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Biosorption of nickel and zinc ions on wheat straw

Khurram Shahzad Baig
Ryerson University

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BIOSORPTION OF NICKEL AND ZINC IONS ON WHEAT STRAW

A Thesis

Presented to

Ryerson University

by

Khurram Shahzad Baig,

B.Eng. Chemical Engineering, Punjab University, Pakistan, 1985

in partial fulfillment of requirements

for the degree of

Master of Applied Sciences

in the program of Chemical Engineering

Toronto, Ontario, Canada, 2008

AUTHOR DECLARATION

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Khurram Shahzad Baig

Biosorption of Nickel and Zinc Ions on Wheat Straw

Abstract:

This study investigates the potential use of wheat straw (*Tritium Sativum*) which is an agricultural by-product for the removal of Ni^{2+} and Zn^{2+} from the waste water discharges. Scanning Electron Microscope was used to obtain images of the surface of wheat straw (WS) and Electron Dispersive Spectroscopy was employed in elemental analysis of wheat straw. Fourier Transform Infrared Spectroscopy was used to get informations about the chemical interaction of the wheat straw surface with the sorbed metallic ions. Simulated wastewater containing Ni^{2+} and Zn^{2+} was subjected to biosorption by WS. The effect of initial concentration, pH and temperature on the removal of metal ions on WS was investigated. For varied initial metal concentrations from 5 to 150 ppm the biosorption equilibrium was achieved between 2.5 to 5 hours. The percentage removal of sorption decreases with increasing concentration.

The experimental data were fitted to Langmuir, Freundlich and Temkin isotherms models and it was found that the Freundlich isotherm model fits better than the other two for single ionic system. For binary ionic system IAS- Freundlich model served best. In addition the sorption data obtained at different temperatures was investigated and found that metal sorption by wheat straw conformed to pseudo second order kinetics with a good value of coefficient of determination ($r^2 > 0.99$). Free energy of biosorption ΔG^0 , enthalpy ΔH^0 and entropy ΔS^0 changes were also estimated and used to predict the nature of biosorption. The capacity of the sorption of wheat straw was compared with other common available sorbent.

On the basis of sorption capacity, regenerate ability and the cost analysis we can conclude that WS could be used as a sorbent material for removal of Ni^{2+} and Zn^{2+} from an aqueous solution.

Khurram Shahzad Baig

M.A.Sc. Chemical Engineering

Ryerson University

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Nomenclature

- a_{ij} the competition coefficient for the Binary system for the first metal ions
- a_{ji} the competition coefficient for the Binary system for the second metal ions
- b_i Individual Langmuir adsorption constants of the first metal ions related to the affinity of the binding site, respectively,
- b_j Individual Langmuir adsorption constants of the second metal ions related to the affinity of the binding site, respectively,
- C_e is the residual concentration in solution (mg/L)
- C_0 is the initial concentration of adsorbate in solution (mg/L),
- C_i Unadsorbed concentrations of the first metal ions at equilibrium, (amount remaining in solution), (mg/L)
- C_j Unadsorbed concentrations of the second metal ions at equilibrium, (amount remaining in solution), (mg/L)
- E is the activation energy of sorption (kJ mol^{-1}),
- I Finite adsorption, at $t=0$, $q_t = I$
- m is the weight of adsorbent per liter of solution (g/L),
- K_l is the Langmuir biosorption constant (L/mg).
- K_f is an indicator of the adsorption capacity, (mg/g)
- k_o is the temperature independent factor ($\text{g mg}^{-1} \text{ min}^{-1}$)
- k_i Intra particle diffusion rate constant
- K_c equilibrium Constant of biosorption
- k_1 is the rate constant of pseudo-first order biosorption (l/min)

- k_2 is the rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$)
- q_e is the equilibrium uptake corresponding to the site saturation (mg/g).
- q_l is the maximum metal adsorbed per gram of biosorbent material, (adsorption capacity) (mg/g)
- $q_{e,i}$ is the adsorbed quantities of the first metal ions per gram of dried biomass (mg/g)
- $q_{e,j}$ is the adsorbed quantities of the second metal ions per gram of dried biomass (mg/g)
- q_t is the uptake of metal ions at time 't' (mg/g)
- Q_i^0 Individual Langmuir adsorption constants of the first and second metal ions show the max amount of metal ions bound to biomass
- Q_1^0 Initial concentration of specie 1
- Q_2^0 Initial concentration of specie 2
- $1/n$ is the adsorption intensity, L/g
- R is gas constant $8.314 \text{ J/mol } ^0\text{K}$
- t is the contact time (min)
- T is temperature (^0K)
- V is the volume of solution (ml)
- W is the volume of dry sorbent in grams
- EDS Energy Dispersive Spectroscopy
- FTIR Fourier Transform Infra Red
- SEM Scanning Electron Microscope

UV Ultra Violet light

h is Planck's constant (4.135×10^{-15} eV.S)

α is Bangham Constant

λ is wavelength (m/S)

r^2 coefficient of determination

R_L separating factor

h Initial biosorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)

ΔG is free energy change, (kJ mol^{-1})

ΔH is the enthalpy change (99 kJ mol^{-1})

ΔS is the entropy change ($\text{J mol}^{-1} \text{K}^{-1}$)

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1. Introduction:

In 1978, the Environmental Protection Agency of USA (US-EPA) prepared a list of priority pollutants which contains 129 organic and inorganic pollutants. These were uncovered in wastewater streams coming from industries, hospitals and municipal areas which and have the potential to constitute serious health hazards [Keith *et al.*, 1979]. The list includes the following thirteen metals: antimony (Sn), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Th), and zinc (Zn). These metals are different from organic compounds [Luckey, 1977, Forstner, 1979; Geldmacher, 1984], because they are non-biodegradable and bioaccumulateable.

In Canada automotive industries are considered as a major contributor to water contamination because they add heavy metals, in Canada. The main operations under the label of this discipline include engine casting, metal cutting, transmission, machining and metal stamping. Wastewater from this industry contains heavy metals like, Cu, Ni, Pb, Zn etc, organic compounds and oil and grease. The table 1.1 shows a small picture of the analysis of daily discharges of only three automotive plants [Kim *et al.*, 2002]

Table 1.1 : Discharge of Metals on a Typical Day from Automotive Industry

units mg/L, except for pH, [Kim *et al.*, 2002]

Plant	A	B	C
Function type	Engine	Transmission	Assembly
Parameters			
Al	0.022	0.67	0.69
Cd	0.72	1.15	1.2
Cr	0.92	2.69	2.77
Cu	1.35	3.28	3.38
Ni	0.35	3.86	3.98
Pb	0.47	0.67	0.69
Zn	0.52	2.53	2.81
pH	6-9	7-9	6-10

Ontario legislation does not cover all type of contamination from an automotive plant. US-EPA has proposed that new categorical pretreatment effluent standards are produced for the waste water generated by the Metal Products and Machinery Industry (MPM) .

Table 1.2 : US-EPA for MPM, 1995

Units mg/L, except pH,

Parameters	Proposed Standards	
	Daily	Monthly
Al	1.4	1.0
Cd	0.7	0.3
CN	0.03	0.02
Cr	0.3	0.2
Cu	1.3	0.6
Fe	2.4	1.4
Ni	1.1	0.5
Pb	b	b
Zn	0.8	0.4
pH	6-9	6-9

Contribution of municipal wastewater in increasing the heavy metal contents in environment can be visualized by the following table 1.3, [Rutherford *et al.* 1994, Golder Associates 1995a & b, Lee *et al* 2002]:

Table 1.3 : Chemicals in Municipal Wastewater Effluents across Canada

Chemicals	Ontario	Edmonton	Nova Scotia
B, N& Acid Extractable	24		
Dioxin and Furans	7		
Pesticides and Herbicides	30		
Volatiles	19		
Metals and cyanides	15	19	
Misc. Organics and Fecal Derivatives		7	48

B,N & Acid : Base, Neutral and Acid , Misc. Miscellaneous

These metals are extensively disseminated in materials that make the earth crust. For example, Zinc occurs at an average of 70 mg/Kg. Rain water released Zn into the environment from soil and rocks. On the other hand, industrial activities are mostly responsible for zinc pollution. Mining, foundry and machining activities, zinc, lead and cadmium refining, steel production, carbon combustion and solid waste incineration add to zinc pollution. Zinc is used to coat iron and other metals for prevention of corrosion. Some zinc salts are used industrially for wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanization, ceramics, textiles, fertilizers, pigments and batteries [USDHHS, 1993]. In case of ingestion of more than 2.0 grams of Zn produces toxic symptoms (fever, diarrhea and gastrointestinal tract irritation) in humans. Hence, there is interest to remove Zn from wastewater because its toxicity level for humans is 100-500 mg/day [Chong *et al*, 1995]. World Health Organization (WHO) recommended the maximum acceptable concentration of Zn in drinking water as 5.0 mg/L.

Nickel being the most abundant, 68.077 %, naturally occurring material. Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc. These alloys are used in making metal coins and jewelry and in industry for making items such as valves and heat exchangers. EPA recommends that drinking water levels for nickel should not be more than 0.1 mg per liter. Plants are known to accumulate nickel and as a result the nickel uptake from vegetables will be eminent. The International Agency for Research on Cancer (IARC) has listed nickel compounds within group 1 (there is sufficient evidence for carcinogenicity in humans) and nickel within group 2B (agents which are possibly carcinogenic to humans). OSHA does not regulate nickel as a carcinogen. American Conference of Governmental Industrial Hygienists placed Nickel at the Notice of Intended Changes as a Category A1 which means it is confirmed human carcinogen.

Uncontrolled discharge of heavy metal containing wastewaters to the environment can be detrimental to humans, animals and the plants. Different methods were developed for removal of heavy metals from wastewater. Chemical methods, such as precipitation, biosorption, ion exchange and solvent extraction require high capital and operating costs and may produce large volumes of solid waste. Studies on the treatment of effluent bearing heavy metal have revealed biosorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent [Chand *et. al.*, 1994]. Despite its

extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material.

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. The low cost agricultural waste by-products such as sugarcane bagasse [Chand, *et al.*, 1994; Mohan and Singh, 2002; Khan *et al.*, 2001; Ayub *et.al.* 1998 & 2001] rice husk [Suemitsu *et. al.*, 1986; Munaf and Zein, 1997; Sirinivasan, *et al.*, 1998; Ajmal *et al*, 2003;] sawdust [Ajmal *et. al.*, 1996; Kadirvelu, 2003; Selvi, 2001] , coconut husk [Tan *et. al.*, 1993], oil palm shell [Khan *et. al.*, 2003], neem bark [Ayub, *et al*, 2001], etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. In the development of activated carbon, use of chemicals, energy and a great deal of time is involved. Apart from added pollution to the environment, the cost of the improvement operations increases the cost of main process. However, cost information about a biosorbent is seldom reported, and the expense of individual biosorbents varies depending on the degree of processing required and local availability. Therefore, there is an urgent need that all possible sources of agro-based inexpensive biosorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. For these reasons, recent research efforts were concentrated on recovery of heavy metals using different biomaterials, such as waste sludge, and waste biomass from commercial bioprocesses.

Biosorption is essentially the passive method of physico-chemical binding of chemical species or ions to the surfaces of biomass. Some advantages of biosorption for removal of heavy metals over chemical and physical methods can be summarized as follows:

1. Easily available.
2. Low cost, free availability.
3. High biosorption capacity because of large surface area.
4. Selective biosorption of metal ions.
5. Operation over a wide range of environmental conditions (pH, ionic strength and temperature).

Wastewater treatment processes have assumed a more important role in the hydrological cycle with the increasing tendency towards water re-use. In particular their capacity for the removal of heavy metals is important in maintaining standards for heavy metal concentrations for drinking water and potable supplies. In the literature biosorption of Ni^{2+} and Zn^{2+} onto wheat straw is not available. In addition, since Ni^{2+} and Zn^{2+} ions are commonly present in industrial effluents, as a result, they are selected as the model metal ion. Because of negative surface charge and its composition, wheat straw is chosen as a biosorbent for metal ions. Therefore, the objectives of this study are to evaluate the biosorptive capacity of Wheat Straw (*Tritium sativum*) for Ni^{2+} and Zn^{2+} . As Canada is in top ten producers of wheat in the world, so, the availability of wheat straw is not a problem. In order to achieve the objectives the following tasks were carried out:

- conducted equilibrium study for biosorption
- determined the kinetic behavior of biosorption of Ni^{2+} and Zn^{2+}
- assessed the thermodynamic behavior of biosorption
- examined the biosorption mechanism
- investigated the effect of temperature, pH and initial concentration of Ni^{2+} and Zn^{2+}
observed the changes on the surface of biosorbent by microscopy and spectroscopy

2. Literature Review

2.1 Treatments Techniques for Wastewater Containing Metal Ions

Several techniques are in use in industry for removal of heavy metals from aqueous solutions. Chemical precipitation, alum coagulation, iron coagulation, ion exchange, reverse osmosis, electro dialysis, ultra filtration, phytoremediation and biosorption are the most commonly used methods.

2.1.1 Chemical Precipitation

Metal precipitation has been the most favored option because it is achieved by using a cheap alkali such as lime (calcium hydroxide). Precipitation, by adjusting the pH value, is not selective for specific ions. Any iron (ferric ion) present in the liquid effluent will be precipitated first, followed by other heavy metals. Consequently, precipitation produces large quantities of solid sludge for disposal, for example, precipitation as hydroxides of 100 mg/L of Cu^{2+} , Cd^{2+} or Hg^{2+} produces as much as ten, nine and five fold mg/L of sludges, respectively. Precipitation processes are highly dependent on solubility of the solutes and effectiveness of the solid-liquid separation. The solubility can be influenced by the presence of complexing agents such as cyanides or whether the metal is capable of existing in an anionic form, e.g. chromium as chromates.

Solid-liquid separation can be improved by the use of polyelectrolyte's or flocculants such as aluminum, but at the expense of sludge generation. Metal precipitation is primarily dependent upon two factors, the concentration of the metal, and the pH of the water. Heavy metals are usually present in wastewaters in dilute quantities (1 - 100 mg/L) and at neutral or acidic pH values (< 7.0). Both of these factors are disadvantageous with regard to metals removal. However, when one adds caustic to water which contains dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids.

Its disadvantages include use of chemicals, reduction of efficiency at high and lower pH and it gives highly heavy metal concentrated sludge. The following figure 2.1 is a schematic diagram of metal removal process by using precipitation:

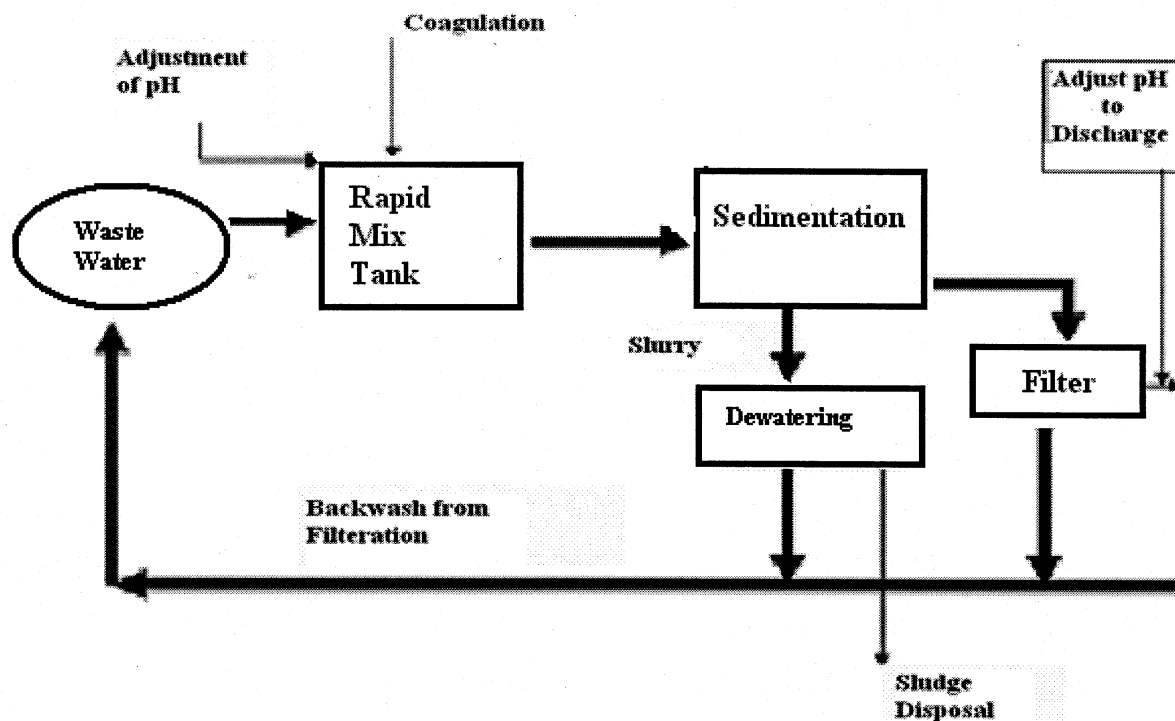


Figure 2.1 : Conventional Methods of Metal Precipitation

2.1.2 Ion-exchange:

This process is applicable to dilute solutions where metal ions are removed by exchanging them with the ions held on resins by electrostatic forces. Synthetic ion exchange resins are based on cross linked polymer matrix typically composed of polystyrene cross linked with vinyl benzene. Charged functional groups are attached to the matrix through covalent bonding. They can be categorized into four groups: strongly acidic, weakly acidic, strongly basic and weakly basic [Clifford, 1999]. These groups are exchanged the ions attached on the surface for similar charge ions in solution that have a stronger exchange (selectivity) for the resin.

This process is not suitable because of its high cost and partial removal of certain ions (selectivity). Its efficiency is affected by the presence of sulfate, nitrates, fluoride ions, total dissolved solids etc. It also uses chemicals for regeneration. The figure 2.2 is representation of an ion exchange process.

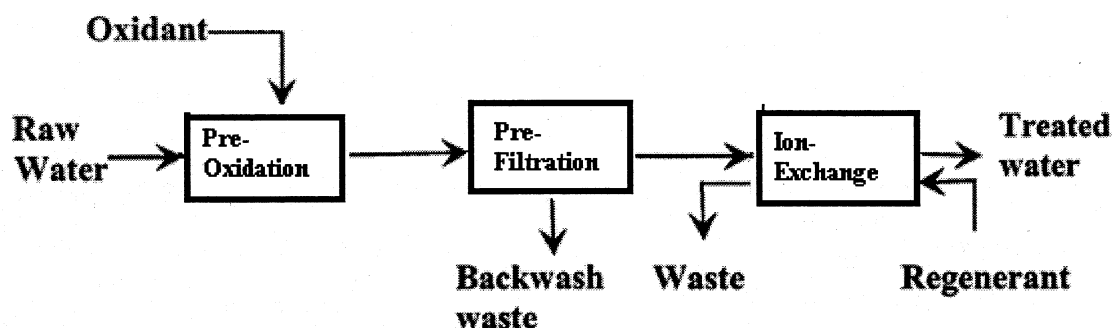


Figure 2.2 : Ion Exchange process, US-EPA 2003

2.1.3 Electrodialysis:

This is an electromembrane process in which ions are transported through ion permeable membranes, from one solution to another, under the influence of a potential gradient. The electrical charges on the ions allow them to be driven through the membranes. By applying a voltage between two end electrodes the required potential field is generated. Since the membranes used in electrodialysis have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge. Removal of unrequited concentrations or separation of electrolytes can be achieved by Electrodialysis.

The disadvantages are formation of metal hydroxide which clogs the membranes; costly, needs oxidizing agents and additional treatment of concentrates (brines) for disposal.

2.1.4 Adsorption:

Among several physical and chemical methods, the adsorption on activated carbon has been found to be superior as compare to other available techniques. Coal is a non-renewable source; its use for adsorption is not much appreciated [Chand, *et al.*, 1994].

The effectiveness of this process is based on the contaminant type, concentration and rate of water usage. It needs careful monitoring because bacteria may grow on the surface if activated alumina is used as adsorbent.

Using agricultural and industrial wastes or by-products to generate activated carbon was another try; however, that is still considered expensive. Its efficiency depends on the ash contents of carbon and the metal concentration in the ash [khan, *et al.*, 2004].

The presence of trace elements in the waste water is so numerous that a search for new technologies has got attention to biosorption. It is based on metal binding capacities of various biological materials

2.1.5 Biosorption

Biosorption and bioaccumulation of metals is not a novel technique rather it is a new approach. For several thousands of years, nature has been using these fascinating and intricate interactions. Scientists, however, have been attempting and in many instances succeeded to understand these subtleties for only five or six decades, whilst the process technologists are still wondering how we can benefit by or put to use this ingenious science [Eccles, 1995].

Biosorption is the passive adsorption and complexation process of metal ions by biological materials. If it is obtained by using microorganisms then it is called bioaccumulation (based on their biosorption mechanism). For all other materials like live, dry, dead plants and agro wastes it is called biosorption. The use of living organisms is often successful in the treatment of toxic organic contaminants; living organisms in conventional biological treatment systems generally have not been useful in the treatment of solutions containing heavy metal ions. Once the metal ion concentration becomes too high or sufficient metal ions are adsorbed by the micro-organism, the organism's metabolism is disrupted, thus causing the organism to die. This disadvantage does not exist if non-living organisms or biological materials derived from microorganisms are used to absorb metal ions from solution.

The biomass, however, unlike mono functional ion exchange resins, will contain a number and variety of functional sites. These sites, contributed by the cell biopolymers include carboxyl, imidazole, sulphydryl, amino, phosphate, sulphate, thioether, phenol, carbonyl, amide and hydroxyl moieties. Various algal species and cell preparations have quite different affinities for

different metal ions. Thus, certain algal species may be much more effective and selective than others for removing particular metal ions from aqueous solution [Darnall *et al.*, 1986]

The advantages of biosorption over conventional methods for the removal of metals from dilute solutions include:

- High efficiency of removal from dilute metal solutions. Biosorption is particularly suited for the purification of wastewaters with a metal concentration of about 1-100 ppm [Schiewe and Volesky, 2000]
- Potential for metal recovery, accelerated depletion of natural resources and rising prices of metals makes metal recycling very attractive
- Low price of biosorbents [Volesky, 2001]
- No sludge generation
- Abundance of material, many effective biosorbents are either abundant in nature or cheap waste products of other industries [Abdul-Halim *et al.*, 2003]
- Regenerative properties, costly and strategic metals are desorbed and biosorbent is reused with a minimal decrease in biosorption performance [Davis *et al.*, 2003]
- Metal selectivity potential, the metal biosorption capabilities of different types of biomass can vary in selectivity for different metals.

However, biosorption hasn't been widely applied in large scale process. This may be remedied in the future through progressive research and development as well as advanced pilot projects.

2.2. Biosorbent Materials

Lately, biosorption experiments have focused on waste materials which are by products or the waste materials from industrial processes.

Table 2.1 : Removal of Heavy Metals by Using Biomass

Waste type/ Industry	Contaminant	Reference
Microorganisms	Cr, Hg, Fe, As	Lovely, et al, 1997
Bacteria	Pb, Zn	Puranik et al., 1997

Dried Activated Sludge	Cr, Ni	Aksu, et al, 2002.
Activated Sludge	Cu, Cd and Zn	Hammaini et al, 2003
Wet Activated Sludge	Zn	Norton et al, 2003
Sargassum algal	Cu, Fe	Kratochvil et al, 1998
<i>Sargassum</i> sp., <i>Padina</i> sp., <i>Ulva</i> sp., and <i>Gracillaria</i> sp	Cu Pb, Cu, Cd, Zn, Ni	Sheng, et al, 2004
Green micro alga	Cu^{2+} , Cd^{2+} , and Pb^{2+}	Apiratikul et al
Aquaphytes,	Cu	Schneider et al, 2001,
<i>Ceratophyllum demersum</i> (Coontail or hornwort)	Pb. Cu, and Zn	Keskinan et al, 2003
Macrophyte <i>Lemna minor</i> L.	Cd, Cu, and Ni	Sayqideger S., et al, 2005
<i>Caladium bicolor</i>	Pb^{2+} and Cd^{2+}	Horsfall, et al, 2005,
<i>Tectona grandis</i> L.f. leaves	Zn	Kumar et al, 2006
Sawdust	Cu	Yu et al, 2000
Sawdust	Heavy metals	Shukla, et al, 2002
Maple Sawdust	Cr	Yu et al, 2003,
<i>T. cuspidata</i> , <i>P. jezoensis</i> and <i>P. abies</i> (barks)	Cd, Cu and Zn	Seki et al., 1997
Modified barks	Cr and Cu	Gaballah, et al, 1998,
Coirpith (Activated Carbon)	Cu	Namasivayam et.al. 1997
Olive mill solid Residues	Hg, Pb, Cu, Zn and Cd	Pagnanell et al , 2002
Modified Apple wastes	Zn & Ni	Maranon, et al, 1991
Fruit peel of orange	Zn, Ni, Cu, Pb and Cr	Ajmal et al, 2000
Sugar beet pulp	Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+}	Reddad et al, 2002
Ago wastes	Cr, Cd, and Al	Orhan et al. , 1992
Waste Tea Leaves	Pb, Fe, Zn and Ni	Ahluwalia, et al., 2005
Low cost Adsorbents	Cr^{6+}	Dakiky et al, 2002

Corncobs	Heavy Metals	Elina, et al., 1995
Rice Hulls	Cr ⁶⁺	Low et al., 1999
Pretreated Rice Husk	Cd ²⁺	Kumar, et al., 2006
Husk of Lathyrus sativus	Ni ²⁺ and Cd ²⁺	Panda et al., 2007
Wheat Bran	Pb	Bulut et al., 2006,
Wheat shells	Direct Blue Dye	Bulut, et al., 2007

2.3 Literature on Biosorption:

Friedman and Waiss, 1972, worked on biosorption capacities of some agricultural products viz., wool albumin, blood meal, chicken feathers, soy flour, silk, gelatin, and wheat gluten and wheat flour. They noticed that wool modified by N-vinyliminazole, N-vinylpyrrolidone and 2-vinylpyridine enhanced mercury uptakes by 30-70 % compared with the non-modified wool. Odozi *et al*, 1985, described the preparation and properties of polymerized corncob powder (treated by sulphuric acid and phenol) and its composite (with saw dust and onion skin) ion-exchange resins for binding heavy metal ions. The static and dynamic tests were carried out with solutions of Pb²⁺, Ni²⁺, Cu²⁺, Mg²⁺, Zn²⁺ and Ca²⁺. Their results showed the concentration of these metal ions were greatly reduced and the exchange capacity of the cation resin for the metal ions studied was the order of 1 meq/g. Odozi and Emelike, 1985, demonstrated that the biosorption capacity of the biosorbent made from corncob-red onion skin with various solution, for the studied ions was in the following order: Pb²⁺>Ni²⁺>Zn²⁺>Ca²⁺>Hg²⁺>Mg²⁺>Mn²⁺. Elina, *et al.*, 1995, studied the separation of cupric ions from aqueous solution by biosorption onto modified corncobs (hemicellulose-free). The equilibrium was attained in 15 minutes with continuous agitation at 35°C. The process was found to be pH-dependent, with increasing biosorption as pH increased up to 6.00. The maximum adsorbed concentration attained was 0.3441 mmol/g. As corncobs are mainly cellulose and lignin based (hemicellulose was extracted because of its instability and complex structure). There was evidence that the biosorption mechanism was based on ion-exchange involving carboxylate groups and it also showed that two binding sites may be present at the biosorbent.

Peterson, 1989, evaluated the removal efficiencies of Cd²⁺ from water using biological biosorbents viz., human hair, bone, apricot seed shell, walnut shell, peanutshell, orange skin,

irish peat, natural compost, zygorhynchus, rhizopus, Mucor ramannianus, penicillium caps, aspergillus terrus, IRA-400 (ionex) and activated charcoal. Among all these tested materials, ten biosorbents showed higher biosorption capacities than that of activated charcoal and ion exchange resin. Ajmal et al, 2000, investigated the ability of fruit peel of orange to remove heavy metals of Zn, Ni, Cu, Pb and Cr from aqueous solution. The adsorbed amounts were in the order of $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cr}^{2+}$. The extent of removal of Ni^{2+} was found to be dependent on biosorbent dose, initial concentration, pH and temperature. The heavy metal cations were completely released under circumstances of extreme acidic conditions. The percent biosorption was minimum (40%) at pH of 2 and increased as the pH was increased. The maximum biosorption occurred at pH 6 (97.5%) but biosorption decreased when pH was increased further., with a maximum biosorption of 96% at 50°C for an initial concentration of 50 mg l⁻¹ at pH 6. Thermodynamic parameters were also evaluated. The positive value of ΔH indicates that the process was endothermic. The free energy of the process at all temperatures was negative and decreased with increase in temperature which indicated that the process was spontaneous and spontaneity increased with increase in temperature. The entropy of the overall system was negative and almost constant showing the favorable biosorption.

Dakiky et al, 2002, investigated the removal of Cr^{6+} from industrial wastewater by using different low-cost adsorbents. Wool, olive cake, sawdust, pine needles, almond shells, cactus leaves and charcoal were used as sorbents. The selected biosorbents were from two different classes of fibers. Wool which is a protein-based animal fiber with many amino and carboxylic groups those may play a major role in metal binding. The other biosorbents were cellulose-based plant fibers with many hydroxy groups those may bind the Cr^{6+} . The presence of a particular functional group or binding site does not necessarily guarantee its accessibility as a biosorption site, due to the possible coexistence of steric, conformational, or other types of barriers. The biosorption process was found to follow a first-order rate mechanism and the rate constant was evaluated at 30°C. In the case of wool, the rate constant was the highest ($39.6 \times 10^{-3} \text{ min}^{-1}$) and the cactus leaves gave the lowest value ($6.8 \times 10^{-3} \text{ min}^{-1}$). Langmuir and Freundlich isotherms were applicable to the biosorption process and their constants were evaluated.

At 8 g l^{-1} of biosorbent, the removal of Cr^{6+} was found to be between 68.7% for wool and 19.8% for almond shells. The nature of the biosorbent and its compactness affected the time needed to reach equilibrium. For wool, this time was 1.5 h and for the other biosorbents, a contact time of 2 h. The dominant form of Cr^{6+} at pH of 2 was HCrO_4^- . Increasing the pH shifted the concentration of HCrO_4^- to other forms, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$.

It is worth mentioning that on conducting similar experiments on Cr^{3+} under the same conditions, no removal of Cr^{3+} by any of the biosorbents was observed. This was due to repulsion of the positive Cr^{3+} ions by the positively charged active centers on the biosorbents at the pH of 2. This means that this process was very selective for the removal of the toxic form of chromium from any matrix under these conditions (pH of 2). On the other hand, the biosorption of Cr^{3+} occurred at higher pH values and reaches a maximum at pH of 5. At this pH, the number of negatively charged groups on the biosorbent matrix increased and enhanced the removal of the Cr^{3+} species by coulombic attraction.

The Gibbs free energy is an indicator of the degree of spontaneity of the biosorption process, where more negative values reflect a more energetically favorable biosorption process. The thermodynamic equilibrium constant and the Gibbs free energy were calculated for each system. The ΔG° for the biosorption by wool $-2.26 \text{ kJ mol}^{-1}$ and that for the cactus leaves 2.8 kJ mol^{-1} supported the findings that wool was the best among the selected sorbents for the selective removal of Cr^{6+} at pH of 2.

Gaballah, *et al*, 1998, discussed the use of tree barks for chelating heavy metal ions from synthetic solutions and industrial effluents. They gave detail about the description of bark and its treatment, the experimental devices used in this work, the results were obtained by decontamination of synthetic solutions, industrial effluents on laboratory and pilot scales and the regeneration, pyrolysis or incineration of the saturated bark.

The rate of removal of heavy metal ions (HMI) varies from 50 to 99% and the bark capacity for different metal ions varies from 12 to 460 kg of metal per ton of dry substrate. The main mechanisms proposed for reaction of Cu^{2+} species with wood constituents were:

- reaction between Cu^{2+} and carboxylic (RCOO^-) groups of polysaccharides
- hydrogen bonding of hydrated Cu^{2+} ions ($\text{Cu}(\text{H}_2\text{O})_6^{2+}$) with cellulose
- formation of complexes with (OH) of the phenolic groups of lignin

Little differences in efficiency were observed, in the pH range of 1 to 4, among the different types of barks used for copper cation removal. However, at pH of 5, it appeared that pine was more efficient in removing copper, followed by oak, spruce and beech. Copper cation precipitation had been experimentally determined and reported. For pH lower than 5, copper removal by barks could not be attributed to precipitation. At pH of 3.8, the removal of Cr^{6+} by modified bark is 98% of the initial chromium concentration. Under the same experimental conditions, the percentages were 80 and 95 with untreated oak and pine bark, respectively.

The kinetics of chelating Cr^{6+} was studied using modified Scotch pine bark at different pH values. At pH of 1 maximum metal removal was attained after 5 min. At a later time, the chromium concentration in the solution increased slightly as function of time. This phenomenon could be explained by the partial dissolution of the chromium bound to the bark. At pH of 3.8, the extraction of Cr^{6+} from the solution took 10 min to remove 95% of the Cr^{6+} . Equilibrium seemed to be reached after 30 min. At pH 6.0, the kinetics of Cr removal was slower and it did not seem to reach equilibrium even after 4 h shaking.

The most favorable extraction of As^{5+} was performed at a pH of 4 corresponding to the presence of H_2AsO_4^- . The solution pH increased as As^{5+} is bound to the bark.

The interaction of cadmium ions with the modified bark generated H_3O^+ leading to a decrease of the pH. It was found that the chelating of one mole of cadmium ions by the bark liberated about 2.2 mol of H_3O^+ . This may suggest that the bark acted as an ion exchanger. At higher pH values, trivalent chromium ions precipitate as $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, and the removal of one mole of trivalent chromium by the modified bark generated about 9 mol H_3O^+ . It was deduced that the chelating of metals was dependent on the predominant chemical specie in the solution. It was observed that Fe^{2+} was better chelated by the bark than FeOH^+ . Precipitation of ferrous hydroxide occurs at a

pH of 5.5 to 9.0 depending on the ferrous ion content of the solutions and the interaction of one mole of ferric ions with the modified bark will release about 13 mol of H_3O^+ .

The amount of Ni^{2+} bound to the bark increased as the pH increases in the zone of Ni^{2+} . As could be expected, precipitation of Ni^{2+} as $\text{Ni}(\text{OH})_2$ at pH higher than 7 decreased the amount of Ni^{2+} reaction with the bark and the interaction of a mole of nickel generated about 2.5 mol of H_3O^+ . At pH of 6, maximum interaction between the bark and the lead ions occurred. The presence of $\text{Pb}_3(\text{OH})_4^{2+}$ in the solution decreased the chelating capacity of the bark and the interaction of Pb ions lead to the release of 2 mol H_3O^+ . The proportion of zinc ions chelated to the modified bark increases as the pH augmented. The reaction of zinc ions with the bark generated 2 mol H_3O^+ .

Marshall *et al*, 1993, investigated the biosorption capability of rice milling by-products (hulls and bran) for metal ions from aqueous solution. Hulls adsorbed low level (13% - 27 %) of Cr^{3+} , Co^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} at 100 mg metal ion concentration. A defatted extrusion stabilized bran was found to have a high biosorption capacity for Cr^{3+} , Cu^{2+} , Zn^{2+} but a much lower capacity for Co^{2+} and Ni^{2+} . Low *et al.*, 1999, investigated the potential of quaternized rice hull in removing Cr^{6+} from synthetic solutions and industrial wastes in column experiments. It was observed that with the increase in column bed depth resulted in a longer service time at $C_t/C_0 = 0.5$ breakthrough. The presence of SO_4^{2-} (commonly available in waste streams) resulted in the earlier breakthrough. It was reported that quaternized rice hulls show better biosorption capacity in the pH range of 2-10. Kumar, *et al.*, 2006, investigated the biosorption of Cd^{2+} from aqueous solution by rice husk. Simple and low-cost chemical modifications were made those resulted in increasing the biosorption capacity of raw rice husk (RRH) from 8.58 mg/g to 11.12, 20.24, 16.18 mg/g. This attempt reduced the equilibrium time from 10 h of RRH to 2, 4 and 1 h for epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH) and sodium bicarbonate treated rice husk (NCRH), respectively. It was found that biosorption kinetics agreed for pseudo second-order kinetic model. The highly efficient low cost and the rapid uptake of Cd^{2+} by NCRH indicated that it could be an excellent alternative for the removal of heavy metal by biosorption process. Biosorption behavior of Ni^{2+} , Zn^{2+} , Cd^{2+} and Cr^{2+} on untreated and phosphate treated rice husk (PRH) by Ajmal *et al*, 2003, showed that biosorption of Ni^{2+} and Cd^{2+} was greater when PRH was used as biosorbent. Biosorption of Cd^{2+} was dependent on contact time,

concentration, temperature, adsorbent doses and pH of the solution. It was also reported that the maximum biosorption (> 90%) was obtained at a pH value of 12. Manuf and Zein, 1997, studied the use of rice husk for removal of toxic metals from wastewater. They have reported, at optimal conditions, the Cu^{2+} , Zn^{2+} , Cd^{2+} , and Cr^{2+} removals from aqueous solution and stated as 79%, 85%, 80% and 85%, respectively. Roy *et al*, 1993, studied on biosorption of heavy metals by green algae and ground rice hulls. They concluded that metal biosorption by algal and rice hull biomass from the aqueous test systems, was greater than 90% for all the metals tested (Sr, Cd, Ni, Pb, Zn, Co, Cr, As) except Ni, for which removal was nearly 80%.

Marshall and Champagne, 1995, investigated the adsorptive capacities of soybean hulls, cottonseed hulls, rice straw and sugarcane bagasse for some metal ions in aqueous solutions. Their capacities' follow the following order:

Soybean hulls > Cottonseed hulls > Rice straw > Sugarcane bagasse

At an unsaturated concentration of metal ion, 100 mg/l, soybean and cotton seed hulls adsorbed 95-99.7% of Cr^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} or Ni^{2+} . Capacities varied from 0.06 to 0.52 meq / g dry weight of adsorbents. Marshall *et al*., 1999, studied metal biosorption by soybean hulls. Soybean hulls contain protein, lipid ash, lignin, cellulose, hemicelluloses and silica which are 109, 10.0, 36.4, 49.1, 676, 137 and < 10, respectively. The hulls were modified with citric acid. A method was developed to improve metal ion biosorption for wastewater treatment using Cu^{2+} as a typical metal ion. Hulls extracted with 0.1 N NaOH, were modified with different citric acid (CA) concentration (0.1 – 1.2 M) at 120°C for 90 minutes. CA-modified hulls had biosorption capacities for Cu^{2+} from 0.68 to 2.44 m moles/g which was much higher than for unmodified hulls (0.39 m moles/g). They have also concluded that, soybean hulls treated with NaOH and modified with $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ (citric acid), especially at concentration of 0.6 M and above it was removed over 1.7 mmoles of copper ion from solution per g of hulls. This is due to the increase in carboxyl group imparted onto the hulls by reaction with citric acid. Bosinco *et al*, 1996, Al-Asheh and Duvjak, 1996, used canola meals for biosorption of copper. The uptake of metal ions by canola meals decreased with an increase in the concentration of the canola meal in solution and improved the biosorption with decreasing canola particle size. Lehrfeld, 1996, prepared

cation exchange resins based on oat hulls, corncob and sugar beet. Their reactive order was following:

sugar pulp > corncob > oat hull

Mohan, 2002, studied bagasse pitch which was a waste product from sugar refining industry. Bagasse pitch is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pitch was composed largely of cellulose, pentosan and lignin. Peternele *et al*, 1999, studied biosorption of Cd^{2+} and Pb^{2+} onto functionalized formic lignin from sugar cane bagasse. They have stated that the Pb^{2+} biosorption process obeys Langmuir's model and Cd^{2+} presents biosorption in multilayer, especially when the temperature is higher than 30°C . When ionic strength increases, the maximum biosorption capacity reduces. The carboxymethylated lignin from sugar cane bagasse can adsorb Pb^{2+} selectively rather than Cd^{2+} under special conditions of pH of 6.0, 30°C and ionic strength of 0.1 mol/dm^3 when both ions are present in the mixture. Factorial analysis of Pb^{2+} biosorption suggested that temperature was the most important factor in single ionic system and biosorption increased with increasing temperature. Khan, 2001, reported that an adsorbent dose of $0.8 \text{ g} / 50 \text{ ml}$ was sufficient to remove 80 – 100% Cr^{6+} from aqueous solution having an initial metal concentration of 20 mg/l at a pH value of 1 but the efficiency reduced sharply to 15% at pH of 3. Chand, 1994, studied the removal of Cr^{6+} from wastewater by biosorption on bagasse and coconut jute. The effect of solution pH, Cr^{6+} concentration, biosorbent dosage and contact time were studied in a batch experiment. The removal was in general most effective at low pH values and low Cr^{6+} concentration.

Reddad *et al*, 2002, studied sugar beet pulp (a waste of sugar-refining factories) for the removal of heavy metals from aqueous solutions. The structural components related to the metallic biosorption being determined, batch biosorption studies were performed for several metal ions, namely, Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} . Two simple kinetic models, that is, pseudo-first-order and pseudo-second-order were tested to investigate the biosorption mechanisms. The equilibrium data fitted well with the Langmuir and Freundlich models and showed the following affinity order of the material: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$.

Even though the same experimental conditions were used, it was interesting to note that the fixation capacities were different according to the metal adsorbed. Quantitatively, more Pb^{2+} ions were adsorbed than Cu^{2+} , than Cd^{2+} , than Zn^{2+} , and least of them were Ni^{2+} ions. The differences between Cd^{2+} and Zn^{2+} cations were very small. The fast metal uptakes were certainly related to the large availability of the carboxyl groups along the pectic backbone of the polysaccharide.

The concentration of Ca^{2+} ions in solution was also measured. The release of Ca^{2+} from the adsorbent was faster than the metal biosorption kinetic and revealed an ion exchange mechanism for all metal ions. The Ca^{2+} concentration was always correlated with the quantity of metal fixed on the material. In fact, beet pulp itself contains enough calcium to neutralize most of the carboxylic moieties of the galacturonic acid. It was considered that this calcium may be endogenous but may be added from the pressing stage during the sugar recovery process. The removal of metal ions by the polysaccharide was found highly dependent on pH. It increased in a narrow pH range, as 2-3 pH units but never reached 100% because chemical precipitation was always avoided under the experimental conditions used. At any fixed pH, the effectiveness of removal for each metal ion was reflected in the percentage of biosorption obtained. For example, at pH of 3.5, the order of removal efficiency was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. By increasing the pH, the biosorption limits were reached in the sequence as $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. This affinity order holds for most pH values until pH 4.5, at which Cd^{2+} seemed to become more adsorbed than Cu^{2+} and Zn^{2+} cations. In the case of Cu^{2+} , Zn^{2+} , and Cd^{2+} ions, the differences were small while the high affinity of Pb^{2+} for the adsorbent was confirmed by its biosorption limits. It was interesting to note that at pH of 2.5 about 20% of lead was removed whereas the biosorption of other metals was insignificant. The preference of several solids for metals has always been related to the equilibrium constant of the first metal hydrolysis reaction. It was found that a higher value of hydrolysis constant lowered the degree of salvation of metal ions, hence, enabling them to approach the solid surface and exhibiting significant biosorption as for Pb^{2+} and Cu^{2+} elements. Pagnanell *et al* , 2002, In this study olive mill solid residue was used as heavy metal adsorbent material for its wide availability as agricultural waste and also for its cellulosic matrix, rich of potential metal binding active sites. Preliminary studies concerned with the removal of different heavy metals (Hg, Pb, Cu, Zn and Cd), the effect of pre-treatments by water and *n*-hexane and the regeneration possibility.

Olive mill solid residue resulted able to remove heavy metals from aqueous solutions with an affinity series reflecting the hydrolytic properties of the metallic ions. It was supposed that biosorption phenomenon occur by a general ion exchange mechanism combined with a specific complexation reaction for copper ions. It has been observed that *n*-hexane pre-treatment reduces the biosorption properties of this material.

They performed a preliminary investigation of the active sites to show the presence of two different site affinities depending on the metal concentration that confirms a previous hypothesis of two kinds of metal uptake mechanisms for copper biosorption.

