

**NEW SOLID PHASE EXTRACTION (SPE)
METHODS FOR THE PRECONCENTRATION AND
DETERMINATION OF TOXIC HEAVY METALS
USING INDIGENOUS BIOSORBENTS**



Ph. D Thesis

By

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**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN
MARCH 2011**

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DISSERTATION

**SUBMITTED TO THE UNIVERSITY OF PESHAWAR IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
IN CHEMISTRY**

INSTITUTE OF CHEMICAL SCIENCES

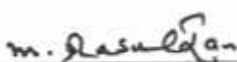
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PAKISTAN

MARCH 2011

INSTITUTE OF CHEMICAL SCIENCES
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PAKISTAN

Certified that **Mr Atta ul Haq S/O Fida Muhammad** has carried out his research and experimental work on the topic entitled as **“New Solid Phase Extraction (SPE) methods for the Preconcentration and Determination of Toxic Heavy Metals using Indigenous Biosorbents”** under our guidance and supervision. His research work is original and his dissertation is worthy of presentation to the university of Peshawar for the award of degree of **Doctor of Philosophy in Chemistry.**



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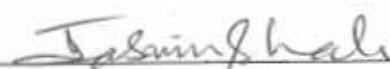
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EXTERNAL EXAMINER

To My Loving Parents

Who introduced me to the joy of learning since birth and whose prayers enabled me to accomplish such an arduous task.

To My Sisters

Who have been my emotional anchors throughout my entire life.

To My Brother

Who has always provided me with the spiritual guidance, love, wisdom, and encouragement through my every endeavor.

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LIST OF ABBREVIATIONS

%	Percent
°C	Degree Celsius
µg	Microgram
µg mL ⁻¹	Microgram per milliliter
µm	Micrometer
AAS	Atomic absorption spectrophotometer
AOP	Acid treated orange peels
BET	Brunauer Emmet Teller
C _e	Equilibrium concentration
C _f	Final concentration
C _i	Initial concentration
cm	Centimeter
cm ⁻¹	Per centimeter
COP	Carbonized orange peels
CSDC	Chemically treated sawdust carbon
CTSD	Chemically treated sawdust
DR	Dubinin-Radushkevich
EDX	Energy dispersive X-ray
FTIR	Fourier transform Infrared
g	Gram
IR	Infrared
K ₁	Pseudo-first-order rate constant
K ₂	Pseudo-second-order rate constant
L	Liter

ln	Natural logarithm
log	Common logarithm
M	Molarity
mg	Milligram
mg g ⁻¹	Milligram per gram
min	Minute
mL	Milliliter
mol	Mole
mol L ⁻¹	Mole per liter
q _e	Sorption capacity at equilibrium
Q ₀	Monolayer sorption capacity
q _t	Sorption capacity at time t
R ₂	Correlation coefficient or regression coefficient
SD	Sawdust
SDC	Sawdust carbon
SEM	Scanning electron microscopy
t	Time
Wt.	Weight
ΔG°	Change in standard Gibbs free energy
ΔH°	Change in standard enthalpy
ΔS°	Change in standard entropy

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ATTA UL HAQ

SUMMARY

The main objective of our work is to develop cost effective, rapid and efficient solid phase extraction methods utilizing indigenous biosorbents like mulberry sawdust, orange peel etc. for the pre-concentrations, separations and decontamination of toxic heavy metals like nickel, cadmium and lead with the potential application to environmental samples.

The first chapter of this dissertation consists of a brief introduction of biosorption process including the techniques used for wastewater treatment containing heavy metals. This chapter consists of discussion of biosorption and its importance over other methods. It focuses on biosorbents for the removal of heavy metals specifically used in the last two decades. It also describes the applications of agricultural/forestry wastes or by-products and several other biosorbents. This chapter also covers the mechanisms involved in this process including factors which affect this process like pH, sorbent dose, contact time, initial metal concentrations, temperature, ionic strength, sorbent size and agitation rate. The end of this chapter consists of indigenously available biosorbents and their mode of actions.

The second chapter focuses on a thorough and comprehensive review of the relevant but recent literature reported for the treatments of wastewater containing heavy metal ions using a variety of agricultural/forestry by-products or wastes.

The third chapter comprises of experimental methods applied for the removal of heavy metals using indigenous biosorbents and the effect of various parameters like solution pH, contact and shaking time, sorbent dosage, initial metal ion concentrations and temperature. The conversion of biosorbents into carbon was carried out in indigenous batch reactor and various chemicals were used to enhance the sorption ability. Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive x-ray and surface area and pore size analyzer were used for the characterization of biosorbents. The concentrations of heavy metals were determined by atomic absorption spectrophotometer.

The fourth chapter is concerned with results and discussions of the experimental data. The operational conditions like pH, sorbent dose, contact and shaking time, temperature and initial metal concentrations were optimized for maximum sorption of heavy metals. The equilibrium sorption data were fitted into two most common isotherm models i.e. Freundlich and Langmuir and the constant parameters for each model were evaluated from the linear form of these models. The kinetics of the sorption processes were described using four common kinetic models i.e. pseudo-first, pseudo-second, intraparticle diffusion and Elovich models and the constant parameters for each model were calculated. The effects of coexisting ions on the sorption processes were also investigated. The regeneration of investigated biosorbents was carried out using several desorbents. The proposed methods were applied to real samples.

The part A1 of fourth chapter consists of comparative study of the sorption of Ni(II) using silica gel, amberlite IR-120 and sawdust. It was observed that maximum sorption (98%) was achieved at pH 3 after equilibration for 60 min. Equilibrium sorption data of Ni(II) were fitted in to Freundlich and Langmuir models and maximum loading capacities (mg g^{-1}) for three investigated materials were found to be 33.33, 25.19 and 33.67 respectively. The sorption data were also fitted in four kinetic models like pseudo-first, pseudo-second, intraparticle diffusion and Elovich and was found that pseudo-second-order is the best choice among them. Desorption of the binded Ni(II) was carried out using various desorbents and was found that sodium chloride (3.0 M) shows efficient results. Sawdust was found to be the best among the three materials investigated for recovery (97%) and thus has not only the potential for preconcentration and decontamination of Ni(II) but also for the reuse for the same purpose.

The part A2 of fourth chapter composed of the removal of Ni(II) from aqueous solution using sawdust carbon. The mulberry wood sawdust was converted into carbon using indigenously designed glass reactor and sorption capacity for Ni(II) was enhanced by chemical treatment with NaOH, HCl and H_2SO_4 . On comparison, NaOH-activated sawdust carbon showed efficient results among them. Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive x-ray and surface area and pore size analyzer were used for the characterization of chemically untreated sawdust

carbon (SDC) and chemically treated sawdust carbon (CSDC). The effects of various parameters like pH, initial metal concentration and contact time on sorption of Ni(II) on CSDC were studied. Maximum % uptake of Ni(II) (86.50 %) was achieved at pH 7.0 after equilibrated for 70 min. The batch sorption data were analyzed by Freundlich and Langmuir models and showed best fit into Langmuir model. The sorption data were also correlated with kinetic models and was found that the data followed pseudo-second-order kinetic model.