Guibal *et al*, 1998, studied the effects of agitation speed and particle size on biosorption by chitosan beads for metal ions with 0.95-2.8 mm did not influence the equilibrium time while it was observed that the biosorption kinetics were mainly controlled by intraparticlular diffusion and an increase in radius of chitosan flakes from less than 0.125 mm to 0.25 to 0.50 mm decreased the biosorption capacities from 3.4 to 1.5 milli mol/g , with the result showing that controlling mechanism involved both external and intraparticlular diffusion. The intraparticlular diffusivity range was between 10^{-13} and 10^{-10} m²/min depending on the biosorbent size and the condition.

2.4 The Factors Affecting Biosorption Process

2.4.1 The Effect of Initial pH:

pH is considered as one of the most important factors that significantly affect the biosorption of metals. Biosorption is a process of interaction between biosorbent (biomass) and the adsorbate (metallic ions). The biosorption capacity is a function of the degree of interaction which in turn depends on the properties of both the adsorbent and the adsorbate materials. This interaction is favored by the surface charge on the adsorbent material and the metallic specie. pH controls the ionization of the functional groups present on the biomass surface, contributing to the surface charge. The interaction should occur when the biosorbent material provide a negative or a partially negative surface charge for the cationic metallic species viz., Ni²⁺ and Zn²⁺ to bind. The

co-occurrence of positively charged metallic ions and negatively charged biomass surface at a common pH or pH range is necessary for the effective interaction to take place.

Decreasing pH values to extreme acidic conditions may damage the structure of the biosorbent material. Kuyucak and Volesky, 1989a, have observed distorted cells, significant weight loss and decrease in biosorption capacity under high acidic conditions. Moreover, the pH of a solution can be changed as a result of biosorption. Crist *et. al.*, 1981, observed a decreased in pH value when they were studying acid washed bio mass for biosorption. Kuyucak and Volesky, 1989b, observed an increase of pH during biosorption study of *Ascophyllum* and they attributed the pH increase to the release of carbonate ions into solution.

pH influence on ionic dissociation and solution chemistry of the heavy metals: hydrolysis, complexation by organic and /or inorganic ligands redox reactions, precipitation. On the other hand pH strongly influences speciation and the biosorption availability of the heavy metals [Sheng, et al., 2004].

Biosorption of Ni on biomass like Husk of Lathyrus Sativus (HLS) has been found to increase with increase in pH to reach maximum at pH of 5 and then decrease with further increase in pH up to 8. At pH of 8, Ni precipitated as hydroxide. At low pH, Ni ions compete with protons for binding sites of HLS resulting low biosorption of Ni. It has been suggested that at low pH values H_3O^+ are close to the binding sites of the biomass and this restricts the approach of Ni ions due to repulsion [Deng and Ting, 2005]. With increase in pH more ligands with negative charges are expected to be exposed and this will attract more positive charged Ni ions for binding. At the pH beyond maximum, a noted decrease in biosorption may be attributed to reduce solubility and precipitation of Ni [Harris and Ramelow, 1990; Zhou and Kiff, 1991].

It is well known that solution pH is an important parameter affecting biosorption of metal ions on adsorbents as it does not only affects metal species in solution, but also influences the surface properties of the biosorbents in terms of dissociation of functional groups and surface charge. As the protonation of the amine groups occurs on the biomass surface, the surface should be positively charged at pH below 6.5 [Deng and Ting, 2005]. Therefore, the electrostatic

interactions between the biomass and the metal ions to be adsorbed were repulsive under the pH studied since Cu^{2+} , Pb^{2+} and Ni^{2+} were the major species in the solutions at pH below 6.5. At lower pH, the positively charged hydrogen ions may compete with the metal ions for binding on the functional groups on the biomass surface. Once the amine groups were protonated, the strong electrical repulsion prevented the metal ions from contacting the biomass surfaces, resulting in almost no biosorption of the metal ions on the biomass at pH below 2.2. The increase of solution pH resulted in the electrical repulsion force being weaker and the metal ions could be adsorbed on the biomass surface. For all the three metals, the increase of metal uptake at pH beyond 4 was not significant, indicating the electrostatic interaction may be no longer the dominant factor for the metal ions approaching the binding sites [Deng and Ting, 2005].

2.4.2 Effect of Temperature:

In general, the rates of chemical reactions decrease with decreasing temperature. The relative concentrations of reactants and products in chemical equilibria can also change with temperature. The magnitude of this change basically depends on the change in Gibbs free energy of the reaction in question [Sheng *et. al.*, 2004].

Temperature has a pronounced effect on the biosorption capacity of the adsorbents. Ozer *et. al.*, studied the biosorption of dyes on *Spirogyra rhizopus* and found that the equilibrium uptakes increased with increasing temperature up to 30 °C for dye AB 290 and 25 °C for dye AB 324 and then decreased. The decrease of the equilibrium uptakes with further increase in temperature means that the dye biosorption process is exothermic. If biosorption is considered to be controlled only by physical phenomena, the increase in temperature would decrease the biosorption capacity. Temperature could influence the desorption step and consequently the reversibility of the biosorption equilibrium. In general, an increase in temperature is followed by an increase in the diffusivity of the ion, and consequently by an increase in the biosorption rate if diffusion is the rate controlling step [Benguella and Benaissa, 2002].

Mane *et. al.*, studied the biosorption of Brilliant Green (BG) dye on rice husk ash at temperature range of 288 to 318 K and found that the biosorption capacity of BG increased with increase in

temperature. If the biosorption process is controlled by the diffusion mechanism (intra-particle transport-pore diffusion) then the biosorption capacity will show an increase with an increase in temperature. This is basically due to the fact that the diffusion process is an endothermic process [Weber, 1972]. With the increase in temperature, the mobility of the BG ions increased and the retarding forces decreased, thereby the biosorptive capacity of adsorbent was increased. The authors also discussed that the diffusion of adsorbate into pores of the biosorbent was not the only rate controlling step but the diffusion process could be ignored with adequate contact time. Therefore, the increase in biosorption capacity with an increase in temperature may be attributed to chemisorption [Srivastava *et al.*, 2006a].

Benguella, and Benaissa, 2002, studied the biosorption of Cadmium on chitin; the results indicated that an increase of the temperature in the interval 10–30°C dealt with an increase in the capacity of cadmium biosorption at equilibrium: 5.54 mg/g at 10°C and a high capacity of biosorption about 12.5 mg/g between 20°C and 30°C. Beyond 30°C, a reduction in the capacity of cadmium biosorption at equilibrium was noticed: 10.48 mg/g for 40°C and 8.01 mg/g for 50°C.

The reduction in the removal in the interval of temperature 30–50°C meant that the process of cadmium biosorption by chitin was exothermic. Santana-Casiano, and Gonzalez-Davilla, 1992, reported different results for the biosorption of lindane by chitin in seawater at three temperatures 5°C, 22°C and 45°C. While going through different steps of experimentation they concluded that the diffusivity of cadmium ions through chitin was not affected by temperature under the set of experimental conditions.

The temperature dependence of Zn^{2+} by chitosan was studied over the range of 293–323 °K by Kanbalagan and Indal, 2004. The considerable increase in the amounts of Zn^{2+} adsorbed with temperature confirmed the endothermic nature of the process. The enhancement of biosorption capacity of chitosan with temperature was attributed to the possible increase in the number of active sites available for biosorption on the surface. Ozer and Ozer, 2003, suggested that high temperature was not favorable to biosorption reactions. In addition the surface of biomass may be damaged at high temperature and thus the ability of metal sequestering would be lowered.

2.4.3 Effect of Initial Metal Concentration:

The effect of initial concentration on the biosorption capacity was examined. Different initial concentrations for a fixed concentration of biomass were investigated. In case of low concentration, a relatively slower transfer due decreased diffusion coefficient and decreased mass transfer were observed which was in accordance with the observations made by Aksu and Ferda, 2004. The higher concentrations the available sites of biosorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The inverse relationship between initial metallic concentration and biosorption rate has been well documented. Binding sites are quickly filled at higher concentration resulting a decrease in breakthrough time [Pant and Singh, 2006].

2.4.5 Co-adsorption of metals

Biosorption is mainly used to treat wastewater which may contain more than one type of metal ions. The removal of one metal ion may be influenced by the presence of other ions. For example it has been observed that the uptake of Uranium was not affected by the presence of Mn, Co, Cu, Cd, Hg, and Pb in solution. In contrast the presence of Fe^{+2} and Zn^{+2} influenced the biosorption [Deng and Bhai, 2004; Deng and Ting, 2005].

Industrial waste waters are composed of various kinds of metallic ions. They influence the biosorption phenomena due to competition between them. Benjamin and Leckie, 1981, put forward the biosorption edge curve model according to the model, metal uptake was observed with pH change while metal ions concentration was kept constant. Cowan *et al.*, 1991, gave another approach, to observe the metal uptake by change in metal ion concentration at initial pH value. The approach was simple to work with biosorption isotherms. Gadde and Laitinen, 1974, studied biosorption by competitive ions and founds that 645 of Zn^{2+} displacement when equal amount of Pb^{2+} was added to the solution at a pH of 6. The results showed no significant difference when the order of metal addition was reversed. Zasoski and Burau, 1988, examined the competitive behavior of Cd^{2+} and Zn^{2+} on hydrous manganese oxide they found that the biosorbent sites have two energy levels. Higher energy site accepts Cd^{2+} more and the visa versa. While Cd^{2+} biosorption decreased by 25% in the presence of equi molar Zn^{2+} concentration

while it declined to 50% for Zn^{2+} in the presence of Cd^{2+} . Christophi and Axe, 2000, investigated competitive biosorption of lead, copper and cadmium on goethite. They found that the equilibrium constant for lead was greater than that of copper which was not in agreement with their hydrated radii i.e. $\text{Pb} < \text{Cu}, \text{Cd}$.

Biosorption models can be classified into two kinds: equilibrium and kinetic models. If the model is considering time as a variable, they are called kinetic models or otherwise they are equilibrium models.

3. Biosorption Isotherms and Kinetics

The analysis and design of biosorption process require the relevant biosorption equilibrium isotherms, which is the most important piece of information in understanding the biosorption process. The different parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insight into both the biosorption mechanism and the surface properties and affinity of biosorbent.

The biosorption isotherms are the plots of solute concentration in the adsorbed state as a function of its concentration in the solution at constant temperature. When an isotherm is made by plotting residual equilibrium concentration of the solute in solution versus concentration of the solute on the biosorbent, it provides valuable informations about biosorption phenomena which are useful for the selection of a biosorbent. It also helps to evaluate the feasibility of the biosorption process for a given application. In our studies three models for biosorption of metals, viz. Langmuir, Freundlich and Temkin models, are used for the evaluation of the biosorption data.

3.1 Single Component System

3.1.1 The Langmuir model

The Langmuir model is for monolayer biosorption. The equation for this model is derived from simple mass action kinetics. This model is based on two assumptions

- the forces of interaction between adsorbed molecules are negligible and
- Once a molecule occupies a site no further biosorption takes place

The saturated monolayer biosorption capacity can be represented by the expression [Langmuir, 1918]:

$$\frac{C_e}{q_e} = \frac{1}{q_l} C_e + \frac{1}{q_l K_l} \quad (3.1)$$

q_l is the maximum metal adsorbed per gram of biosorbent material, (biosorption capacity) (mg/g)

C_e is the residual concentration in solution (mg/L)

q_e is the equilibrium uptake corresponding to the site saturation (mg/g)

K_l is the Langmuir biosorption constant (L/mg)

The Langmuir equation is applicable to homogeneous biosorption where the biosorption of each adsorbate molecule onto the surface has equal biosorption activation energy [Aksu, 2004]

3.1.2 The Freundlich model

Freundlich model was used for biosorption as a special case for heterogeneous surface energy in which the energy term in the Langmuir equation varies as a function of surface coverage strictly due to variation of the biosorption [Aksu, 2004]. The Freundlich equation is given as [Freundlich, 1906]:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (3.2)$$

where K_f is an indicator of the biosorption capacity (mg/g)

$1/n$ is the biosorption intensity L/g, i.e.,

K_f and $1/n$ can be determined from the linear plot of $\log q_e$ versus $\log C_e$. These Freundlich biosorption constants, K_f describes the biosorbent capacity and $1/n$ tells about the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium [Keith *et. al.*, 1999].

3.1.3 The Temkin model

Temkin and Pyzhev considered the effects of indirect adsorbate-adsorbate interactions on biosorption system. The authors noted that the heat of biosorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbate interactions. This isotherm assumes that a solid surface is composed of small areas of equal size, at every area of which Langmuir's isotherm holds independently.

Temkin isotherm, which considers the effects of the heat of biosorption that decreases linearly with coverage of the adsorbate and biosorbent interactions, is given as [Temkin and Pyzhev, 1940].

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \quad (3.3)$$

The linear form of above equation is

$$q_e = B \ln A + B \ln C_e \quad (3.4)$$

Where $\frac{RT}{b} = B$

R is gas constant 8.314 J/mol $^{\circ}$ K

T is temperature, $^{\circ}$ K

The biosorption data can be analyzed according to the above equation. Therefore, a plot of q_e versus $\ln C_e$ enables the determination of the constant A and b where B is the slope.

3.2 Multicomponent System

The problem associated in describing the biosorption of metal ions from waste streams is that the waste waters contain more than one type of metal ions. When several components are present then there is an interference and competition phenomenon for biosorption sites. Multicomponent system of metal ions leads to a more complex mathematical formulation of the equilibrium. One of the isotherms proposed to describe equilibrium and competitive biosorption for such a system is a modified Langmuir model.

3.2. 1 The Modified Langmuir model

This model based on the same hypotheses as for the single-component Langmuir model and also assumes identical saturation capacities for all components. It was first modified by Butler and Ockrent [McKay et al., 1989]. For several components in one biosorption system the isotherm equation is given below:

$$q_{e,i} = \frac{Q_i^o b_i C_i}{1 + \sum_{j=1}^n b_j C_j} \quad (3.5)$$

- $q_{e,j}$ the adsorbed quantities of the first and the second metal ions per gram of dried biomass, (mg/g)
- Q_i^o Individual Langmuir biosorption constants of the first and second metal ions show the max amount of metal ions bound to biomass
- b_i, b_j Individual Langmuir biosorption constants of the first and the second metal ions related to the affinity of the binding site, respectively,
- C_i, C_j Unadsorbed concentrations of the first and second metal ions at equilibrium (mg/L)

This model is only applicable when each of the adsorbate in the multicomponent system obeys the Langmuir single component biosorption behavior. For a bisolute system, the linear form of the isotherm is given as [Bellot and Condoret, 1993]:

$$\frac{C_1}{C_2 q_{e,1}} = \frac{b_2}{b_1 Q_1^0} + \frac{C_1}{C_2 Q_1^0} \quad (3.6)$$

$$\frac{C_2}{C_1 q_{e,2}} = \frac{b_1}{b_2 Q_2^0} + \frac{C_2}{C_1 Q_2^0} \quad (3.7)$$

Where the subscripts 1, 2 representing the two species in the bisolute system.

The basic assumptions for this model are the same as that of the Langmuir component model : homogeneous surface energies of biosorption; no interaction between adsorbed species ; single-layer biosorption; equal availability of biosorption sites to all species ; reversible biosorption, and maximum biosorption equivalent to saturated monolayer biosorption of solutes [Weber, 1972; McKay *et. al.* , 1989]. One major criticism of this model is that it violates the Gibbs biosorption equation and it is thermodynamically inconsistent [Radke *et. al.* , 1972b].

The fact that the Langmuir isotherm does not usually fit single-solute isotherm data very well may discourage one from using its multicomponent form. In spite of this the Langmuir isotherm is probably the most commonly known model.

3.2.2 The Langmuir extension first-approximation model

As the Langmuir multicomponent isotherm is very general and sometime does not fit data very well, some researchers modified it to predict biosorption of two competitive isomers [Lin *et al.* , 1989]. For this purpose one additional assumption is made i.e., the rate of biosorption and desorption of each compound are linear functions of the concentrations of both the compounds' in the stationary and the mobile phases respectively. This means that there are molecular interactions in both the solution and the adsorbed monolayer.

As a first approximation, the influence of species 'i' concentration on species 'j' and the rate of desorption is neglected. The modified isotherm for the binary system takes the shape as:

$$q_1 = \frac{A_1 C_1 + A_{12} C_1 C_2}{1 + B_1 C_1 + B_2 C_2 + B_{12} C_1 C_2} \quad (3.7)$$

$$q_2 = \frac{A_2 C_2 + A_{21} C_1 C_2}{1 + B_1 C_1 + B_2 C_2 + B_{12} C_1 C_2} \quad (3.8)$$

This isotherm has no linearized form for plotting. Apart from the Langmuir single-solute parameters A_i and B_i which correspond to Q^0 and b in the Langmuir multi component isotherm for species i , the cross terms A_{ij} and B_{ij} are used to account for the interactions between the two components in the mixture. These cross terms depend on the rate constant of biosorption and biosorption of the two components, and their molecular interaction. One can use least squares fitting to determine these cross terms, but the process is rather time-consuming. The researchers who derived this isotherm restricted its application to competitive isomers but its application for other compounds has not yet been explored. It has been noted that the biosorption experiment of the competitive isomers, the experimental data and the calculated values from the isotherm was better for high concentration than for low concentration [Lin *et al.*, 1989].

The disadvantages of this model are

- It violated Gibbs biosorption equation and thermodynamically inconsistent
- Difficult to find biosorption behavior following Langmuir behavior, too ideal; or Langmuir model cannot provide reasonable fit for many single solute isotherm data.

3.2.3 The Langmuir partially competitive multicomponent model

Since the Langmuir multicomponent isotherm assumes complete competition, Jain and Snoeyink, 1973, modified the isotherm so that it would allow partial competition during biosorption of two species. The isotherm is as follows:

$$q_1 = \frac{(Q_1^0 - Q_2^0) b_1 C_1}{1 + b_1 C_1} + \frac{Q_1^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (3.9)$$

$$q_2 = \frac{Q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (3.10)$$

Where

$$Q_1^0 > Q_2^0$$

$$Q_1^0 = \text{Initial concentration of specie 1}$$

The assumptions for this isotherm are

- Biosorption without competition occurs when Q_1^0 does not equal to Q_2^0 , and
- The number of sites for which there is no competition is equal to $(Q_1^0 - Q_2^0)$, where $Q_1^0 > Q_2^0$.

When $Q_1^0 = Q_2^0$ there is no competition and hence, this isotherm will reduce to the original Langmuir multicomponent isotherm.

The first term of the q_1 accounts for the mass of species 1 biosorbed without competition on surface area which is proportional to $(Q_1^0 - Q_2^0)$. The second term, which is based on the original Langmuir multicomponent isotherm, refers to the mass of species 1 biosorbed on surface area that is proportional to Q_2^0 under competition with species 2. The q_2 expression is the mass of species 2 adsorbed on surface areas that is proportional to Q_2^0 under competition with species 1. This isotherm is only applicable to bisolute systems which involve solutes with large differences in molecular size or chemical properties [Jain et al., 1973; McKay et al., 1989].

This model is valid for bisolute systems involving dissimilar solutes, account for partial competition instead of complete competition, parameters are derived from single-solute data. The only disadvantage associated is that the isotherm is not applicable for more than two species.

3.2.4 The Freundlich multicomponent model

The Freundlich single component isotherm can be expressed in two different ways; even so, the basic concept is generally the same. The main decisive factor for using this model is that each

component individually obeys the Freundlich single component isotherm. It is assumed that for each component, there is an exponential distribution of biosorption energy which is equivalent to the distribution function in the single component system. On the other hand the multicomponent isotherm takes the form [Fritz and Schlunder, 1974]:

$$q_i = K_i C_i \left(\sum_{j=1}^k a_{ij} C_j \right)^{n_i-1} \quad (3.11)$$

For a bisolute system, the isotherm will be as

$$\frac{C_1}{C_2} = \frac{1}{C_2} \beta_1 - a_{12} \quad (3.12)$$

$$\frac{C_2}{C_1} = \frac{1}{C_2} \beta_2 - a_{21} \quad (3.13)$$

On simplification the above equations become

$$C_1 = \beta_1 - a_{12} C_2 \quad (3.14)$$

$$C_2 = \beta_2 - a_{21} C_1 \quad (3.15)$$

where $\beta_i = \left(\frac{K_i C_i}{q_i} \right)^{1/1-n_i}$

a_{ij} = the competition coefficient for the system , and

$$a_{ij} = 1/ a_{ji}$$

There are two ways to determine a_{ij} and the method of determination depends on the biosorption process. If one component's concentration is kept constant throughout the biosorption process, the slope of the plot of C_i versus β_i will be 1 and the intercept will be $a_{ij} C_j$. If both components

vary in concentration during biosorption, then the slope of the plot C_i/C_j versus β_i/C_j when $i \neq j$ will be 1 but the intercept will be $-a_{ij}$. If one set of single-solute Freundlich parameters (K_i, n_i) represents a restricted range of equilibrium concentrations, then various sets of biosorption coefficients are necessary to describe other ranges of concentrations .

LeVan *et al*, 1981, criticized the Freundlich isotherm that it has failed to satisfy the Gibbs biosorption isotherm. Since the Freundlich isotherm fits many single-solute systems very well, there is incentive to use its multicomponent form. Sheintuch *et al*, 1988, reported that this model has been successful in fitting bisolute and trisolute systems.

The model is suitable for highly heterogeneous surface. The disadvantages attached with its operations are

- Its only an empirical isotherm
- It may need to use various sets of biosorption parameters to describe all ranges of concentration
- It needs multicomponent data to find a_{ij}

3.2.5 The Crittenden *et al.*'s IAS-Freundlich isotherm model

There have been many tries to simplify the IAS Model and its combination with Freundlich isotherm was successful because it uses only one set of Freundlich parameters. The explicit nature of this isotherm also makes calculations easier [Crittenden *et al.*, 1985]. For several components the IAS-Freundlich equation is:

$$C_i = \frac{q_i}{\sum_{j=1}^N q_j} \left(\frac{\sum_{j=1}^N n_j q_j}{n_j K_i} \right)^{n_i} \quad (3.16)$$

Where i, j are the sorbates in the multi component system. For a binary system, we can write the above equation as:

$$C_1 = \frac{q_1}{q_1 + q_2} \left(\frac{n_1 q_1 + n_2 q_2}{n_1 K_1} \right)^{n_1} \quad (3.17)$$

$$C_2 = \frac{q_2}{q_1 + q_2} \left(\frac{n_1 q_1 + n_2 q_2}{n_2 K_2} \right)^{n_2} \quad (3.18)$$

C_1 and C_2 are the amounts of solute 1 and 2 remaining in the solution at the equilibrium with the amounts adsorbed q_1 and q_2 on the surface of biomass, respectively. n_1 and n_2 are the inverse of slopes of Freundlich isotherms for the species 1 and 2 respectively. K_1 and K_2 are the intercepts of Freundlich isotherms for the species 1 and 2 respectively.

Crittenden *et al.*'s IAS-Freundlich isotherm is based on the Freundlich equation

$$q_e = KC^{1/n}$$

and it requires only one set of Freundlich parameters for each component because it is used where no curvature is observed in their single-solute isotherms. As a result, any system that utilizes this isotherm, its adsorbate is assumed to have linear behavior in the Freundlich single solute log-log plots. This model is simpler than other models and is claimed to fit experimental data better than other models. It is based on single-solute data only.

Some of the disadvantages of this model are:

- i-This model cannot be used if single-solute isotherm data show curvature on Freundlich log-log plot.
- ii. It can be used only if extrapolation of Freundlich isotherm to high and zero surface coverages do not result in significant errors in calculating.

3.3 Biosorption Kinetics

3.3.1 Pseudo-First-Order Model

The pseudo-first order of the equation of Lagergren and Kunglia is expressed as

$$\frac{dq_e}{dt} = k_1(q_e - q_t) \quad (3.19)$$

k_1 is the rate constant of pseudo-first order biosorption (1/min)

q_e is the amount adsorbed corresponding to monolayer coverage on solid (mg/g)

q_t is the amount adsorbed at any time t (mg/g)

After integration and applying initial boundary conditions, $t=0$ to t and $q_t=0$ to q_t the above equation becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3.20)$$

The plot of $\ln(q_e - q_t)$ versus time t . the values of pseudo-first order rate constant were obtained from the slope of the straight line. The variation in rate should be proportional to the first power of concentration for strict surface biosorption. In spite of this, the relationship between initial solute concentration and rate of biosorption will not be linear when pore diffusion limits the biosorption process.

Ho and McKay, 1998, testified that the Lagergren first-order model represent only for the rapid initial phase of biosorption that occurs for a contact time of 0–30 min [Ho and McKay, 1998]. This suggests that it is not appropriate to use the Lagergren kinetic model to predict the biosorption kinetics for the entire biosorption period.

3.3.2 Pseudo-Second-Order model

The pseudo second order model which is known as Ho and Mc Kay model is given by

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3.21)$$

Integrating the equation for boundary conditions $q_t=0$ to q_t and $t=0$ to t , we get

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (3.22)$$

This is the integrated rate law for a pseudo second order reaction which can be rearranged to get a linear form as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.23)$$

Where

t is the contact time

q_e is the biosorption capacity at equilibrium, mg/g

q_t is the biosorption at time t , mg/g

k_2 is the rate constant, $\text{g mg}^{-1} \text{min}^{-1}$

The plot of t/q_t against t would give a linear relationship from which the q_e and k_2 can be determined, these are the slope and intercept of the plot.

4. Materials and Methods

4.1 Preparation of Biomass

The biological material used in this study was Wheat straw (*Triticum sativum*). Common available type of crop was obtained from a farm outside Toronto. Wheat straw could be pretreated with alkali or acid. But in our study it was preferred to use this in natural form. The biomass was dedusted and freed from any possible foreign material. Further it was washed with tap water. And it rinsed with distilled water. It was dried at 60 °C till the achievement of constant weight, using an oven from Labline, Inc., Chicago, USA, which was equipped with hot air recirculation system. The dried material was cut into size of 5 mm for use in study.

All chemicals used in this study were of analytical grade and solutions were made with distilled water. Stock solutions of 1500 ppm were prepared for target metals by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (J. T. Baker., Mallinckrodt Baker Inc., New Jersey, USA) in distilled water. For further studies these solutions were diluted as per requirement.

0.1M solution of HCl and NaOH were used to adjust the initial pH of the solutions for experiments. For all batch experiments, glassware and bottles were washed with 6M HCl before use and washed and rinse with distilled water.

4.2 Concentration of Remaining Ions in Solution

Atomic biosorption Spectroscopy (AAS) has been used for years for the analysis of metals. Today these procedures are used more than ever in materials and environmental applications. This is due to the need for lower detection limits and the need for trace analysis in a wide spectrum of samples.

For every experiment 200 ml of metallic solution and 1000 mg of biomass was used. Different concentrations of solution 5.0, 25.0, 50.0, 100.00, 150.00 ppm were used to study the biosorption

behavior. The biomass suspensions were shaken at 120 rpm on a Jubalo Shaker (Germany) at different temperatures 20, 25, 30, 35 and 40 degree Celsius. The first 3 runs were monitored for 24 and 48 hours and no significant difference was found after 5-6 hours of biosorption process. So, for rest of experiments the length of a run was taken as 9 hours. The figure 4.1 gives a scheme for the sample collection

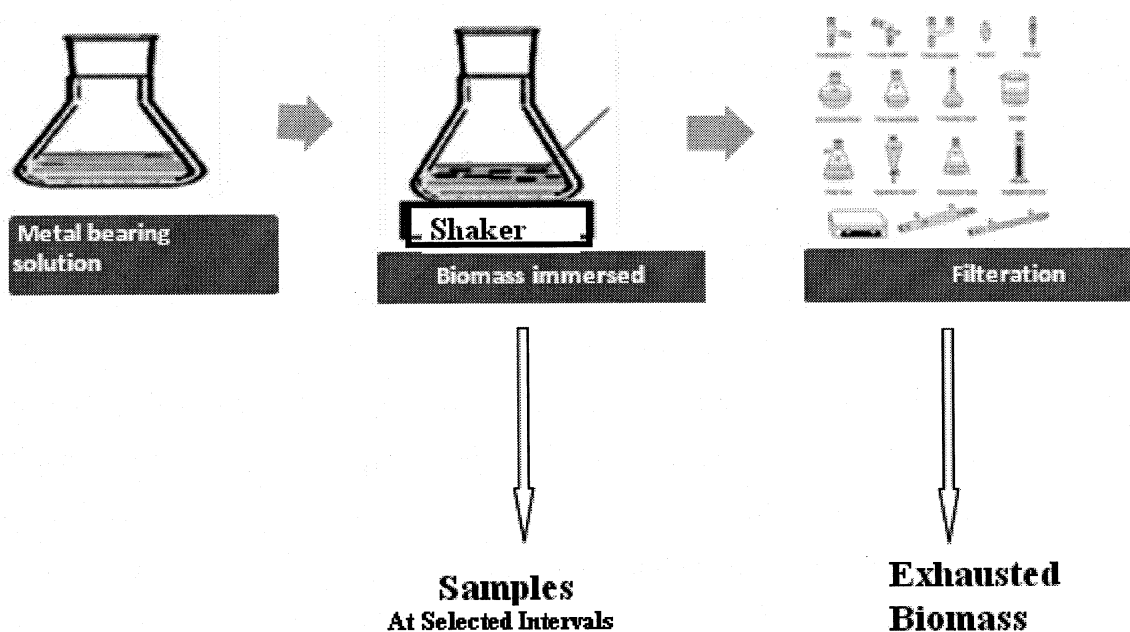


Figure 4.1: A Schematic for the Procedure of Sample Collection for Present Study

Samples were collected after every 30 min for whole length of experiment and the collected samples were stored at 4°C. At the end of experiment, the exhausted biomass was obtained by filtration of the reaction mixture. This biomass was subjected to microscopy i.e. Scanning Electron Microscopy (SEM). During the study the pH was also monitored. The liquid samples were collected in 100 ml glass bottle and then, Perkin-Elmer AAnalyst 300 atomic biosorption spectrophotometer with graphite furnace and flame technique was used to detect the metallic ions present in the solution. The figure 4.2 shows the changes in chemical composition during a typical biosorption on wheat straw. The lower curve represents the concentration remaining in the solution. The upper curve shows amount of metal ions adsorbed on the wheat straw throughout all the experimental run.

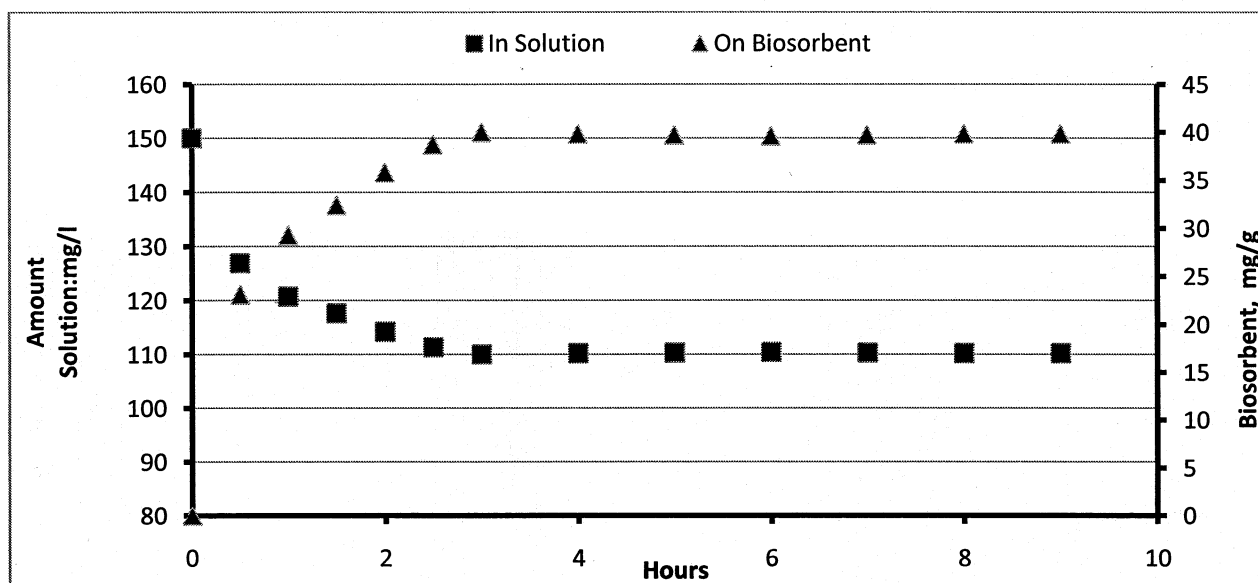


Figure 4.2: Equilibrium of the Amount of Metal Ions Adsorbed on the Solid Surface and the Amount Remaining in the Solution

Each element in the periodic table will have a specific ΔE that will absorb a specific wavelength of uv light. The relationship between the energy transition and the wavelength (λ) can be described by:

$$\Delta E = h/\lambda$$

where h is Planck's constant. Atomic biosorption uses this relationship to determine the presence of a specific element based on biosorption in a specific wavelength. For example, Ni absorbs light with a wavelength of 232 nm. Zn absorbs light at 213.9 nm.

The technique of atomic absorption spectroscopy (AAS) requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 °C. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths, as shown in the figure 4.3. The characteristic wavelengths are element specific and accurate to 0.01-0.1nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photon multiplier can detect the

amount of reduction of the light intensity due to biosorption by the analyte and this can be directly related to the amount of the element in the sample.

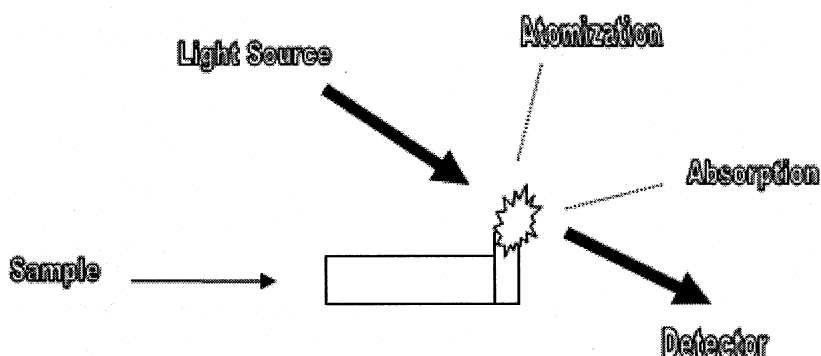


Figure 4.3: Operation of Atomic Absorption Spectroscopy

To examine the concentration of the unknown samples obtained from the biosorption experiments following steps were involved. First of all the blank adjustment was made with the distilled water. Secondly, calibration standards were used to generate calibration curves of Nickel and Zinc, separately. One element was detected at one time, within the set calibration range. Finally, properly diluted samples were subjected to analysis. And the report of the concentration of the element remaining in the solution under study was generated by software AAwinlab from Perkin Elmer.

4.3 Changes on the Surface of Wheat Straw Due to Biosorption

To discover any structural changes due to biosorption on wheat straw Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) were used where unused or natural wheat straw was taken as a reference. The SEM is a type of electron microscope capable of producing high-resolution images of a sample surface. It scans electrons across the target which reflects onto a fluorescent screen where the image is captured by a camera and enlarged. These images are three-dimensional appearance and are useful for judging the surface structure of the sample. Scanning electron microscope measurement was performed using JEOL, JSM-6380 LV, with accelerating voltage 20 kV and elemental analysis was performed by Energy

Dispersive Spectrometry (EDS) measurements using a INCA X-sight (Oxford instruments, UK.). As figure 4.4 shows, normally SEM is coupled with EDS.

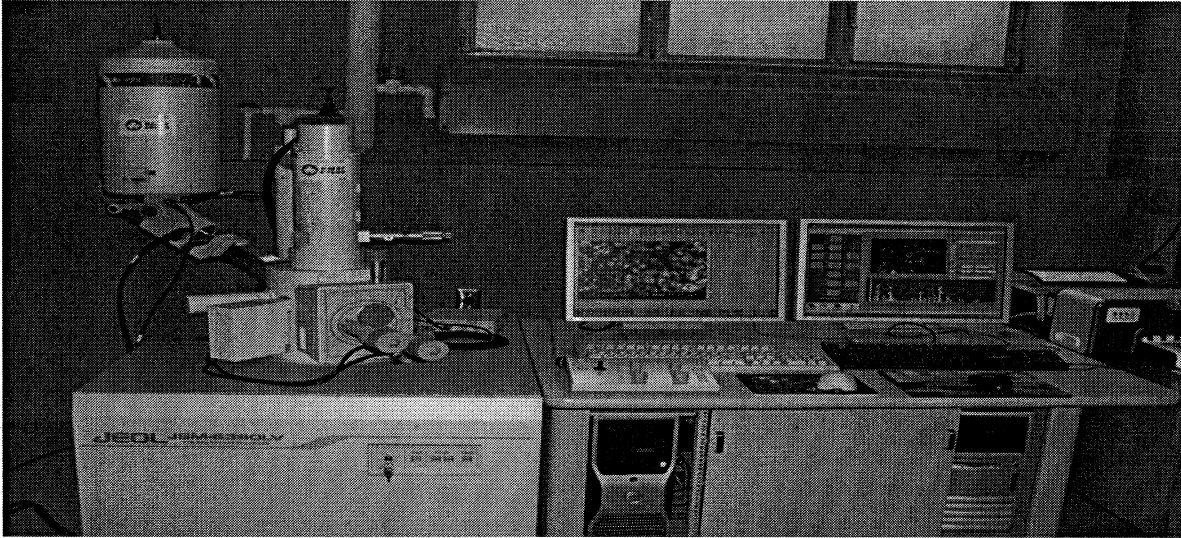


Figure 4.4: SEM Coupled with EDS

Being a type of spectroscopy, EDS relies on the investigation of a sample through interactions between light and matter. Its fundamental principle is that each element of the periodic table has a unique electron structure and thus, a unique response to electromagnetic waves. EDS operates by using a crystal of silicon or germanium to detect the x-rays. The x-ray spectrum can eventually be displayed as a histogram of x-ray intensity as a function of energy. The SEM is equipped with energy dispersive spectroscopy (EDS). EDS operates by using a crystal of silicon on germanium to detect the x-rays. The x-ray spectrum can eventually be displayed as a histogram of x-ray intensity as a function of energy. The detection crystal is kept under vacuum at liquid nitrogen temperature. In this process, x-rays of specific energies (hence of wavelengths) are generated when electrons transition from outer to inner orbital. Initial inner orbital electrons are kicked out by the impinging high energy electron.

In the figure 4.5 an electron in the K shell is ejected from the atom by the electron beam and creating a vacancy. An electron from K or l or M shell jumps in to the K shell to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and intern produce a vacancy

in the L or M shell. The low incident energies preferably of M then L and then K orbital can be detected.

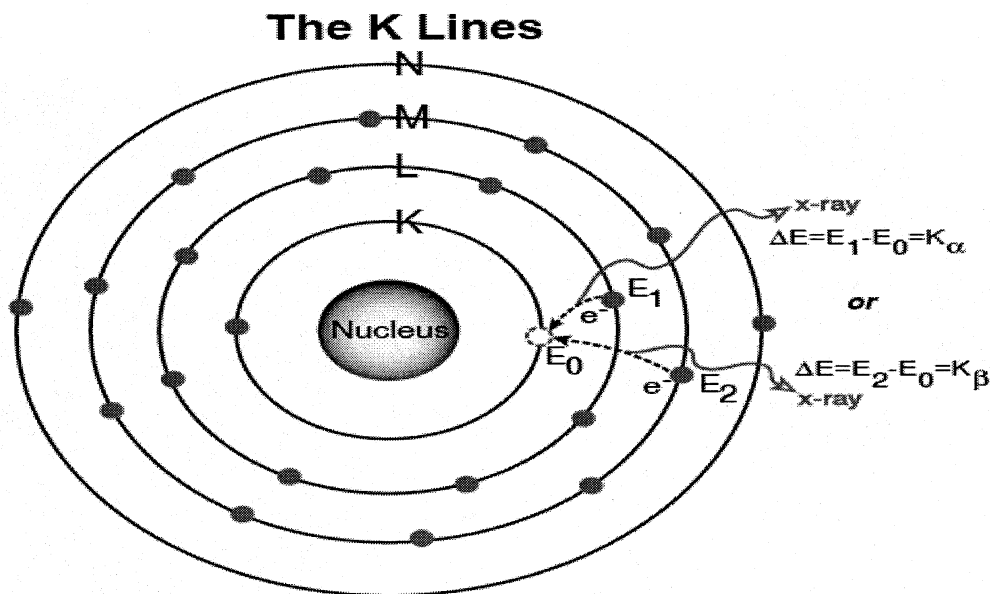


Figure 4.5: A Vacancy Formation

The SEM study is appreciated because, under normal conditions, it doesn't need any treatment of samples. It scanned, enlarged and presented what was actually present on the surface of wheat straw. If a sample surface is difficult to study the gold coating of sample is recommended. Samples were carefully selected and they were represented of the biosorption process. Next precaution was made while placements of samples on the analytic disk that that sample were completely dried. As microscopy was performed under vacuum conditions and with electron bombardment, a non-dry sample will be damaged.

4.4 FTIR

FTIR spectroscopic studies were performed on wheat straw samples using a Perkin-Elmer Spectrum One spectrophotometer. Fourier Transform Infrared (FTIR) spectroscopy is a chemical analytical technique, which measures the infrared intensity against wavelength (wave number) of light. Based upon the wave number, infrared light can be categorized as follows:

far infrared ($4 \sim 400\text{cm}^{-1}$),
 mid infrared ($400 \sim 4,000\text{cm}^{-1}$) and
 near infrared ($4,000 \sim 14,000\text{cm}^{-1}$).

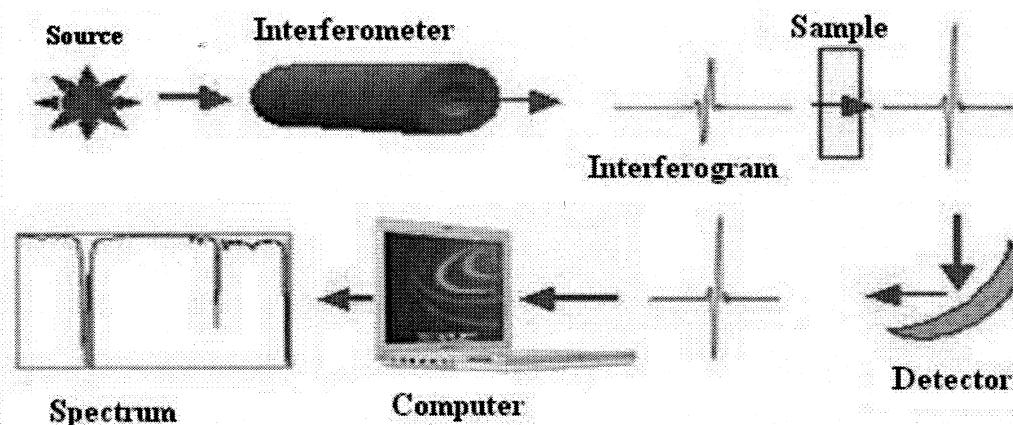


Figure 4.6: Schematic Illustration of FTIR

Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wave number range regardless of the structure of the rest of the molecule. For example, the C=O stretch of a carbonyl group appears at around 1700cm^{-1} in a variety of molecules. Hence, the correlation of the band wave number position with the chemical structure is used to identify a functional group in a sample. The wave number positions where functional groups adsorb are consistent, despite the effect of temperature, pressure, sampling, or change in the molecule structure in other parts of the molecules. Thus the presence of specific functional groups can be monitored by these types of infrared bands, which are called group wave numbers.

Carefully selected samples of wheat straw were ground to a size of -0.00126 inches mesh (32 microns) because the particle size was a key variable in a transmission measurement with the pellet method. Large particle size could result in the scattering of the energy, leading to the shift of the spectrum baseline and the broadening of IR bands might lead to misleading results. KBr pellet method was used to mount samples. Wheat straw samples were pulverized with KBr and

pelletized by help of a stainless steel micro-cup and a pneumatic press. Pellets prepared were placed in a desicator. All the pelletizing steps were taken in controlled temperature.

The prepared samples are mounted on the FTIR sample holder. The first step was to make a background scan. The purpose of the background was to remove contaminating peaks from the spectra of wheat straw sample. The in-built computer program does this automatically, by subtracting the background peaks from the spectrum. It was necessary to keep the background because we were going to take more spectra. Then FTIR was asked to analyze sample. Then the peak pick command was given to label the peaks of sample spectra and the final spectra for each sample were achieved. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam.

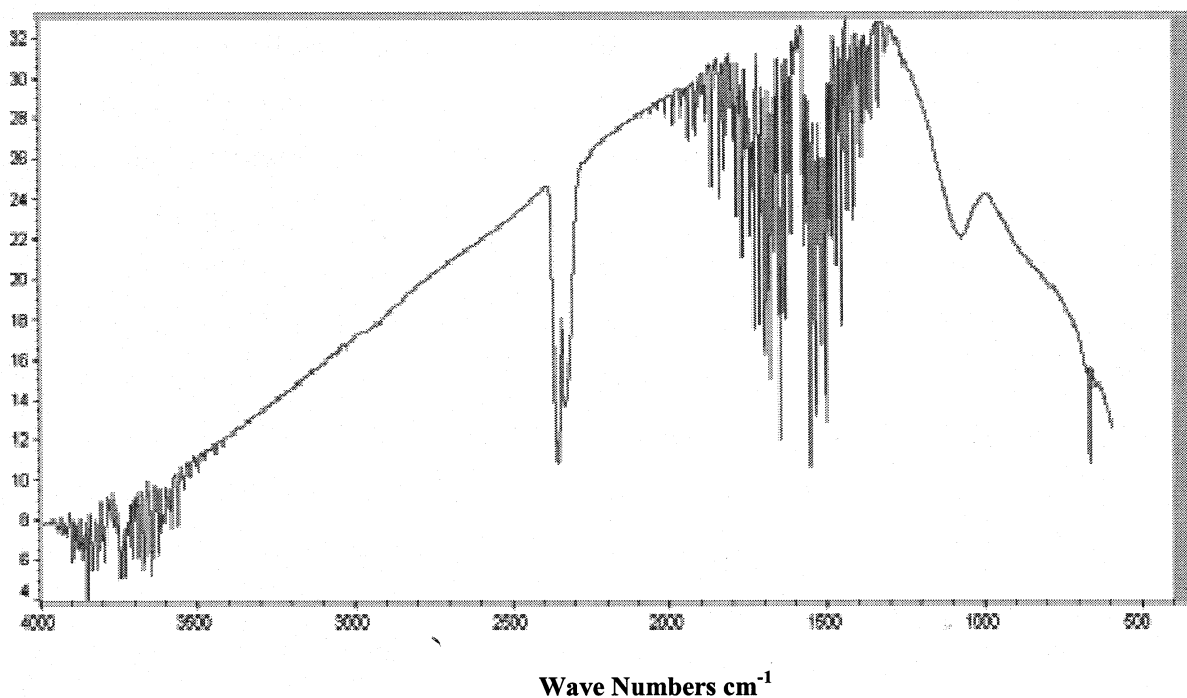


Figure 4.7 : Background Spectrum of KBr for FTIR Analysis

The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR biosorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library.

Unlike SEM inspection or EDX analysis, FTIR spectroscopy does not require a vacuum since neither oxygen nor nitrogen absorbs infrared rays. FTIR analysis can be applied to minute quantities of materials, whether solid, liquid, or gaseous. When the library of FTIR spectral patterns does not provide an acceptable match, individual peaks in the FTIR plot may be used to yield partial information about the specimen.

5. Results and Discussions

5.1 SEM Analysis:

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of a biosorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Thus the resolution of SEM is much higher than an optical microscope. Scanning electron micrographs of wheat shells were obtained by Bulut *et al*, 2007 while studying biosorption of direct dye blue on wheat shells. From the micrographs, they observed that wheat shells have considerable numbers of pores where there was a good possibility for dyes to be trapped and adsorbed into these pores. Wheat straw consists of cellulose, hemicelluloses and lignin chemically in the amount of 34-40 %, 30-35 % and 14- 15 %, respectively [Sun *et al*, 1998].

Cellulose, $(C_6H_{10}O_5)_n$, is an organic compound. It is a structural polysaccharide derived from beta glucose. Cellulose is the primary structural component of green plants. The primary cell wall of green plants is made of cellulose.

Hemicelluloses can be any of several hetero polymers (matrix polysaccharides) present in almost all cell walls along with cellulose. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicelluloses have a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicelluloses enzymes.

Hemicelluloses contain many different sugar monomers. In contrast, cellulose contains only anhydrous glucose. For example besides glucose, sugar monomers in hemicelluloses can have xylose, manose, galactose, rhamnose and arabinose. Hemicelluloses contain most of the D-pentose sugars and occasionally small amounts of L-sugars as well. Xylose is always the sugar monomer present in the largest amount but mannuronic acid and galacturonic acid also tend to be present. Unlike cellulose, hemicellulose (also polysaccharide) consists of shorter chain-around 200 sugar units as opposed to 7000-15000 glucose molecules per polymer seen in cellulose. Hemicellulose is branched polymer, while cellulose is unbranched.

Lignin is found in all vascular plants, mostly between the cells, but also within the cells, and in the cell walls. It makes vegetables firm and crunchy, and gives us what we call "fiber" in our food. It functions to regulate the transport of liquid in the living plant (partly by reinforcing cell walls and keeping them from collapsing, partly by regulating the flow of liquid), and it enables trees to grow taller and compete for sunshine. And researchers see it as a disposal mechanism for metabolic wastes. In nature it is very resistant to degradation, being held together with strong chemical bonds; it also appears to have a lot of internal H bonds. It is bonded in complex and various ways to carbohydrates (hemicelluloses) in wood. Lignin is actually not one compound but many. All are complex, amorphous, three-dimensional polymers that have in common a phenyl propane structure, that is, a benzene ring with a tail of three carbons. In their natural unprocessed form, they are so complex that none of them has ever been completely described, and they have molecular weights that may reach 15,000 or more. Lignins are not acids, though most of them contain certain carboxylic acids, and wood gives off acids as it deteriorates, as do paper and board that contain lignin.

Macroscopically, a wheat straw stem consists of internodes and nodes. Nodes are hard points where leaves are attached to the stem. The internodes are formed as concentric rings, leaving a void or cavity in the center, as shown in the figure 5.1.

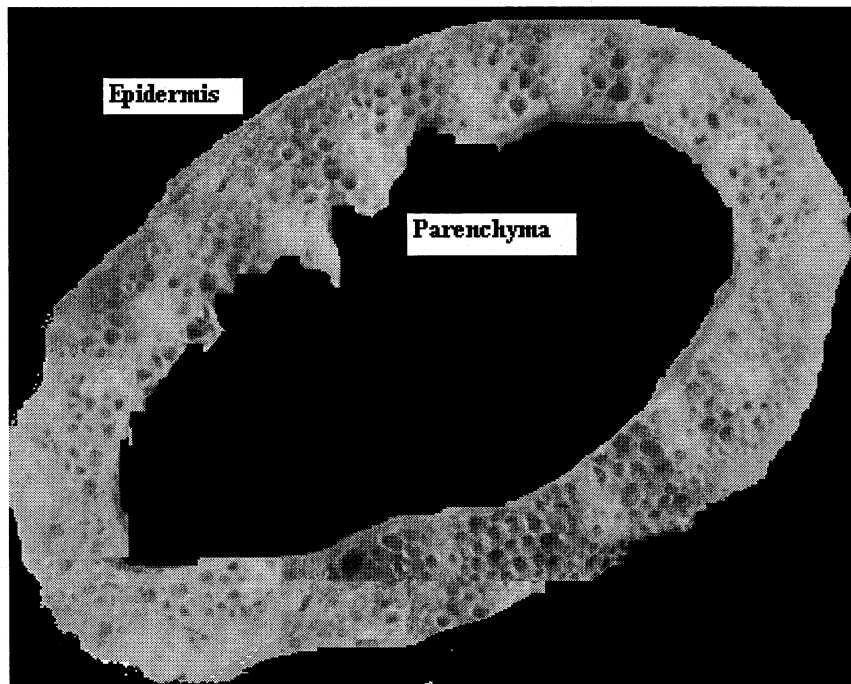


Figure 5.1: Structure of Wheat Straw (Transverse View of Internodes)

The outer most layer is a cellulose rich dense layer, called epidermis. Epidermis has a coating of silica on the surface. Beneath the epidermis is a loose layer containing parenchyma and vascular bundle [Hornsby *et al*, 1997a]. Parenchyma: Soft plant tissue made up of thin walled cells that form the greater part of leaves, stem pith, roots and fruit pulp. Vascular Tissues: Fluid carrying vessels e.g., sap-carrying vessels in plants, as shown in the figure 5.2.

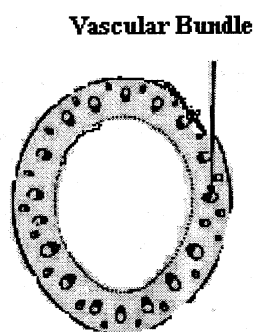


Figure 5.2: Conceptual Drawing of Vascular Bundles in Wheat Straw

In vascular bundles, some parts of dense lignified thickenings in the secondary wall arrange as the annular rings or the spiral structure to form the vessels. It was indicated that cellulose is the framework of the vascular bundles. The out layer is the primary wall and the annular and spiral structure is the lignified thickening secondary wall, which mainly consists of cellulose and surrounded by the primary wall [Liu *et al.*, 2005].

In the present study cellulose chains in the epidermis of wheat straw were observed with their orientation along the growth direction of wheat straw while those in parenchyma were observed with almost no preferred orientation. The surface shows heterogeneity of the smooth outer surface. There are thick lines of fiber, holes, silica particles, some rapture in the surface. Hole is in its natural features, Silica on particles is from cellulosic material or from the natural layer of wax made by silica. The silica is concentrated in the outer part of straw. The outer most internodal layer is comprised predominantly of epidermal cells and waxy protective layer, the cuticle. The epidermis is highly lignified and it contains silica. It has been suggested that in plant cells many cellulose chains are held together by hydrogen bonding between hydroxyl groups of the glucose monomers to form a cellulose fibril with indefinite length and varying degrees of crystallinity which embedded in a gel matrix composed of hemi cellulose, lignin and other

carbohydrates. Morphology and orientation of cellulose in the vessels of vascular bundles of wheat straw were studied by Merdy *et al*, 2002. The results indicated that cellulose acts as the framework in the vascular bundles and cellulose chains are high in orientation. In the thickening part of the vessels, cellulose exists in the form of cellulose crystalline lamellae. There are two kinds of morphologies on the surface of wheat straw. As in the figure 5.3, one is the fiber structure with fibrils of about 5 μm diameter (part a), and the other is the fiber structure with serration morphology at the edge of the fiber. The diameter of the latter one is about 10 μm (part b) which are shown in part c. The part d represents natural holes in surface for ventilation and metabolism.

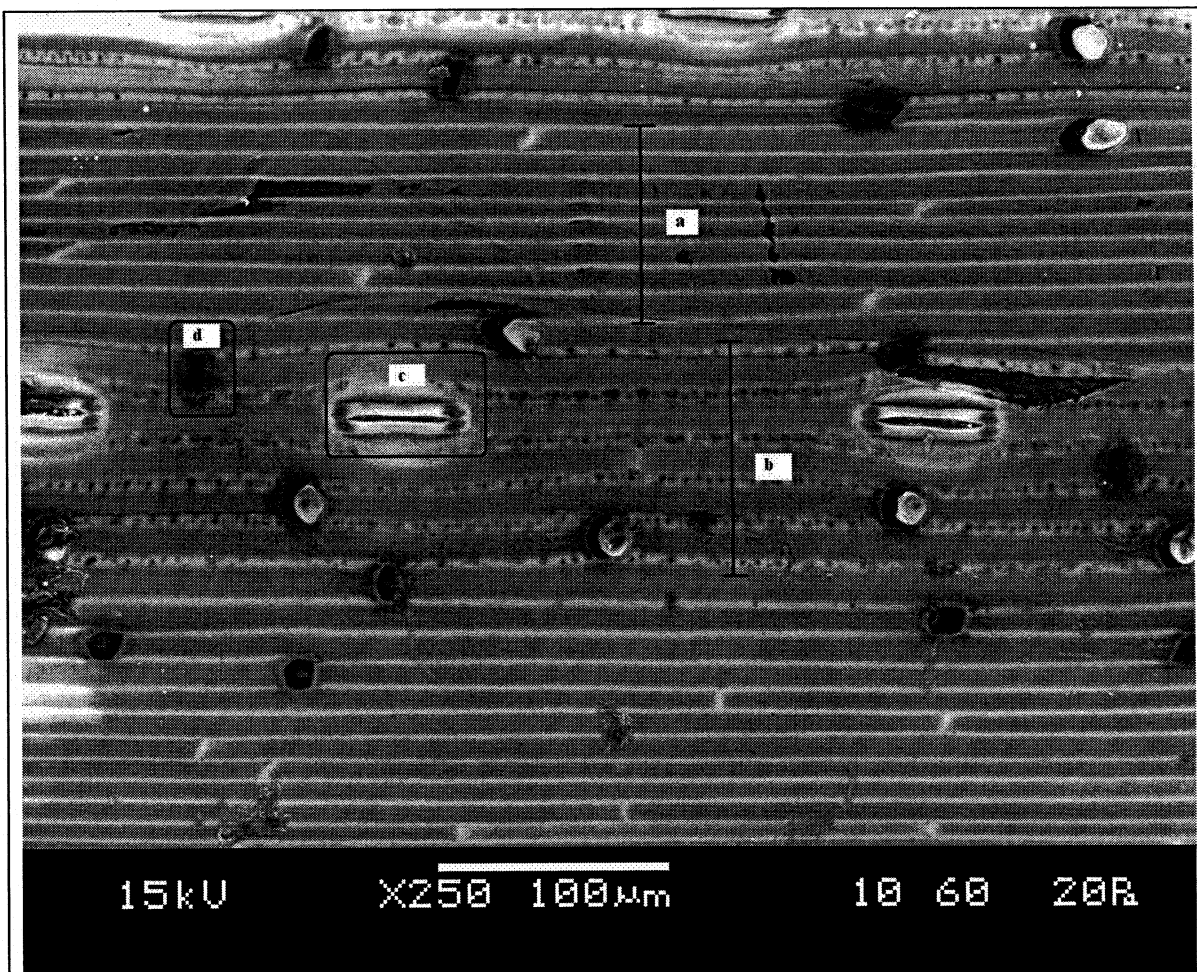


Figure 5.3 : Features of Outer Surface of Wheat Straw

Cellulose sugar molecules have -OH groups, between two threads these -OH groups make strong bonding with H groups of sugars and from. Water because of its polarity tries to get some affinity from this bonding and develop hydronium ions H_3O^+ . A part of the uptake of metal ions on the inner surface is because of making linkage between OH groups (as some are free because of some chain rupture etc) or because of some adjustment with H_3O^+ for H^+ .



Figure 5.4 : Inner Surface of Wheat Straw

The figure 5.4 shows vascular bundle their longitudinal view. The annular or spiral form structure in vessels is quite bright. The other bright holes show protoxylem trashed cells have dense lignified thickening in the surrounding walls. The other part is lignin which exists all around the cellulosic cells, between the cells and in vascular bundles. It provide bigger portion of sites for metal uptake due to its, large number of phenolic groups, hydroxyl groups, methoxy groups and carboxylic groups. With the degradation or breakage of higher aliphatic hydroxyl linkage, the carboxylic sites are increased, Thomson 1999 agreed with this observation made in this study. In the case of cereal straw, the outer most layer is compromised predominantly of epidermal cells and a waxy protective layer. The epidermis is highly lignified and it contains

silica [Yu *et al*, 2005]. In the present study it is presumed that wheat straw has similar characteristics as that of barley because they are in same biological family. It means that lignin in the outer surface is mainly responsible for the biosorption of metal on the outer surface. Figure 5.5 contains representative pictures of EDS studies for the microscopy of WS after immersion in distilled water. Spectrum 1 is obtained by analyzing a fiber, we know that fibers are made of cellulose which contain C, O, Si some other ions are also

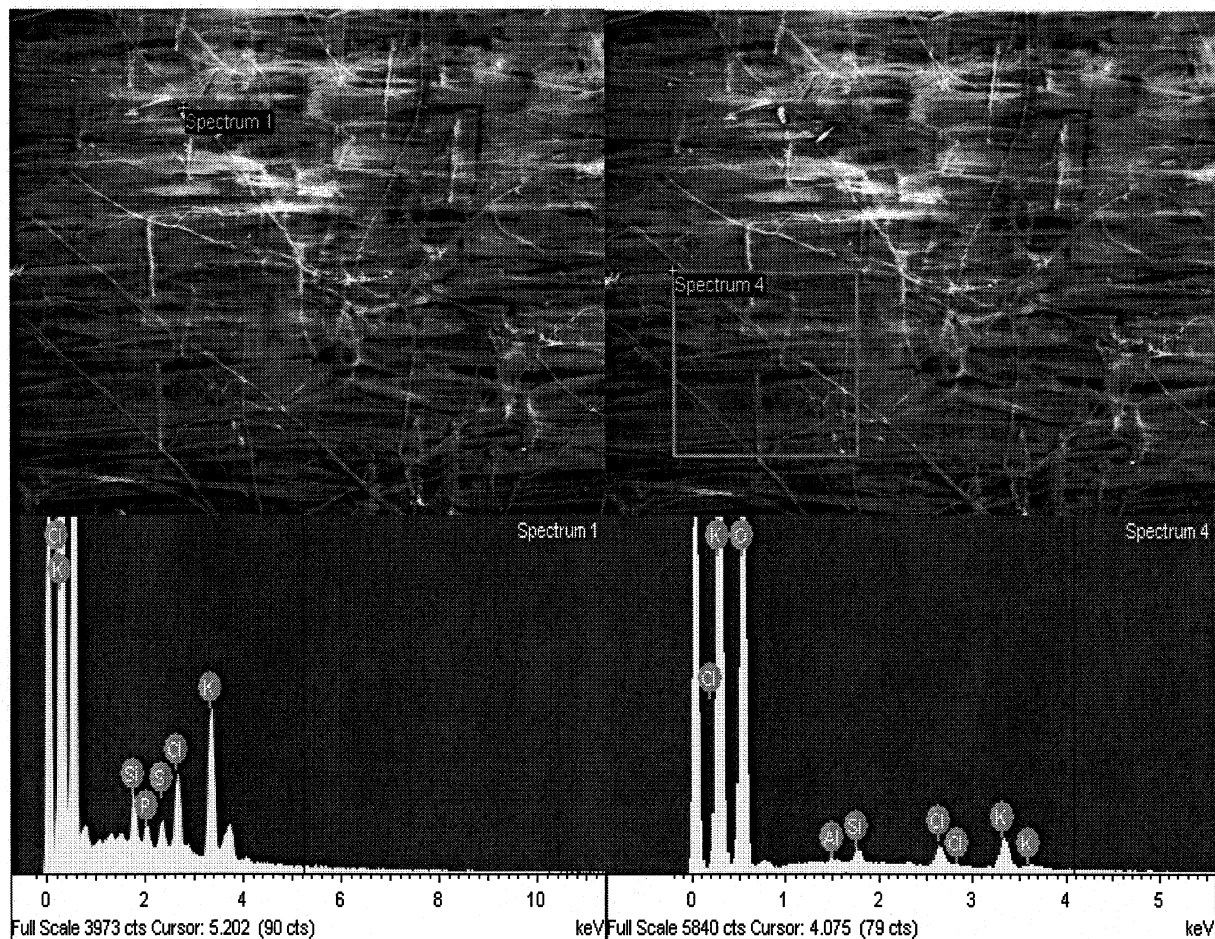


Figure 5.5 : Inner Surface of Wheat Straw on EDS (After Soaking with Distilled Water)

attached with these like, N, K, Al, Ca, S, Cl etc. The figure 5.6 b is of an area about 100 x 100 microns. Both pictures showed no attachment of any heavy metal in its native state. This idea was confirmed by testing over 40 samples of wheat straw collected from different places, randomly selected.

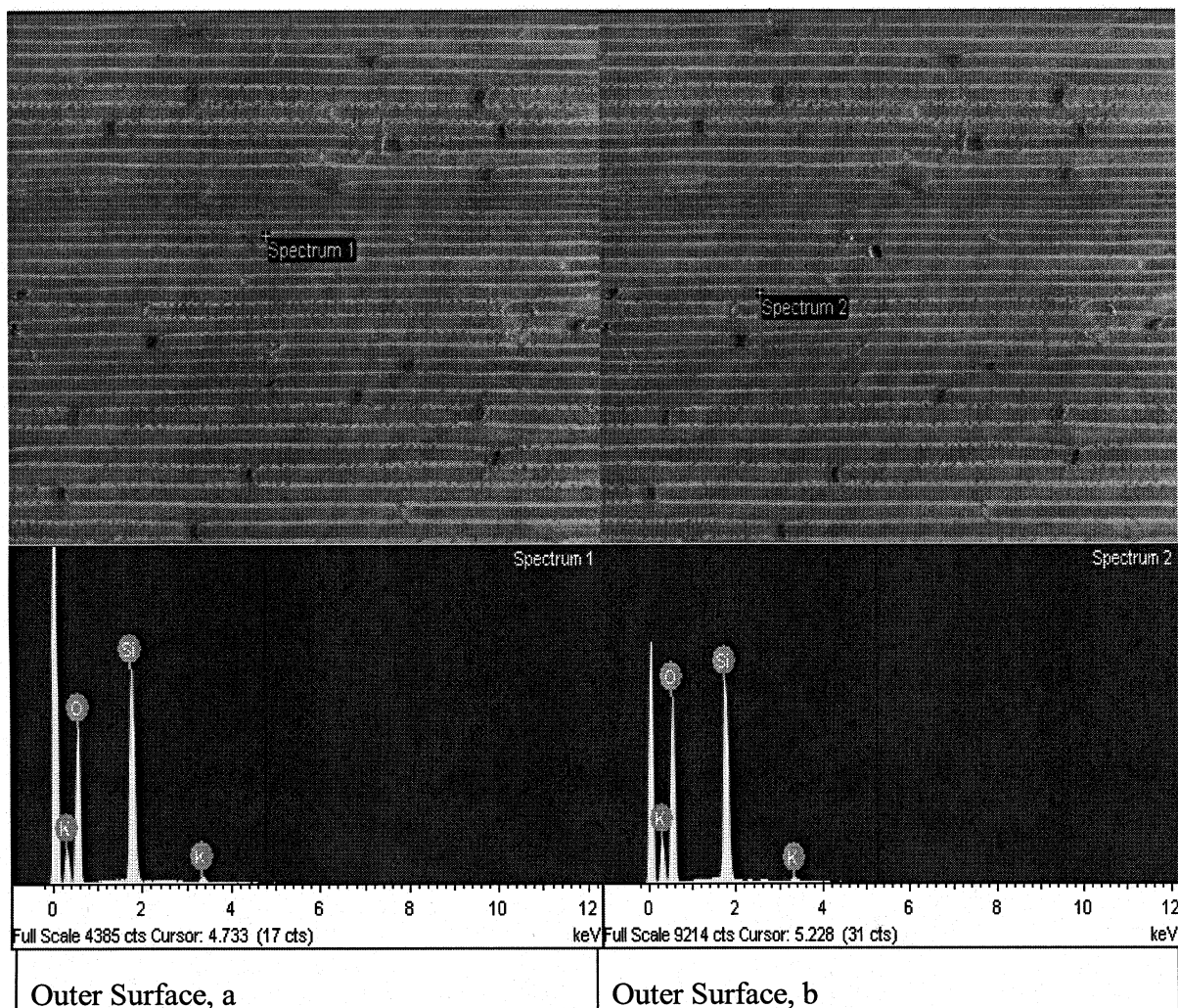


Figure 5.6 : Outer Surface of Wheat Straw at Biosorption with Ni^{2+}

Spectrum 1 and Spectrum 2 in figure 5.6 of these pictures have shown the elements which WS has in its structure. The big peak, not labeled is C (carbon). The following figure 5.7 is about the biosorption of Ni^{2+} on the inner surface of WS. The Part 'a' is analysis of a fiber which shows attachment of Ni^{2+} while the three big peaks are C, O and Si. A small amount of Al is present in the structure. The part 'b' is about an area $100 \times 100 \mu\text{m}$ and Ni^{2+} is present in that area. Figure 5.8 is about biosorption of Zn^{2+} ions on the inner surface of wheat straw. Part 'a' is about the biosorption on a fiber and part 'b' is about the area $100 \times 90 \mu\text{m}$. This area was selected because of some irregularities on the surface still it shows biosorption.

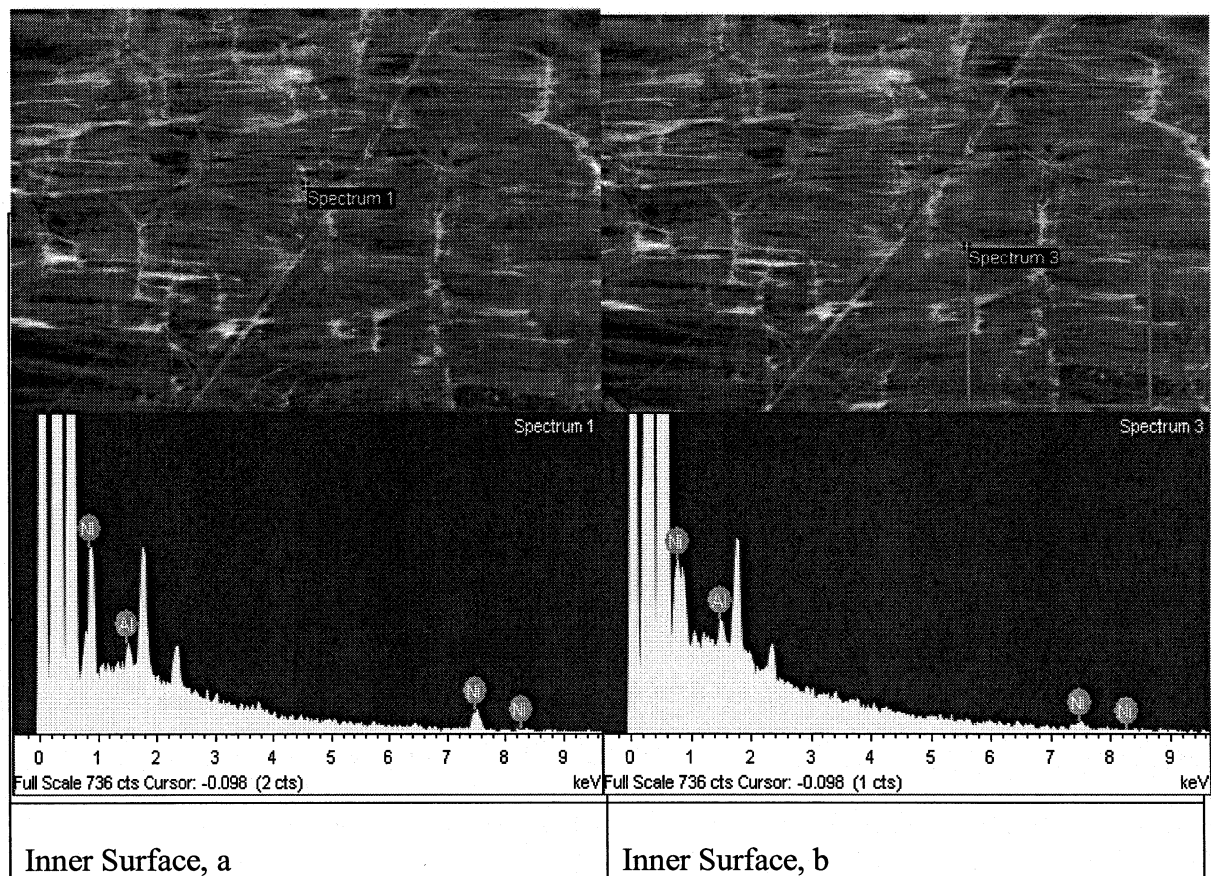


Figure 5.7: Biosorption of Ni²⁺ at the Inner Surface of WS

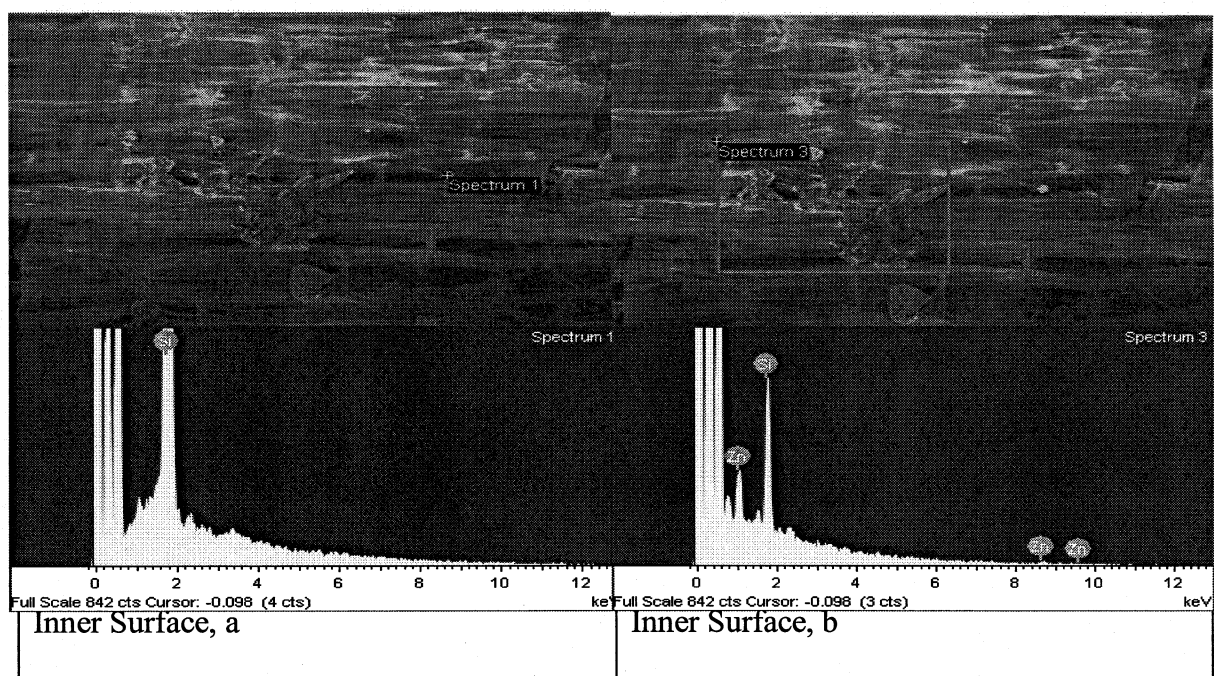


Figure 5.8 : Biosorption of Zn²⁺ on the Inner Surface of WS

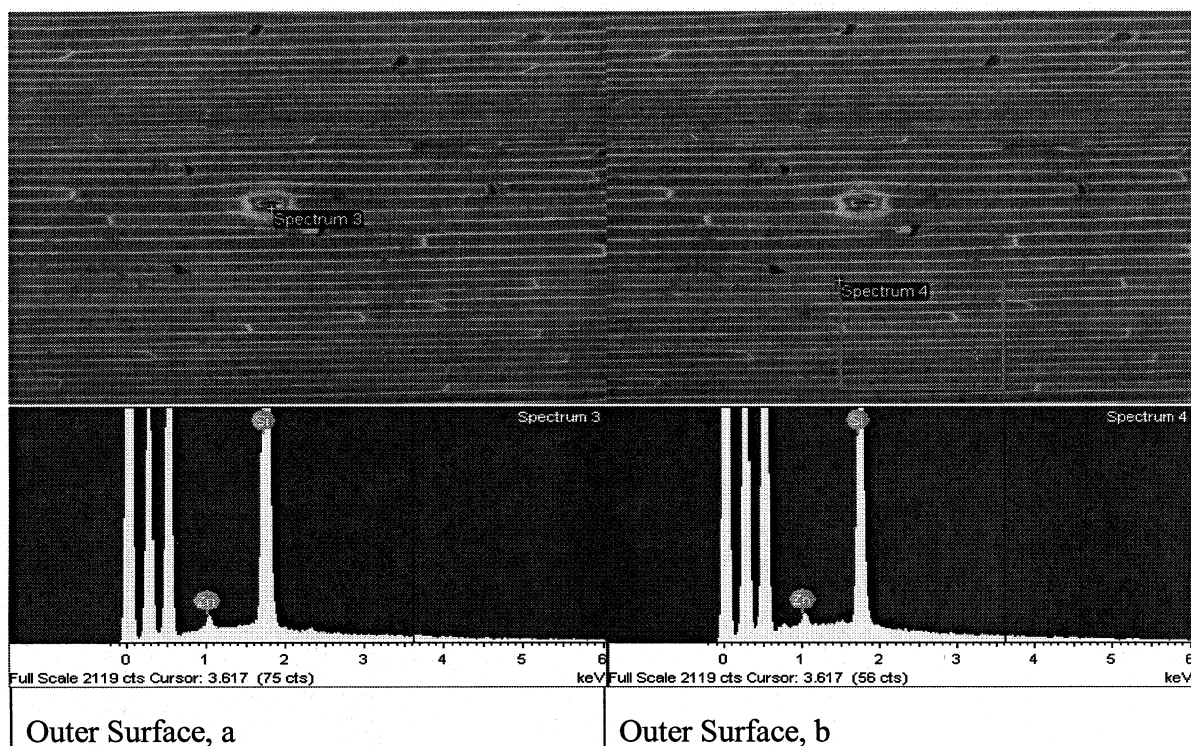


Figure 5.9 : Biosorption of Zn^{2+} on the Outer Surface of WS

Similarly figure 5.9 shows the biosorption on stomata cells (spectrum 3) which shows better biosorption of Zn as the other parts of WS. Figure 5.10 and figure 5.11 show biosorption behaviors of N^{2+} and Zn^{2+} . Irregularity of surface while studying outer surface, was of interest. But its biosorption behavior studied by microscopy under all biosorption experimentation conditions was about the same as other places. These micrographs give us chance to consider the relative degree of biosorption of Nickel and Zinc ions, at particular point under consideration. It has been observed that biosorption of Zn^{2+} is higher than the Ni^{2+} . It has been observed that the outer surface does not behave the same for two metals in a binary mixture. At 150 ppm, 25 °C at pH 6.3 the amount of Ni^{2+} adsorbed at stomata was almost double than that of Zn^{2+} . At the hole, the amount of Zn^{2+} adsorbed was three times of that Ni^{2+} . The fibrous structure was giving same opportunity for Ni^{2+} and Zn^{2+} to adsorb.

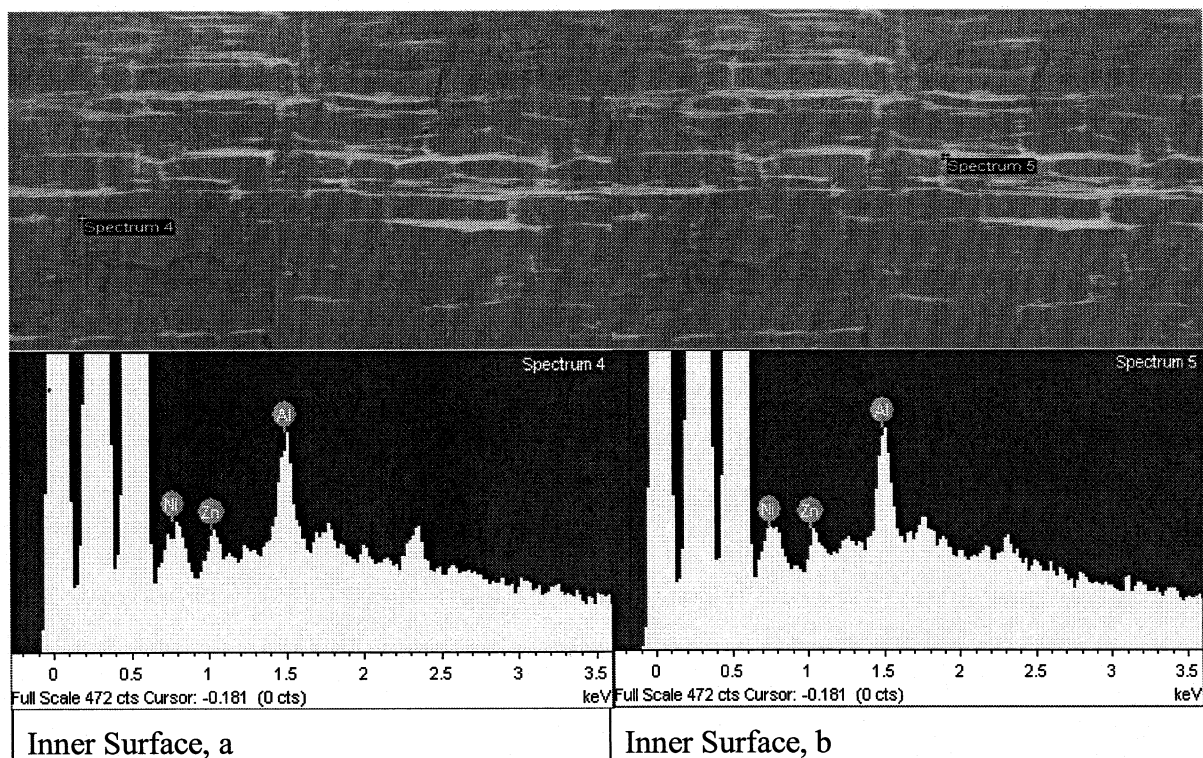


Figure 5.10 : Biosorption of Ni^{2+} and Zn^{2+} on the Inner Surface of WS

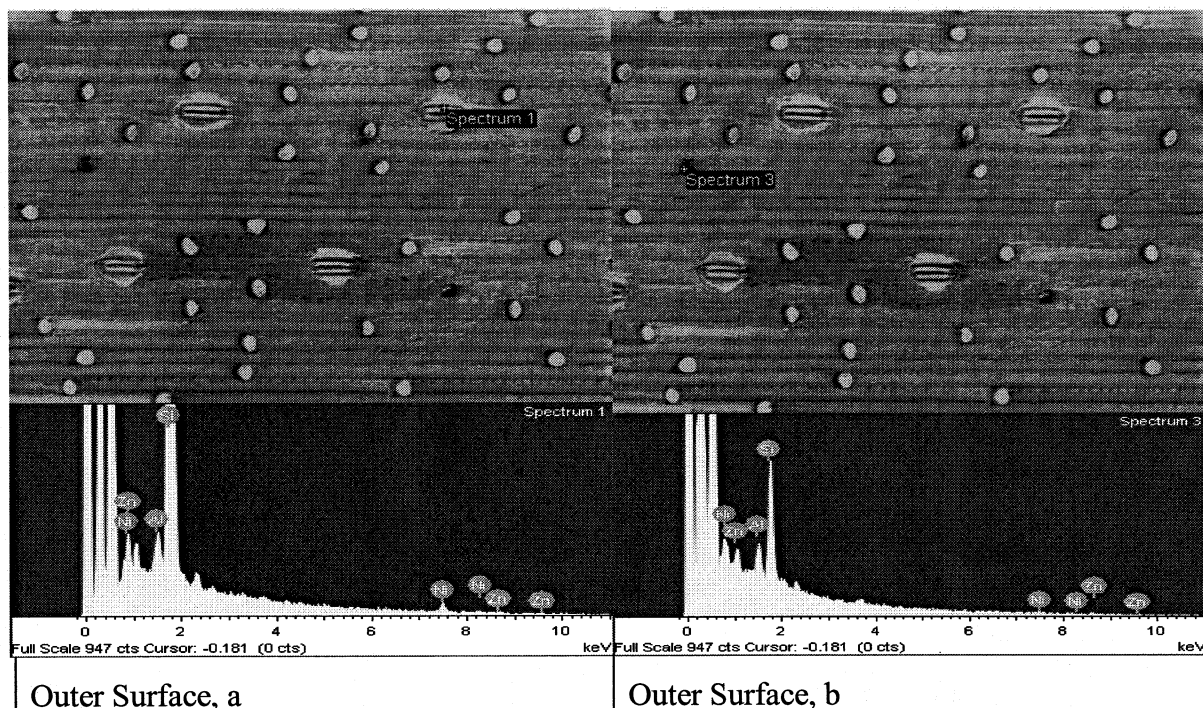


Figure 5.11: Biosorption of Ni^{2+} and Zn^{2+} on the Outer surface of WS

The biosorption of Cu^{2+} by wheat straw cell wall residue (CWR) was studied by Merdy, 2002, and revealed a relatively stable surface complexation on the acid sites of the substrate (carboxylic and phenolic moieties). A competitive effect on copper complexation has been shown which is presumably due to the calcium ability to form outer-sphere complexes far less stable than Cu^{2+} ones. Electron spin resonance and X-ray biosorption spectroscopy were combined to obtain information on the geometry and structure of Cu bound to CWR. At least two different binding sites for Cu^{2+} were found to take place in CWR. From ESR parameters, it can be deduced that Cu^{2+} when complexed with CWR are coordinated in a square-planar arrangement with four oxygen-containing groups. EXAFS and XANES experiments revealed that Cu^{2+} is surrounded by four oxygen atoms, with an average Cu-O equatorial

Several biopolymers such as humic substances of different types and origins (pine bark, moss, coals) or lignin showed an ESR signal at $g = 2.00$, attributed to organic free radicals [al Asheh *et al*, 1998], The important role of metal ions as acceptor of electrons is linked with the formation of these organic free radicals of semiquinone type. It has been established that the free radical concentration was highly dependent on the metal concentration.

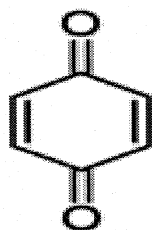


Figure 12 : P-benzo quinone

Though cellulose and hemicelluloses take part in biosorption but the lignin with its entire available radical and functional groups is the important material for biosorption process. The mechanism by which the metal reacts with the surface remained uncertain, and to our knowledge, no spectroscopic study of Zn^{2+} -wheat straw and Ni^{2+} -Wheat Straw complexes has been published yet.

5.2 FTIR Studies

As we know wheat straw is composed of cellulose, hemi cellulose and lignin. Lignin is well-known to have a good binding ability for minerals because it is composed of various complex chemical compounds hence offer various functional groups to interact [Lalvani *et al*, 1997] and it has been established that cellulose is a less efficient biosorbent because cellulose is a linear polymer which has more or less a stable structure due to its hydrogen bonding. [Wieber *et al*, 1988]. Lignin from wheat straw was analyzed by Merdy *et al*, 2002, their analysis is given in table 5.2.1:

Table 5.2.1 : Lignin Samples Analysis

Cell Wall Residues	
Saccharide Contents	µg/l
Arabinose	29.3
Galactose	5.1
Glucose	423.6
Xylose	296.7
Metal Contents	mol/g, dry weight
Cu	3.3×10^{-8}
Fe	1.6×10^{-8}
Mn	6.1×10^{-7}
Ca	4.5×10^{-5}
Mg	6.0×10^{-5}
Microanalysis Results	%
C	43.91
H	5.73
N	0.25
O	≈ 50
S	<0.05

They evaluated minerals by acid mineralization. It appeared that magnesium and calcium contents in cellulose wall residues were not negligible and occupies a part of the complexation sites. Some authors reported that they were strongly bound to the organic matter matrix, not displaced by acid washing, and not reduced or oxidized by chemical reagents [Sensi, 1990;

Jerzykiewicz, *et al.*, 1999]. In our EDS analysis Al, Na and Si were found on the wheat straw surface. It meant that numerous sites were also occupied by various metal cations (iron, copper, manganese and aluminum) and were not yet available for biosorption experiments. So, the displacement of alkaline earth cations bound by transition metal ions is expected during surface complexation. The major functional groups contributing in the biosorption were carboxylic and phenolic groups. They were present in an amount of 30 % and 70 % on the basis of total number of functional groups respectively [Merdy *et al.*, 2002]. Other active functional groups were guaiacyl, syringyl, methoxy, phenyl and phenylpropanoid radicals. The following table 5.2.2 is derived from the study of Lawther *et al.*, 1996,

Table 5.2.2 : Source of Functional Group

Functional Groups	Source in Wheat Straw
C-C or C-H	Lignin, hemicellulose
C-O	Lignin, carbohydrate
C=O	Lignin
O-C-O	Cellulose
O	O-C=O, Ph-C-O, Ph-, Ph-O-Ph C=O C-O, C-O-O, O-C-O
O=N=O	Lignin

Xylose was a predominant component sugar in all the hemi cellulosic fractions. Arabinose, glucose, and galactose were also present and vanillin and syring-aldehyde were found to be the major phenolics [Sun *et al.*, 2002]. Kiefer *et al.*, 1997, pointed out the FTIR beam can penetrate about 5 μm into the sample, so the functional groups identified from the spectrum could be only due to the surface of biosorbent.