The part A3 of fourth chapter focuses on the use of waste tea leaves for the removal of Ni(II) from aqueous solution. The effect temperature, pH, contact and shaking time, sorbent dose and initial metal concentration on sorption of Ni(II) using waste tea leaves was investigated in batch experiments. The Langmuir model shows best fit into equilibrium data as compared to Freundlich model and maximum sorption capacity was found to be 120.50 mg g^{-1} . The kinetics of the sorption data showed best fit into pseudo-second-order model as compared to the other analyzed models. The spontaneous and exothermic nature of the sorption process was revealed from thermodynamic parameters such as standard entropy, free energy and enthalpy. The results showed that waste tea leaves have the potential to be used as a low cost biosorbent for the removal of Ni(II) from aqueous solution.

The part B of fourth chapter consists of comparative sorption study of Pb(II) on acid modified orange peels (AOP) and carbonized orange peels (COP) in batch modes at optimum solution pH, contact and shaking time, initial metal concentration and temperature. The sorption of Pb(II) on AOP and COP was found to be strictly pH dependent and maximum uptake (100%) was achieved at pH 6.0 and 5.5 respectively. Both Freundlich and Langmuir model were fitted into equilibrium data and the monolayer sorption capacities of AOP and COP were found to be $1040 \text{ (mg g}^{-1}\text{)}$ and $993.11 \text{ (mg g}^{-1}\text{)}$ using Langmuir isotherm respectively. It was observed that pseudo-second-order model was best fitted into kinetic data as compared to other models. Thermodynamic parameters ΔG° , ΔH° and ΔS° were calculated using Van't Hoff equation which indicated that Pb(II) sorption on studied sorbents is spontaneous and endothermic in nature. It was observed that interfering ions like Na^+ , K^+ , Mg^{2+} , and Ca^{2+}

has not affected the sorption of Pb(II). Various desorbents were used for regeneration of loaded sorbents and was found that HNO₃ is the most efficient among them.

The part C of chapter fourth focuses on the removal of Cd(II) from aqueous solution using sawdust, an inexpensive material, obtained from mulberry wood after treatment with hydrochloric acid in batch experiments at optimum conditions. The sorption of Cd(II) was found to be pH dependent and maximum biosorption was achieved at pH 6 after 30 min shaking. The maximum sorption capacity of chemically treated sawdust (CTSD) obtained from Langmuir isotherm was 403.73 (mg g⁻¹) for Cd(II) and the equilibrium data followed Langmuir model. The kinetic data shows that pseudo-second-order model ($R^2 = 0.9887$) was the best choice among the kinetic models studied for description of biosorption of Cd(II) on CTSD. The effect of interfering ions (Na⁺, K⁺, Mg²⁺ and Ca²⁺) was also studied and the results showed that the presence of these ions has no appreciable effect on sorption of Cd(II). For desorption of retained Cd(II), various eluents were investigated and HCl (1.5 M) was found to be the most effective among them.

INTRODUCTION

1. INTRODUCTION

1.1. Biosorption

A number of traditional techniques like ion exchange, precipitation, chemical reduction and oxidation, filtration, evaporative recovery and electrochemical treatment are employed for the removal of heavy metal ions present in wastewater. Nevertheless, by using these techniques a lot of serious problems have been faced, including incomplete removal of metal ions, requirement of costly instruments and reagents, energy and the disposal of waste products or toxic sludge formed after analyses. To overcome these problems, new methods having reasonable cost are required for the treatment of wastewater containing heavy metals to reduce the concentrations of these metals to environmentally acceptable limits [1-3]. Among such methods, biosorption has drawn great attention recently due to its low cost, high sorptive efficiency, recycling of the biosorbents, minimal volume of the reagents and no requirement of nutrients [4, 5]. The passive uptake of toxicants by biologically inactive/dead materials or by materials derived from biological sources is known as biosorption [6]. On comparison with other techniques, the biosorption has the following advantages [7, 8].

- The materials have high sorption capacities.
- The materials are abundantly available as by-products or wastes and have low cost or free of cost.
- This sorption process is quick, suggesting that non-living material acts as ion exchangers.
- There is no need of specific conditions.
- Minimum biological or chemical sludge formation.
- The expensive growth media is not required.
- The physiological limitations of living cells have no effect on this process.
- The metals can be desorbed easily due to the reversibility of the process; therefore the materials can be easily recycled.

1.2. Biosorbent

Materials derived from biological sources like animals or plants and used for the removal of contaminants are called biosorbents [9-14]. Mostly, these materials have high efficiency to remove metal ions from very dilute solutions [15] for instance rice husk, bone, crushed egg shells, cotton waste and peat [16]. On the basis of cost, biosorbents may be divided in two categories; low and high cost biosorbents. The materials which are directly collected from the environment or industries, as by-products or wastes are included in first category [17] while the materials, which propagate specially for biosorption purposes can be including in second category [18]. The concentration of heavy metal ions are decreased from ppt to ppb level due to high sorption properties of the biosorbents and these materials efficiently and rapidly remove heavy metal ions from dilute complex solutions [19, 20, and 17]. Recently, a number of low cost and abundantly available biosorbents like rice husk [21], agricultural husk [22], rice milling [23], chaff [24], woody materials [25], activated sludge [26], agricultural waste biomass [27], etc. have been investigated for the treatment of wastewater containing heavy metal ions [28].

1.3. Agricultural/forestry wastes as biosorbents

Similar to synthetic adsorbents and ion exchangers, these biomaterials have been used for the removal of heavy metal ions due to its cost and recycling ability [29-42]. Recently, agricultural wastes or by-products like banana pith, sunflower, pine bark, wood, peat, wheat bran, wool etc. have received much attention for the treatment of wastewaters due to high sorption capacities, low cost, abundant availability, less care and maintenance, easily regeneration and reduction of disposal operation required for these waste materials [43-45]. A number of agricultural by-products and wastes have been employed for the removal of heavy metals from water samples such as pectin-rich waste [46], grape stalk [47], eucalyptus bark [48] *Moringa oleifera* bark [49], rice polish [50], rice husk [51], coconut trees [52], tea waste [53] etc.