The spectrum of wheat straw before biosorption was taken as a reference. The tables of biosorption peaks are given in the appendix B as B-7, B-8, B-9 and B-10 at page 158. In order to have a clear view the spectra of wheat straw would be considered first. The peaks in the range of 2924 cm^{-1} to 2850 cm^{-1} were due to methyl, methylene and methane group vibrations [Panteleeva *et. al.*, 1995]. The methyl group gave symmetric stretching vibrations at 2872 cm^{-1} and asymmetric stretch at about 2962 cm^{-1} . The peaks in the range of $1715 \pm 100\text{ cm}^{-1}$ were normally due to the presence of C=O group in the molecule [Panteleeva *et. al.*, 1995]. An

intensive broad band at 1646 cm^{-1} is indicative of the adsorbed water. A small sharp band at 903 cm^{-1} is characteristic of glucosidic linkages between the sugar units. [Rowell *et al.*, 1994]. The absorbance at 1520 , 1474 , and 1427 cm^{-1} relate to the lignin aromatic ring vibrations [Rana *et.al.*, 1997]. The point at 1509.37 cm^{-1} indicates that phenolic units were more abundant than carboxyl groups. The 1454.42 cm^{-1} is due to bending of CH_3 - while 1425.32 cm^{-1} is the OH and / or aromatic ring vibration [Klemm, *et. al.*,1998] . 1372.63 cm^{-1} represent C-H, OH or CH_2 bending. The peaks at 1320.72 , 1259.75 and 1162.65 cm^{-1} represent C-O bond vibration. At 1056.08 cm^{-1} is vibration of C-O-C and O-H of polysaccharides. 897.697 cm^{-1} is characteristic of glucosidic linkages between the sugar units in hemicelluloses and celluloses [Gupta, *et. al.*, 1987]. At 805.62 cm^{-1} and 697.45 cm^{-1} are out of C-H plane vibrations of monosubstituted hydrogen atom of benzene ring [Nakanisi, 1965].

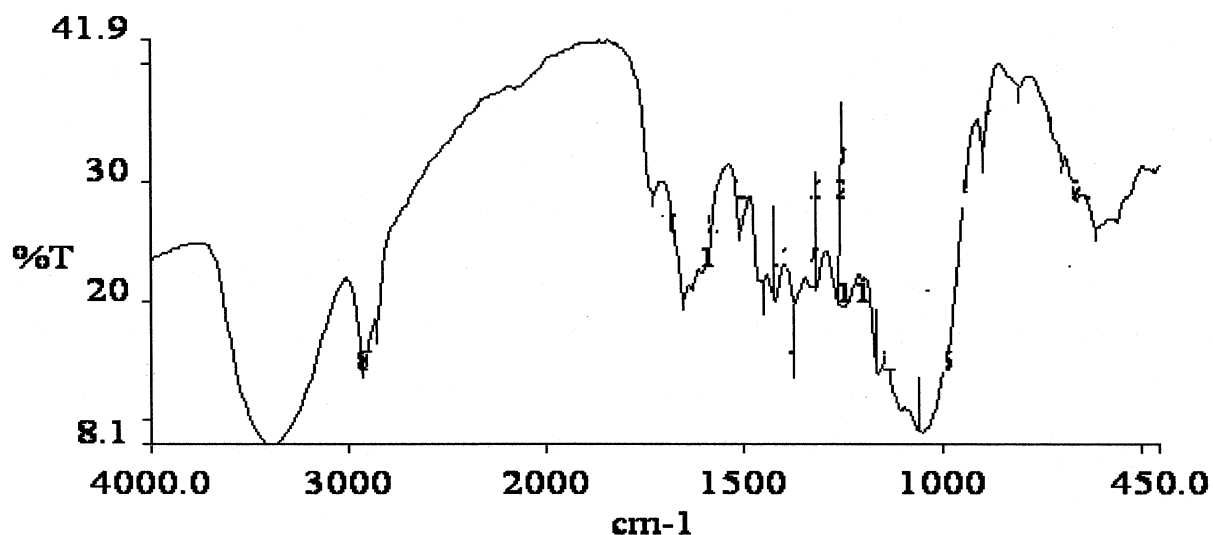


Figure 5.2.1: FTIR Analysis of Wheat Straw

Figure 5.2.2 shows the behavior of Ni^{2+} adsorbed on the surface of WS. A decrease in absorbance at 3366.51 cm^{-1} has been observed which is due to O-H stretching of carboxylic acid group and the presence of water molecule. The water could be in the sample or in the moisture captured during pellet preparation or due to atmospheric contribution in background spectrum. A stretch from 1730.25 cm^{-1} to 1734.03 cm^{-1} indicates a strong ester carbonyl absorbance [Pavia, 2001]. A new peak is observed at 1633.34 cm^{-1} which is attributed to C=O of non-conjugated aromatic vibrations. A stretch in 1510.35 cm^{-1} from 1509.37 cm^{-1} is due to guaiacyl group. Sun and Sun, 2002, considered it a weak biosorption that arise from the aromatic ring vibrations and

ring breathing with C-O stretching in lignins. At 1467.06 cm^{-1} a new peak is observed while the peak at 1425 cm^{-1} of virgin WS is missed which indicates vibration of methyl groups and deformation of methyl group which is asymmetric in $-\text{CH}_3$ and $-\text{CH}_2$. Similarly the peak at 1320.72 cm^{-1} was stretched to 1371.67 cm^{-1} which is due to participation of $-\text{C}-\text{CH}_3$ linkage in biosorption,

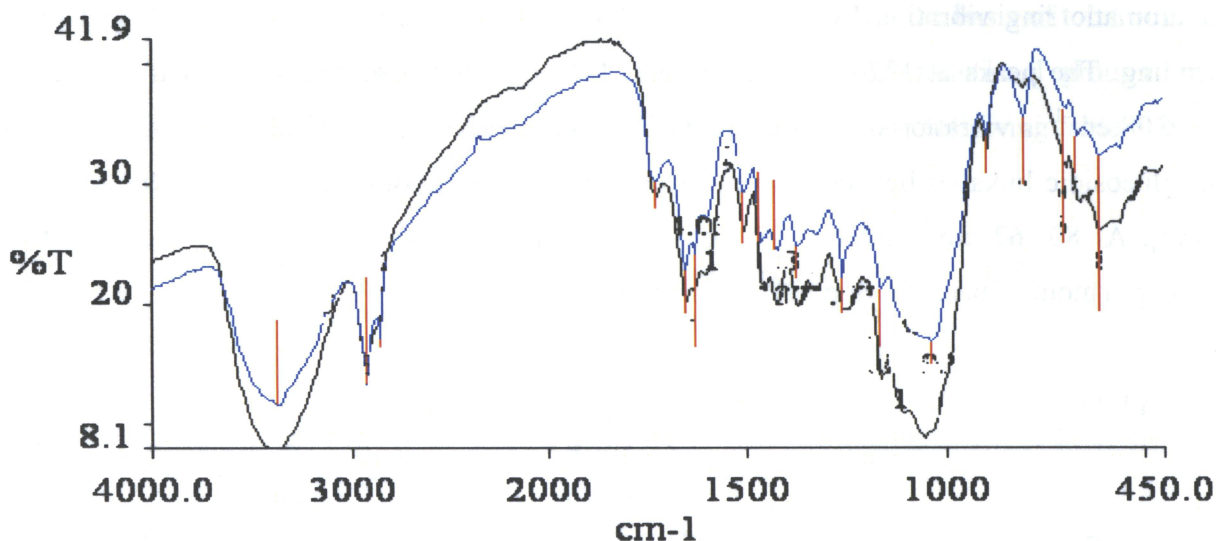


Figure 5.2.2 : Ni^{2+} (Blue lines) on WS

Sun and Sun 2002 has similar views. The stretch from 1259.75 cm^{-1} to 1261.59 cm^{-1} is due to breathing of guaiacyl ring. Similarly a shift is observed from 1056.08 cm^{-1} to 1034.83 cm^{-1} which is due to C-O deformation in its plane [Panteleeva, 1995].

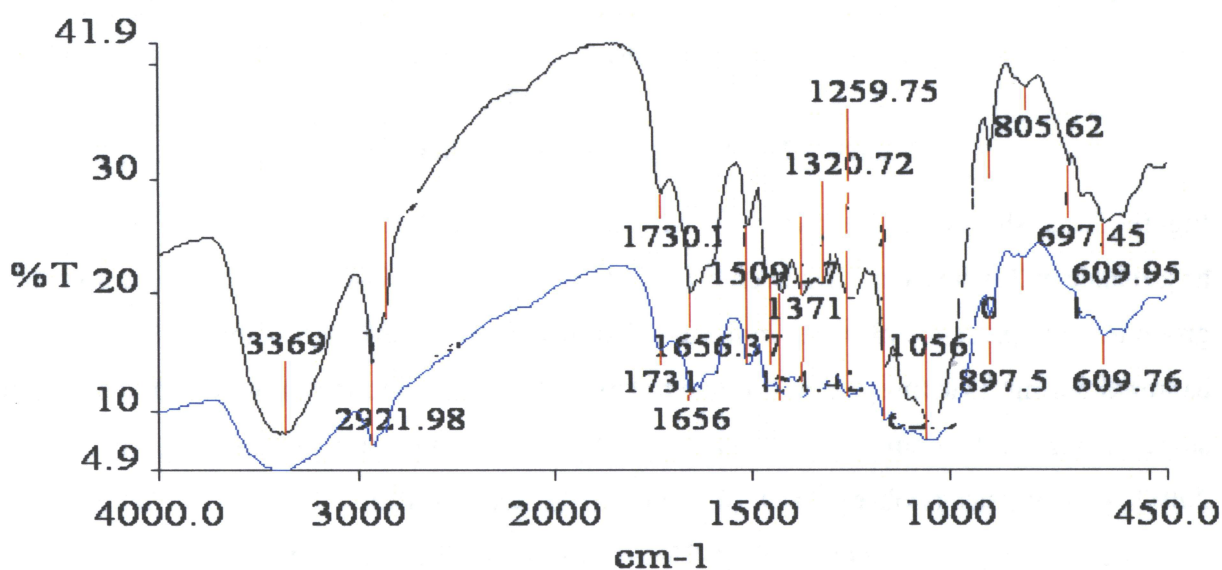


Figure 5.2.3: Zn^{2+} on Wheat Straw

Aravindhana *et al.*, 2004b got a similar observation. They found that the peak at 1730 cm^{-1} shifted to lower frequencies for the *Turbinaria ornata* seaweeds biomass after metal biosorption. They concluded that it could be due to the complexation of carboxyl group (RCOO) by coordination of metal ions.

Fourest and Volesky, 1996, investigated the binding of H, Cd and Pb by alginic acid and *Sargassum fluitans* biomass before and after modification of the carboxyl group. A linear correlation between the binding capacity for Cd and between the content of the weak acidic group probably carboxylate, resulting from different degrees of blocking was noted. A 48 hour treatment with propylene oxide almost reduced the removal of Cd by 90 % and 80 % of Pb. This indicated that the majority of the metals bound to the carboxylic groups. The carboxylic acid group was suggested as a key component for Fe uptake at pH of 4.5.

One way of confirming the role of carboxylic group (CG) in the uptake of ions is the analysis of the control biomass by FTIR. This was the strategy of the Fourest and the Volesky to investigate the mechanism of Cd biosorption by *Sargassum* biomass. The protonated biomass was used as a free biosorbent control since the presence of K, Na, Mg, Ca etc could interfere in the FTIR peaks. These techniques helped to identify the shifts of two absorbing peaks. As in the case of Cd uptake CG were confirmed to be involved in the uptake of Ca and Fe. The spectrum of protonated biomass typically displays absorbance peaks of 1738 cm^{-1} corresponding to the stretching band of the free carbonyl double bond from the CG.

In the present study, a band at 1646 cm^{-1} is indicative of the adsorbed water. There is shift from 1454.42 cm^{-1} to 1426.48 cm^{-1} which is attributed to adjustment of Zn^{2+} with the aromatic rings and decreasing their vibrations. Similar behavior was observed by Rana *et al* 1997, and they relate this to the lignin aromatic ring vibrations. Another peak from 1320.72 cm^{-1} has been shifted to 1260.08 cm^{-1} which is attributed to syringyl group whose vibrations has been reduced due to biosorption of Zn^{2+} . Similar stretch was observed by Ashkenazy *et al.* 1997, for lead laden acetone washed yeast biomass. They believe that there was a change in the ions associated with carboxylate ions. The other peaks from 816.47 cm^{-1} to 1163.63 cm^{-1} there is a small stretch in

their vibrations from 0.07 % to 0.98% of transmittance. The range of bands between 750-1000 cm^{-1} corresponds to S=C, -C-C- and C-Cl functional groups.

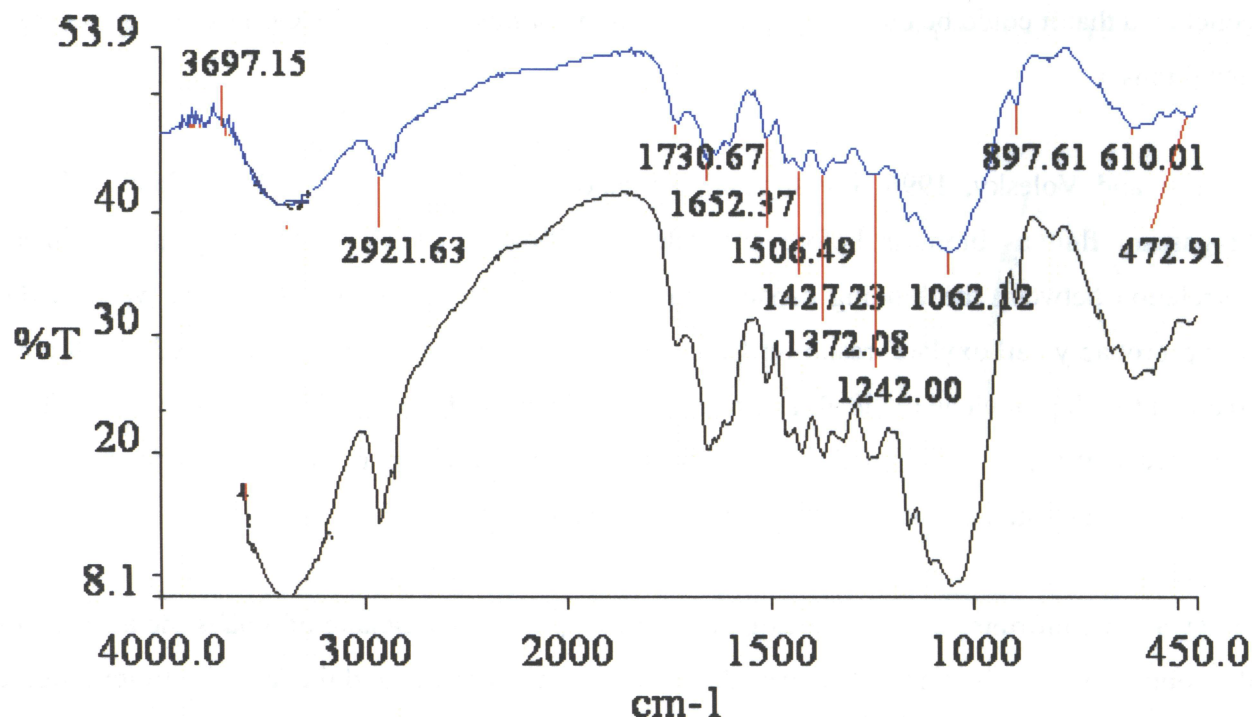


Figure 5.2.4 : Comparison of Biosorption of Ni^{2+} and Zn^{2+} on Wheat Straw with Virgin Wheat Straw

Both the plots in the figure 5.2.4 look similar. A new peak has been observed at 1242.08. at the same time the peaks at 1320.72 and 1259.75 cm^{-1} has been disappeared which means there is an increasing trend of ester bonding. It indicates that C=O stretching of syringyl and guaiacyl groups has been satisfied by both the metal ions. Saikia *et al*, 1995, while working on *Hibiscus cannabinus* L., considered it the same stretching. From the changes of band areas, it is also reasonable to assume that most of the ester groups had been converted to carboxylic and alcoholic groups when wheat straw is loaded with both the metal ions. A stretch of peak at 1056.08 to 1062.12 cm^{-1} has been observed which means vibrations at C-O linkage have been increased. Sheng *et al* 2004 assigned this to the -C-O stretching of alcoholic groups which means the metal ions are disturbing the linkage. This is attributed to the C-O, C-C stretching or C-OH bending in hemicelluloses. Mainly vibrations in the range of 1130-1000 cm^{-1} are considered due to C-O-C and O-H of polysaccharides.

Disturbance in the normal resonance of functional groups give us a lead to think if the adsorbate specie, Ni^{2+} or / and Zn^{2+} will be able to adsorb. In general, the more disturbances in the functional groups location the more biosorption will take place. The use of FTIR studies told us that several group like $\text{C}=\text{O}$, $-\text{O}-\text{H}$, $\text{C}-\text{O}$, $\text{C}-\text{C}$, $\text{C}=\text{C}$ and $-\text{O}=\text{N}=\text{O}$ interact with metal ions and accommodate them.

5.3 Effect of Temperature

Temperature dependence of biosorption is associated with various thermodynamic parameters. To study the effect of temperature on biosorption, the biosorption studies were carried out at 20, 25, 30, 35, and 40 °C (the sampling incubator was equipped in-built temperature control system). It was found that the biosorption capacity decreased from 10.2 to 4.4 mg g^{-1} with temperature increase from 20 to 40 °C for Zn^{2+} for an initial concentration of 150 mg / L in single ion - wheat straw biosorption system at a pH of 5. For Ni^{2+} it was found that biosorption decreased from 5.2 mg/l to 3.6 mg/l in a single ion system. This study was conducted at different initial pH values of the solution as 4, 5 and 6.3 for the same initial concentration and same range of temperature as that for Zn^{2+} .

Kalavathy *et al.*, 2005, found that the biosorption capacity decreased from 3.168 to 2.102 mg /g with temperature increase from 20 to 40 °C for an initial concentration of 20 mg /L while studying the biosorption of Cu^{2+} onto rubber wood sawdust. Ozer *et al.*, 2006, observed that the amount of the adsorbed metal ion per unit mass passes through a maximum value at 25°C and then begins to decrease with increasing temperature from 25 to 50 °C. Kuyucak and Volesky noted that binding of C_0 with brown alga *Ascophyllum nodosum* increased by 50-70 % when the temperature was raised from 4-23 °C. Further increase in temperature from 23 to 40 °C caused only a slight binding increase. Temperature 60 °C and above caused a change in the texture of the biosorbent and a loss in biosorbent capacity due to material deterioration.

Effect of temperature on the biosorption of ions in a binary system of ions was also studied. The equilibrium was reached up to 180 minute in all the biosorption conditions of temperature range

20 to 40 °C at all pH values of 4, 5 and 6.3. Always more than 50 % of biosorption was achieved at first 30 minutes at all temperatures.

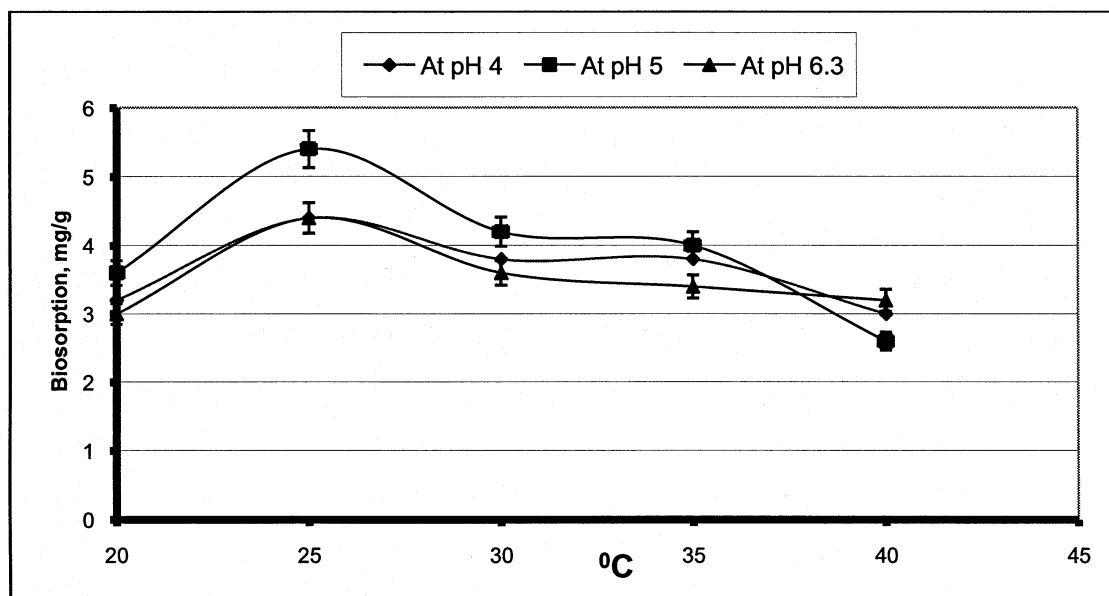


Figure 5.3.1: Effect of Temperature on the Biosorption of Ni²⁺ in a Binary System

The figure 5.3.1 represents biosorption behavior of Ni²⁺ in a binary system as a function of temperature. The maximum uptake of Ni²⁺ by WS was observed as 0.0954 mmol at 25 °C and then there is a slight decrease in trend as the temperature was increased. Error bars represents an experimental error of $\pm 5\%$. Its calculation is shown in the appendix C page 169. Similar results were obtained by Kilic *et al.*, 2008. They studied the effect of temperature on biosorption by increasing temperature from 10 to 30 °C for Pb²⁺ and Hg²⁺. In their study, the equilibrium was reached around 90 min though 62% of the biosorption capacity for Pb²⁺ was completed in first 15 min. The highest biosorption capacity was observed at 30 °C as 0.091 mmol Pb²⁺ per gram of biomass. They found that, for Hg²⁺ around 75% of the biosorption capacity was completed in 45 min and steady-state was reached at around 105 min. The highest biosorption capacity was observed at 20 °C as 0.097 mmol Hg²⁺ per gram of biomass. Optimum temperature for Pb²⁺ and Hg²⁺ biosorption were found to be 30 °C and 20 °C, respectively. It was concluded that optimum uptake temperature for biosorption on the same biomass was dependent on the nature of adsorbing specie.

The figure 5.3.2 is about the biosorption capacity of Zn^{2+} in the single ion system as a function of temperature. The maximum uptake of Zn^{2+} was 0.177 mmol at equilibrium. The uptake increased upto 25 °C, with further increase in temperature it was decreased. The decrease of metal uptake by biomass is a common behavior which is attributed to the decrease in surface acceptance for the ions. Because increase in temperature activates functional groups on the surface that satisfy the charge demand from each other which result in decrease in affinity to the metal ions, hence the metal uptake is decreased.

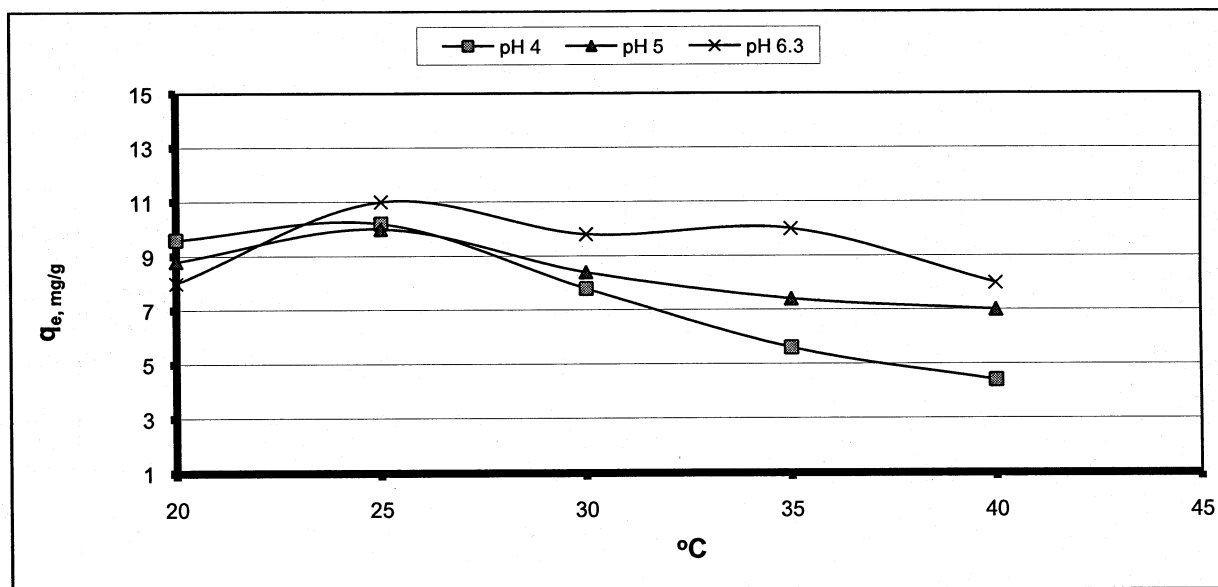


Figure 5.3.2: Effect of Temperature on the Biosorption of Zn^{2+} at Various pH Values

The increase of metal uptake to an optimum value and then decrease in uptake with increase in temperature is discussed by a number of authors because it is considered as a common behavior of biomass. Ho, 2003, studied the removal of Pb^{2+} and Cd^{2+} in aqueous solution by *Caladium bicolor* (wild cocoyam) which is a plant, by varying the temperature between 30 and 80°C. The data showed that biosorption of metal ion by the *C. bicolor* biomass increased with increase in temperature, which is typical for the biosorption of most metal ions from their solution. However, the magnitude of the increase continued to decline as temperatures are increased from 30 to 80°C. He postulated that with increasing temperature, the attractive forces between biomass surface and metal ions were weakened and the biosorption decreased. The data revealed that most of the metal ions were removed between the temperatures of 30 to 50°C. As temperature increased above 50°C, an initial slow biosorption was observed followed by a relatively constant

biosorption process. The equilibrium concentrations for higher temperatures (60-80°C) were not significantly different for those of lower temperatures. This indicates that increasing the initial metal ion concentrations above the equilibrium concentrations of 50 – 70 mg/L did not have any significant increase in the biosorption of metal ions by *C. bicolor* biomass.

The biosorption of metal ions is influenced by temperature but to a limited extent. Considering this behavior of biosorption Wang 2002, suggested that ion exchange mechanism exists in biosorption to some extent. Biosorption process is usually not operated at high temperature because it will increase the operational cost. Brady and Duncan 1994, found that temperature range 5–40 °C had minor effect on the accumulation level of Cu^{2+} , Co^{2+} or Cd^{2+} by free cells of *S. cerevisiae* in suspension. Biosorption reactions are normally endothermic, so biosorption capacity increases with decrease of temperature [Kapoor and Viraraghavan, 1997]. Ozer and Ozer, 1993, worked in the range of 15– 40 °C to observe biosorption of Pb^{2+} , Ni^{2+} and Cr^{2+} on the inactive *S. cerevisiae* and they found that the maximum equilibrium biosorption capacity was reached at temperature of 25 °C. The decrease in capacity at higher temperature between 25 and 40 °C revealed that the processes of biosorption for these metal ions by *S. cerevisia* were exothermic. They assumed that the decrease of biosorption capacity at higher temperature may be due to the damage of active binding sites in the biomass.

However, Goyal *et al.* [2003] found that the metal biosorption of Cr^{6+} by *S. cerevisiae* increased with increasing temperature in the range of 25–45 °C, they explained that higher temperature would lead to higher affinity of sites for metal or binding sites on the yeast. The energy of the system facilitates Cr^{6+} attachment on the cell surface to some extent. When the temperature was too high, there was a decrease in metal biosorption due to distortion of some sites of the cell surface available for metal biosorption.

Ramos *et al*, 2002, investigated the effect of temperature on biosorption by determining the biosorption isotherms at 15, 25 and 35 °C on different activated carbons. The isotherm of Zn^{2+} onto carbon either was independent of temperature or the effect of temperature was so minimal as to be masked by experimental error. For F-400 carbon, the biosorption isotherm decreased as temperature increased for concentrations less than 30 mg/l. At greater concentrations, the

isotherm increased as temperature was increased from 15 to 25 °C, and it remained constant or increased only slightly as temperature was increased from 25 to 35 °C. This unexpected behavior could be explained by assuming that Zn^{2+} biosorption onto F-400 carbon was occurring by two mechanisms, one of which is favored while the other is inhibited by the increase in temperature. Biomass usually contains more than one type of sites for metal binding. The effect of temperature on each kind of site could be contributed to the overall metal uptake. This was confirmed in biosorption of Cu by potassium-saturated microbial biomass [Weppen and Hornburg, 1995]. At high temperature, the metal ion tends to escape from the biomass surface to the solution phase, which results in a decrease in biosorption as temperature increases [Aksu and Kutsal, 1991]. The decrease in biosorption with increasing temperature suggested that there were weak interaction between biomass surface and the metal ion which supported the idea of physisorption.

The above discussions support the situation in our study i.e. biosorption of Ni^{2+} and Zn^{2+} is increased from 20 to 25 °C with further increase in temperature from 25 to 40 °C it decreases. We attribute this to the distortion of sites, a decrease bonding affinity between the functional groups and the metal ions, more attraction by polarity of water molecules to pull the physically adsorbed metal layers back to the solution. The free energy of the process at all temperatures is positive and increased with increase in temperature, which indicates that the process is non-spontaneous in nature, it drives heat from the surroundings which is confirmed by the positive values of ΔH . The positive ΔH means an endothermic reaction. It means heat is adsorbed by the system due to the products of the reaction having a greater enthalpy than the reactants. Though temperature significantly influences the chemical processes, it has little influence on mass transfer processes [Liou, 2005]. Higher temperature helps to reach equilibrium faster while it reduces the biosorption capacity [Buiteman, 1994]. Our study supports the idea that there is less significant influence on the biosorption of Ni^{2+} and Zn^{2+} in the temperature range of 20 to 40 °C. A little promising situation arrived at temperature 25 °C which can be considered as optimum temperature for the biosorption of Ni^{2+} and Zn^{2+} on wheat straw. The increase in biosorption is also attributed to the swelling of biosorbent that makes more active site available for metal ions [Cox et al, 2000]

In conclusion biosorption is applicable to reasonably narrow temperature range. In this range the effect of temperature is small.

5.4 Effect of pH

The solution pH is an important factor affecting the amount of heavy metal ions adsorbed by biomass. Under acidic conditions, H^+ can protonate the surface functional groups of the biomass and enhance ion exchange with metal ions. At high pH, the metal ions would precipitate and reduce the extent of biosorption. However, at very low pH, a large amount of H^+ in solution would compete with the metal ions for active binding sites on the biomass surface.

Biosorption of Zn^{2+} ions were measured on wheat straw at pH of 3, 4, 5 and 6.3. pH value above 6.5 was avoided because Zn^{2+} began to precipitate from dilute solutions at pH of 6.5. The change in concentration of Zn^{2+} in the biosorption processes observed at temperatures range 20 °C to 40 °C. it was observed that at pH of 4 and pH of 5 behaved similar in terms of uptake of metal ions. The surface of the wheat straw has positive charge when pH is 3 because cations compete with H^+ ions at binding sites when pH decreased to 3. In other words, binding sites were protonated by H^+ ions when pH was low. This phenomenon prevented metal ions from binding to functional groups on the wheat straw. Kumar *et al*, 2006, experienced that there was an increase in zinc biosorption with an increase in the pH from 2 to 6 beyond which it decreased due to precipitation. The results obtained indicated that the optimum pH range for the biosorption of zinc by *S. cinnamomeum* biomass was in the range of 5.0–6.0 Optimum pH was different for each type of metal ion and biomass for efficient biosorption [Veglio, 1997].

Mapolelo and Torto, 2004, proved that the biosorption capacity of Cd^{2+} , Cr^{3+} , Cr^{6+} , Cu^{2+} , Pb^{2+} and Zn^{2+} was dependent on pH. For these metal ions, the optimal pH values were all higher than 5. It has been observed that further increase in pH the biosorption capacity has subsequently decreased. It could be that at low pH, the affinity with the proton at the binding site of yeast was much greater than that of the metal ion. Vianna *et al*, 2000, reached on the similar conclusion that the biosorption capacity of metal cations was strongly dependent on pH value. For Cu, Cd and Zn, the biosorption capacity at pH 4.5 was far higher than that at pH 2.5 and pH 3.5.

Electrostatic attraction of the negatively charged functional groups could be one of the specific biosorption mechanisms. In their study at pH 4.5, the most important group was phosphate and the other two main active molecular groups were carboxyl and sulphate

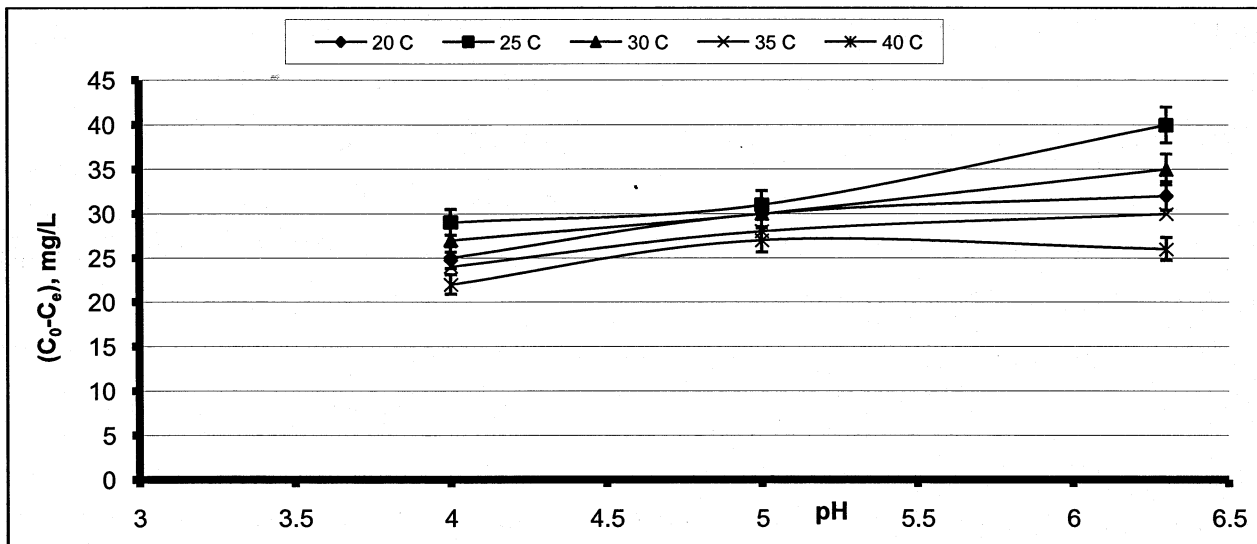


Figure 5.4.1 : Effect of pH on the Biosorption of Zn^{2+} on Wheat Straw in Binary System

As shown in figure 5.4.1 that increase in pH increased the metal ions biosorption in the presence of other ions as in this case it is Zn^{2+} . For example at 25 °C, at 120 rpm, with the increase in pH value from 4 to 6.3 the amount adsorbed at equilibrium was increased from 5.6 mg /g to 8.0 mg /g. Some studies suggests that biosorption favored at increase pH >4.5, [Kratochvil, 1997 and Schiewer 1995]. This depends on the characteristics of the biomass as well as considering the specifications of metals in the solution. It is known that pH effects on biosorption in three ways as:

- 1- The condition of active sites could be changed by the change in pH of solution. If the metal binding groups are weakly acidic or basic (as carboxylic groups in our case), the availability of free sites is dependent on the pH. [Gilles and Hassan, 1958].
- 2- Under the extreme pH values, the distortion of cell was observed under microscope accompanied by significant biomass weight loss and decrease in the biosorption capacity [Kuyucak and Volesky, 1989].

- 3- Metals in aqueous solutions occur as hydrolyzed ions when pH is low, in particular for metallic anions of high charge density, in general the speciation of the metal in solution is pH dependent.

In a multi ion system for a given biosorbent, it is quite possible that one type of ions have optimum pH values different than the other one. Kilic *et.al*,2008, observed optimum pH value of 3.5 and 5.8 for Pb^{2+} and Hg^{2+} respectively in a bimetal biosorption study.

As we have discussed that the speciation of metal ions is highly dependent on pH: different species of metal ions have different binding affinities with the binding sites. pH is an effective parameter in biosorption because it significantly affects cell wall and solution chemistry. The effect of pH on the biosorption of Ni^{2+} was studied at various temperatures ranging from 20 to 40 °C by varying pH of metal solution – wheat straw system from 4 to 6.3 same as that of Zn^{2+} . The change in concentration of solution at biosorption is depicted in the following figure:

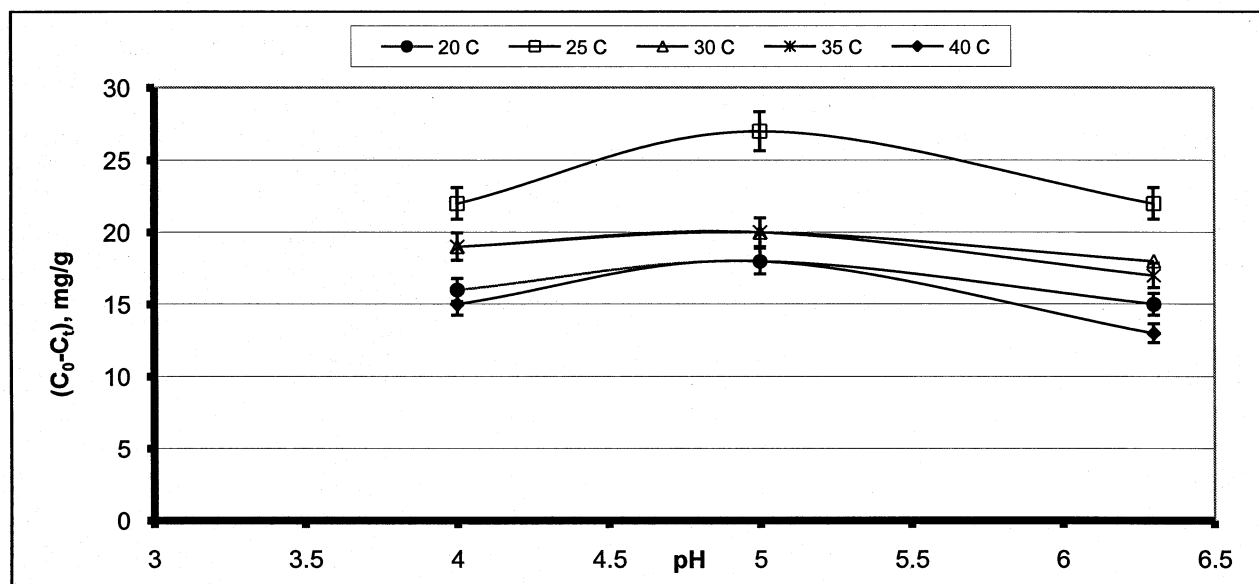


Figure 5.4.2: Effect of pH on the Biosorption of Ni^{2+} in Binary ionic System

The increase in the rate of biosorption for Ni^{2+} on wheat straw was observed as pH changes from 4 to 6.3. Similar results were obtained in the Binary ionic system as shown in the figure 5.4.2. Unsal *et al*, 2004, while studying biosorption of Ni^{2+} on dried activated sludge observed

that the uptake of Ni^{2+} increased by increasing initial pH and was the greatest at pH 4.5. Further increase in pH (i.e. beyond 4.5) brought a decrease in biosorption. They attribute this decrease to the formation of nickel hydroxide complexes and reduced solubility that would prevent biosorption. Chandra, et al, 1998, presented same reason for the decrease in biosorption of Ni^{2+} at high pH while they were studying removal of metal ions using industrial biomass. Some other researchers have similar theory for the decrease in biosorption of Ni^{2+} at pH of above 6 [Harris and Ramelow, 1990; Zhou and Kiff, 1991; Yu *et al*, 2003; Panda *et al.*, 2007].

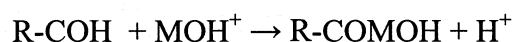
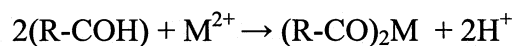
The different pH binding values for these components could be due to the nature of the chemical interactions of each component with the WS. The low level of Ni^{2+} uptake at lower pH values could be attributed to the increased concentration of hydrogen (H^+) and hydronium (H_3O^+) ions competing for Ni^{2+} binding sites on the biomass. In acidic medium the electromeric effect of the $-\text{C}-\text{C}-$ group in wheat straw leads to surface protonation and possesses net positive charge on the surface which inhibits the approach of positively charged metal cations. The effect of pH on biosorption of Cu^{2+} on rubber wood sawdust activated carbon (RSAC) was studied by Kalavathy *et al*, 2005, at a temperature of 30 °C. At pH of 8.0, a decrease in biosorption of Cu^{2+} was observed due to the formation of soluble hydroxyl complexes. The optimum removal was achieved at pH of 6. Chandra and Sekhar, 1998, thought that the decrease of the Ni^{2+} biosorption for pH higher than 5 could be due to the formation of nickel hydroxide complexes and reduced solubility that would prevent biosorption.

Researchers are agreed that a single biosorption mechanism due to the initial pH is not sufficient to explain the biosorption of both components observed at all the pH values studied. It is thought that additional types of biosorption mechanisms such as ion exchange, complex formation, chelation, and micro precipitation or membrane transport and physicochemical forces such as van der Waals and hydrogen binding are also important for the removal of Cr^{6+} and Ni^{2+} ions by the biomass [Aksu, 1998; Volesky, 1990; Par *et al.*, 1999].

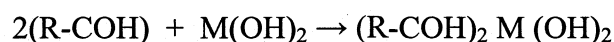
In a certain pH range, for one specific heavy metal there may be a number of species present in solution, such as M , MOH^+ , $\text{M}(\text{OH})_2$, etc. At lower pH, the positive charged metal ion species may be adsorbed at the surface of the wheat straw by ion exchange mechanism. With an increase

in pH, metal ion species, mainly neutral, may be adsorbed by hydrogen bonding mechanism along with ion exchange. These mechanism are shown in the following equations [Shukla *et al.*, 2002]:

Ion Exchange



Hydrogen Bonding



Where R is the matrix of the wheat straw, biosorption of metal ions from solutions by solid phase can occur with formation of surface complex between the adsorbed ligand and the metal. The biosorptive capacity of metal cations increases with increasing pH of the biosorption system, but not in a liner relationship. On the other hand, too high pH value can cause precipitation of metal complexes, so it should be avoided during experiments. For different biosorption system of metal ions, the optimal pH is different. It was reported that the optimal pH value was 5–9 for copper biosorption by *S. cerevisiae*, and 4–5 for uranium [Volesky 1990b. 156]. Ozer and Ozer, 2003, found that optimal pH value for Pb^{2+} and Ni^{2+} ion uptake was 5.0.

At lower pH, cell wall ligands were closely associated with the hydronium ions $[\text{H}_3\text{O}^+]$ and restricted the approach of metal cations as a result of the repulsive force. At higher pH, e.g. 5.0, divalent positive ions were suitable to interact with negatively charged groups in wheat straw. On the other hand, the wheat straw consists of protein, which can cause a charge through dissociation of ionizable side groups of the amino acids. The ionic state of ligands such as carboxyl, imidazole and amino groups will promote reaction with the positively charged metal ions.

5.5 Effect of Metal Concentration

The biosorption capacity of Wheat Straw would be varied by changing the surrounding metal concentration. At low metal concentration, due to the low availability of metal ions, the amount

adsorbed was small and it increased as the metal concentration increased. Consequently, biosorption can be regarded as ionic strength dependence as displayed in the figure 5.5.1. The amount of Ni^{2+} adsorbed increased with increase in initial concentration and remained nearly constant after equilibrium as shown in the figure 5.5.1.

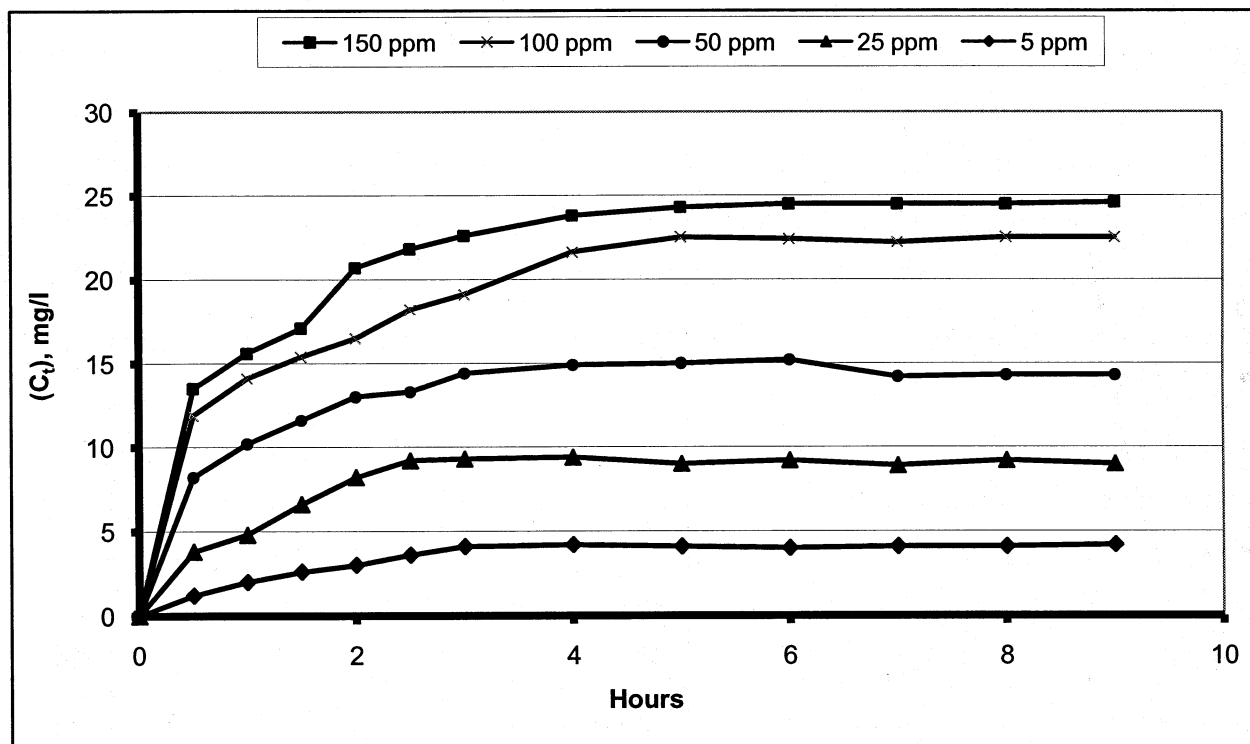


Figure 5.5.1 : Amount of Ni^{2+} Removed from Solutions of Ni^{2+} and Zn^{2+} at 25 °C, 6.3 pH

Equilibrium was attained and the equilibrium times were found not to be the same for all concentrations studied. The equilibrium time ranges between 2.5 hours to 5 hours, it increased with increase in concentration. Similar behavior was observed for biosorption of Zn^{2+} ions.

It could be observed that the percentage of metal ions adsorbed were larger at the lower ionic concentration. About 82 % of Zn^{2+} was adsorbed at initial concentration of 5 ppm while it was 80 % for the Ni^{2+} in the binary solution of nickel and zinc ions. Their individual biosorption was 88 % for Zn^{2+} and 84 % for Ni^{2+} . It could be concluded that the influence of ionic concentration of both metal ions was specific for their single and multiple existence.

Schiewer and Wong, 2000 and Small *et al*, 2001 discovered that the metal removal decreased with increasing ionic concentration if the biomass used was bacteria and algae. Some others [Smith *et al.*, 1996; Gao and Mucci, 2001] projected that the formation of outer sphere complexes would depend on ionic concentration. Formation of these complexes was a major step in the biosorption mechanism and a high ionic concentration was not beneficial for these complexes. Several biosorption studies made by Chen and Lin, 2001, with activated carbon, Manohar *et al*, 2002, with clay mineral and Raval *et al*, 2000, with natural organic matter extracts also showed that the amount of metal adsorbed increased as the ionic concentration increased. The removal of Zn^{2+} increased with time and attains saturation in due course of time. Basically, the removal of adsorbate was rapid but it gradually decreased with time until it reached equilibrium. The results for 5, 25, 50, 100, 150 mg/l concentrations of Zn^{2+} are presented in figure. 5.5.2.

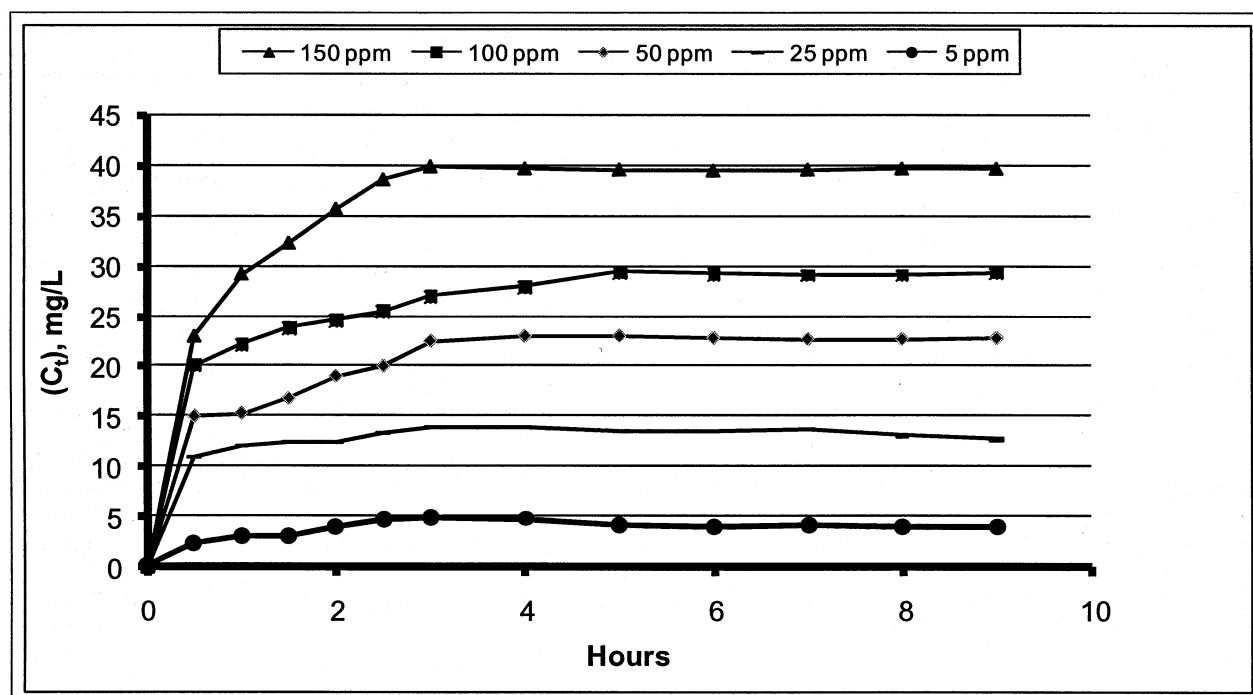


Figure 5.5.2: Amount of Zn^{2+} Removed from Solutions of Nickel and Zinc at 25 °C, 6.3 pH

The plots represent the extent of removal of Zn^{2+} versus the contact time for the initial metal concentrations. The plots reveal that maximum percent metal removal was specific for specific initial concentration. The similar shape of the curves at each initial concentration shows that the

percentage uptake of Zn^{2+} decreased with increasing initial concentrations. This may be due to the fact that for a fixed adsorbent dose, the total available biosorption sites were limited thereby adsorbing almost the same amount of adsorbate thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increased initial adsorbate concentration. The rate of percent metal removal was higher in the beginning due to a larger surface area of the wheat straw being available for the biosorption of the metals. As the biosorption proceeds, the rate of percent removal became almost insignificant due to exhaustion of the biosorption sites. Almost 30 % to 50 % of Ni^{2+} was adsorbed in first 30 minutes of the process while in case of Zn^{2+} it was over 50 %. The proposition is that after the adsorbed material forms a 1 molecule (actually ion) thick layer, the capacity of the adsorbent was exhausted and then the uptake rate was controlled by the rate at which the adsorbate was transported from the exterior to the interior sites of the biosorbent. The data indicates that the initial metal concentration determines the equilibrium concentration, and also determines the uptake rate of metal ion and the kinetic character.

In the case of low concentrations, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional biosorption became independent of initial concentrations. However, at higher concentrations the available sites of biosorption became fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The percent equilibrium biosorption was 82 % and 80 % at 5 ppm of initial metal ionic concentrations and it decreases to 16 % and 26 % at 150 ppm for Ni^{2+} and Zn^{2+} respectively. Raji and Anirudhan, 1988, found that at an initial concentration of the biosorbent of 2.0 g/L the removal of Cr^{4+} decreased from 45.06 mg/g (90.12%) to 135 mg/g (67.94%) by increasing the Cr^{4+} concentration from 100 to 400 mg/g.

Corapioglu and Hung, 1987, explained that the biosorption would be hindered because of the interaction of the adsorbate-adsorbent at high metal concentration. Since the surface of biomass is usually negatively charged. The presence of positive metal ions could bind the biomass particle together, leading to the reduction in the available biomass surface area. Xue, 1988, presented a different approach that the metal ions would first bind to the high affinity site of the biomass surface and then with low affinity. This result in the reduction of biosorption percentage in a more metal concentrated environment owing to site saturation.

5.6 Effect of Co-adsorption

It is very important for the treatment of metal laden waste water to identify all metal ions existing in a stream, normally, the wastewater streams are mixture of heavy metal ions. Due to their electrostatic interaction, divalent metal ions would compete for the same binding sites and thus the biosorption capacity would be diminished in the presence of other cations. A comparison of the maximum biosorption of metal ions is given by the table 5.5.1:

Table 5.5.1: Comparison Maximum Biosorption on Wheat Straw, at 25 °C

Concentration ppm	Single Ions in Solution mg/g		Binary Solution mg/g	
	Ni ²⁺	Zn ²⁺	Ni ²⁺	Zn ²⁺
150	7	10	5	8
100	6.2	7.8	4.	6
50	5	5.2	3	4.6
25	2.5	3.2	2.2	2.8
5	0.82	0.86	0.1	1

Table 5.5.2 : Biosorption of Biomasses [Larsen and Schierup, 1981]

Sorbent	Single Ions		Binary Solution	
	Ni ²⁺	Zn ²⁺	Ni ²⁺	Zn ²⁺
Barley Straw (untreated)	6.4	5.3	0.5	0.6
Barley Straw (Washed)	4.6	4.3	0.4	0.5
Saw dust	1.3	2.7	0.0	0.0
Activated Carbon	8.1	6.2	0.9	1.5
Initial concentration	20 mg/l		4 mg/l	

By comparing the tables 5.5.1 and table 5.5.2 it is obvious that at 20 ppm of initial concentration, biosorption capacity of wheat straw for Ni²⁺ and Zn²⁺ is better than that of saw dust and it is less than that of barley straw. At initial concentration of 5 ppm biosorption capacity of wheat straw for the same metallic ions is better than the other biomasses of barley straw and saw dust. Activated carbon is taken as a reference for higher limit.

5.7 Isotherms

Before studying the bisolute biosorption of Ni^{2+} and Zn^{2+} onto wheat straw it is important to understand the independent biosorption behavior of each component. Single-solute biosorption can provide a basis for comparing the change in the biosorption behavior in a 2-component system. The suitability of the single-solute biosorption data to classical isotherms will help eliminate inapplicable isotherms. If a monocomponent isotherm cannot fit the single-solute data well, its corresponding multicomponent form will also not fit well.

5.7.1 Biosorption of Nickel and Zinc Ions on Wheat Straw:

The Langmuir, the Freundlich, and the Temkin isotherms are the three classical isotherm models. At least one of these models can fit most monocomponent isotherm data. Individual biosorption isotherm experiments were conducted for Ni^{2+} and Zn^{2+} , and the data were used to fit the linearized form of the three isotherms and plotted in figures 5.7.1, 5.7.2 and 5.7.3

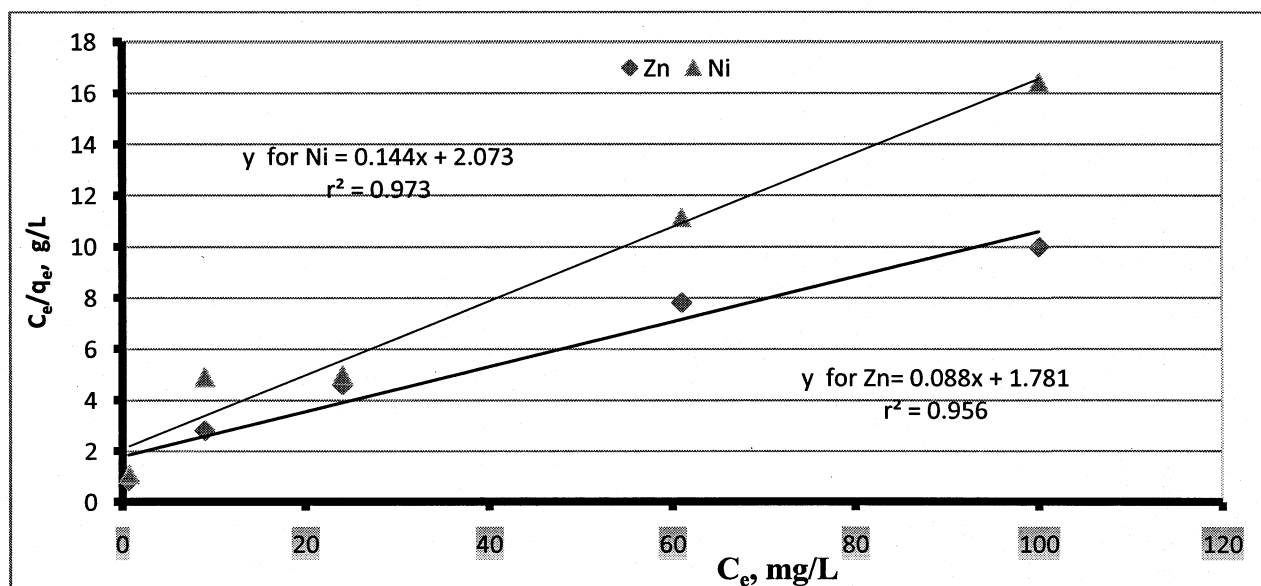


Figure 5.7.1: Langmuir Model for Ni^{2+} and Zn^{2+} in Single Ion System at 25 °C, pH 6.3.

The results indicated that the Freundlich isotherm fitted data the best for the given equilibrium concentration range as the r^2 values for Langmuir are 0.97 and 0.956, for Freundlich these are 0.97 and 0.999 while Temkin gives the values of 0.90 and 0.903 Ni^{2+} and Zn^{2+} respectively. For the entire Langmuir isotherm gave a moderate fit for the same concentration range. The

Langmuir isotherm did not fit the data well because its assumptions were not much practical as he assumed that the surface was homogenous, all active sites on the surface has equal energy and

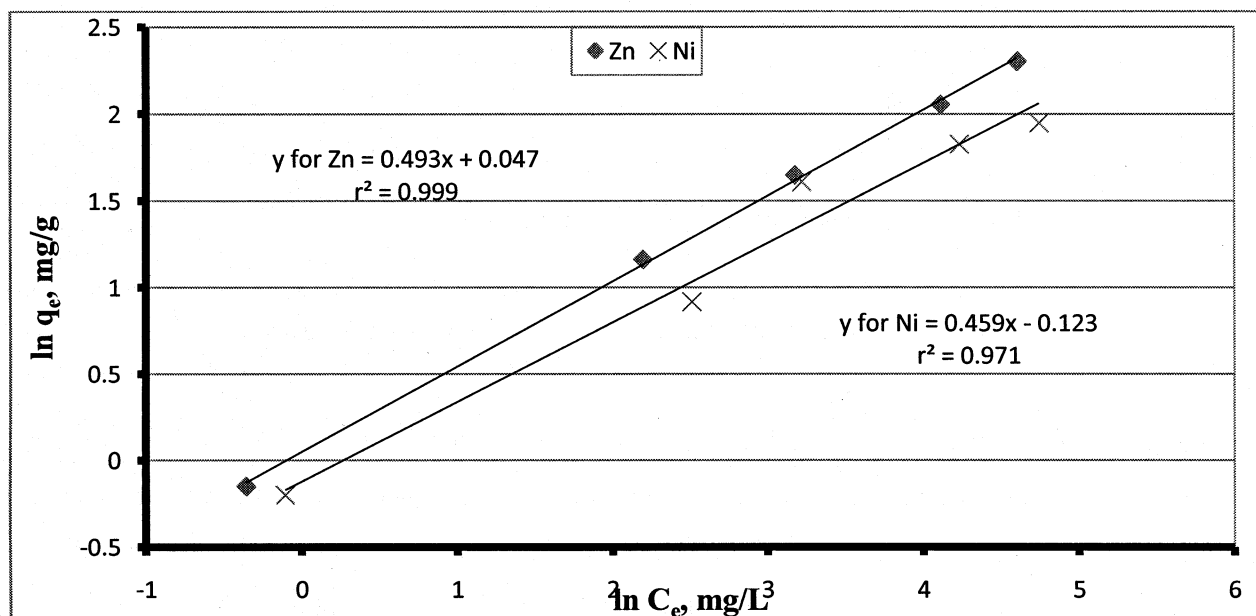


Figure 5.7.2: Freundlich Isotherm for Ni^{2+} and Zn^{2+} in Single Ion System, at 25°C , pH 6.3

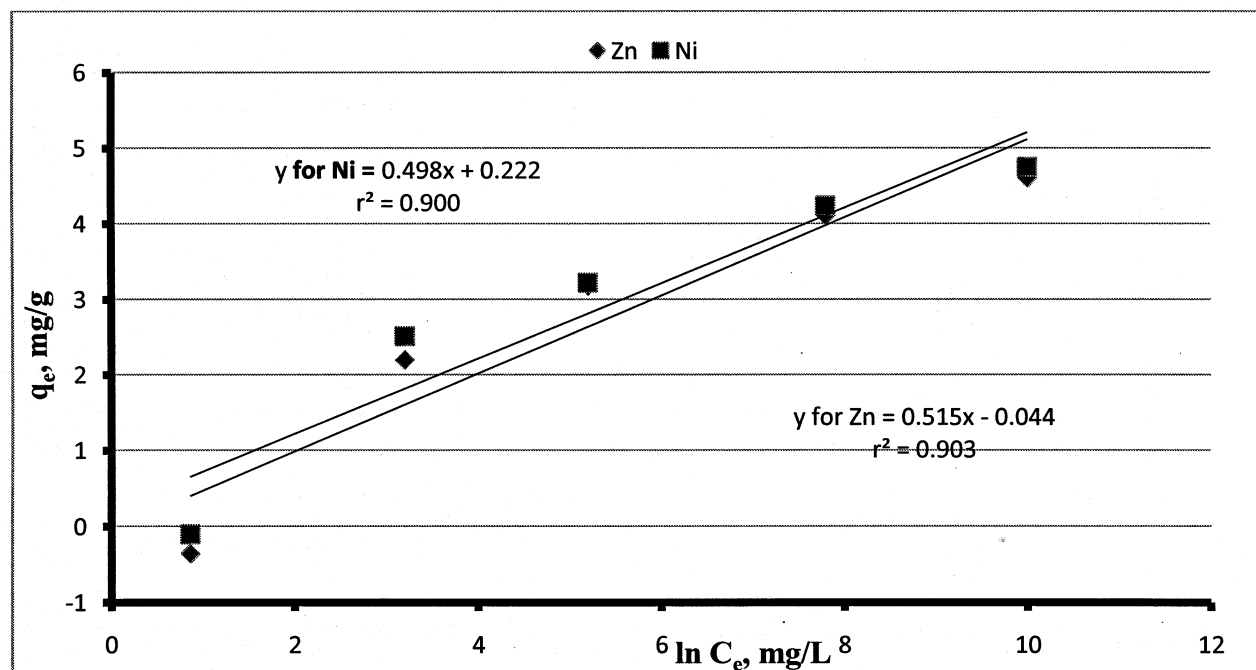


Figure 5.7.3 : Temkin Model for Ni^{2+} and Zn^{2+} in Single Ion System, at 25°C , pH of 6.3

there is no interaction between adsorbate molecules. ; However, the Langmuir isotherm is used as a reference for the discussion in this chapter because of its widespread acceptance.

From the graph of Langmuir isotherm, the maximum capacity of Ni^{2+} and Zn^{2+} removal by WS is about 11.4 and 7 mg/g respectively, from a solution of 150 ppm. About 80 % of all adsorbed amount was taken up by WS in first 30 min at 150 ppm. The Langmuir constants for single ionic system were calculated for Ni^{2+} and Zn^{2+} as given in table 5.7.1:

Table 5.7.1: Langmuir Constants for Ni^{2+} and Zn^{2+}

	$q_l = \text{mg/g}$	$K_l = \text{L/mg}$	r^2
Ni	6.94	0.07	0.97
Zn	11.4	0.05	0.95

The actual amount of biosorption of Zn^{2+} on wheat straw was 10 mg/g and it was 7 mg/g for Ni^{2+} , in single ionic system, as shown in table 5.5.1. The prediction made by Langmuir model for Zn^{2+} was about 14 % higher than the experimentally obtained value. The biosorption capacity of wheat straw for metallic ions uptake could be evaluated by using the following relationship called the separating factor R_L

$$R_L = \frac{1}{1 + K_l C_0}$$

K_l is Langmuir constant

C_0 is the initial concentration metallic ion

Table 5.7.2: R_L Values for Ni^{2+} and Zn^{2+}

C_0	Ni^{2+}	Zn^{2+}
150	0.088	0.119
100	0.126	0.168
50	0.225	0.2889
25	0.367	0.447
5	0.743	0.802

Regarding Langmuir isotherm model, R_L separation factor was found out between 0.088 to 0.743 for Ni^{2+} and between 0.119 to 0.802 for Zn^{2+} . R_L value between 0 and 1 indicated that biosorption of these metal ions on the biomass is favorable. In the light of the assumptions of Langmuir model, the fitting of the biosorption data of Ni^{2+} and Zn^{2+} to Langmuir isotherm showed that the binding energy on the whole surface of the wheat straw biomass was uniform. In

other words the whole surface has identical biosorption activity. It was also derived the adsorbed metal ions do not interact or compete with each other and they are adsorbed by forming a monolayer.

Kratochvil and Volesky, 1998, mentioned that a favorable biosorbent should have a low Langmuir constant K_L . The values of K_L determined by Gulnaz *et al.*, 2004, higher than 1 in a biosorption test of dye by activated sludge. Chen *et al.*, 2002, determined Langmuir constant K_L as 0.741 for Cu^{2+} biosorption by nonviable activated sludge. In the present study, K_L and q_{\max} value were found out 0.07 and 7 mg g^{-1} for Ni^{2+} and 0.05 and 11.4 mg g^{-1} for Zn^{2+} which indicated that wheat straw biomass is an encouraging biosorbent for the tested metal ions.

The experimental data was applied to other isotherms as well. Since the Freundlich isotherm represent the Ni^{2+} and Zn^{2+} biosorption data very well, further study of the two linear plots should give more information about their biosorption behavior. As shown in figure 5.7.2, both linearized Freundlich isotherms for Ni^{2+} and Zn^{2+} have similar slopes, but the intercept of the Zn^{2+} isotherm is clearly higher than that of the Ni^{2+} . The slope and the intercept of a linearized Freundlich isotherm represent roughly the biosorption intensity and the biosorption capacity respectively. This indicates that Zn^{2+} has a higher biosorption intensity and capacity than Ni^{2+} . Zn^{2+} should thus be more efficiently removed than Ni^{2+} at all concentration ranges. Ni^{2+} 's biosorption intensity ($1/n$) was found to be 0.46 and Zn^{2+} was 0.49. The numeric similarity implies that their biosorption intensities are quite comparable. On the contrary, the clear difference between the two intercepts indicates that wheat straw definitely has higher capacity for Zn^{2+} than for Ni^{2+} .

The experimental biosorption capacity and the biosorption capacity predicted by the three isotherms are compared and the corresponding Langmuir, Freundlich, and Temkin isotherm parameters, along with the regression coefficients. Freundlich values of $1/n$ 0.46 for Ni^{2+} and 0.49 for Zn^{2+} lies between $0 < 1/n < 1$ shows the favorability of biosorption process. The Freundlich linear isotherm's slope is also an indication of the biosorption energy. Since the n values for Ni^{2+} is consistently higher than that of Zn^{2+} (as shown in the table 5.7.3), Ni^{2+} may be attracted to high energy sites while Zn^{2+} is attracted to low energy sites.

Table 5.7.3 : n Values from the Slops of Freundlich Isotherms

Ionic Specie	Single Ionic	Binary Ionic
Ni ²⁺	2.18	2.68
Zn ²⁺	2.03	2.07

The degree of mutual inhibition between two competing biosorbates is also governed by the relative molecular sizes of the biosorbates and the relative affinities for biosorption.

Table 5.7.4 : Coefficient of Determination for Isotherms

Ionic Specie	Langmuir	Freundlich	Temkin
Ni ²⁺	0.97	0.97	0.90
Zn ²⁺	0.96	1	0.90

Despite the numeric differences calculated from the two isotherms, the two isotherms agreed that there were more biosorption sites for Zn²⁺ than for Ni²⁺ on the WS. Since Zn²⁺ has higher biosorption capacity and slightly higher biosorption intensity, it is logical to assume that Zn²⁺ should be preferentially adsorbed in the bisolute system; however, Zn²⁺ should not suppress Ni²⁺ biosorption too much because the biosorption intensities for both are quite similar. Generally, the degree of inhibition during biosorption depends partially on the initial concentration ratio of the two species. Throughout the discussion in this chapter, the initial concentration of Ni²⁺ and Zn²⁺ are similar ; therefore, there has no preferential biosorption subject to large concentration differences . The biosorption capacities for both Ni²⁺ and Zn²⁺ were slightly decreased in the multicomponent biosorption system. However, Zn²⁺'s biosorption capacity was consistently higher than Ni²⁺'s under this competition.

It is difficult to decide whether the two species are partially competing or fully competing for all biosorption sites. Studying various multicomponent isotherms may lead to further insights on the bisolute system .

5.7.2 Multi Component System

It has been a practice to use single-component isotherms to account for multicomponent biosorption data. While the isotherms might provide adequate fit for the data, this method of data analysis is not satisfactorily accurate because it fails to account for the interaction between the biosorbates. In general when two species are present at the same time during biosorption, they either mutually

- enhance each other's biosorption, or
- they adsorb onto the surfaces independently, or
- they interfere with each other by competing for the same biosorption sites.

The Ni^{2+} - Zn^{2+} biosorption behavior resembles the third behavior. Biosorption of both Ni^{2+} and Zn^{2+} individually was worse in the bisolute system than in the single-solute systems, nevertheless, the overall biosorption efficiency did not seem to change significantly. Ni^{2+} and Zn^{2+} must have competed for at least part of the activated sites on the WS.

For a bisolute system a model is selected on the following basis:

- 1- the isotherm must be able to represent or model biosorption over a wide range of concentration
- 2- it must be simple to apply mathematically ;
- 3- it must account for non idealities, such as heterogeneous and irreversible biosorption .
- 4- It is also preferable if this isotherm can be derived from the single-solute data.

Upon examining the three classical isotherms which are the Langmuir isotherm, Temkin isotherm and the Freundlich isotherm. The Langmuir isotherm was not able to fit the single-solute Ni^{2+} and Zn^{2+} data well at low concentration range. However, the Langmuir isotherm was the most well-known multicomponent isotherm, therefore, it would be informative to include the Langmuir multicomponent Isotherm for comparing other multicomponent isotherms. The Freundlich monocomponent isotherm fitted the data the best among the three and it has been widely used for describing multicomponent. Consequently the Freundlich multicomponent isotherm appeared to be the best candidate among the three classical isotherms. Among the

multicomponent isotherms discussed in the literature review, the applicable ones consist of the Langmuir Partially Competitive Isotherm, the Freundlich multicomponent isotherm and the IAS-Freundlich isotherm.

5.7.3 Modified Langmuir Isotherm

A Langmuir multicomponent isotherm or Modified Langmuir isotherms is given as:

$$q_{e,i} = \frac{Q_i^0 b_i C_i}{1 + \sum_{j=1}^n b_j C_j} \quad (5.7.1)$$

The bisolute form of this isotherm is as:

$$q_{e,1} = \frac{Q_1^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (5.7.2)$$

$$q_{e,2} = \frac{Q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (5.7.3)$$

The subscript 1 represents Ni^{2+} , and 2 represents Zn^{2+} . Q_1^0 , Q_2^0 , b_1 , b_2 are 5.6 mg/g, 9.17 mg/g, 0.057, and 0.04 respectively and they are derived from the single solute isotherm experiments.

The representative plots are in figure 5.7.4.

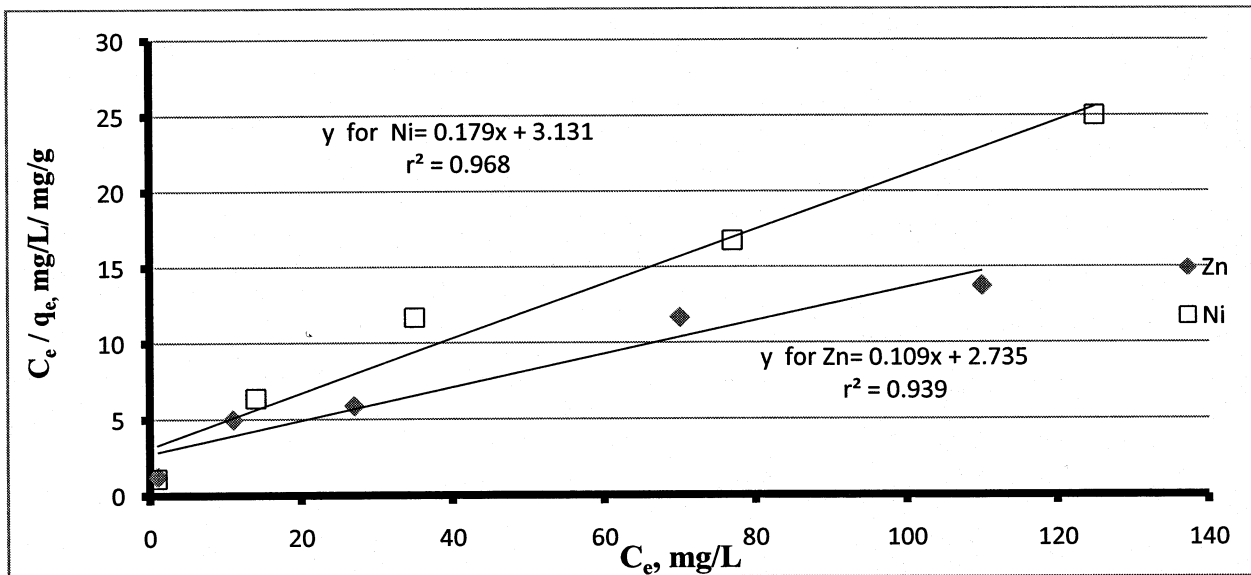


Figure 5.7.4 : Langmuir Isotherm for Multicomponent System

These isotherms fit the experimental data very well. But the Langmuir multicomponent isotherm tends to underestimate the Ni^{2+} and Zn^{2+} biosorption data. The maximum experimental Ni^{2+} adsorbed concentration was above 5 mg/g, but the isotherm calculated a maximum value of about 3.2 mg/g only. It can be noticed that the isotherm is also underestimating the Zn^{2+} biosorption. It means that the isotherm is misrepresenting the biosorption trend in these areas.

The main reason which contributes to the poor fit is that the competitive biosorption violates most of the Langmuir assumptions and it does not fit the single solute data very well. Since Ni^{2+} and Zn^{2+} biosorption is competitive, biosorption without interaction between the biosorbates is not likely; this is a violation of Langmuir assumption.

5.7.4 Langmuir Partially Competitive Isotherm

The values of q_1 and q_2 obtained by using Langmuir Partially Competitive Isotherm's equations 3.9 and 3.10 were not matching with the experimentally obtained values. The table 5.7.5 presents this situation

**Table 5.7.5: Prediction of the Biosorption of Metallic Ions
(Langmuir Partially Competitive Isotherm)**

Initial	Ni^{2+}		Zn^{2+}	
C_0	Predicted	Actual	Predicted	Actual
150	3.2	5	4.9	8
100	3.0	4.6	4.5	6
50	2.7	3	3.3	4.6
25	1.2	2.2	2.2	2.8
5	0.26	0.82	0.34	0.8

The modified Langmuir isotherm is unique in a way that no other isotherm explicitly considers partial competition between the two sorbates. Most isotherms usually assume the bisolute biosorption process to be fully competitive. The Langmuir Partially Competitive Isotherm's general assumptions are the same as that of the Langmuir Multicomponent Isotherm, but the assumption of partial competition has improved the isotherm's ability to predict the Zn^{2+} biosorption values. Since the isotherm equations for Ni^{2+} in the Langmuir Multicomponent

Isotherm and the Langmuir Partially Competitive Isotherm are the same, there is no improvement in predicting the Ni^{2+} biosorption values.

5.7.5 Freundlich Multicomponent Isotherm

Multicomponent Freundlich isotherms obtained from the experimental data are given below:

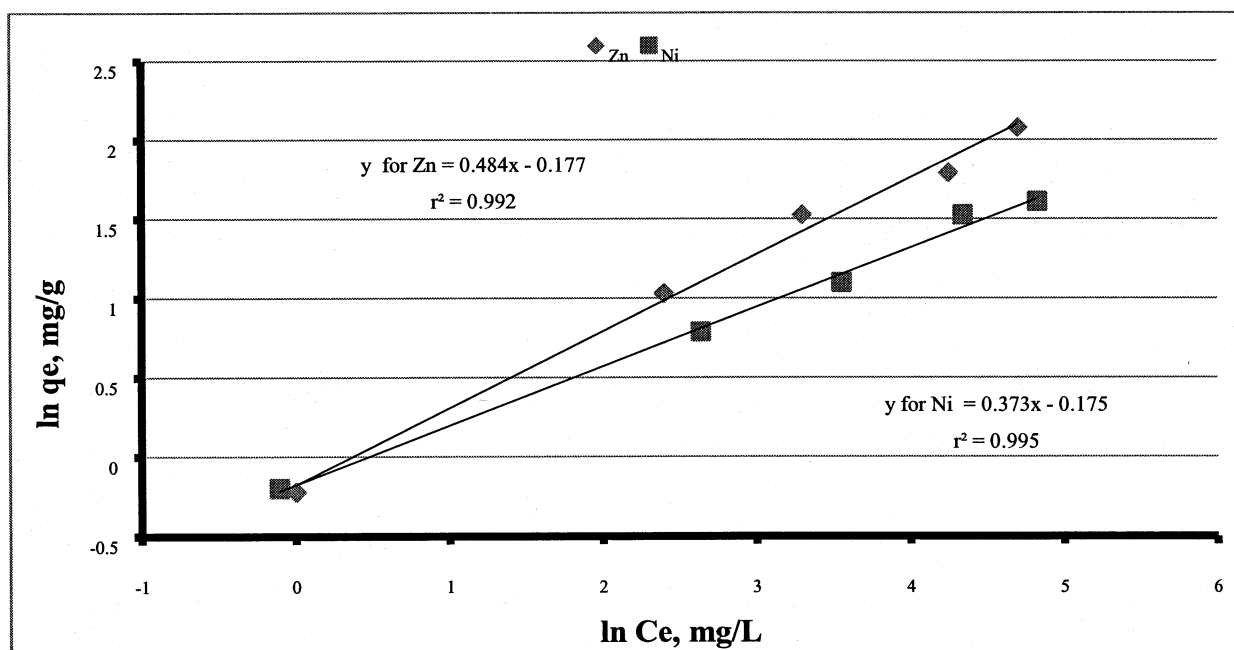


Figure 5.7.5 : Freundlich Isotherm for Binary Component System at 25 °C and pH of 6.3

The IAS-Freundlich Multicomponent Isotherm was the best, among the four isotherms discussed (Langmuir multicomponent isotherm, Langmuir partially competitive isotherm, Freundlich multicomponent isotherm), at modeling both the Ni^{2+} and the Zn^{2+} data. But these isotherms gave the erroneous results about prediction of the amount adsorbed during the biosorption processes. The amounts remaining in solution at equilibrium were calculated by using IAS-Freundlich multicomponent isotherm equations 3.17 and 3.18 for the Ni^{2+} and the Zn^{2+} . The prediction made was very much close to the actual experimental values. The table 5.7.5 gives a comparison for the two values. Zn^{2+} were more efficiently adsorbed than Ni^{2+} for two reasons: first, Zn^{2+} has higher molecular weight and lower aqueous solubility than Ni^{2+} ; second, the extra carboxylic group or electron withdrawal group on Zn^{2+} allows it to form a stronger complex than Ni^{2+} .

Table 5.7.6: Prediction of The Metallic ions Remaining in Solution by IAS-Freundlich Multicomponent Isotherm

Initial C_0	Ni^{2+}		Zn^{2+}	
	Predicted	Actual	Predicted	Actual
150	123.60	125	108.03	110
100	80.711	77	67.00	70
50	39.41	35	35.25	27
25	14.64	14	14.08	11
5	0.84	0.9	1.25	1

Since Ni^{2+} - Zn^{2+} bisolute biosorption was a competitive process, the two species inhibited each other's biosorption. Gadde and Laitinen, 1974 used the isotherms to study heavy metal biosorption competition on hydrous manganese oxides. They found 64% displacement of Zn^{2+} when an equal Pb^{2+} concentration of 10^{-3} M was there at a pH 6. Al-Asheh and Duvjak, 1998, investigated the biosorption of binary metal ions by pine bark. The binary system was Cu^{2+} Cd^{2+} , Cu^{2+} Ni^{2+} and Cd^{2+} Ni^{2+} . They concluded that the capacity of the bark for each metal in the binary systems was lower than in the single metal system.

Crittenden *et al.*, 1985, presented the IAS-Freundlich model; the nature of this isotherm makes calculations easier. This model is good in giving us the amounts of metallic species left in binary solutions after the biosorption on a biosorbent surface.

The Freundlich isotherm gave a better fit for the Ni^{2+} and Zn^{2+} single-solute data than the Langmuir and the Temkin isotherms over the concentration range of 5 ppm to 150 ppm at 25 °C. The Langmuir Partially Competitive Isotherm, the Freundlich Multicomponent showed that the biosorption of Zn^{2+} was better than the Ni^{2+} biosorption in binary solutions. Overall the IAS-Freundlich Isotherm was the most reliable in representing the Ni^{2+} - Zn^{2+} biosorption behavior.

5.8 Kinetics

The rate of reaction of wheat straw was determined by equilibrium batch tests. The data obtained was applied to proposed models. The equilibrium data was collected for biosorption at temperatures of 20, 25, 30, 35 and 40 °C for pH of 3, 4, 5, and 6.3 for Zn^{2+} ions and pH of 4, 5, and 6.3 for Ni^{2+} . The behavior of Ni^{2+} and Zn^{2+} for binary ionic system was studied at same

temperature range from 20 to 40 °C and at pH of 4, 5 and 6.3. In order to see the effect of concentration on the rate of reaction, a concentration range of 5 ppm to 150 ppm at temperature of 25 °C and pH of 6.3.

5.8.1 The pseudo-first order

The plot of $\ln(q_e - q_t)$ versus time t , the values of pseudo-first order rate constant were obtained from the slope of the straight line.

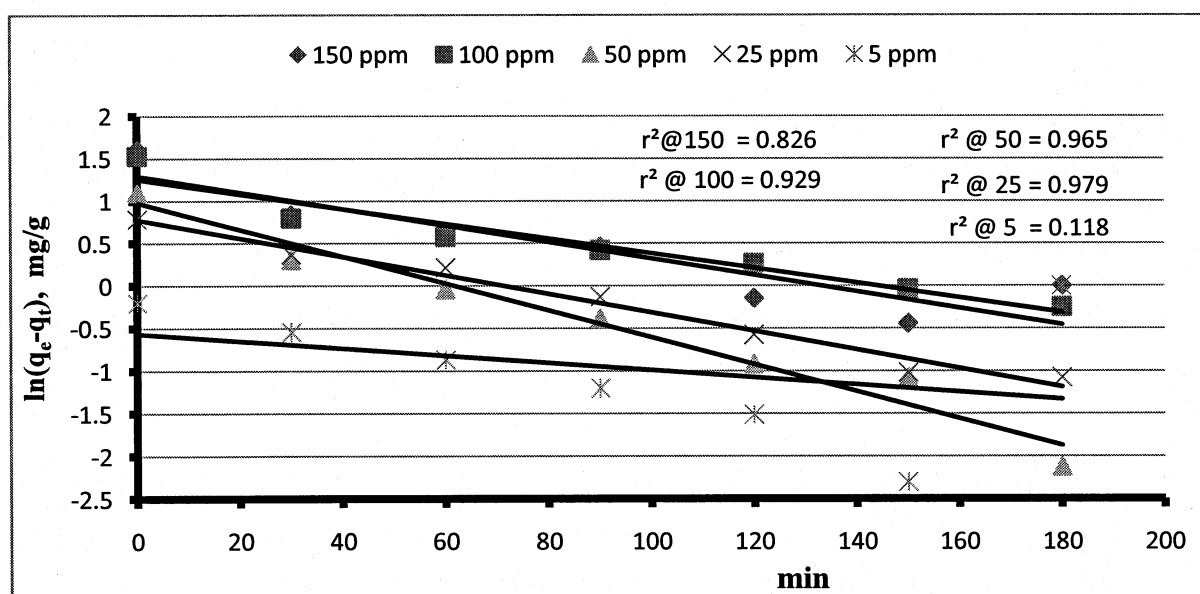


Figure 5.8.1: Pseudo First Order for Ni^{2+} in Binary System at 25 °C and pH of 6.3

For the same experimental conditions of pH, temperature and concentrations the data was obtained for Zn^{2+} as that of Ni^{2+} and plotted for pseudo second order in figure 5.8.2. The straight line plot of $\ln(q_e - q_t)$ vs. t at different temperatures indicates the validity of Lagergren equation for the system and it indicates that the process follows first-order kinetics. In such a case, a relationship is established between the rate constant and the biosorption. This will indicate if rate constant is decreases with increase in temperature then the biosorption is higher at lower temperatures. The first-order rate constant k_1 were obtained from the slope of the plot of $\ln(q_e - q_t)$ vs. time. The first-order rate constants for biosorption were found to 0.0042, 0.0109, 0.0158,

0.0134 and 0.0097 min^{-1} for initial Ni^{2+} concentrations of 5, 25, 50, 100 and 150 mg L^{-1} , respectively. For Zn^{2+} these were obtained as 0.0014, 0.0082, 0.0168, 0.0105 and 0.0146

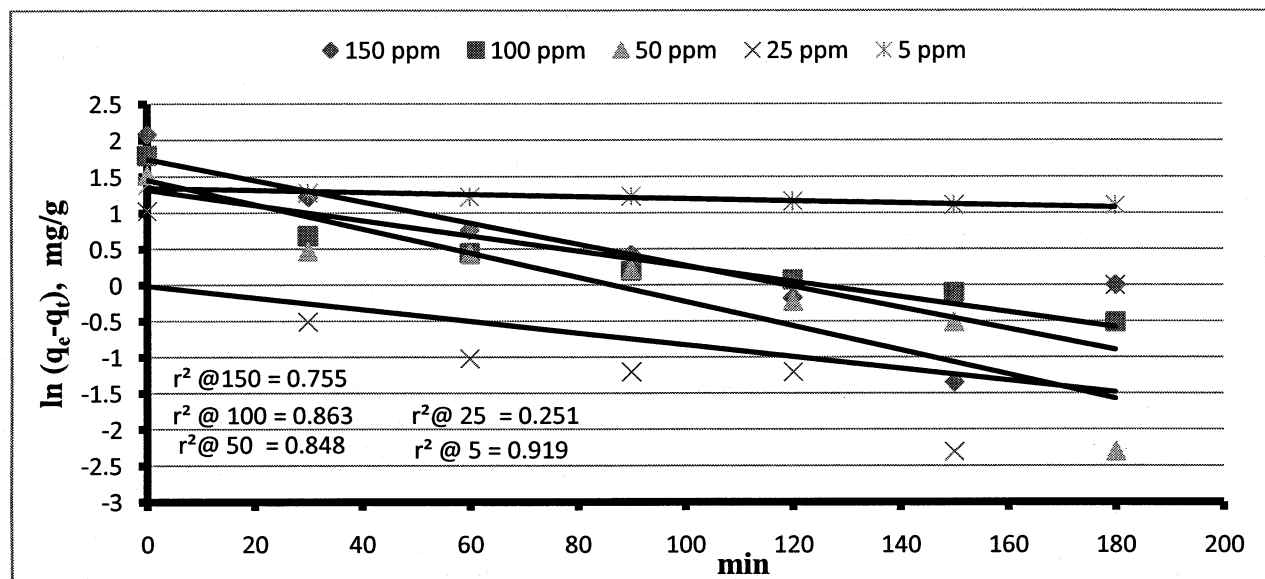


Figure 5.8.2: Pseudo First Order for Zn^{2+} in Binary System at 25°C and pH of 6.3

respectively. The variation in rate should be proportional to the first power of concentration for strict surface biosorption. However, the relationship between initial solute concentration and rate of biosorption will not be linear when pore diffusion limits the biosorption process.