1.4. Mechanisms involved in biosorption process

Different mechanisms have been expected to be involved in biosorption process due to the complex structure of biological materials, their origins and the process through which these materials come into usable forms but still these mechanisms are not crystal clear in many cases. Generally, the biosorption mechanism may be classified into two types: physical and chemical. The Van der Waal forces and electrostatic forces are involved in the physical biosorption mechanism between sorbate and sorbent while in the chemical biosorption mechanism; microprecipitation, chelation, complexation and microreduction are involved. The cell wall of the biomaterials contains proteins, polysaccharides and lipids which contain various functional groups like hydroxyl, amino, phosphoryl and carboxylate, are responsible for biosorbate-biosorbent interactions [54]. Additionally, the polysaccharides act as ion-exchangers [55-57]. Nevertheless, due to conformational, steric or other barriers, the presence of these functional groups do not assure their involvement in metal binding [58].

1.5. Factors affecting biosorption

There is a variety of factors which are important in the evaluation of the biosorption potential and are discussed below:

1.5.1. Solution pH

Among the important factors, pH is a controlling parameter which plays a vital role in biosorption process and it affects the activity of the functional groups present on the biomass and the solution chemistry of metals. The biosorption availability and speciation of the metal ions are strictly affected by pH of the solutions [59, 60]. The sorption process becomes very complicated at higher pH, due to decrease in solubility of metal-complex and results in precipitation while at lower pH, there is a competition among protons and metal ions. The adjustment of the pH also changes the activity of binding

sites. The favorable pH for the binding of metal ions is 3 to 6, due to the involvement of negatively charged carboxyl groups through ion exchange mechanisms.

1.5.2. Initial metal concentration

The uptake of solute is increased with increase in initial solute concentration, suggesting that it strongly affect the biosorption process [61-63]. The fractional sorption becomes independent of the initial concentration at lower initial solute concentrations due to low ratio of the initial moles of solute to the available surface area. Nevertheless, the removal of solute depends upon the initial solute concentrations at higher initial concentration owing to saturation of the sorption sites. The biosorption experiments have been conducted at the highest possible initial concentration for the identification of maximum loading capacity of the biosorbent.

1.5.3. Sorbent dose

The biosorption can be strictly affected by sorbent dose. Higher uptakes and lower percent removals have been obtained at low sorbent dose [64, 65]. As the concentration of the biomass increases, the numbers of the binding sites are also increased and hence large amount of metal ions get biosorbed [66]. Contrary, a decrease in biosorbed solute per unit weight of biosorbent occurs with increase in sorbent dose perhaps due to the complex interaction of many factors. One of the important factors among these is that at higher sorbent dose the total exchangeable sites on the biosorbent are not completely covered by available solute molecules due to insufficiency and resulting in low metal uptake [67]. Additionally, a decrease in specific uptake results by the interference between binding sites which are due to increase in sorbent dose [68].

1.5.4. Temperature

The biosorption is affected by temperature to a small extent in the range of 20 to 35 °C [69]. The sorption properties increases by increase in temperature owing to increase in

kinetic energy and surface activity of the solute [70, 71]; however, at higher temperature there may be possibility of damaging of the biomaterials. The sorption capacity of the biomaterials reduced with increase in temperature due to the exothermic nature of some biosorption processes [72, 73]. Therefore, the conduction of the biosorption experiments at room temperature is most suitable and replicate results can be easily obtained.

1.5.5. Agitation rate

The rate of biosorption could be affected by external film diffusion in some cases and this mass transfer might be reduced with appropriate agitation. A decrease in the thickness of the liquid boundary layer and the enhanced turbulence results into higher diffusion rate of a solute from the bulk liquid to the boundary layer surrounding particles [74]. An increase in the value of the external diffusion occurs under these circumstances [75]. At last, rate of the diffusion of the solute through the boundary layer is enhanced by the thinness of the boundary layer at higher agitation rates.

1.5.6. Size of biosorbent

The extent of biosorption is also affected by the size of the biosorbent. The biosorption increases with decrease in particle size due to higher surface area and equilibration is established in a short time. Additionally, the particle must have sufficient resistance to the applied pressure during biosorption process and the extreme conditions applied for regeneration [76]. Therefore, a suitable size of the biosorbent is required for preliminary experiments. The mechanical strength like granulation should be improved for a biosorbent; available in powdered form such as industrial waste in order to use it effectively in biosorption columns.

1.5.7. Ionic strength

The biosorption of metal ions to the biomass surface is also affected by an important parameter, the ionic strength [77, 78]. The changes in metal activity lead to changes in

the properties of electrical double layer. Also competition between metal ions is thought to be responsible for the effect of ionic strength on the extent of biosorption. An electrical double layer due to electrostatic interaction surrounds the two phases i.e. solute in aqueous solution and biomass surface. Hence, an increase in ionic strength decreases the extent of biosorption [79]. The sorption process is also affected by some inorganic ions like chlorine due to the formation of complexes with metal ions [80, 6].

1.6. Sawdust

The timber and wood-based industries produce sawdust on a large scale as a waste which is used for different purposes like packing material and as a fuel for cooking [81-83]. Recently, the wood sawdust, an agricultural waste or by-product has been used for the treatment of wastewater containing heavy metal ions [84] due to its low cost, abundant availability, renewability, mechanical stability and its regeneration ability [85-87]. The wood sawdust is made of different organic compounds like cellulose and lignin in the range of 45 to 50% and 23 to 34% respectively [88]. These compounds bear various functional groups like carboxylic, hydroxyl and phenolic [89], which capture the heavy metal ions through ion exchange, chemical reaction, lone pair electron sharing, chemisorption or physical sorption [90].

1.7. Orange peels

The orange is 75% of the total citrus fruit production in the world [91, 92]. The residue of the orange; peels are the wastes or by-products of the juice providing industry and used as animal food [93, 94]. The peels mainly consist of two parts i.e. outer yellow called flavedo and the inner white called albedo [95]. The main components of the orange peels are lignin, hemi-cellulose, cellulose and pectin which bear many functional groups like hydroxyl, phenolic and carboxylic [96, 97]. The orange peels have serious disposal problems and little economic value [98, 99]. In recent years, research has been focused on the use of orange peels as a biosorbent for the removal of heavy metal ions from

wastewaters due to low cost, local availability, insolubility in water, special structure and chemical stability [100-106].

1.8. Aim and objective of the present work

There is a need to investigate and develop new biomaterials, which should be inexpensive, abundantly available and possess high capacity for biosorption of heavy metals. Mulberry is one of the common woods in the K.P.K province of Pakistan which is mostly used in furniture manufacture and timber industries due to its relatively low cost and abundant availability. Mulberry wood sawdust is one possible material to be used as a biosorbent because it is produced in large quantities at sawmills as a solid waste. Similarly, orange is also produced in large quantity in Pakistan especially in mountainous area of K.P.K province. Orange peels are solid wastes which are found abundantly and so far have no proper utilizations. The main objective of our work is to utilize these materials for the pre-concentrations, separations and decontamination of toxic heavy metals like nickel, cadmium and lead with the potential application to environmental samples.