The values of the rate constant for Brilliant Green Dye (BG) determined from the plot of $\ln(q_e - q_t)$ against t by Mane *et al*, 2006. The values were 0.0198, 0.0269 and 0.0152 per minute for C_0 of 50, 100 and 200 mg / L , respectively. These were considered close to the rate constant values of 0.0073 and 0.0061 per minute, respectively, for the BG biosorption on neem leaf powder [Bhattacharyya and Sharma, 2003] and modified peat-resin particles [Sun and Yang, 2003]. Kalavathy *et al*, 2005, studied the biosorption of Cu^{2+} on activated carbon of rubber wood saw dust. The first-order rate constants were found to be 0.0336, 0.0182, 0.0181, and 0.0262 min^{-1} for initial Cu^{2+} concentrations of 10, 20, 30, and 40 mg L^{-1} , respectively.

Table 5.8.1 : Estimated and Actual Amount of Metal ions Adsorbed

Conc.	Zn^{2+}		Ni^{2+}	
	qe	Actual qe	qe	Actual qe
150	5.7	8	3.65	5
100	1.3	6	22.05	4.6
50	1.45	4.6	2.66	3
25	1.01	2.8	2.2	2.2
5	3.83	0.8	0.57	0.82

The table 5.8.1 is about the equilibrium adsorbed amounts found by experimentation and the amounts estimated by the model equation 3.20. The sample calculations are shown in the appendix. The regression coefficient values obtained from the plots were found to be in the range of 0.7344–0.8680. This suggested that it was not appropriate to use the Lagergren kinetic model to predict the biosorption kinetics for Zn^{2+} on to WS for the entire biosorption period. Again its behavior, in the case of Ni^{2+} suggested that the model can be applied but was not appropriate to describe the entire concentration range.

5.8.2 Pseudo-Second-Order Model

Pseudo-Second-Order Model (Ho and McKay Model) is used in order to investigate the biosorption mechanism of Ni^{2+} and Zn^{2+} and potential rate controlling steps such as mass transport and chemical reaction processes.

If the Ho and McKay model holds then the plot of t/q_t against t would give a linear relationship from which the q_e and k_2 can be determined, these are the slope and intercept of the plots. The rate constants measured for Zn^{2+} by pseudo second order reaction are 0.027, 0.053, 0.014, 0.022 and 0.007 $g\ mg^{-1}\ min^{-1}$ for the concentrations of 5, 25, 50, 100 and 150 ppm respectively. The following figure 5.8.4 shows biosorption of Zn^{2+} under same conditions of 25 °C and at pH of 6.3.

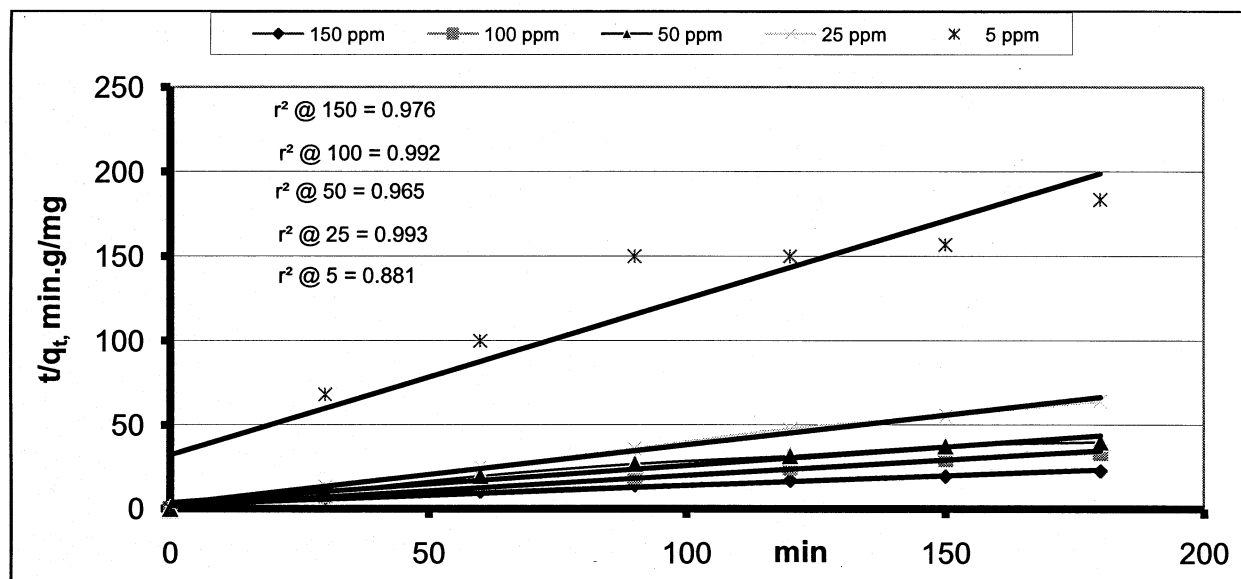


Figure 5.8.3: Pseudo Second Order for Zn^{2+} in the Binary System at 25 °C and pH of 6.3

The rate constants measured for Ni^{2+} by pseudo second order reaction are 0.067, 0.011, 0.018, 0.007 and 0.011 $\text{g mg}^{-1} \text{min}^{-1}$ for the concentrations of 5, 25, 50, 100 and 150 ppm respectively. In general, rate of reaction decreased for increase in initial concentration. In general, there is a decrease in the values of reaction rate constant with increase in initial concentration.

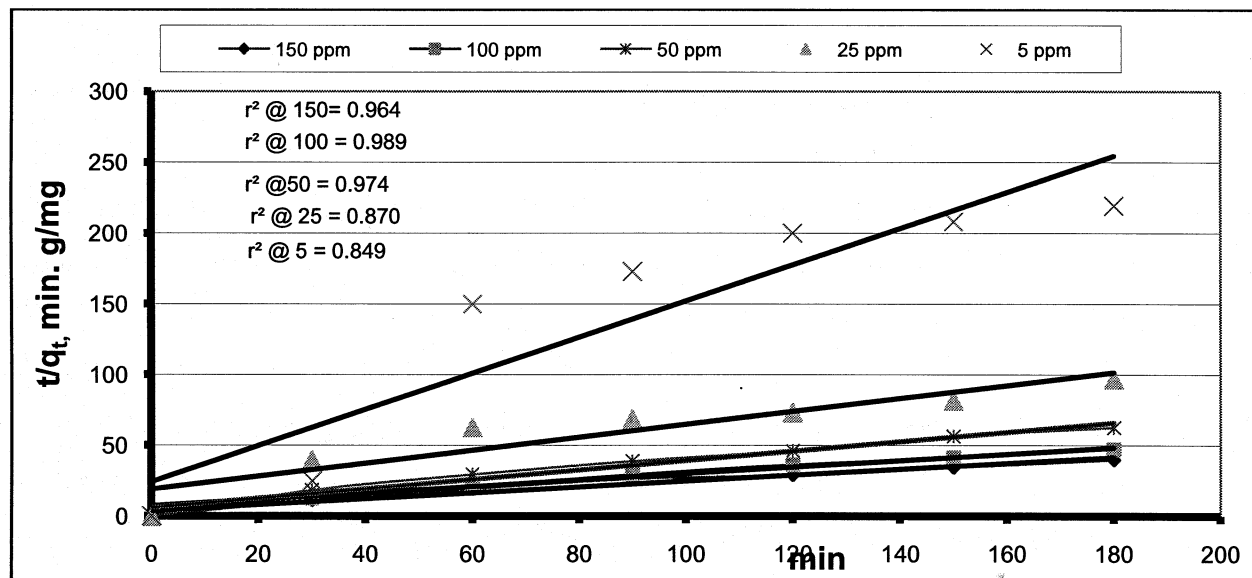


Figure 5.8.4 : Pseudo Second Order for Ni^{2+} in the Binary System at 25 °C and pH of 6.3

The decrease in k_2 values with an increase in metal concentration is a common phenomena observed with variety of adsorbents such as chitosan and 2-mercaptobenzimidazoleclay, moss peat, activated carbon and cross-linked chitosan bead used for the biosorption of Hg^{2+} , Ni^{2+} , Cr^{2+}

and reactive dye, respectively [Anoop Krishnan and Anirudhan, 2002; Manohar et al., 2002; Chiou and Li, 2002]. In a report by El-Shafey, 2007, percentage removal of Cd^{2+} and Hg^{2+} has increased with the decrease in the initial concentration and with temperature rise.

It is important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design a biosorption treatment plant. In order to investigate the mechanism of biosorption, characteristic constants of biosorption rate were determined using a first order equation, second order equation, pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on solid phase biosorption

Table 5.8.2: Coefficient of Determination for Binary System at 25 °C and pH of 6.3

Concentration	Zn^{2+}		Ni^{2+}	
	Pseudo Ist order	Pseudo 2 nd Order	Pseudo Ist order	Pseudo 2 nd Order
150	0.7552	0.976	0.9469	0.9647
100	0.8633	0.9926	0.9857	0.9893
50	0.8483	0.965	0.9658	0.9746
25	0.2511	0.9932	0.9775	0.8706
5	0.9192	0.8812	0.9775	0.8494

For our studies we can ignore coefficient of determination for 1st and 2nd order because of their low values. On this basis r^2 values for pseudo 1st order reaction for Ni^{2+} in the binary system cannot be neglected because they are ranging from 0.97 to 0.99. This has to be done because it is not fit to predict the suitable values for the amount adsorbed per unit mass of biosorbent as given in the table 5.8.3. At the higher concentration of metal ions, wheat straw can remove more metal ions from the solution but has a lower uptake per unit mass. As it decreased from 80% to 26 % for Zn^{2+} and for Ni^{2+} the decrease was from 82% to 16 %. Because of mal-predictability of the pseudo first order reaction as shown in the table 5.8.3, we have to go for the pseudo second order reaction. The table 5.8.4 is self explanatory for the predictions made by the second order reaction model for both Ni^{2+} and Zn^{2+} . Bulut *et. al*, 2007, found that their system follow the

Table 5.8.3: Predicted q_e values from Pseudo First Order Model for a Binary System, mg/g

Concentration ppm	Zn^{2+}		Ni^{2+}	
	Predicted q_e	Actual q_e	Predicted q_e	Actual q_e
150	5.7	8	3.65	5
100	1.3	6	22	4.6
50	1.45	4.6	2.66	3
25	1.01	2.8	2.17	2.2
5	3.83	0.8	0.59	0.82

pseudo second order model for biosorption of direct Blue dye 71 on wheat shells. A similar phenomenon was observed in the biosorption of direct red 12B and methylene blue onto Fe(III)/Cr(III) hydroxide [Namasivayam] , direct acid dyes on soy meal hull [Arami, 2006] ,basic dyes on kudzu [Allen, 2005] , direct red 23 and direct red 80 on orange peel [Ardejani, *et al*, 2006].

Table 5.8.4: Predicted q_e values from Pseudo Second Order Model for a Binary System, mg/g

Concentration ppm	Zn^{2+}		Ni^{2+}	
	Predicted q_e	Actual q_e	Predicted q_e	Actual q_e
150	8.4	8	4.8	5
100	5.43	6	4.4	4.6
50	4.5	4.6	2.99	3
25	2.8	2.8	2.18	2.2
5	1.0	0.8	0.78	0.82

The second-order rate constants were used to calculate the initial biosorption rate, given by

$$h = k_2 q_e^2$$

Table 5.8.5: Calculated Initial Biosorption Rates

Concentration	Zn ²⁺	Ni ²⁺
150 ppm	0.485578	0.249881
100 ppm	0.644621	0.136099
50 ppm	0.277293	0.169848
25 ppm	0.412031	0.052709
5 ppm	0.031124	0.041292

From the pseudo second-order rate constants, the calculated initial biosorption rate values are shown in table 5.8.5. It was observed that the initial biosorption rate (h) was found to increase with increased initial concentration of Ni²⁺ and Zn²⁺. The calculated q_e values agree very well with the experimental values, and a regression coefficient of above 0.89 shows that the model can be applied for the entire biosorption process and confirms the chemisorption of Ni²⁺ and Zn²⁺ onto wheat straw.

It was observed that the pseudo-second-order rate constant k_2 decreased with increased initial concentration and the initial biosorption rate h was found to increase with increased initial Cu²⁺ concentration while studying biosorption of Cu²⁺ on modified rubber wood saw dust by Kalavathy, 2005.

5.9 Effect of Temperature and pH on Kinetics

In order to determine the effect of temperature and pH on biosorption of wheat straw, temperatures of 20, 25, 30, 35 and 40 °C and pH of 3, 4, 5 and 6.3 were used. To isolate the effect of temperature only the temperature was varied within the said range while other parameters like pH, initial concentration (150 ppm), shaking speed (120 rpm), volume of solution (200 ml) and amount of biosorbent (1000 mg) were kept constant. Same strategy was used while studying pH. Following model was studied as it was done during the study of effect of concentration:

Pseudo Second Order Model

Pseudo second order model was tried to find suitable representation of experimental data obtained under various conditions of temperature and pH for biosorption process of wheat straw. The plots of t / q_t against 't' obtained were straight lines, only the set obtained for pH of 5 is given in figure 5.9.1 and those for pH of 4 and 6.3 are shown in appendix as figures B-1 and B-2 on page 158 :

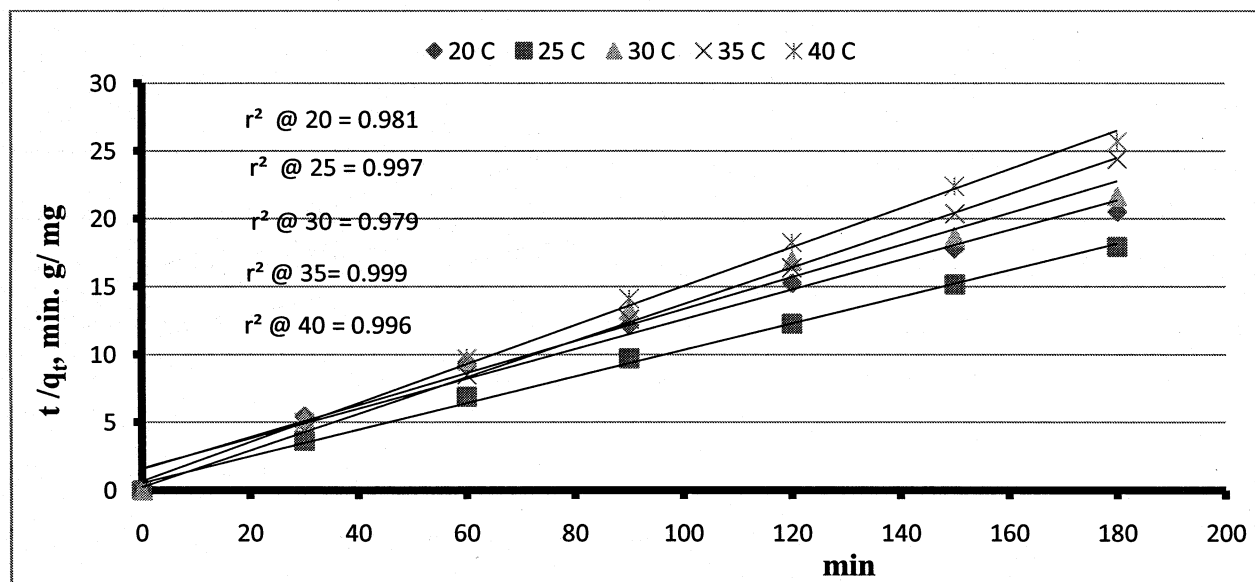


Figure 5.9.1 : Pseudo Second Order for Zn^{2+} in a Single ion System at pH of 5 and 150 ppm

Comparison of the accuracy of the estimated and actual q_e values, for Zn ions by using Pseudo Second Order Model in a Single Ion System was made as shown in table 5.9.1. It was found that the estimated values and the actually found values are almost the same. As the next step, the behavior of Zn ions was checked for a binary system. The table 5.9.2 gives a comparison of the predicted values and the practical values of the amounts adsorbed on wheat straw in a binary system. The estimated and actual values are in good agreement. Similar, good agreement between predicted and experimental values was observed for the Ni^{2+} in single as well as in binary ionic systems. The tables representing these results are given in the appendices p-155 in tables B-1 and B-2.

Table 5.9.1: Comparison of the Accuracy of the Estimated and Actual $*q_e$ Values, for Zn^{2+} by Pseudo Second Order Model in a Single System.

°C	pH 4		pH 5		pH 6.3	
	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e
20	10	9.6	9.17	8.8	8.13	8
25	10.41	10.2	10.30	10	10.87	11
30	8.47	8	8.54	8.4	10.10	9.8
35	5.84	5.6	7.46	7.4	10.10	10
40	4.80	4.4	6.99	7	8.06	8

$*q_e$: is the amount of Zn^{2+} adsorbed at equilibrium

Table 5.9.2 : Comparison of the Accuracy of the Estimated and Actual $*q_e$ Values, for Zn^{2+} by Pseudo Second Order Model in a Binary System.

°C	pH 4		pH 5		pH 6.3	
	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e
20	5.19	5	6.12	6	6.47	6.4
25	5.96	5.8	6.26	6	8.4	8
30	5.6	5.6	6.1	6	7.5	7
35	4.93	4.8	5.7	5.6	6	6
40	4.5	4.4	5.3	5.4	5.13	5.2

$*q_e$: is the amount of Zn^{2+} adsorbed at equilibrium

The rate constants of second order and amount adsorbed at equilibrium were used to estimate the initial amounts adsorbed on the surface of wheat straw and found that with increase or decrease in temperature, there was no regular trend for initial concentration biosorbed. For Ni^{2+} , same strategies were applied, the plots obtained from the experimental data is given in figure 5.9.2.

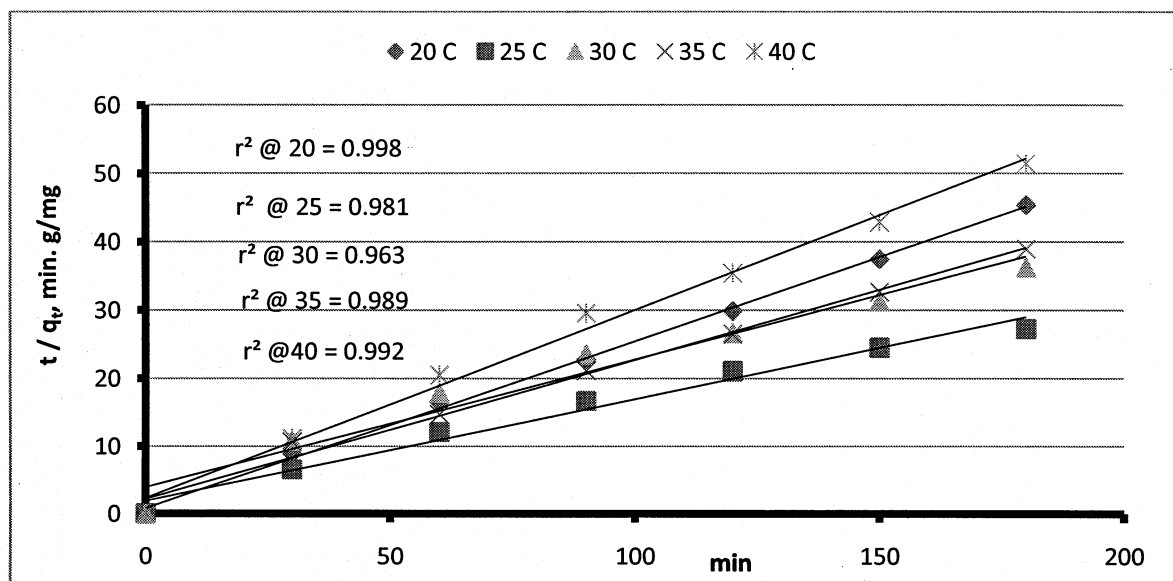


Figure 5.9.2: Biosorption of Ni^{2+} in Single Ions System

Similar behavior was observed for Ni^{2+} in binary solution. The plots obtained were studied and their rate constants values were calculated. The rate constants for a single ionic system are given below along with rate constants for other set of pH values of 5 and 6.3.

Table 5.9.3 : The Second Order Rate Constants for the Plots of Ni^{2+} in Single ionic System

°C	r^2	pH 4	r^2	pH 5	r^2	pH 6
20	0.985	0.019	0.998	0.07	0.984	0.017
25	0.988	0.028	0.981	0.012	0.988	0.017
30	0.994	0.005	0.963	0.009	0.998	0.030
35	0.975	0.046	0.99	0.019	0.975	0.018
40	0.987	0.028	0.99	0.032	0.987	0.037

Similarly, no trend is observed for Zn^{2+} in single ionic binary ionic system as shown in the tables B-3 and B-4 in appendices at page 156. For the binary system of Ni^{2+} , the values are given in table B-5 at page 157 and the plots are shown in the figures B-7, B-8 and B-9 in the appendix B at the pages 162 and 163. The rate constants of second order and amount biosorbed at equilibrium were used to estimate the initial amounts biosorbed on the surface of wheat straw by using following equation:

$$h = k_2 q_e^2$$

Table 5.9.4: Initial Biosorption Rate for Ni ion in a Single Ion System mg/g . min

°C	pH 4	pH 5	pH 6
20	0.305	0.26	1.03
25	0.49	0.53	0.93
30	0.59	0.11	0.26
35	0.26	0.69	0.47
40	0.44	0.34	0.44

No regular trend can be observed for the values of h , initial biosorption rate. The rate constants for Ni^{2+} in single ion system at pH of 6, increased from 0.017 to 0.037, at pH of 5 there was a decrease from 0.07 to 0.037 no regular trend was followed and at pH of 4 with increase in temperature from 20 to 40 °C. A slight increase in initial biosorption rate was observed at pH of 4 and 5, at pH of 6 the initial biosorption rates decrease from 1.03 to 0.44 with increase in temperature from 20 to 40 °C. In binary ionic system, as shown in table B-6 of page 157, at pH of 6.3 the rate constant increased from 0.016 to 0.266 at pH of 5 there was no significant change and at pH of 4, there was a trend to increase from 0.017 to 0.041 with increase in temperature from 20 to 40 °C for Ni^{2+} . All data is given in appendix. Initial rate constant are almost the same at pH of 5, at pH of 4 and 6.3 no regular trend was observed for Ni^{2+} . No regular trends were observed for Zn^{2+} at all the values of pH. The reduction of the removal of Cd in the interval of temperature 30–50°C has been reported by the Aksu, 2004. They concluded that the process of cadmium biosorption by chitin was exothermic. Similar results have been reported for the biosorption of lindane by chitin in seawater at three temperatures 5°C, 22°C and 45°C by Santana and Davilla, 1992. In a report by El-Shafey, 2007, percentage removal of Cd^{2+} and Hg^{2+} has been reported that was increased with the decrease in the initial concentration and with temperature rise.

According to the literature, results of study of the effect of the temperature on biosorption for different metal–biomaterials systems are disparate. An increase of the temperature, in the range 5–45°C, rose the biosorption [Shumate et al. 1978, Strandberg *et al*, 1981, Townsley *et.al*, 1985,

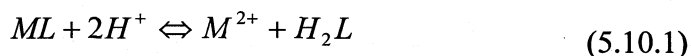
Tsezos *et al* 1986,] while variations of temperature in the range 5–25°C did not affect the biosorption[De Rome and Gadd] . If biosorption is governed only by physical phenomena, an increase in temperature will be followed by a decrease in biosorption capacity. Temperature could influence the desorption step and consequently the reversibility of the biosorption equilibrium. Within the temperature range investigated, it is impossible to come to a conclusion.

The predictions made by pseudo second order for the amounts adsorbed per gram of wheat straw were very precise for both the single and binary ion system for both the nickel and zinc ions.

5.10 Mechanism

The interactions of metals with wheat straw surface molecules are complex. Probably a lot of reactions run simultaneously like ion exchange and chelation or complexation, but the biosorption is the dominating one. The pH dependence of biosorption may suggest that metal ions are adsorbed according to the ion-exchange mechanism, and deacetylation dependence of biosorption may indicate the chelation mechanism [Lawther *et. al.*, 1996].

There are two major types of metal–organic interactions to be considered in an aquatic system. The first type is complexation, usually chelation when organic ligands are involved. A reasonable definition of complexation by organics applicable to wastewater systems is a system in which a species is present that reversibly dissociates to a metal ion and an organic complexing species as a function of hydrogen ion concentration [March, 1986]:



In this equation, M^{2+} is a metal ion and H_2L is the acidic form of a complexing—frequently chelating—ligands, L^{2-} , illustrated here as a compound that has two ionizable hydrogens the metals bound to organic entities by way of a carbon atom and do not dissociate at lower pH or greater dilution. Organ metallic compound could have the following functional groups that bind to metal ions:

1. Alkyl group such as C_2H_5- .
2. Carbonyls $C \equiv O$.
3. Those in which the organic group is a π electron donor, such as ethylene or benzene. $CH_2=CH_2$ (ethylene) C_6H_6 (benzene).

Secondly, a possible mechanism of metal ions removal is ion exchange that could be considered as a heavy metal ion (M^{n+}) attaching itself to adjacent hydroxyl groups and oxyl groups which could donate two pairs of electrons to metal ions, forming chelated compounds and releasing hydrogen ions are released back into solution.

In order to study the binding of metal ions to the wheat straw, the IR spectra of wheat straw and the metal were recorded. It was hoped that there would be a large number of metal ions bonded strongly to sites on the wheat straw. The IR spectra showed broad peak at 3400 cm^{-1} and weaker but more highly separated peak systems in $500\text{--}1500\text{ cm}^{-1}$ region. It could be seen that there were some changes in the IR spectra of metal loaded wheat straw as compared to that of untreated wheat straw. On the study of Ni^{2+} on wheat straw, a new peak was observed at 1633.34 cm^{-1} which was attributed to $C=O$ of non-conjugated aromatic affiliations. At 1467.06 cm^{-1} a new peak is observed while the peak at 1425 cm^{-1} of virgin WS was missed here. This may be considered as stretched to 1467.06 cm^{-1} which indicated vibration of methyl groups and deformation of methyl group. For Zn^{2+} loaded wheat straw another peak at 1320.72 cm^{-1} from virgin wheat straw was shifted to 1260.08 cm^{-1} which could be attributed to syringyl group whose vibrations was reduced due to biosorption of Zn^{2+} . Similarly, the loading of Ni^{2+} and Zn^{2+} simultaneously showed the involvement of $-C-OH$, $-C-O-C$ and $-C-C$ bonds in the biosorption of Ni^{2+} and Zn^{2+} on wheat straw at peaks of 1056 cm^{-1} , 1130 cm^{-1} and 1370 cm^{-1} respectively. Therefore, the IR is capable of giving useful information about interaction of the metal with sites on the wheat straw.

From our experimental data it can be seen that the initial biosorption rate was very high for almost all values of the initial concentration and that it rapidly decreased with time, especially at high initial Ni^{2+} and Zn^{2+} concentrations. Since the initial rate was mainly related to the external

mass transfer resistance, this implied that the external diffusion was very rapid and hence it was concluded that the external mass transfer was not the rate limiting step of the metal removal.

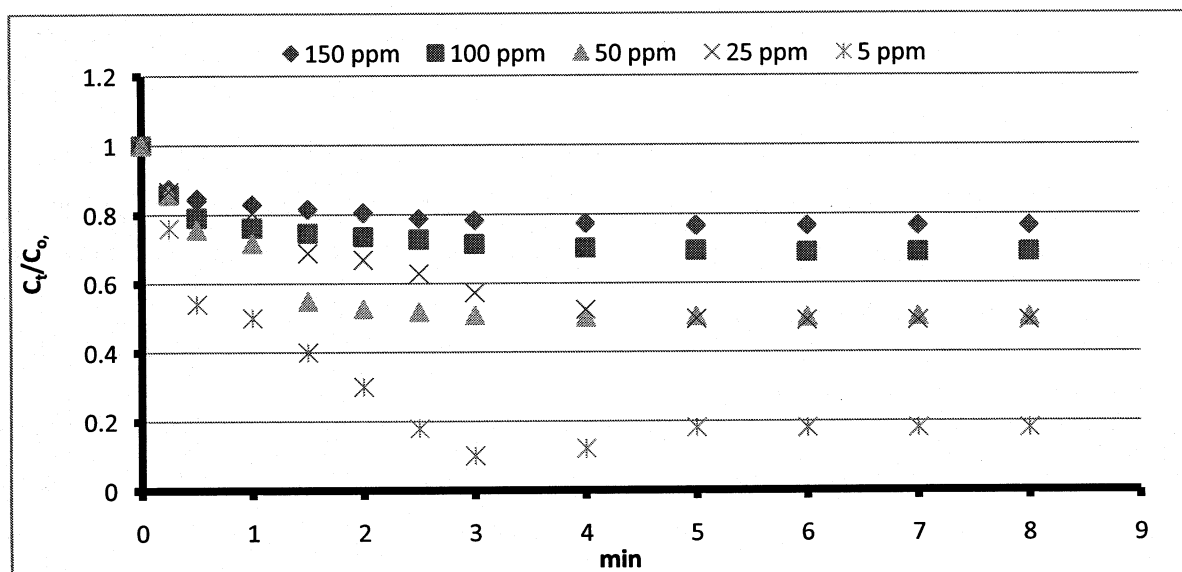


Figure 5.10.1 : Non-Dimensional Concentration Vs Time for Zn²⁺

In addition to identify the limiting step, among reaction rate and intraparticle diffusion, it was important to note that the biosorption rates were different for various initial concentrations. The biosorption rates showed a tendency to increase as the initial amount of Ni²⁺ and Zn²⁺ ions decreased. It suggested that the limiting step of biosorption kinetics could be the intraparticulate diffusion inside the solid surface.

The biosorption of solute onto the biosorbent surface from the solution phase occurs in several steps, such as film or external diffusion, pore diffusion, surface diffusion and biosorption on the pore surface. The overall biosorption process may be controlled by one or more steps. The possibility of pore diffusion was explored using the Bangham equation [Aharoni *et al.*, 1979].

$$\log \log \left(\frac{C_0}{C_0 - q_t m} \right) = \log \left(\frac{k_o m}{2.303V} \right) + \alpha \log t \quad (5.10.2)$$

here C_0 is the initial concentration of adsorbate in solution (mg/L),

V is the volume of solution (ml),

m is the weight of adsorbent per liter of solution (g/L),

q_t is the amount of adsorbate retained at time t , (mg/g) and

$\alpha < 1$ (min^{-1}) and k_o (L^2/g) are constants

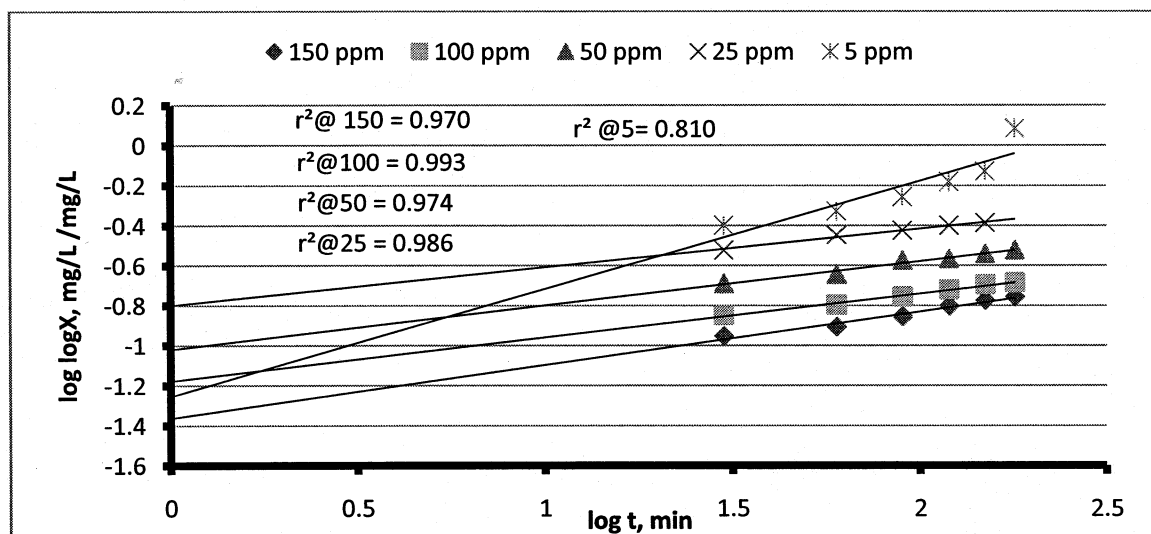


Figure 5.10.2 : Bangham Model for the Biosorption of Zn^{2+} in Single ionic System

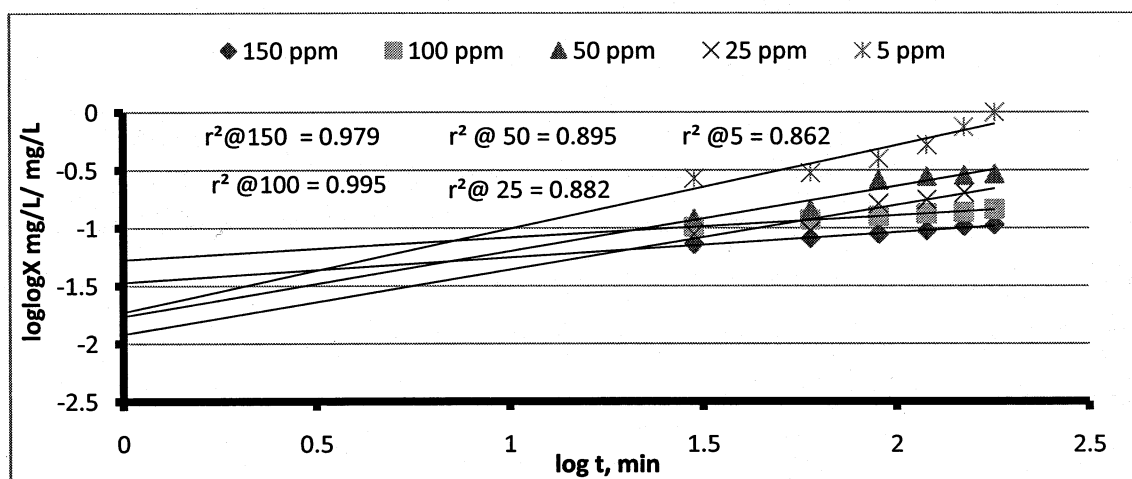


Figure 5.10.3 : Bangham Model for the Biosorption of Ni^{2+} in Single ionic System

The slopes obtained from the plots of double log against $\log t$ were very well within the limits, i.e. less than 1 which suggested that the biosorption was pore diffusion process. The α values were obtained from the slopes of the plots of figures 5.10.2 and 5.10.3, the α values are given in the table 5.10.1

Table 5.10.1 : Bangham Constant ‘ α ’ for Single and Bisolute Systems

Concentration ppm	Zn^{2+}		Ni^{2+}	
	Single	Bisolute	Single	Bisolute
150	0.266	0.347	0.218	0.325
100	0.218	0.180	0.192	0.284
50	0.220	0.180	0.563	0.354
25	0.191	0.157	0.557	1.143
5	0.538	1.049	0.723	0.984

The r^2 values are in the range of 0.81 to 0.99. It means that the pore diffusion is there but it is not the only rate-controlling step in the biosorption process.

The prediction of the rate-limiting step is an important factor to be considered in the biosorption process. It is governed by the biosorption mechanism, which is generally required for design purposes. For a solid–liquid biosorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or intraparticle diffusion, or both. The three steps analyze the mechanisms of biosorption as follows [Ozer *et al.*, 2005]:

- 1- Transport of the solute from bulk solution through liquid film to the biosorbent exterior surface;
- 2- Biosorption of the sorbate on the exterior surface of the biosorbent.
- 3- Transport of the sorbate within the pores of the biosorbent (particle diffusion);

Weber and Morris, 1963, model can be described by the equation 5.10.3. According to this model, the amount adsorbed varies almost proportionately \sqrt{T}

$$q_t = k_i \sqrt{T} + I \quad (5.10.3)$$

Where q_t : Amount adsorbed per gram of biosorbent (mg/g)

k_i : Intra particle diffusion rate constant, $\text{mg g}^{-1} \text{min}^{-0.5}$

I : Finite biosorption, mg/g, at $t=0$, $q_t = I$

T: time, min

The intercepts I and the intraparticle rate constant values calculated from the slopes of the linear portions of the plots which are obtained by plotting q_t versus \sqrt{T} . As it has been observed that for both Ni^{2+} and Zn^{2+} , the k_i values increased with increasing initial concentrations and the r^2 values are from 0.87 to close to unity indicating the applicability of this model.

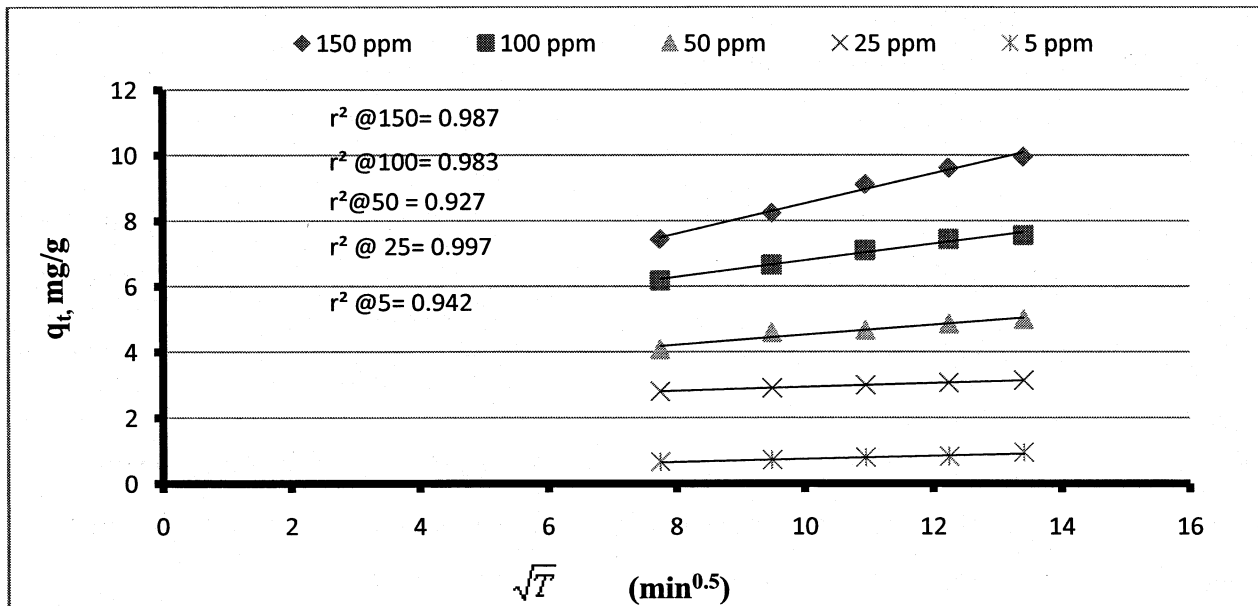


Figure 5.10.4: Weber Model for Zn^{2+} in Single Ionic System

The observed increase in k_i values with increasing initial metal concentration can be explained by the growing effect of driving force, the concentration gradient. Values of intercepts give an idea about the thickness of the boundary layer, i.e., the larger intercept the greater is the boundary layer effect, means higher initial rate of biosorption. The higher k_i values obtained for Zn^{2+} (0.046 to 0.458) biosorption system than the Ni^{2+} biosorption (0.058 to 0.246) system suggests that intraparticle for Zn^{2+} in biosorbent is faster than that of Ni^{2+} .

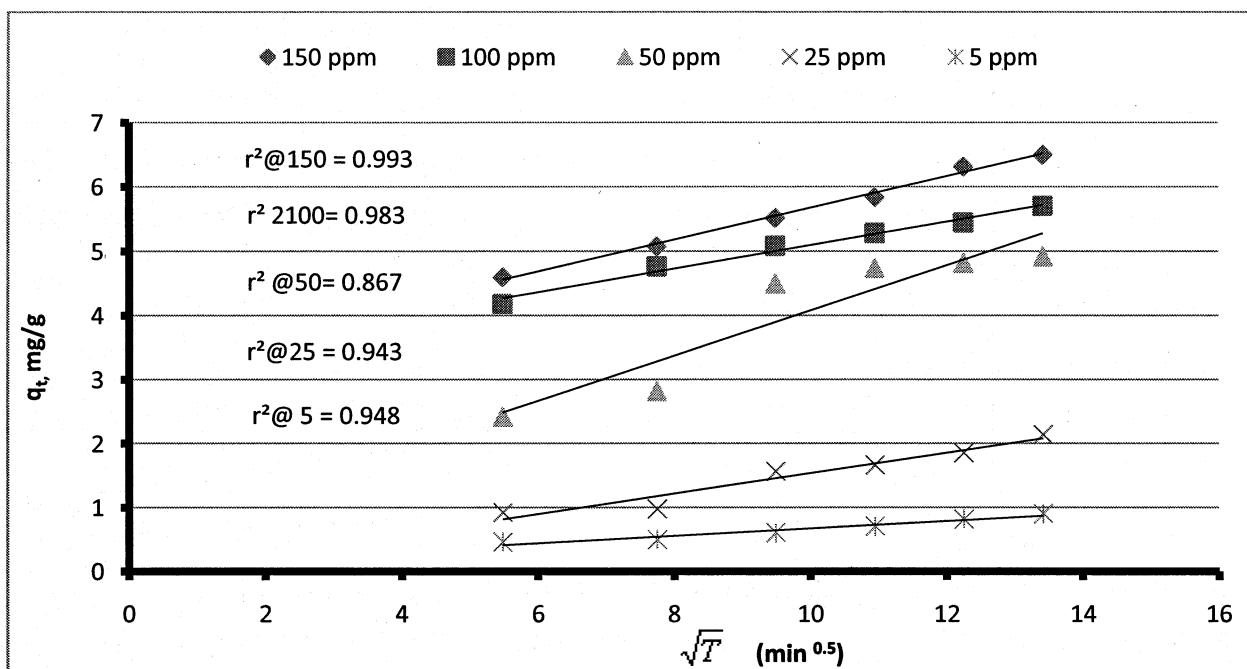


Figure 5.10.5 : Weber Model for Ni^{2+} in Single Ionic System

The intraparticle rate constant values, the higher intercept values for Zn^{2+} are also higher (0.28 to 3.94) than those obtained for Ni^{2+} (0.09 to 3.2) indicating that the effect of the external mass transfer on the Zn^{2+} biosorption was higher. The increasing trend of intraparticle rate constant values with initial solute concentrations was reported before by various investigators [Namasivayam et al, 2002, Otero et al, 2003].