References

1. M. Gavrilescu, "Removal of heavy metals from the environment by biosorption", *Engineering in Life Sciences*, 4, 219–232 (2004).
2. Z. Aksu, F. Gonen, Z. Demircan, "Biosorption of chromium(VI) ions by Mowital B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon", *Process Biochemistry*, 38, 175–86 (2002).
3. Y. Sag, D. Ozer, T. Kutsal, "A comparative study of the biosorption of lead(II) ions to *Z. ramigera* and *R. arrhizus*", *Process Biochemistry*, 30, 169–74 (1995).
4. Y. Goksungur, S. Uren, U. Guvenc, "Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass", *Bioresource Technology*, 96, 103–109 (2005).
5. L. Norton, K. Baskaran, T. Mckenzie, "Biosorption of zinc from aqueous solutions using biosolids", *Advance Environmental Research*, 8, 629–635 (2004).
6. K. Vijayaraghavan, Y. Yeoung-Sang, "Bacterial biosorbents and biosorption", *Biotechnology Advances*, 26, 266–291 (2008).
7. J. M. Modak, K. A. Natarajan, "Biosorption of metals using non-living biomass – a review", *Minerals and Metallurgical Processing*, 12, 189–196 (1995).
8. U. Farooq, J. A. Kozinski, M. A. Khan, M. Athar, "Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature", *Bioresource Technology*, 101, 5043–5053 (2010).
9. H. K. Alluri, S. R. Ronda, V. S. Settalluri, J. Singh, "Biosorption: An eco-friendly alternative for heavy metal removal", *African Journal of Biotechnology*, 25, 2924–31 (2007).
10. M. S. Asma, W. Akhter, M. Iqbal, "Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent", *Separation and Purification Technology*, 45, 25–31 (2005).
11. R. Gupta, P. Ahuja, S. Khan, R. K. Saxena, "Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solutions", *Current Science*, 78, 967–973 (2000).

12. A. H. Ivo, J. R. R. Schneider, W. Ross, "Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation?", *International Journal of Mineral Processing*, 62, 111–120 (2001).
13. T. R. Muraleedharan, L. Iyengar, C. Venkobachar, "Screening of tropical wood-rotting mushrooms for copper biosorption", *Applied and Environmental Microbiology*, 61, 3507–8 (1995).
14. C. W. S. C. White, G. M. Gadd, "The role of microorganisms in biosorption of toxic metals and radionuclides", *International Biodeterioration and Biodegradation*, 35, 17–40 (1995).
15. K. Kuyucak, "Feasibility of biosorbents application. In: Volesky B, editor. *Biosorption of Heavy Metals*", Boca Raton: CRC Press, pp. 371–378 (1997).
16. Z. Aksu, "Application of biosorption for the removal of organic pollutants: A review", *Process Biochemistry*, 40, 997–1026 (2005).
17. J. Wang, C. Chen, "Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review", *Biotechnology Advances*, 24, 427–451 (2006).
18. K. Chojnacka, "Biosorption and bioaccumulation – the prospects for practical applications", *Environment International*, 36, 299–307 (2010).
19. F. Veglio, F. Beolchini, "Removal of metals by biosorption: A review", *Hydrometallurgy*, 44, 301–16 (1997).
20. B. Volesky, "Biosorption and biosorbents", In: Volesky B, editor. *Biosorption of Heavy Metals*. Florida: CRC press, pp. 3–5 (1990).
21. M. Ajmal, R. A. K. Rao, S. Anwar, J. Ahmad, R. Ahmad, "Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater", *Bioresource Technology*, 86 (2), 147–149 (2003).
22. S. P. Dubey, K. Gopal, "Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: A comparative study", *Journal of Hazardous Materials*, 145, 465–470 (2007).
23. C. R. T. Tarley, M. A. Z. Arruda, "Biosorption of heavy metals using rice milling by products. Characterization and application for removal of metals from aqueous effluents", *Chemosphere*, 54 (7), 987–995 (2004).

24. R. P. Han, J. H. Zhang, W. H. Zou, H. J. Xiao, J. Shi, H. M. Liu, "Biosorption of copper(II) and lead(II) from aqueous solution by chaff in a fixed-bed column", *Journal of Hazardous materials*, 133 (1–3), 262–268 (2006).
25. M. A. Hanif, R. Nadeem, M. N. Zafar, K. Akhtar, H. N. Bhatti, "Kinetic studies for Ni(II) adsorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass", *Journal of Hazardous Materials*, 145, 501–505 (2007).
26. M. Kilic, M. E. Keskin, S. Mazlum, N. Mazlum, "Effect of conditioning for Pb(II) and Hg(II) adsorption on waste activated sludge", *Chemical Engineering and Processing*, 47, 31–40 (2008).
27. E. Malkoc, Y. Nuhoglu, "Investigations of Ni(II) removal from aqueous solutions using tea factory waste", *Journal of Hazardous Materials*, 127, 120–128 (2005).
28. Y. Nuhoglu, E. Malkoc, "Thermodynamic and kinetic studies for environmentally friendly Ni(II) biosorption using waste pomace of olive oil factory", *Bioresource Technology*, 100, 2375–2380 (2009).
29. J. A. Laszlo, F. R. Dintzis, "Crop residues as ion exchange materials—treatment of soyabean hull and sugar beet fibre (pulp) with epichlorohydrin to improve cation exchange capacity and physical stability", *Journal of Applied Polymer Science*, 52, 531–538 (1994).
30. W. E. Marshall, E. T. Champagne, "Agricultural by-products as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater", *Journal of Environmental Science and Health A*, 30, 241–261 (1995).
31. V. M. Dronnet, C. M. G. C. Renard, M. A. V. Axelos, J. F. Thibault, "Binding of divalent metal cations by sugar-beet pulp", *Carbohydrate Polymers*, 34, 73–82 (1997).
32. M. C. Basso, E. G. Cerrella, A. L. Cukierman, "Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater", *Industrial and Engineering Chemistry Research*, 41, 3580–3585 (2002).
33. Z. Reddad, C. Gerente, Y. Andres, P. L. Cloirec, "Comparison of the fixation of several metal ions onto a low cost biopolymer", *Water Science and Technology*, 2, 217–224 (2002).

34. Z. Reddad, C. Gerente, Y. Andres, R. M. Christine, J. F. Thibault, P. L. Cloirec, "Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp", *Carbohydrate Polymers*, 49, 23–31 (2002).
35. Z. Reddad, C. Gerente, Y. Andres, P. L. Cloirec, "Modeling of single and competitive metal adsorption onto a natural polysaccharide", *Environmental Science and Technology*, 36, 2242–2248 (2002).
36. Z. Reddad, C. Zerente, Y. Andres, P. L. Cloirec, "Adsorption of several metal ions onto a low cost biosorbent: kinetic and equilibrium studies", *Environmental Science and Technology*, 36, 2067–2073 (2002).
37. Z. Reddad, C. Zerente, Y. Andres, P. L. Cloirec, "Mechanisms of Cr(III) and Cr(VI) removal from aqueous solutions by sugar beet pulp", *Environmental Toxicology*, 24, 257–264 (2003).
38. L. Dupont, E. Guillon, "Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran", *Environmental Science and Technology*, 37, 4235–4241 (2003).
39. L. Dupont, J. Bouanda, J. Dumonceau, M. Aplincourt, "Metal ions binding onto a lignocellulosic substrate extracted from wheat bran: a NICA-Donnan approach", *Journal of Colloid Interface Science*, 263, 35–41 (2003).
40. K. K. Krishnani, V. Parimala, X. Meng, "Detoxification of hexavalent chromium from coastal water using lignocellulosic waste", *Water SA*, 30, 541–545 (2004).
41. V. Parimala, K. K. Krishnani, B. P. Gupta, M. Jayanthi, M. Abraham, "Phytoremediation of chromium from seawater using five different products from coconut husk", *Bulletin of Environmental Contamination and Toxicology*, 73, 31–37 (2004).
42. K. K. Krishnani, S. Ayyappan, "Heavy metals remediation of water using plant and lignocellulosic agro-wastes", *Reviews of Environmental Contamination and Toxicology*, 188, 59–84 (2006).
43. B. Volsky, "Biosorption and me", *Water Research*, 41, 4017–4029 (2007).
44. S. Larous, A. H. Meniai, M. B. Lehocine, "Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust", *Desalination*, 185, 483–490 (2005).

45. A. Ahmad, M. Rafatullah, O. Sulaiman, M. H. Ibrahim, Y. Y. Chii, B. M. Siddique, "Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood", *Desalination*, 247, 636–646 (2009).
46. S. Schiewer, S. B. Patil, "Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics", *Bioresource Technology*, 99, 1896–1903 (2008).
47. M. Martinez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, "Removal of lead(II) from aqueous solutions using grape stalk waste", *Journal of Hazardous Materials*, 136, 203–211 (2006).
48. I. Ghodbane, O. Hamdaoui, "Removal of mercury(II) from aqueous media using eucalyptus bark: kinetic and equilibrium studies", *Journal of Hazardous Materials*, 160, 301–309 (2008).
49. D. H. K. Reddy, K. Sessaiah, A. V. R. Reddy, M. M. Rao, M. C. Wang, "Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetic studies", *Journal of Hazardous Materials*, 174, 831–838 (2010).
50. K. K. Singh, R. Rastog, S. H. Hasan, "Removal of cadmium from wastewater using agricultural waste 'rice polish'", *Journal of Hazardous Materials*, 121, 51–58 (2005).
51. K. Upendra, B. Manas, "Sorption of cadmium from aqueous solution using pretreated rice husk", *Bioresource Technology*, 97, 104–109 (2006).
52. K. Kadirvelu, M. Palanival, R. Kalpana, S. Rajeswari, "Activated carbon from an agricultural by-product, for the treatment of dyeing industry wastewater", *Bioresource Technology*, 74, 263–265 (2000).
53. B. M. W. P. K. Amarasinghe, R. A. Williams, "Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater", *Chemical Engineering Journal*, 132, 299–309 (2007).
54. U. Dziwulska, A. Bajguz, B. G. Zylkiewicz, "The use of algae *Chlorella vulgaris* immobilized on Cellex-T support for separation/preconcentration of trace amounts of platinum and palladium before GFAAS determination", *Analytical Letters*, 37, 2189–2203 (2004).

55. Y. Sag, T. Kutsal, "The selective biosorption of chromium(VI) and copper(II) ions from binary metal mixtures by *R. arrhizus*", *Process Biochemistry*, 31, 561–572 (1996).
56. F. Veglio, F. Beolchini, A. Gasbarro, "Biosorption of toxic metals: an equilibrium study using free cells of *Arthrobacter* sp.", *Process Biochemistry*, 32, 99–105 (1996).
57. A. I. Zouboulis, E. G. Rousou, K. A. Matis, I. C. Hancock, "Removal of toxic metals from aqueous mixtures", *Journal of Chemical Technology and Biotechnology*, 74, 429–436 (1999).
58. B. Volesky, Z. R. Holan, "Biosorption of Heavy Metals", *Biotechnology Progress* 11, 235–250 (1995).
59. J. Yang, B. Volesky, "Modeling the uranium-proton ion exchange in biosorption", *Environmental Science and Technology*, 33, 4079–4085 (1999b).
60. A. Esposito, F. Pagnanelli, F. Veglio, "pH-related equilibria models for biosorption in single metal systems", *Chemical Engineering Science*, 57, 307–13 (2002).
61. Y. S. Ho, G. McKay, "The sorption of lead(II) ions on peat", *Water Research*, 33, 578–584 (1999).
62. Y. S. Ho, G. McKay, "The kinetics of sorption of divalent metal ions onto sphagnum moss peat", *Water Research*, 34, 735–742 (2000).
63. A. R. Binupriya, M. Sathishkumar, D. Kavitha, K. Swaminathan, S. E. Yun, S. P. Mun, "Experimental and isothermal studies on sorption of Congo red by modified mycelial biomass of wood-rotting fungus", *Clean*, 35, 143–150 (2007).
64. Z. Aksu, S. S. Çagatay, "Investigation of biosorption of Gemazol Turquoise Blue-G reactive dye by dried *Rhizopus arrhizus* in batch and continuous systems", *Separation and Purification Technology*, 48, 24–35 (2006).
65. K. Vijayaraghavan, K. Palanivelu, M. Velan, "Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles", *Bioresource Technology*, 97, 1411–1419 (2006).