Ozer *et. al.*, 2006, studied the biosorption behavior of *S. rhizopus* for the dyes AB 290 and AB 324. They applied Webber and Morris model and found that the linear portions of the curves do not pass through the origin indicating that the mechanism of AB 290 and AB 324 biosorption on *S. rhizopus* is complex and both the surface biosorption as well as intraparticle diffusion contribute to the actual biosorption process. The deviation of straight lines from the origin can be explained by the difference between the rate of mass transfer in the initial and final stages of biosorption. We observe same deviation in our study for both single and bisolute systems and all conditions of temperatures 20 °C to 40 °C and all pH values from 4 to 6.3.

The plots obtained for Ni^{2+} and Zn^{2+} in a bisolute system have almost the same trends as the plots shown in figs 5.10.3 and 5.10.4 for single solute systems for the ions under study. Plots for

bisolute system are in appendices as figures B-13 to B-15 at pages 164 to 165. The larger the intercept, the greater is the boundary layer effect [Kannan and Sundaram, 2001]. Further, such deviation of straight lines from the origin indicates that the pore diffusion was not the sole rate controlling step [Poots et al., 1978] .

Several studies reported that the plot of q_t vs. $t^{0.5}$ represents the initial curved and final linear portion, which characterized the two or more steps involved in the biosorption [Sun and Yang, 2003; Walker et. al., 2003]. Biosorption process could proceed by surface biosorption and intraparticle diffusion. The initial curved portion of the plot indicates a boundary layer effect (film diffusion) while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot represented the intraparticle diffusion rate constant. On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface biosorption in the rate-controlling step.

Table 5.10.2: Parameters of Weber and Morris Model for Bisolute System

Concentration ppm	Zn^{2+}			Ni^{2+}		
	k_i $mg\ g^{-1}\ min^{-0.5}$	Intercept	r^2	k_i $mg\ g^{-1}\ min^{-0.5}$	Intercept	r^2
150	0.43	3.1	0.99	0.24	1.39	0.97
100	0.19	2.4	0.99	0.18	1.29	0.99
50	0.16	0.17	0.91	0.15	0.83	0.96
25	0.07	0.13	0.93	0.15	0.13	0.97
5	0.07	0.02	0.94	0.07	0.16	0.99

Similar to the observations with single ionic solutions for the binary solution K_i values increased with the initial solute concentration.

The biosorption mechanism of Zn^{2+} and Ni^{2+} was complex combination of ion exchange, complexation and physical and chemical biosorption. The rate determining steps appeared to be pore diffusion and film diffusion.

5.11 Thermodynamic Parameters

Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) can be estimated using equilibrium constants changing with temperature. The free energy change of the biosorption reaction is given by the classic Vant Hoff's equation:

$$\Delta G = -RT \ln K_c \quad (5.11.1)$$

where ΔG is free energy change, J/mol;

R is universal gas constant, 8.314 J/mol K and

T is absolute temperature, K.

The free energy change indicates the degree of spontaneity of the biosorption process and the higher negative value reflects a more energetically favorable biosorption. The equilibrium constant of biosorption is defined as:

$$K_c = \frac{C_0 - C_e}{C_e} \quad (5.11.2)$$

C_e is the equilibrium concentration.

**Table 5.11.1: K_c Values for Metallic Ions
In a Single Ionic System**

C_0 , ppm	Ni^{2+}	Zn^{2+}
150	0.5	0.30
100	0.64	0.45
50	1.08	1
25	1.77	1.08
5	6.14	4.55

The table 5.11.1 shows K_c values for the biosorption of Ni^{2+} and Zn^{2+} on wheat straw at 298.16 °K at pH of 6.3, of the initial dye concentration as shown for their single ionic system. The K_c

values decreased with increasing concentration resulting a shift of the biosorption equilibrium to the left for both biosorption systems.

**Table 5.11.2 : ΔG Values for Metallic Ions for Single Ion System
at 25 °C, J/mol**

C_o , ppm	Ni^{2+}	Zn^{2+}
150	1718.24	2948.86
100	1108.84	1983.42
50	-198.42	0
25	-1426.27	-198.42
5	-4499.92	-3758.88

The reaction of metal ions with wheat straw is spontaneous from 5 ppm to 50 ppm for Ni^{2+} . For Zn^{2+} it is spontaneous up to 25 ppm. The increase in concentration the spontaneity of the reaction decreases till at 150 ppm where ΔG has large positive values. The similar trend for free energy change is observed for the binary solute system i.e. negative at 5 ppm and increases to positive value for 150 ppm. We can say free energy of a system is a direct function of initial concentration of system.

Further to investigate the effect of temperature and pH on free energy change, concentration of ions kept constant (150 ppm). The temperature was varied from 20 to 40 °C and pH from 3 to 6.3.

$$\Delta G = \Delta H - T \Delta S \quad (5.11.3)$$

According to equation 5.11.3 a plot of free energy change versus temperature (°K) is linear and the enthalpy and entropy change values are determined from the slope and intercept of the plot. The calculated values are tabulated in appendix at pages 167 and 168 for single ionic system and binary ionic system. The enthalpy change values for the biosorption of Ni^{2+} and Zn^{2+} on *wheat straw* were found to be 28 to 38 kJ/mol and 21.1 to 63.8 kJ/mol for single ions system and for binary ionic system the values are from 20.2 to 31.09 kJ/mol 9.3-28.7 kJ/mol for bisolute system,

respectively. The entropy change values for the biosorption of Ni^{2+} on wheat straw were found to be -0.108 to -0.139 J / mol K for single ion system and it was -0.082 to -0.118 J/mol K for bisolute system for variations in temperatures from 293.16 $^{\circ}\text{K}$ to 313.16 $^{\circ}\text{K}$. Similarly the values for Zn^{2+} in the single ion system were -0.075 to -0.218 J/mol $^{\circ}\text{K}$ for single ion and -0.042 J/mol K to -0.104.6 J/mol K. The positive value of ΔH shows that the biosorption of Ni^{2+} And Zn^{2+} on wheat straw is endothermic in nature; an increase in T causes an increase in K_c .

Bulut and Aydm, 2005, while working on wheat shells observed that biosorption of dye methylene blue (it is a basic dye) had a positive enthalpy change value indicating the that the biosorption was endothermic. The negative ΔS value obtained in the present study corresponds to a decrease in randomness at the solid/liquid interface during the biosorption of metallic ions on biosorbent while low value of ΔS indicates that no remarkable change on entropy occurs.

The free energy changes for Ni^{2+} and Zn^{2+} biosorption processes were obtained as 1.7 and 2.95 kJ/mol at optimum biosorption temperature 25 $^{\circ}\text{C}$ respectively for single ions system. For the bisolute system the values were 3.99 and 2.50 for Ni^{2+} and Zn^{2+} respectively.

Generally, the change of free energy for the physical and chemical biosorption are in the range of 0 to 20 kJ/mol and 80 to 400 kJ/mol, respectively [Ho et al., 2002]. From here we can postulate that the biosorption of Ni^{2+} and Zn^{2+} on wheat straw is a physical phenomena.

5.12 Activation Energy

The pseudo second order rate constant is expressed as a function of temperature by the following Arrhenius type relationship [Srinivasan,1988]:

$$k_2 = k_0 \exp \left[\frac{-E}{RT} \right] \quad (5.12.1)$$

Where

k_0 is the temperature independent factor ($\text{g mg}^{-1} \text{ min}^{-1}$),

E is the activation energy of biosorption (kJ mol^{-1}),

R is universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and

T is the absolute temperature (K).

The activation energy of biosorption was also calculated from the linearized Arrhenius equation:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (5.12.2)$$

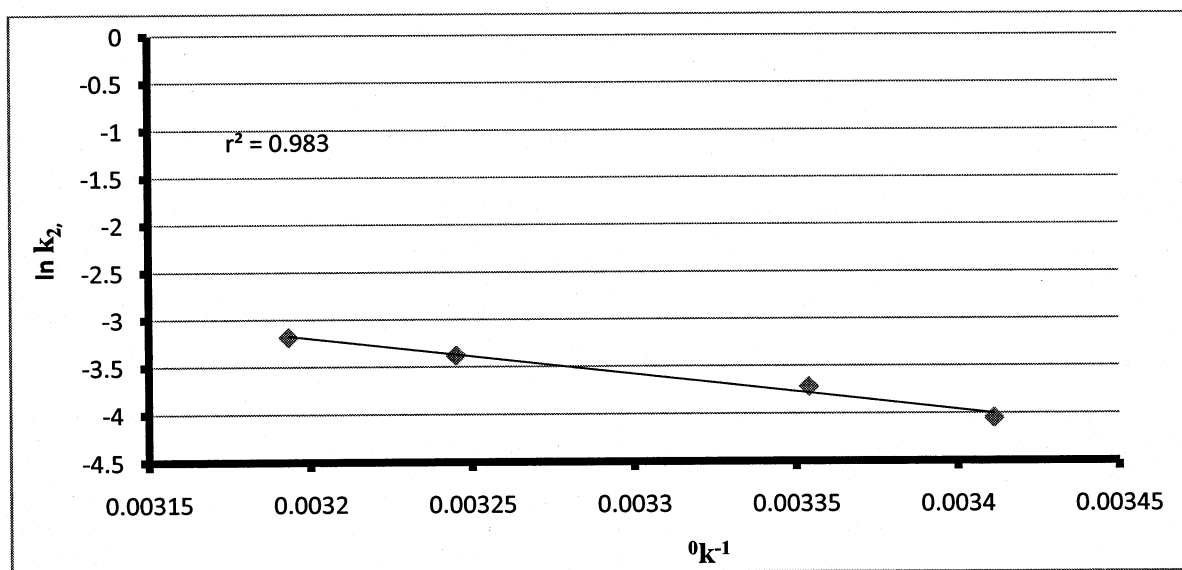


Figure 5.12.1: Activation Energy for Zn^{2+} in Binary Solution for pH of 4

The magnitude of activation energy may give an idea about the type of biosorption. Two main types of biosorption may occur, physical and chemical. A plot of $\ln k_2$ versus $1/T$ gives a straight line, and the corresponding activation energy was determined from the slope of the linear plot.

The results obtained under optimum conditions were 51.57 and 14.7 kJ mol^{-1} for the biosorption of Zn^{2+} on WS, for single and bisolute systems, respectively, at initial concentration 150 mg/L , while the temperature range used was 20 to 40°C and pH range was 5 . Similarly the results obtained for Ni^{2+} under optimum conditions of biosorption process (pH of 5 and 25°C) were $-19.39 \text{ kJ mol}^{-1}$ and $-64.2 \text{ kJ mol}^{-1}$.

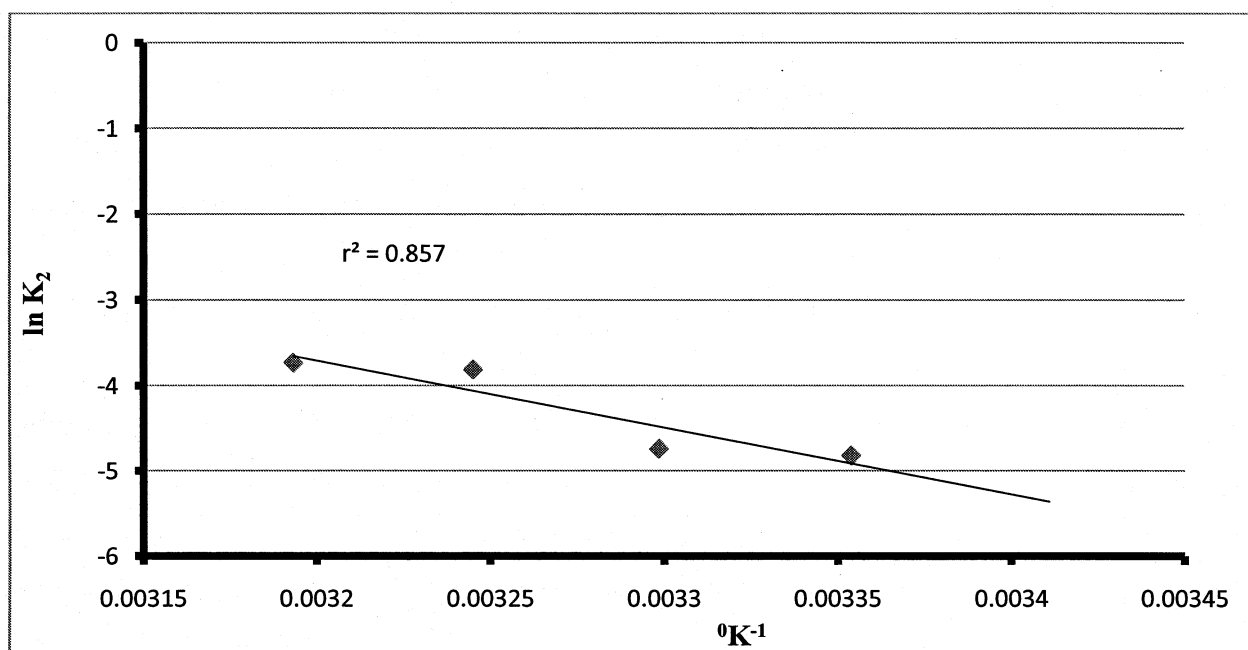


Figure 5.12.2 : Activation Energy for Ni^{2+} in Binary Solution for pH of 4

The activation energy for physical biosorption is usually no more than 1 kcal gmol^{-1} i.e., 4.2 kJ mol^{-1} . Since the forces involved in physical biosorption are weak [Treybal, 1980; Smith, 1981]. Chemical biosorption is specific and involves forces much stronger than in physical biosorption. So the activation energy for chemical biosorption is of the same magnitude as the heat of chemical reactions $5 \text{ to } 100 \text{ kcal mol}^{-1}$ [$21\text{--}420 \text{ kJ mol}^{-1}$]. Two kinds of chemisorption are normally, encountered: activated and nonactivated. Activated chemisorption means that the rate varies with temperature according to finite activation energy in the Arrhenius equation. However, in some systems chemisorption occurs very rapidly, suggesting activation energy near zero. This is termed as non-activated chemisorption. Bulut *et al*, 2007, investigated the activation energy of Cu^{2+} onto *C. crispate* (algae). The authors reported that for the temperature up to $25^{\circ}C$ for which the activation energy was 51.5 kJ mol^{-1} and from $25 \text{ to } 50^{\circ}C$ was found to be -35 kJ mol^{-1} with the observed activation energy values for the biosorption of Cu^{2+} were of the same magnitude as the heat of chemisorption. An increase in the biosorption of Cu^{2+} by *C. crispata* deals with an increase in the uptake capacity of *C. crispate* up to $25^{\circ}C$ and then followed by an exothermic uptake process with further increase in temperature.

The values of activation energy obtained for nickel show that the system follows physical biosorption while the values obtained for Zn ions obtained is ranged between 14.7 to 108.7

kJ mol^{-1} for biosorption suggest that the biosorption holds both the phenomena i.e. physical and chemical biosorption.

5.13 Desorption:

Desorption studies helps to elucidate the mechanism of biosorption and recovery of the adsorbate and biosorbent. The regeneration of the biosorbent may make the treatment process economical. The per cent desorption increases with decrease in pH of the aqueous medium. This was just opposite to pH effect, indicating that ion exchange was a part of biosorption process. Attempts were also made to reuse the exhausted biosorbent after its regeneration by chemical treatment. The wheat straw was exhausted in two different ionic concentrations of 25 ppm and 100 ppm for both Ni^{2+} and Zn^{2+} . Distilled water, and 0.1 M H_2SO_4 solution were used to desorb and the results are presented in the figures 5.13.1 and 5.13.2. With distilled water only 91% and 40 % desorption of Ni^{2+} and Zn^{2+} occurred at the initial concentration of 25 ppm metallic ions whereas it was 58 % and 32% for Ni^{2+} and Zn^{2+} at the concentration of 100 ppm. In the acidic environment when the pH was 1 only the desorption for 25 ppm was 100% and 98% while at 100 ppm the desorption was 93% and 64 % respectively. This is an indication of the ion exchange nature of the biosorption process. The higher percentage desorption at lower pH may be due to the presence of a large concentration of OH^- ions which release the metal ions from the biosorbent surface to the solution. The low desorption of metallic ions in distilled water can be attributed to the fact that at a lower pH, a lower concentration of OH^- ions replaces the smaller amounts of metallic ions from the biosorbent.

The data showed that the used biosorbent can be regenerated, 91% Ni^{2+} can be regenerated with distilled water when the biomass is exhausted at 25 ppm. Implying that the biosorption was very weak physical bonding. The desorption of Ni was increased to 100 % in conditions for the same concentration. Ajmal *et al*, 2000, investigated the ability of fruit peel of orange to remove heavy metals of Zn, Ni, Cu, Pb and Cr from aqueous solution. The adsorbed amounts were in the order of $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cr}^{2+}$. The extent of removal of Ni^{2+} was found to be dependent on biosorbent dose, initial concentration, pH and temperature. The heavy metal cations are

completely released under circumstances of extreme acidic conditions. For Zn^{2+} the acidic concentration gave 98% regeneration.

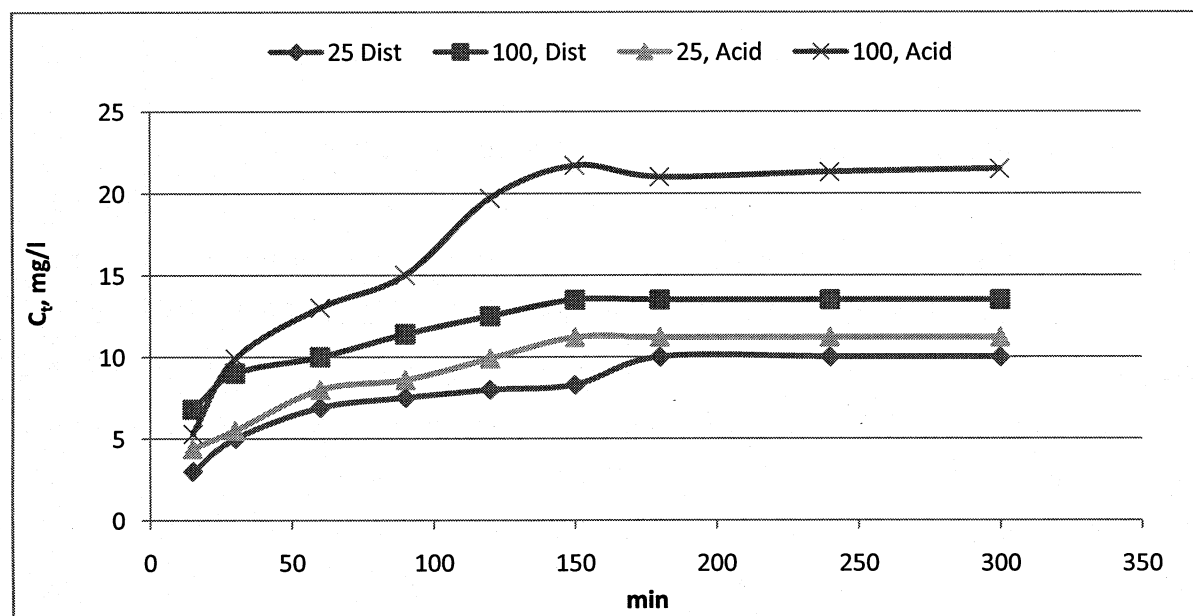


Figure 5.13.1: Desorption of Ni^{2+}

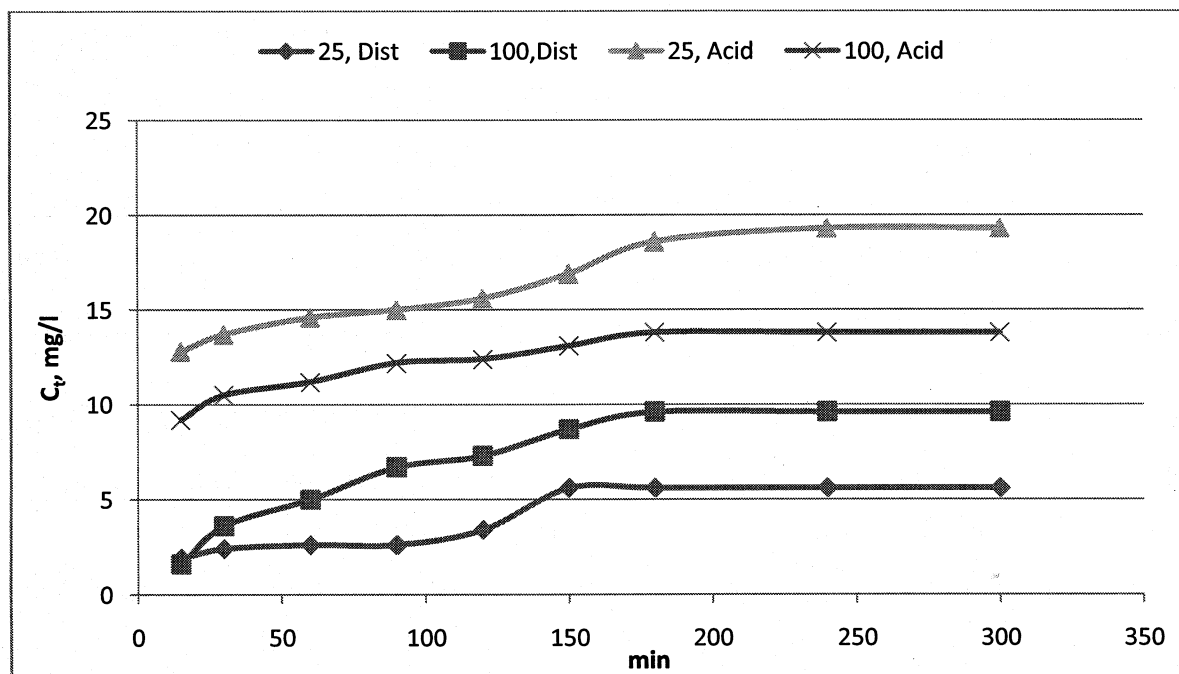


Figure 5.13.2: Desorption of Zn^{2+}

At 100 ppm concentration of metallic ions, the desorption was almost doubled for Zn^{2+} and for Ni^{2+} ions it was about 64 % increased. At this stage desorption proceeds via physico-chemical (electrostatic) interaction and reversible chemical reaction. 64% desorption of Zn^{2+} at the concentration of 100 ppm shows some involvement of chemical biosorption which support our observation at microscopy. Because molecules that undergo chemical biosorption, or activated biosorption, or chemisorption are not free to move along the biosorbent surfaces. Since the adsorbates form strong bonds and react with the biosorbent during chemisorption, the process involves high energies of biosorption and the process is irreversible. The $\text{M}^{2+}-\text{H}^+$ ion exchange is easily reversible, depending upon pH. In a study by Sukla *et al* 2002, in which sawdust samples have been exposed to heavy metal solutions and adsorbed up to 97% copper and lead were stripped with 0.1M HNO_3 (pH = 1.3). The heavy metal cations were almost completely removed from the sawdust after 6 h. These concentrations represent almost a complete exchange of H^+ ions from the stripping acid to the sawdust. The regenerated sawdust samples were washed several times with distilled water until its pH reached the regular range. After dried in an oven at 101°C , the regenerated sawdust was employed to sorb heavy metals again. The results showed that the regenerated sawdust has even higher capacity for heavy metals than the untreated material dose. That may be due to the impurities of sawdust being removed after regeneration and more exchangeable surface area becoming available. A decrease in percent biosorption, however, was observed after a couple of cycles of regeneration, since a small fraction of adsorbed metals not recoverable by regeneration presumably represents the metals which are bound through stronger interaction. As in our case, we are not able to remove 36 % of Zn^{2+} ions from the wheat straw when the sample was subjected to desorption and the samples were exhausted at 100 ppm of Zn^{2+} ions. In this case the capacity of biosorption of wheat straw will be decreased.

Effective desorption can help in reducing the volume of waste (biomass) by recycling it was well as the safe disposal of recovered contaminant. The efficiency of a desorbing agent or elutant is often expressed by the S/L ratio i.e. solid to liquid ratio. The solid represent the solid sorbent (mg dry weight) and the liquid ratio. The liquid represents the amount of elutant applied. High values of S/L are desirable for complete elution and to make the process more economical. [Gupta *et al.* 2000]. In our case the S/L ratio is about 270. Desorption should ensure three major issues: high

elution efficiency, low biomass damage and low cost. Acids like HCl, H₂SO₄, HNO₃ and salts like NaCl, CaCl₂ are used as elutant depending on the mechanism of desorption [Aldor *et al* 1995]

5.14 Capacity

The amount of metal bound to a biomass depends not only the biosorbent but also on the type of metal ions, its concentration as well as other physico-chemical factors such as the solution temperature, pH, ionic strength and ions interference with other metals present.

Kapoor and Viraraghavan, 1997, reported that biosorption of metal ions by *R. arrhizus* was linearly influenced by the ionic radius but independent of the ionic charge or electrostatic strength. Avery and Tobin, 1993; Remacle, 1990, classified metallic ions based on a “hardness scale” defined by their binding strength with F⁻ and I⁻ under the consideration of the thermodynamics but not the kinetics. Nierboer and Ruchardson proposed a refined classification of metals for biological systems in determining their relativeness, considering the electro negativity charge and ionic radius of metals. Hard metals such as Na⁺, K⁺, Ca²⁺, Mg²⁺, are usually nontoxic and often are essential macronutrients for microbial growth they bind preferentially to oxygen-containing (hard) ligands such as OH⁻, HPO₄²⁻, CO₃²⁻, R-COO⁻ and -C=O whereas soft metals such as Hg²⁺, Cd²⁺ and Pb²⁺ which often display greater toxicity, form stable bonds with nitrogen- or sulfur-containing (soft) ligands such as CN⁻, R-S⁻, -SH⁻, NH₂⁻ and imidazol. Borderline or intermediate metals are less toxic and can even be detected in certain biomolecules where they assist in mediating specific biochemical reactions, e.g., Zn²⁺, Cu²⁺ and Co²⁺ [Avery and Tobin, 1993]. Based on the hard-and-soft principle of acids and bases, they investigated the metal biosorption characteristics for metabolism-independent uptake of the metal ions, including Sr²⁺, Mn²⁺, Zn²⁺, Cu²⁺, Cd²⁺, Ti²⁺ by *S. cerevisiae*. The results showed that the complex characteristics of microbial metal uptake conformed well to the hard-and-soft principle.

The determination of the metal uptake rate by the biosorbent is often based on the equilibrium state of biosorption system. The biosorption uptake rate, *q*, is usually expressed in milligrams of metal adsorbed per gram of the (dry) biosorbent for the basis for engineering process—mass

balance calculations or mmol g⁻¹ or meq g⁻¹ when stoichiometry and/or mechanism are considered [Kratochvil and Volesky, 1998]. There are different ways by which the biosorption capacity is expressed. At the same time, uptake rate 'q' should be compared in almost the same equilibrium concentration of metal in solution for the purpose of evaluating performance of the biomaterial [Kratochvil and Volesky, 1998].

In particular, there is no standard measurement of dry weight of biomass, i.e. no standard of dry temperature and dry hours when drying biomass. Park *et al.*, 2003, obtained the dry-cell weight by drying cells at 70 °C until the weight of the cells became constant. Liu *et al.*, 2002a, measured the dry weight of *S. cerevisiae* after drying in a stove for 2 h at 100–120 °C to calculate the biosorption capacities. Ozer and Ozer, 2003, dried the yeast at 100 °C for 24 h. Rapoport and Muter, 1995, determined dry weight by drying the sample at 105 °C until the constant weight was achieved. Obviously, the numeric value of dry weight of biomass obtained in different drying conditions is different. For our experimentation we dried Wheat Straw (WS) at 60 °C for the first 8 hours and then continued till it got constant weight. The amount of Metal ions adsorbed on WS were calculated by the following equation:

$$q_e = (C_0 - C_e) \frac{V}{W}$$

Where

q_e is the amount adsorbed per gram of dry biomass, mg/g

C_0 is the initial concentration of metal ions, mg/l

C_e is the equilibrium concentration of metal ions, mg/l

V is the volume of solution in liters

W is the volume of dry sorbent in grams

Table 5.14.1 : Amount of Metal Adsorbed on Wheat Straw in Binary Ionic System, mg/g

Initial Concentration	Ni ²⁺	Zn ²⁺
150	5	8
100	4.6	6
50	3	4.6
25	2.2	2.8
5	0.82	0.8

It can be seen from the table 5.14.1 that the amount adsorbed is dependent on the on the initial concentration of metal ions in the solution. The reported capacities of various biosorbents such as live and dead biomass from natural sources and lignocellulosic wastes are given in the Table 5.14.2 as:

Table 5.14.2 : Zinc Ion Biosorption on Biomass

biosorbent	Type	Amount	Reference
Waste Tea leaves	Agro Waste	4.6 mg/g	Ahluwalia and Goyal, 2005
<i>Saccaromyces cerevisiae</i>	Yeast	14	Volesky and Philips, 1995
<i>Bacillus</i> sp	Bacteria	3.4	Barierley et al, 1986
<i>Penicillium spinulosum</i>	Fungi	0.2	Townsley et at, 1986
<i>Solanum elaeagnifolium</i>	weed	6. 96	Baig et. al., 1999
<i>A.nodosum</i>	Marine Algae	25.6	Bakkaloglu et al. ,1998
<i>P.chrysogenum</i>	Fungi	19.2	Bakkaloglu et al. ,1998
<i>F.vesiculosus</i>	Marine algae	17.3	Bakkaloglu et al. ,1998
<i>Activated Sludge</i>	waste	9.7	Bakkaloglu et al. ,1998
<i>S.rimosus</i>	Bacteria	6.63	Bakkaloglu et al. ,1998
<i>S.cerevisiae</i>	Yeast	3.45	Bakkaloglu et al. ,1998
<i>Waste of fermentation industry</i>	Yeast	3.45-1.95	Bakkaloglu et al. ,1998 120 °C
<i>Abies sachalinensis</i> Masters	Bark	3.6	Seki et al, 1997
<i>Pinus densiflora</i> Sieb. et Zucc	Bark	4.6	Seki et al, 1997

However, lignocellulosic materials have an edge on other biosorbents because of their great availability, very low cost and simple operational process. In general, a biosorbent can be assumed as low cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry (Bailey *et al.* 1999). Biosorbents comprise of different type of cells with a highly complexes structure whose various building blocks consists of a multitude of different molecules which can display several binging sites. Moreover even one binding site can participate in different binding mechanisms. For example, carboxyl group can engage both in

complexation and electrostatic attraction of metal cations. Consequently several mechanism often act in combination.

Table 5.14.3 : Nickel Ions Biosorption by Biomass.

Sorbent	Type	Amount, mg/g	Reference
<i>Sargassum natans</i>	Sea weed	24	Holan and Volesky, 1994
<i>Candida tropicalis</i>	Fungi	20	Mattuschka et al., 1993
<i>Rizopus nigricans</i>	Fungi	5	Holan and Velosky, 1995
<i>Absidia orchidis</i>	Fungi	5	Kuyucak and Volesky, 1988
<i>Solanum elaeagnifolium</i>	weed	6.5	Baig et al., 1999
Fly ash Bagasse	agro waste	1.2	Gupta et al. (2003)
Waste Tea leaves	agro waste	11.4	Ahluwalia and Goyal, 2005
Fermentatio industry waste	Yeast	1.47	Bakkaloglu et al. ,1998 120 °C
<i>Picea jezoensis Carr.</i>	Bark	4.2	Seki et al, 1997

Researchers have investigated various types of biomass including bacteria, yeast , fungi , marine algae, activated sludge and agro waste materials. The above tables represents metal biosorption capacities of different biomass for Zinc and Nickel ions. It has been found that *S. cerevisiae*, *A. nodosum*, *F. vesiculosus* and *P. chrysogenum* have high biosorption capacity for Zinc than that of wheat straw. Similarly, *S.nataus*, *C. tropicalis* adsorb more Nickel than that of wheat straw. On the other hand, biosorption capacity of WS is in par with coniferous barks and a lot better than some of marine algae and other biomass shown in the table above. To make it more interesting, elements removed by saw dust and barley straw at 20 ppm initial concentration of metal ions and 1000 mg of biosorbent is given table 5.14.4:

Table 5.14.4: Amount Removed by Some Agro wastes

Element	pH	Amount mg/g	Biomass
Zn	6.3	4.3	Barley Straw (washed),
Zn	6.3	2.7	Saw dust,
Zn	5.5	3.2	<i>Tectona grandis</i> L.f. (teak Leaves), 212 µm size
Ni	5.5	1.3	Pine Saw dust,

Barley is added for comparison because biologically it is of same family as that of wheat. From the single ions solution of 25 ppm of Ni^{2+} and Zn^{2+} the metal removal on wheat straw was observed 3.2 and 2.5 mg / g respectively. Similarly for same amount of biomass with initial concentration of 4 mg of metallic ions Larsen and Schierup, 1981, gave :

Table 5.14.5: Biosorption of Biomass at 4 ppm

Element	pH	Amount mg/g	Biomass
Zn	5.6	0.5	Barley Straw ,washed
Ni	5.6	0.4	Barley Straw, washed
Zn	5..6	0.0	Pine Saw dust,
Ni	5.6	0.0	Pine Saw Dust,
Ni	5.6	0.9	Activated Carbon, pine

Comparing the biosorption capacity of wheat straw with biomasses given in table 5.14.5, we feel stronger because biosorption was 0.82 and 0.86 mg /g for Ni^{2+} and Zn^{2+} respectively. In over all comparison with the biosorption capabilities of all the given biomass material for zinc and nickel, wheat straw is regarded as an addition to the metal biosorbents.

5.15 Feasibility of Biosorption

Feasibility of a project depends on the following factors:

Capital Cost:

- i- Fixed capital: site, building, utilities plants, process equipment, storage facilities, auxiliary facilities and emergency facilities.
- ii- Working capital: raw material inventory, in-process inventory, product inventory, maintenance and repair, receivable carry over, minimum cash reserves.

Total product cost:

- i- Manufacturing cost
- ii- Overhead expenses.

For our purpose here we will skip capital cost and discuss only about the materials. The selection of biosorbent material used for a biosorption process includes:

- ☐ Choice of biosorbent which is based on its uptake performance
- ☐ The source of the raw biomass
- ☐ Processing of biomass if required (granulation and/ or treatment)
- ☐ The regeneration processes used such as desorption.

Very often, the source of the biosorbent has a major impact on the feasibility of the operation. Biosorbents (biomass) should always be obtained from the least-expensive source such as from the effluent of a fermenter, seaweeds from nearby bodies of water, algae, etc. In our case, Canada is among top ten producers of wheat. So wheat straw is commonly available from any farm land. The highest cost for the wheat straw is \$20 /ton. In this process we never give any treatment to biomaterial (to avoid adding more pollution to environment). It means all that processing material, time and energy has been saved.

The spent biosorbents can be regenerated at very low cost using water, so the material can be reused many times. Our study showed that 4 ml of 10% solution of H_2SO_4 was enough to regenerate 98 to 100 % of biomass after it has been exhausted by capturing Ni^{2+} and Zn^{2+} from polluted waters.

Hence, considering the overall unit operations involved in biosorption and other comparative studies made on large scale, we can conclude that the process is generally economically viable.

6 Conclusions

The biosorption of Ni^{2+} and Zn^{2+} on wheat straw was studied for the initial metal concentration range of 5 to 150 ppm and the equilibrium was achieved in 2.5 to 5 hours. And the maximum biosorption achieved was about 86 %. The results obtained showed that wheat straw has a great potential to be used as a biosorbent in treatment of waste water.

From FTIR studies we found that C=O, C-O-, O-H, C-OH, C-C and O=N=O bonds from the wheat straw surface interact with the metal ions to proceed for biosorption.

The pH has a significant effect on the biosorption, for Zn^{2+} the biosorption increases with increase in pH for 3 to 6.3. For Ni^{2+} the optimum was achieved between pH of 4 to 6.3, at pH of 6.3 we observed a decrease in biosorption for Ni^{2+} . As for as temperature is concerned, a decrease in biosorption was observed with increase in temperature from 20 to 40 °C while there was a slight increase in biosorption at 25 °C. Kinetics study of the reaction shows that the system of Zn^{2+} - WS and Ni^{2+} - WS follows the pseudo second order reaction.

The Freundlich isotherm gave a better fit for the Ni^{2+} and Zn^{2+} single-solute data than the Langmuir and the Temkin isotherms over the concentration range of 5 ppm to 150 ppm at 25 °C. The Langmuir Partially Competitive Isotherm, the Freundlich Multicomponent showed that the biosorption of Zn^{2+} was better than the Ni^{2+} biosorption in binary solutions. Overall the IAS-Freundlich Isotherm was the most reliable in representing the Ni^{2+} - Zn^{2+} biosorption behavior in binary ionic system.

The values of activation energy obtained for nickel show that the system follows physical biosorption while the values obtained for Zn ions obtained is ranged between 14.7 to 108.7 kJ mol^{-1} for biosorption suggest that the biosorption holds both the phenomena i.e. physical and chemical biosorption this was confirmed in the desorption experiments.

The regeneration capacity for wheat straw is excellent if it is exhausted in treatment of Ni^{2+} and/or Zn^{2+} at an ionic concentration up to 25 ppm. At ionic concentration of 100 ppm the wheat straw used for Ni^{2+} was regenerated but that used for Zn was only 64 % regenerated.

7 Recommendations

- 1- As our study is a batch study, the system should be evaluated by dynamic studies.
- 2- As the mechanism of biosorption on wheat straw is a complex phenomenon. The physical and chemical parameters on the surface should be study by SEM microscopy, EDS and FTIR analysis.
- 3- Its use should be explored for other heavy metals.

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9 Appendices :

Appendix A: Sample Calculations for Biosorption Isotherms

Langmuir multi component isotherm

$$q_{e,1} = \frac{Q_1^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2}$$

$$q_{e,2} = \frac{Q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2}$$

Q_1^0 for Ni = 5.587

Q_2^0 for Zn = 9.174

b_1 for Ni = Slope/ Intercept= 0.06

b_2 for Zn = Slope / Intercept = 0.04

C_0 = 150 ppm for both Ni^{2+} and Zn^{2+}

C_1 = Ce, Ni = 125

C_1 = Ce, Zn = 110

$q_{e,1}$ for Ni= $(5.6 * 0.06 * 125) / (1 + 0.06 * 125 + 0.04 * 110) = 3.18$

$q_{e,2}$ for Zn= $(9.17 * 0.04 * 110) / (1 + 0.06 * 125 + 0.04 * 110) = 3.22$

Actual $q_{e,1}$ for Ni =5

Actual $q_{e,1}$ for Zn= 8

Table A-1: Comparison of Predicted and Actual q_e Values from Langmuir multi component isotherm

Co	Ni^{2+}		Zn^{2+}	
	Predicted, q_e	Actual, q_e	Predicted, q_e	Actual, q_e
150	3.18	5	3.22	8
100	3.00	4.6	3.13	6
50	2.74	3	2.43	4.6
25	1.99	2.2	1.80	2.8
5	0.26	0.82	0.33	0.8

Langmuir Partially Competitive isotherm

$$q_1 = \frac{(Q_1^0 - Q_2^0) b_1 C_1}{1 + b_1 C_1} + \frac{Q_1^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2}$$

$$q_2 = \frac{Q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2}$$

$$Q_1^0 \text{ for Zn} = 9.17$$

$$Q_2^0 \text{ for Ni} = 5.6$$

$$b_1 \text{ for Zn} = 0.04$$

$$b_1 \text{ for Ni} =$$

$$C_1 = \text{Ce, Zn} = 110$$

$$C_2 = \text{Ce, Ni} = 125$$

$$q_1 = \{(9.17 - 5.6) * 0.04 * 110\} / (1 + 0.04 * 110) + \{(9.17 * 0.04 * 110)\} / (1 + 0.06 * 125 + 0.04 * 110)$$

$$= 6.13$$

$$q_2 = (5.6 * 0.057 * 125) / (1 + 0.04 * 110 + 0.057 * 125)$$

$$= 3.18$$

IAS-Freundlich Multicomponent Isotherm

$$C_i = \frac{q_i}{\sum_{j=1}^N q_j} \left(\frac{\sum_{j=1}^N n_j q_j}{n_j K_i} \right)^{n_i}$$

$$C_1 = \frac{q_1}{q_1 + q_2} \left(\frac{n_1 q_1 + n_2 q_2}{n_1 K_1} \right)^{n_1}$$

$$C_2 = \frac{q_2}{q_1 + q_2} \left(\frac{n_1 q_1 + n_2 q_2}{n_2 K_2} \right)^{n_2}$$

$$C_1 \text{ for Ni} = 125 \text{ mg/L}$$

$$C_2 \text{ for Zn} = 110 \text{ mg/L}$$

$$q_1 \text{ for Ni} = 5 \text{ mg/g}$$

$$q_2 \text{ for Zn} = 8 \text{ mg/g}$$

$$n_1 \text{ for Ni} = 2.18$$

$$n_2 \text{ for Zn} = 2.03$$

$$K_1 \text{ for Ni} = 0.88$$

$$K_2 \text{ for Zn} = 1.05$$

$$C_1 \text{ for Ni} = \text{Predicted value} = 5 / (5 + 8) \{ (2.18 * 5 + 2.03 * 8) / (2.18 * 0.88) \}^{2.18}$$

$$= 122.8 \text{ mg/L}$$

$$C_2 \text{ for Zn} = \text{Predicted value} = 8 / (5 + 8) \{ (2.18 * 5 + 2.066 * 8) / (2.066 * 1.05) \}^{2.03}$$

$$= 107.7 \text{ mg / L}$$

Appendix B: Sample Calculations and Tables for Kinetics Study

Pseudo First Order Model

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The plot of $\log(q_e - q_t)$ versus time t , the values of pseudo-first order rate constant were obtained from the slope of the straight line.

Figure 5.8.1 and 5.8.2 gives values of $\ln q_e$ for Ni^{2+} and Zn^{2+}
 $\ln q_e$ for Ni^{2+} at initial concentration of 150 ppm = 1.294
 or $\text{Exp}(\ln q_e) = 3.65$
 while actual q_e for $\text{Ni}^{2+} = 5$

Similarly,

$\ln q_e$ for Zn^{2+} at initial concentration of 150 ppm = 1.74
 or $\text{Exp}(\ln q_e) = 5.7$
 while actual q_e for $\text{Zn}^{2+} = 8$

Pseudo Second Order Model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

The plot of t/q_t against t gave slope of $1/q_e$, taking inverse of this will give the predicted value of q_e as:

Slope for the plot for Zn^{2+} at initial concentration of 150 ppm = 0.12

Which gave q_e i.e. $(1/\text{slope}) = 8.4$

while actual q_e for $\text{Zn}^{2+} = 8$

Similarly,

Slope for the plot for Ni^{2+} at initial concentration of 150 ppm = 0.21

Which gave q_e i.e. $(1/\text{slope}) = 4.78$

while actual q_e for $\text{Zn}^{2+} = 5$

The second-order rate constants were used to calculate the initial biosorption rate, given by

$$h = k_2 q_e^2$$

k_2 value for Ni^{2+} at initial concentration of 150 ppm = 0.011

q_e from the corresponding plot is = 4.78

h value = initial biosorption rate for Ni^{2+} would be = $0.011 * 4.78 = 0.25$

Similarly,

k_2 value for Zn^{2+} at initial concentration of 150 ppm = 0.0068

q_e from the corresponding plot is = 8.4

h value = initial biosorption rate for Ni^{2+} would be = $0.0068 * 8.4 = 0.48$

Table B-1: Comparison of the Accuracy of the Estimated and Actual q_e Values, for Ni^{2+} by Pseudo Second Order Model in a Single ionic System.