66. A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veglio, "Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations", *Hydrometallurgy*, 60, 129–141 (2001).
67. J. Tangaromsuk, P. Pokethitiyook, M. Kruatrachue, E. S. Upatham, "Cadmium biosorption by *Sphingomonas paucimobilis* biomass", *Bioresource Technology*, 85, 103–105 (2002).
68. G. M. Gadd, C. White, L. D. Rome, "Heavy metal and radionuclide uptake by fungi and yeasts", In: Norri PR, Kelly DP, editors. *Biohydrometallurgy*. Chippenham, Wilts, UK: A. Rowe; (1988).
69. F. Veglio, F. Beolchini, "Removal of metals by biosorption: A review", *Hydrometallurgy*, 44, 301–316 (1997).
70. Y. Sag, T. Kutsal, "Determination of the biosorption heats of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*", *Biochemical Engineering Journal*, 6, 145–151 (2000).
71. K. Vijayaraghavan, Y. S. Yun, "Utilization of fermentation waste (*Corynebacterium glutamicum*) for biosorption of Reactive Black 5 from aqueous solution", *Journal of Hazardous Materials*, 141, 45–52 (2007).
72. N. Mameri, N. Boudries, L. Addour, D. Belhocine, H. Lounici, H. Grib, A. Pauss, "Batch zinc biosorption by a bacterial nonliving *Streptomyces rimosus* biomass", *Water Research*, 33, 1347–54 (1999).
73. I. P. Suhasini, G. Sriram, S. R. Asolekar, G. K. Sureshkumar, "Biosorptive removal and recovery of cobalt from aqueous systems", *Process Biochemistry*, 34, 239–247 (1999).
74. J. R. Evans, W. G. Davids, J. D. MacRae, A. Amirbahman, "Kinetics of cadmium uptake by chitosan-based crab shells", *Water Research*, 36, 3219–3226 (2002).
75. J. Shen, Z. Duvnjak, "Adsorption kinetics of cupric and cadmium ions on corncob particles", *Process Biochemistry*, 40, 3446–3454 (2005).
76. B. Volesky, "Detoxification of metal-bearing effluents: biosorption for the next century", *Hydrometallurgy*, 59, 203–216 (2001).

77. C. J. Daughney, J. B. Fein, "The effect of ionic strength on the adsorption of H^+ , Cd^{2+} , Pb^{2+} and Cu^{2+} by *Bacillus subtilis* and *Bacillus licheniformis*: a surface complexation model", *Journal of Colloid Interface Science*, 198, 53–77 (1998).
78. D. M. Borrok, J. B. Fein, "The impact of ionic strength on the adsorption of protons, Pb, Cd, and Sr onto the surfaces of Gram negative bacteria: testing nonelectrostatic, diffuse, and triple-layer models", *Journal of Colloid Interface Science*, 286, 110–126 (2005).
79. G. Donmez, Z. Aksu, "Removal of chromium(VI) from saline wastewaters by *Dunaliella* species", *Process Biochemistry*, 38, 751–62 (2002).
80. M. A. Borowitzka, "Algal media and sources of algal cultures", In: Borowitzka MA, Borowitzka LJ, editors. *Micro-algal technology*. Cambridge: Cambridge University press; pp. 456–65 (1988).
81. A. Shukla, Y. H. Zhang, P. Dubey, J. L. Margrave, S. S. Shukla, "The role of sawdust in the removal of unwanted materials from water", *Journal of Hazardous Materials B*, 95, 137–152 (2002).
82. S. S. Shukla, L. J. Yu, K. L. Dorris, A. Shukla, "Removal of nickel from aqueous solutions by sawdust", *Journal Hazardous of Materials B*, 121, 243–246 (2005).
83. V. K. Garg, R. Gupta, R. Kumar, R. K. Gupta, "Adsorption of chromium from aqueous solution on treated sawdust", *Bioresource Technology*, 92, 79–81 (2004).
84. S. Alka, Z. Yu-Hui, P. Dubey, J. L. Margrave, S. S. J. Shyam, "The role of sawdust in the removal of unwanted materials from water", *Journal of Hazardous Materials*, 95, 137–152 (2002).
85. F. Asadi, H. Shariatmadari, N. Mirghaffari, "Modification of rice hull and sawdust sorptive characteristics for removal of heavy metals from synthetic solutions and wastewater", *Journal of Hazardous Materials*, 154, 451–458 (2008).
86. M. E. Argun, S. Dursun, C. Ozdemir, M. Karatas, "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics", *Journal of Hazardous Materials*, 141, 77–85 (2007).
87. M. Sciban, M. Klasnja, B. Skrbic, "Modified softwood sawdust as adsorbent of heavy metal ions from water", *Journal of Hazardous Materials B*, 136, 266–271 (2006).

88. Z. A. Zakaria, M. Suratman, N. Mohammed, W. A. Ahmad, "Chromium(VI) removal from aqueous solution by untreated rubber wood sawdust", *Desalination*, 244, 109–121 (2009).
89. M. Sciban, B. Radetic, Z. Kevresan, M. Klasnja, "Adsorption of heavy metals from electroplating wastewater by wood sawdust", *Bioresource Technology*, 98, 402–409 (2007).
90. C. Raji, T. S. Anirudhan, "Preparation and metal-adsorption properties of the polyacrylamide-grafted sawdust having carboxylate functional group", *Indian Journal of Chemical Technology*, 3, 345–350 (1996).
91. X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, "Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 317, 512–521 (2008).
92. X. Li, Y. Tang, Z. Xuan, Y. Liu, F. Luo, "Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution", *Separation and Purification Technology*, 55, 69–75 (2007).
93. Y. Liu, J. Shi, T. A. G. Langrish, "Water-based extraction of pectin from flavedo and albedo of orange peels", *Chemical Engineering Journal*, 120, 203–209 (2006).
94. M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, "Copper biosorption from aqueous solutions by sour orange residue", *Journal of Hazardous Materials*, 149, 269–274 (2007).
95. J. F. Kefford, B. V. Chandler, "The Chemical Constituents of Citrus Fruits", *Advances in Food Research*, Supplement 2, New York, Academic press, pp. 28 (1970).
96. J. T. Matheickal, Q. Yu, G. M. Woodburn, "Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga *Durvillaea potatorum*", *Water Research*, 33, 335–342 (1999).
97. Y. P. Ting, I. G. Prince, F. Lawson, "Uptake of cadmium and zinc by the alga *Chlorella vulgaris* (II): Multi-ion situation", *Biotechnology and Bioengineering*, 37, 445–455 (1991).

98. G. Selvakumari, M. Murugesan, S. Pattabi, M. Sathishkumar, "Treatment of electroplating industry effluent using maize cob carbon", *Bulletin of Environmental Contamination and Toxicology*, 69, 195–202 (2002).
99. T. A. Kurniawan, G. Y. S. Chan, W. H. Lo, S. Babel, "Comparisons of low-cost adsorbents for treating wastewater laden with heavy metals", *Science of the Total Environment*, 55, 402–426 (2005).
100. F. Ning-chuan, G. Xue-yi, L. Sha, "Enhanced Cu(II) adsorption by orange peel modified with sodium hydroxide", *Transactions of Nonferrous Metals Society of China*, 20, 8146–8152 (2010).
101. M. Ajmal, R. A. K. Rao, R. Ahmad, J. Ahmad, "Adsorption studies on *Citrus reticulata* (fruit peel of orange): Removal and recovery of Ni(II) from electroplating wastewater", *Journal of Hazardous Materials B*, 79, 117–131 (2000).
102. A. Annadurai, R. S. Juang, D. J. Lee, "Adsorption of heavy metals from water using banana and orange peels", *Water Science and Technology*, 47, 185–190 (2002).
103. Z. X. Xuan, Y. R. Tang, X. M. Li, Y. H. Liu, F. Luo, "Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically-modified orange peel", *Biochemical Engineering Journal*, 31, 160–164 (2006).
104. X. M. Li, Y. R. Tang, Z. X. Xuan, Y. H. Liu, F. Luo, "Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution", *Separation and Purification Technology*, 55, 69–75 (2007).
105. J. Gross, "Carotenoid pigments in citrus", In: Nagy, S., Shaw, P., Veldhuis, M. K. (Eds.), *Nutrition, Anatomy, Chemical Composition and Bioregulation, Citrus Science and Technology*, 1st Ed. The AVI Publishing Company, Inc, Westport, Connecticut, pp. 74–479 (1977).
106. K. N. Ghimire, K. Inoue, H. Yamaguchi, K. Makino, T. Miyajima, "Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste", *Water Research*, 37, 4945–4953 (2003).

LITERATURE REVIEW

2.LITERATURE REVIEW

Chubar et al., (1) studied the biosorption of heavy metals (Ni, Cu and Zn) using a pretreated cork biomass considering the influence of different chemicals used for pretreatment. The carboxylic groups play an important role in metal binding which was confirmed with pretreatment by Fisher reaction. The sorption capacity of the cork for copper was enhanced up to 30% with pretreatment of the cork biomass using 0.5 M NaOH solution while no appreciable change was observed in the performance of the biomass after pretreatment with a 0.5 M CaCl_2 solution. The washing of the biomass with 0.1 M NaOH and NaCl solutions or boiling in deionized water did not change the sorption capacity of the cork biomass while the sorption capacity of the biomass was improved by heating/boiling in alkaline solutions. The sorption capacity of the biomass was improved with pretreatment with oxidizing agents (NaClO and NaIO_3). When the pretreatment was carried out at room temperature with a solution containing 7% of active chlorine, the sorption capacity of the biomass was improved from 70 to 80%. On comparison with original cork biomass, the sorption capacity of the porous carbon obtained after direct activation of the cork with steam at 700 and 800 °C was four to six times higher.

Pagnanelli et al., (2) studied olive pomace, a solid waste from olive oil production plants as a biomass for the biosorption of heavy metals. Potentiometric titrations were carried out for the determination of acid-base properties of the active sites of olive pomace and two main active sites were represented by a continuous model. The biosorption tests were performed at various equilibrium pH with single (Cd and Cu) and binary metal system (Cd-Cu), to consider the competition among heavy metals and protons in solution. At various equilibrium pH, the non-ideal competitive adsorption model (NICA model) and Langmuir extensions model can be used for the biosorption of Cd and Cu to represent the experimental data. Non-ideal adsorption of various species simultaneously present in solution and site heterogeneity were only described by NICA models, can adequately simulate the competition between Cd and Cu in binary metal systems with the help of parameters fitted to a single system data.

Han et al., (3) reported the removal of Pb(II) from aqueous solutions by using cereal chaff, an agricultural product which is abundantly available in middle-west region of China. The sorption processes were determined and were found to be a function of contact time, temperature and chaff dosage. The characteristic parameters for each model were determined by correlating the experimental data with Freundlich, Langmuir, Temkin and Koble-Corrigan isotherm models. The biosorption data of Pb(II) was shown best fit in Langmuir and Koble-Corrigan isotherms. The maximum biosorption capacity of Pb(II) onto chaff at 293 K was found to be 12.5 mg g^{-1} . Various thermodynamic parameters, like ΔH° , ΔG° and ΔS° were determined using the thermodynamic equilibrium coefficients obtained at different temperatures. The exothermic and spontaneous nature of the biosorption process was indicated from thermodynamic studies of Pb(II)-chaff system. It was observed that the loading of metal ion per unit weight of chaff decreased with rise in temperature.

Al-Qodah (4) investigated the biosorption of Ni(II), Cd(II) and Cu(II) onto different pretreated sludge. The adsorption capacity of the sludge was improved with pretreatment with NaOH while it decreased with HCl. The untreated and treated sludge have less affinity towards Ni(II) and greater affinity towards Cd(II) and Cu(II). The sludge pretreated with NaOH has maximum loading capacity of 93.4 and 131.6 mg g^{-1} for Cd(II) and Cu(II) respectively. The adsorption data followed Freundlich and Langmuir isotherm models. In most cases the R^2 value exceeds 0.95. It was observed that as the temperature increases from 25 to 45 °C the maximum adsorption capacity falls 18.3%. An increase in mixing speed and mass of the adsorbent resulted in an increase of adsorption capacity. It was observed that maximum adsorption was achieved at pH 5. In the first cycle of the desorption studies the desorption efficiency with H_2SO_4 (0.1M) reaches 94% while it drops to 8% in the fourth cycle after recovering $20,700 \text{ mg Cd(II) L}^{-1} \text{ H}_2\text{SO}_4$.

Han et al., (5) studied chaff in a fixed-bed column for the treatment of wastewater samples containing heavy metal ions. The biosorption experiments were conducted to see the effect of flow rate, pH, coexisting ions and influent concentration of solution. The recycled chaff might be used for the removal of heavy metal ions as revealed from the adsorption/desorption recycling studies of chaff. The characteristic parameters and

breakthrough curves were determined at various concentrations of influent and flow rate by applying Thomas model to the biosorption of lead and copper. It was observed that the model described best the biosorption process of the dynamic behavior of the chaff column. The high rate of biosorption and efficient removal ability of the chaff, make it a useful adsorbent for the removal of heavy metal ions from aqueous solutions. Additionally, the adsorption efficiency of the adsorbent was found to be high. The equilibrium adsorption biomass reached up to 6.72 mg g^{-1} and 1.98 mg g^{-1} when the concentration of lead and copper ions was 50.12 mg L^{-1} and 14.82 mg L^{-1} at a flow rate of 3.6 mL min^{-1} respectively. The Pb(II) and Cu(II) metals were also studied in a competitive biosorption process. It may be concluded that the adsorption capacity of chaff did not decrease during competitive biosorption of Pb(II) and Cu(II).