°C	pH 4		pH 5		pH 6.3	
	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e
20	3.48	4	4.06	4	4.2	4
25	5.71	5.6	6.66	6.6	5.34	5.2
30	4.46	4.4	5.31	5	4.33	4.2
35	3.87	4	4.87	4.6	3.75	3.8
40	3.47	3.4	3.61	3.4	3.46	3.6

* q_e : is the amount of Ni^{2+} adsorbed at equilibrium

Table B-2: Comparison of the Accuracy of the Estimated and Actual q_e Values, for Ni^{2+} by Pseudo Second Order Model in a Binary System.

°C	pH 4		pH 5		pH 6.3	
	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e	Estimated q_e	Actual q_e
20	3.5	3.2	3.77	3.6	2.96	3
25	4.9	4.4	5.48	5.4	3.9	4.4
30	4.3	3.8	4.1	4.2	3.66	3.6
35	4	3.8	4.07	4	3.44	3.4
40	3.17	3	3.10	3	3.42	3.2

* q_e : is the amount of Ni^{2+} adsorbed at equilibrium

**Table B-3 : The Second Order Rate Constants and Coefficient of Determination
For Zn^{2+} in Single ionic System**

$^{\circ}\text{C}$	r^2	pH 4	r^2	pH 5	r^2	pH 6.3
20	0.98	0.847	0.98	0.007	0.99	0.005
25	0.99	0.013	0.99	0.0168	0.96	0.011
30	0.97	0.008	0.98	0.009	0.96	0.017
35	0.88	0.004	1	0.069	0.96	0.017
40	0.8	0.004	0.99	0.029	1	0.004

**Table B-4: The Second Order Rate Constants and Coefficient of Determination
for Zn^{2+} in Binary ionic System**

$^{\circ}\text{C}$	r^2	pH 4	r^2	pH 5	r^2	pH 6.3
20	0.99	0.017	0.99	0.024	0.99	0.016
25	0.99	0.024	1	0.033	0.98	0.007
30	0.98	0.011	1	0.126	0.92	0.005
35	0.99	0.034	0.99	0.0163	0.99	0.026
40	0.99	0.041	0.99	0.020	1	0.266

Table B-5: The Second Order Rate Constants and Coefficient of Determination for Ni^{2+} in Binary ionic System

$^{\circ}\text{C}$	r^2	pH 4	r^2	pH 5	r^2	pH 6.3
20	0.99	0.016	0.98	0.019	0.99	0.060
25	1	0.008	0.95	0.007	0.98	0.020
30	0.95	0.008	0.99	0.035	0.99	0.029
35	0.99	0.022	0.97	0.016	0.99	0.032
40	0.98	0.023	0.99	0.038	0.99	0.082

Table B-6: Initial Biosorption Rate Constants for Binary System

$^{\circ}\text{C}$	Zn^{2+}			Ni^{2+}		
	pH 4	pH 5	pH 6.3	pH 4	pH 5	pH 6.3
20	0.47	0.90	0.69	0.20	0.277	0.53
25	0.86	1.29	0.48	0.19	0.23	0.31
30	0.35	4.67	0.27	0.16	0.59	0.38
35	0.82	0.53	0.93	0.35	0.27	0.38
40	0.84	0.57	0.71	0.24	0.37	0.55

Peaks on the Spectrographs Obtained from FTIR Studies

Table B-7 : Peaks Observed Between Location 2000 cm^{-1} to 600 cm^{-1} On Spectrographs of WS Virgin.

Peak	%T	Peak	% T	Peak	% T	Peak	% T	Peak	5T
1730.25	28.93	1656.37	20.21	1509.37	26.01	1454.42	21.55	1425.32	20.02
1372.63	19.83	1320.72	20.97	1259.75	19.54	1162.65	13.86	1056.08	9.05
897.60	32.51	805.62	38.01	697.45	31.34	609.95	26.21		

T: Transmission, WS: Wheat Straw

Table B-8 : Peaks Observed Between Location 2000 cm^{-1} to 600 cm^{-1} On Spectrographs of WS -Ni²⁺ System.

Peak	%T	Peak	% T	Peak	% T	Peak	% T	Peak	%T
1734.03	30.14	1656.99	22.79	1633.34	24.11	1510.35	29.20	1467.06	25.05
1425.43	24.34	1371.67	24.84	1261.59	22.21	1162.92	21.34	1034.83	16.98
897.18	33.93	8-3.35	35.37	698.85	36.08	667.77	33.96	609.31	32.35

Table B-9 : Peaks Observed Between Location 2000 cm^{-1} to 600 cm^{-1} On Spectrographs of WS -Zn²⁺ System.

% T	Peak	%T	Peak	% T	Peak	% T	Peak	% T	Peak
1731.16	15.16	1656.91	11.64	1510.86	14.07	1426.48	11.35	1371.81	11.22
1260	11.22	1163.63	9.12	1056.44	7.46	897.53	18.13	816.47	23.24
609.76	16.46								

Table B-10 : Peaks Observed Between Location 2000 cm^{-1} to 600 cm^{-1} On Spectrographs of WS - Ni²⁺ and Zn²⁺ System.

% T	Peak	%T	Peak	% T	Peak	% T	Peak	% T	Peak
1730.67	47.64	1652.37	44.36	1506.49	46.38	1427.23	43.67	1372.08	43.49
1242	43.34	1062.12	36.73	897.61	48.98	610.01	47.19	472.91	48.15

The Second Order Biosorption of Zn^{2+} on Wheat Straw in Single Ion Solution

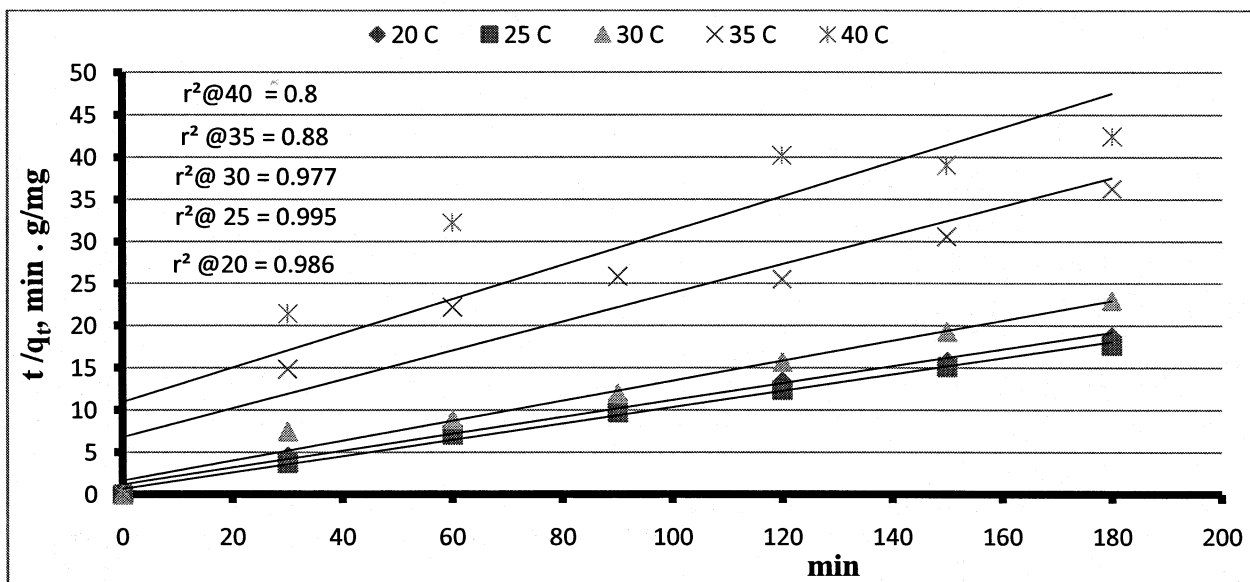


Figure B-1: The Second Order Biosorption of Zn^{2+} on Wheat Straw in Single Ion Solution at 150 ppm and pH of 4

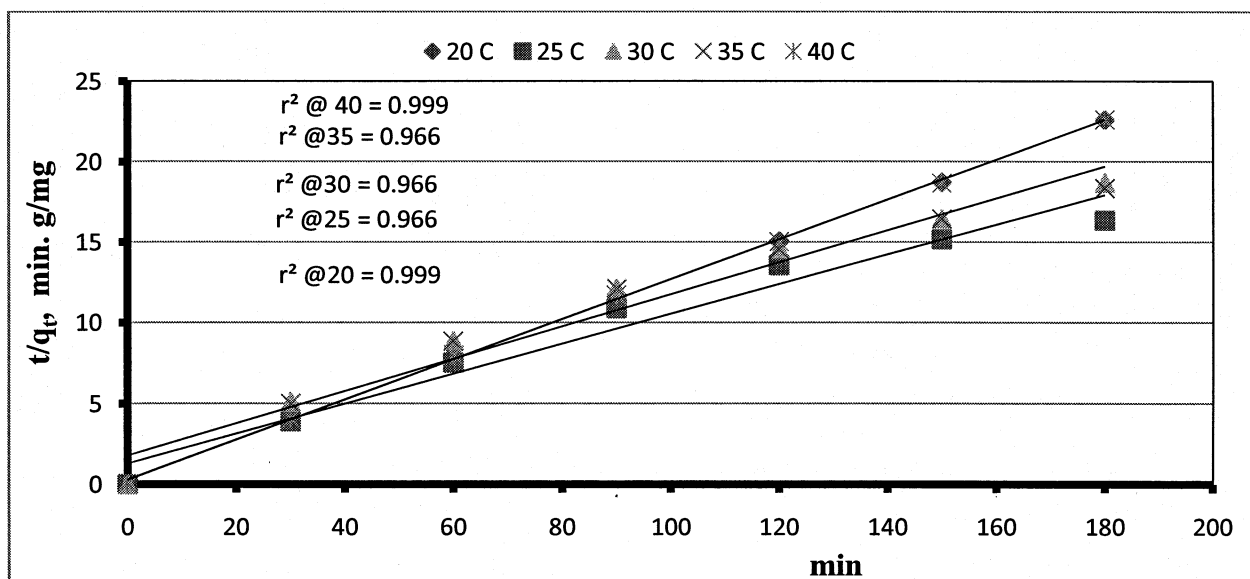


Figure B-2 : The Second Order Biosorption of Zn^{2+} on Wheat Straw in Single Ion Solution at 150 ppm and pH of 6.3

The Second Order Biosorption of Zn^{2+} on Wheat Straw in Binary Solution

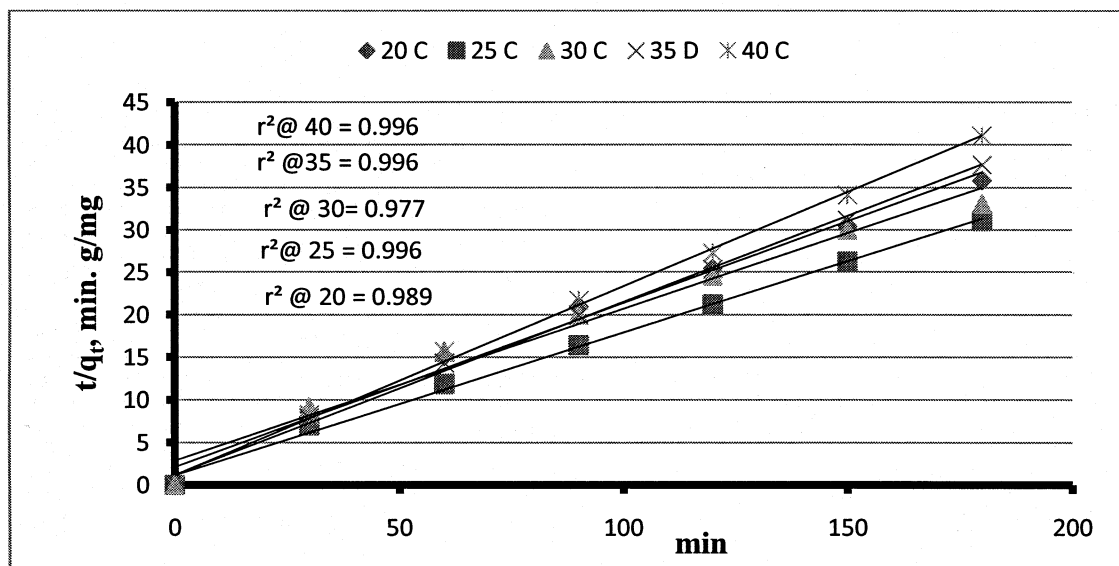


Figure B-3: The Second Order Biosorption of Zn^{2+} on Wheat Straw in Binary Solution at 150 ppm and pH of 4.

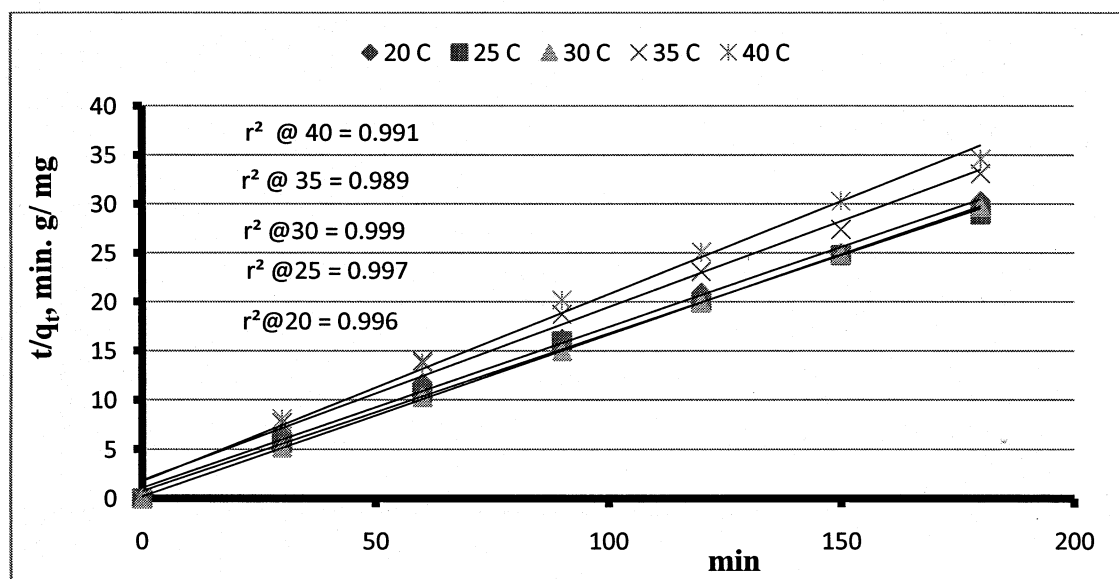


Figure B-4: The Second Order Biosorption of Zn^{2+} on Wheat Straw in Binary Solution at 150 ppm and pH of 5.

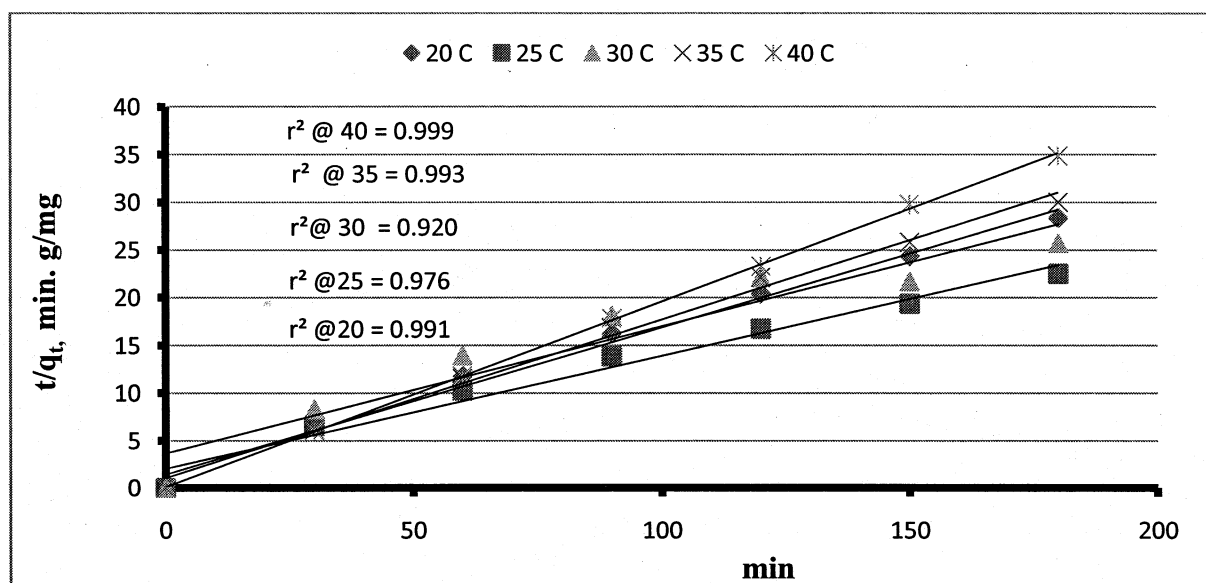


Figure B-5: The Second Order Biosorption of Zn^{2+} on Wheat Straw in Binary Solution at 150 ppm and pH of 6.3.

The Second Order Biosorption of Ni^{2+} on Wheat Straw in Single Solution

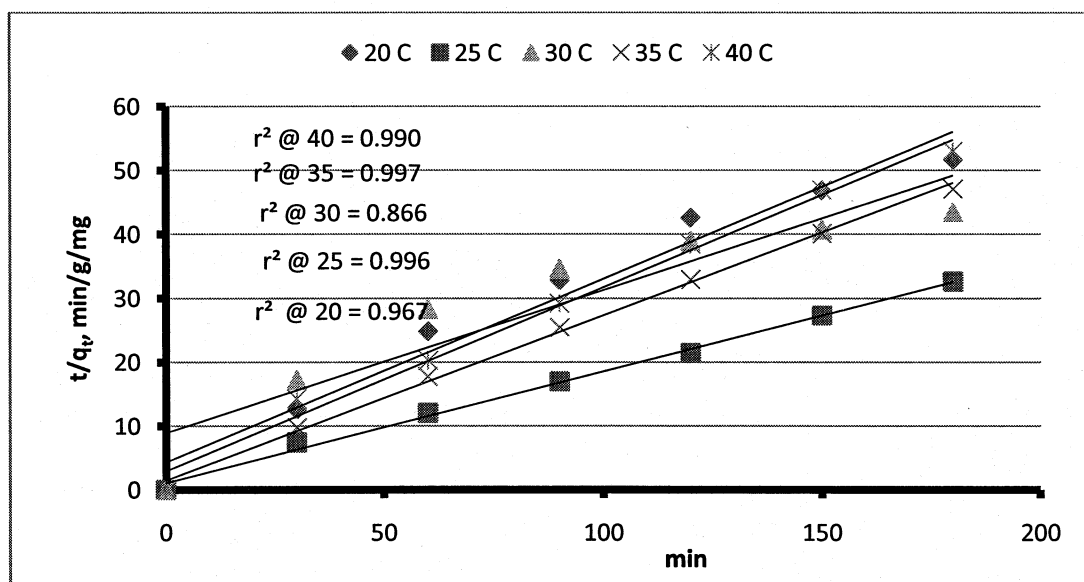


Figure B-6: The Second Order Biosorption of Ni^{2+} on Wheat Straw in Single Ion Solution at 150 ppm and pH of 4.

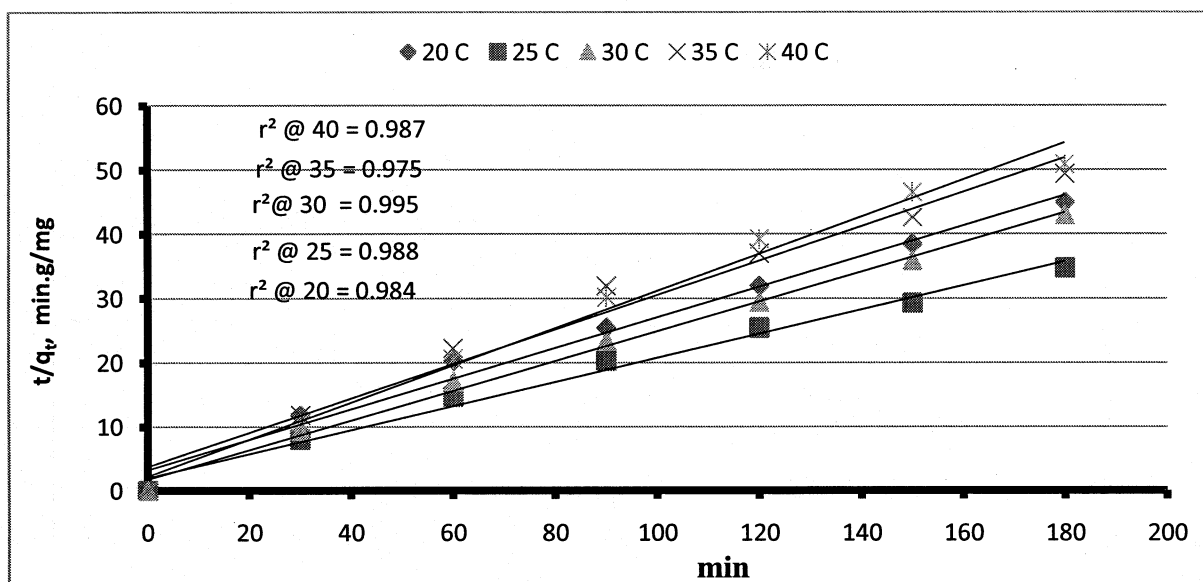


Figure B-7: The Second Order Biosorption of Ni^{2+} on Wheat Straw in Single Ion Solution at 150 ppm and pH of 6.3.

The Second Order Biosorption of Ni^{2+} on Wheat Straw in Binary Solution

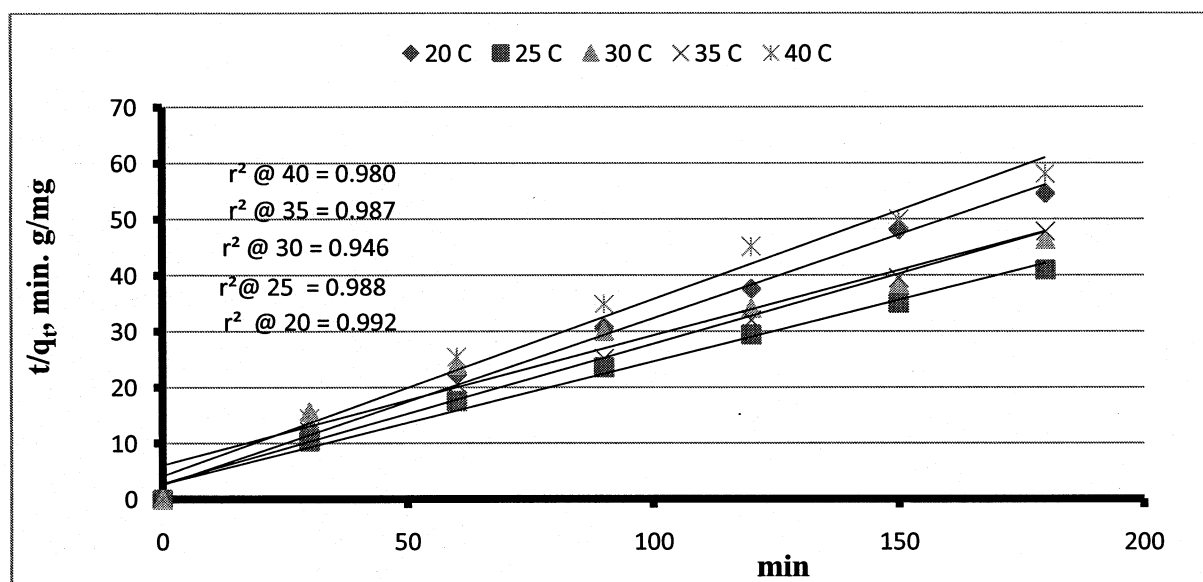


Figure B-8: The Second Order Biosorption of Ni^{2+} on Wheat Straw in Binary Solution at 150 ppm and pH of 4.

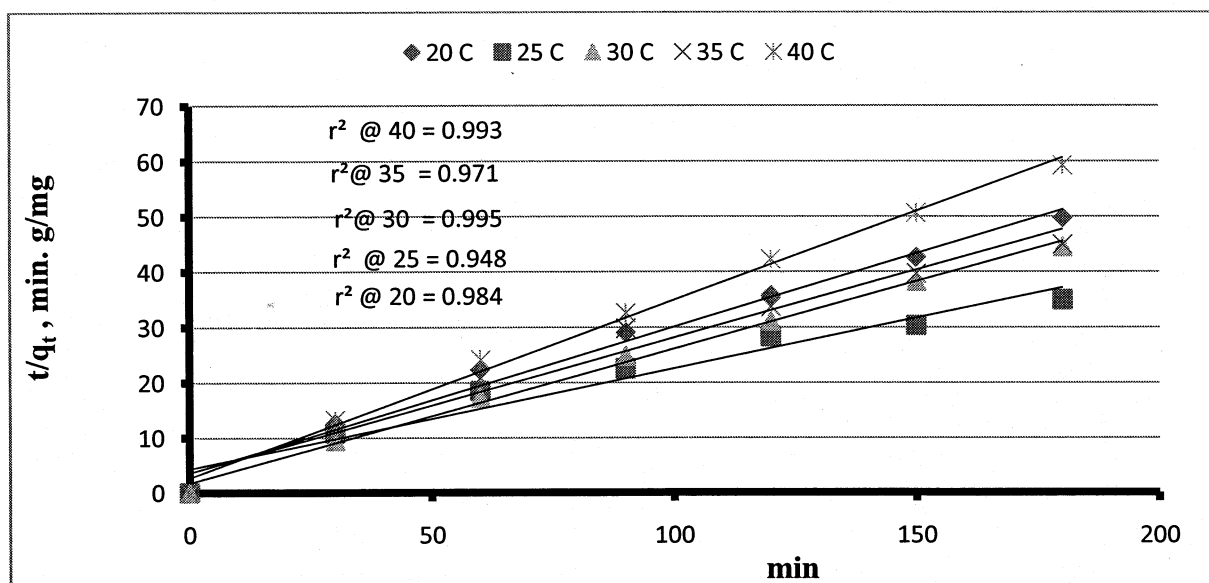


Figure B-9 : The Second Order Biosorption of Ni^{2+} on Wheat Straw in Binary Solution at 150 ppm and pH of 5.

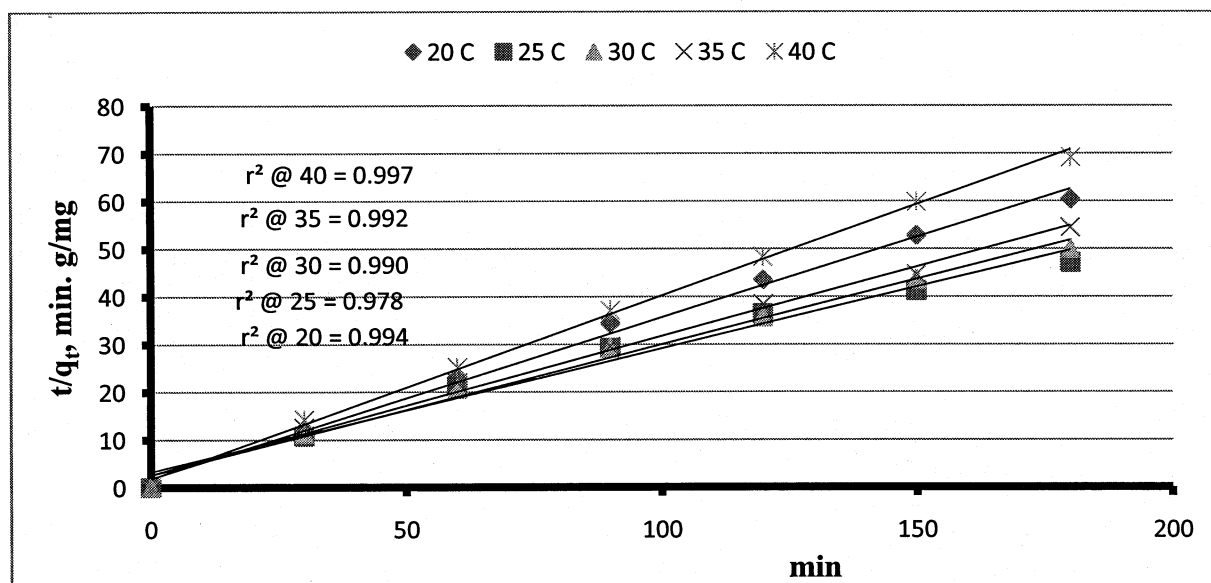
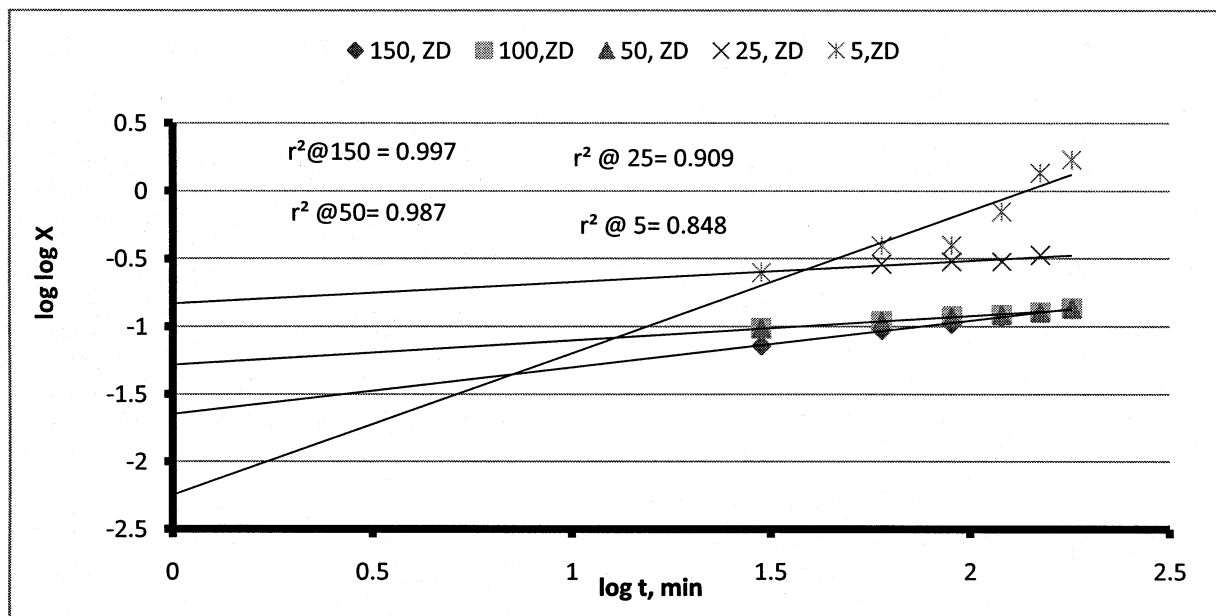


Figure B-10 : The Second Order Biosorption of Ni^{2+} on Wheat Straw in Binary Solution at 150 ppm and pH of 6.3.



FigureB-11 : Bangham Model for Zn^{2+} in Binary System

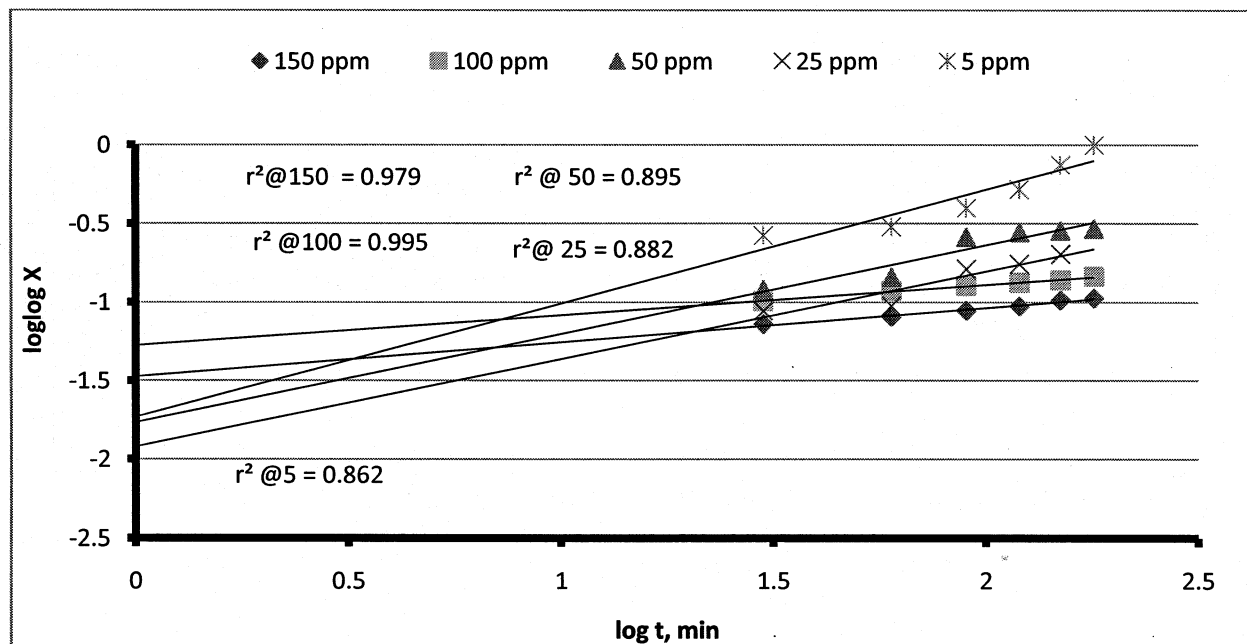


Figure B-12 : Bangham Model for Ni^{2+} in Single Ionic System

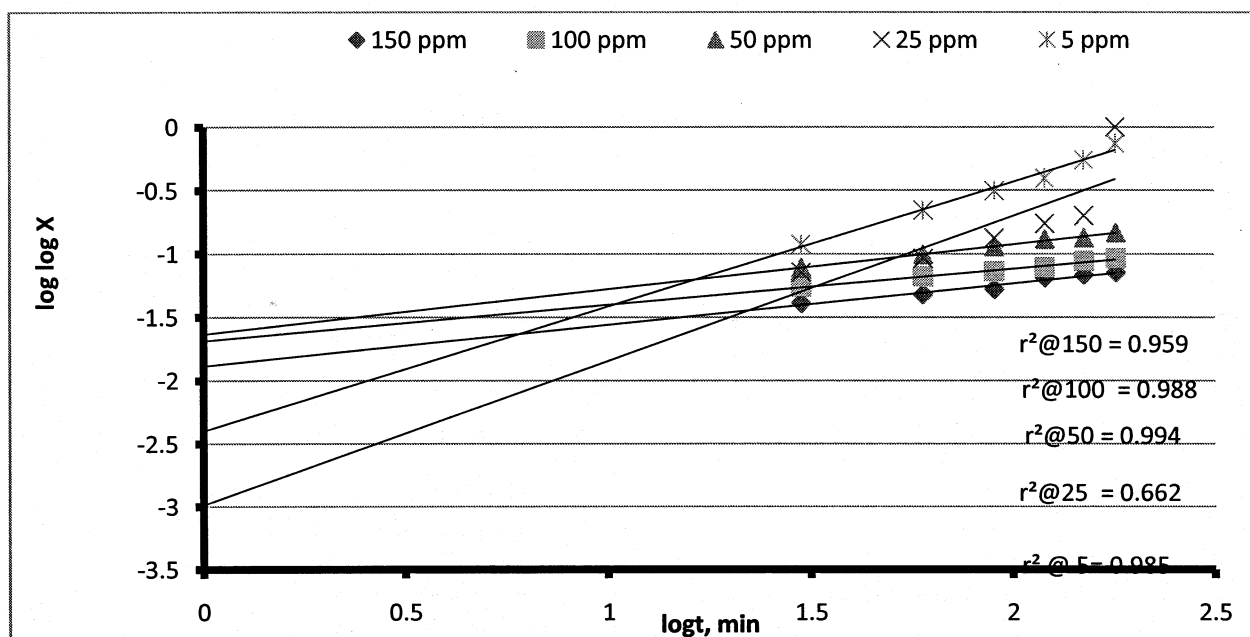


Figure B-13: Bangham Model for Ni^{2+} in Binary System

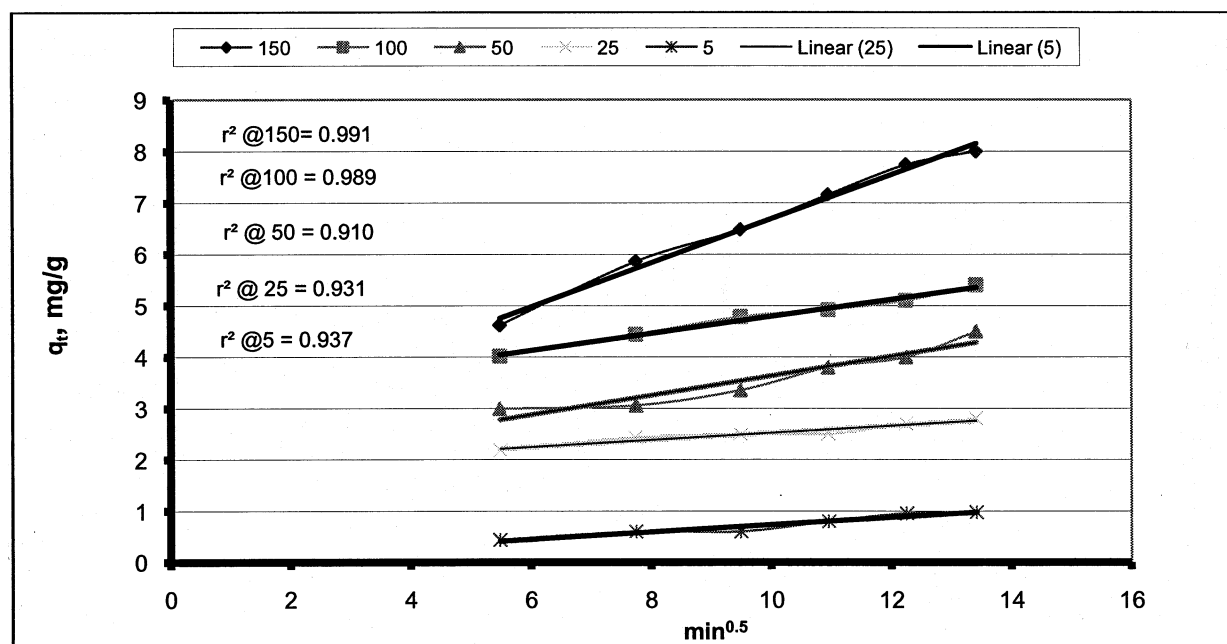


Figure B-14: Weber Model for Zn^{2+} in Binary System

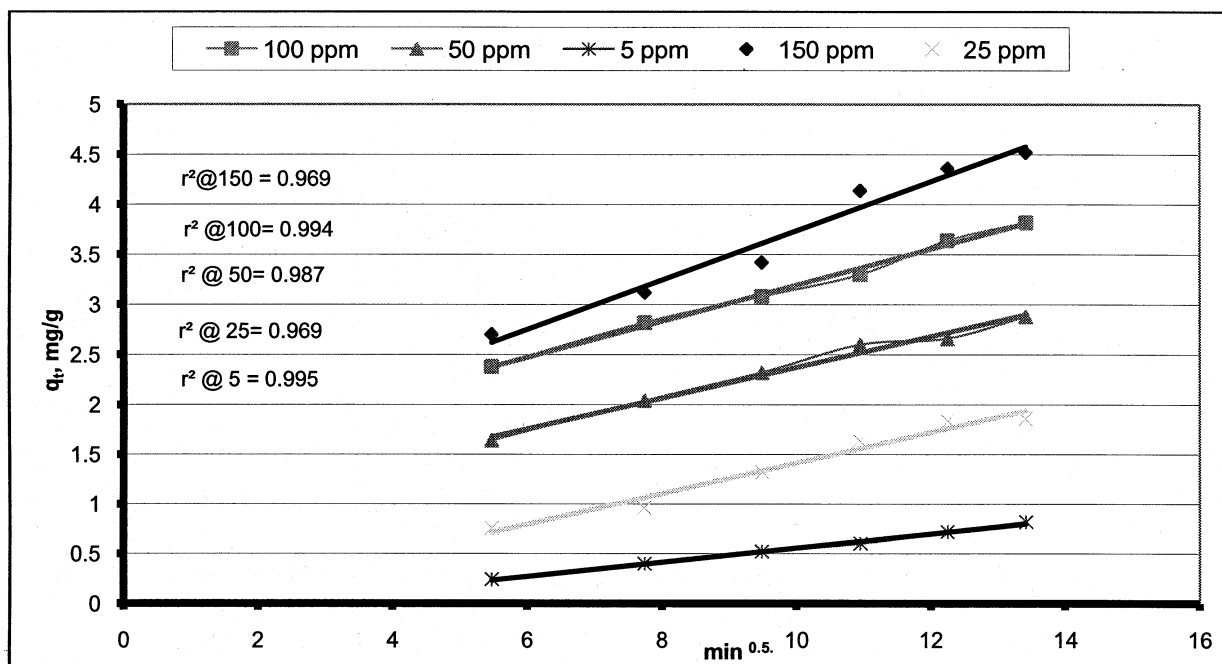


Figure B-15 : Weber Model for Ni^{2+} in Binary System

Appendix C: Thermodynamic Values

Table C-1:
Thermodynamic Parameters for Single Ionic System

Nickel				
pH	T	ΔH	ΔS	ΔG
4	293.16	20261.22	-82.558	44464.51
	298.16			44877.31
	303.16			45290.11
	308.16			45702.91
	313.16			46115.71
5	293.16	29256.97	-110.909	61771.35
	298.16			62325.9
	303.16			62880.45
	308.16			63435
	313.16			63989.55
6.3	293.16	31094.36	-118.641	65874.86
	298.16			66468.06
	303.16			67061.26
	308.16			67654.46
	313.16			68247.66
Zinc				
4	293.16	18347.17	-73.1798	39800.62
	298.16			40166.52
	303.16			40532.42
	308.16			40898.32
	313.16			41264.22
5	293.16	9298.96	-42.3183	21705.49
	298.16			21917.09
	303.16			22128.69
	308.16			22340.29
	313.16			22551.89
6.3	293.16	28695.27	-104.59	59356.87
	298.16			59879.82
	303.16			60402.77
	308.16			60925.72
	313.16			61448.67

Table C-2:

Thermodynamic Parameters for Binary Ionic System

Zinc

pH	T	ΔH	ΔS	ΔG
4	293.16	42866.98	-150.899	1371.551
	298.16			2126.046
	303.16			2880.541
	308.16			3635.036
	313.16			4389.531
5	293.16	25864.85	-92.7842	53064.56
	298.16			53528.48
	303.16			53992.4
	308.16			54456.32
	313.16			54920.24
6.3	293.16	21109.25	-75.2417	43167.19
	298.16			43543.4
	303.16			43919.61
	308.16			44295.82
	313.16			44672.03

Nickel

4	293.16	29024.17	-109.828	61221.93
	298.16			61771.08
	303.16			62320.23
	308.16			62869.38
	313.16			63418.53
5	293.16	38394.05	-139.426	79269.35
	298.16			79966.5
	303.16			80663.65
	308.16			81360.8
	313.16			82057.95
6.3	293.16	28691.61	-108.082	60382.2
	298.16			60922.7
	303.16			61463.2
	308.16			62003.7
	313.16			62544.2

C-3: Experimental Error

Amount remaining in solution at equilibrium, C_e

Sample-1 = $X_1 = 77$ mg/l

Sample-2 = $X_2 = 71$ mg/l

Sample-3 = $X_3 = 70.4$ mg/l

Sample-4 = $X_4 = 73$ mg/l

Sample-5 = $X_5 = 66$ mg/l

Total number of samples, $N = 5$

We know that

Average mean is

$$\bar{X} = \frac{1}{N} \sum_{i=1}^N X_i$$

Average mean, $\bar{X} = 71.48$, where $X_i = X_1, X_2, X_3, X_4, X_5$

Standard Deviation is:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^5 (X_i - \bar{X})^2}$$

$$= \pm 3.58$$