Kalavathy et al., (6) reported the adsorption of Cu(II) from aqueous solution using H_3PO_4 -activated carbon obtained from rubber wood sawdust (RSAC) in batch mode. The influences of different variables like temperature, pH, contact time and initial metal concentration on equilibrium and kinetic studies were conducted. It was observed that adsorption of Cu(II) on RSAC is pH dependent and maximum adsorption was achieved at pH 6.0. Vant's Hoff equation was applied for the determination of thermodynamic parameters like standard entropy (ΔS°), standard enthalpy (ΔH°) and standard Gibbs free energy (ΔG°) which showed the exothermic and spontaneous nature of the Cu(II) adsorption onto RSAC. The equilibrium data at various temperatures were analyzed by using isotherms like Temkin, Freundlich and Langmuir and was found to best fit into Langmuir isotherm. Intraparticle diffusion, pseudo-first and pseudo-second-order kinetic models were used to check the kinetic data. It was observed that pseudo-second-order model was the best choice to describe the kinetics of Cu(II) biosorption. For different initial concentrations of metal ions, the rate constants of intraparticle diffusion, pseudo-first and pseudo-second-order and initial sorption rate were determined and was found that the adsorption process is complex and followed both particle diffusion and surface adsorption. Reichenberg plot was used to determine the effective diffusion coefficient and rate- controlling parameter and showed that at low concentrations, the biosorption occurs through film diffusion while particle diffusion was the rate determining step at higher concentrations.

Acar and Eren (7) used poplar sawdust and activated sawdust to remove the Cu(II) from aqueous solution in batch system. The pH, adsorbent dosage and initial Cu(II) concentration were found to affect the equilibrium adsorption level. Both Langmuir and Freundlich isotherms were applied to the equilibrium data and was found that Langmuir adsorption model was obeyed by the equilibrium data. At natural pH and room temperature, the equilibrium capacity of sawdust and activated sawdust were found to be 5.432 and 13.495 mg Cu(II) per g adsorbent respectively. Maximum adsorption capacity was achieved at the zeta potential value of -48.4 mV (pH 4) for sawdust and -74.5 mV (pH 5) for activated sawdust. The activated sawdust showed greater adsorption capacity for Cu(II) from aqueous solution as compared to sawdust.

Baral et al., (8) investigated the adsorption of Cr(VI) on treated sawdust as a function of temperature, concentration of adsorbate, amount of adsorbent, pH and contact time. The adsorption of Cr(VI) followed pseudo-second-order kinetic and the adsorption capacity of the adsorbent was evaluated by applying Langmuir adsorption isotherm. It was observed that adsorption capacity of the sawdust was pH dependent and reached equilibrium in 3 hours with adsorbent dose of 30 mg L⁻¹. Arrhenius equation was used to calculate the activation energy (E_a) and the rate constant at 303, 308, 313 and 318 K temperature. The adsorption of Cr(VI) onto sawdust was found to be exothermic in nature as shown from the thermodynamic parameters like heat of adsorption (ΔH_f) and Gibbs free energy (ΔG°). An increase in percent adsorption was observed with decrease in pH and for an initial concentration of 5 mg L⁻¹, the removal of Cr(VI) was maximum in the pH range of 4.5-6.5.

Sciban et al., (9) reported that sodium hydroxide treatment of the fir and poplar sawdust enhanced the adsorption capacity about 15 times for zinc ions and 2.5 to 5 times for Cu(II). The results showed that sodium carbonate solution was less efficient than sodium hydroxide solution for activation of sawdust. Therefore 1% sodium hydroxide solution was used for the treatment of sawdust. Adsorption mechanism included both microprecipitation and ion exchange of metal hydroxide in the pores. The modification of the sawdust also decreased the leaching of organic matters by about 23% for fir and 7% for poplar.

Xuan et al., (10) studied the biosorption of Pb(II) on chemically modified orange peel. New biosorbents were prepared using different temperatures, different concentrations of citric acid and alkaline saponification. The adsorption of Pb(II) by different chemically modified biosorbents was investigated as a function of various parameters like solid/liquid ratio, shaking time and pH. The equilibriums were reached in one hour and followed pseudo-first-order kinetics. The biosorption of lead was varied with pH and was found to be maximum (1.22 mol kg^{-1}) in the pH range of 4.5-6.0.

Argun et al., (11) described the removal of Cr(VI), Ni(II) and Cu(II) from aqueous solution by using HCl treated oak sawdust. The parameters, affecting the adsorption behaviors like pH, contact time, mass of adsorbent and shaking speed were optimized. The concentration of the metal ions in the range of 0.1 to 100 mg L^{-1} was used to obtain the adsorption isotherms. The equilibrium data obeyed D-R and Langmuir adsorption isotherm while the kinetic data followed pseudo-second-order kinetic model. The thermodynamic parameters of the adsorption process were studied which showed that the biosorption process was endothermic and spontaneous. The maximum removal efficiencies were found to be 84% for Cr(VI) at pH 3, 82% for Ni(II) at pH 8 and 93% for Cu(II) at pH 4.

Khormaei et al., (12) reported the biosorption of Cu(II) on sour orange residue (SOR). The influences of various parameters like particle size, temperature and pH of the solution were investigated in batch analysis along with kinetics and equilibrium isotherms. Pseudo-second-order kinetic model well fitted into kinetic data. Further Freundlich and Langmuir isotherm models were the best choice to describe the equilibrium data. It was found that maximum adsorption was achieved at pH 5. Approximately 20% decrease in copper removal was observed with an increase in temperature from 20 to 50°C . The uptake capacity of the biosorbent was increased by additional chemical treatment with sodium hydroxide. The biosorption rate was affected by increase in particle size of biosorbent but there was no significant effect of the particle size on the final equilibrium concentration.

Li et al., (13) reported a method for the removal of Cd(II) from water samples by using chemically treated orange peels. The properties of the biosorbent were studied under the

influences of various chemical modifications like concentration of cross-linking reagent, cross-linking temperature, alkali saponification and washing. The effects of solid/liquid ratio, shaking time, pH of the solution and initial concentration were studied on the biosorption of Cd(II). It was found that 0.6SCA₈₀ (orange peel modified with 0.6 mol L⁻¹ citric acid under 80 °C after alkali saponification) has higher biosorption efficiency. The order of various biosorbents for Cd(II) removal was found to be 0.6SCA₈₀ > SOP > CA2 > CA1 > PA1 > PA2 > OP. The maximum biosorption capacity of 0.90 mol kg⁻¹, at optimum conditions was found by using 0.6SCA₈₀ as biosorbent for Cd(II). The desorption of the retained cadmium was carried out with 0.15 mol L⁻¹ HCl solution and the desorption rate was found to be 94%. Langmuir isotherm model was found best fit into equilibrium data when different isotherms were compared. The Lagergren first-order kinetic model was a best choice to describe the biosorption of Cd(II).

Perez-Marin et al., (14) described a method for the removal of Cd(II) from aqueous solutions using orange wastes obtained from orange juice industry. Fourier transform infrared spectroscopy was used to characterize the biosorbent and adsorption capacity was determined using batch experiments. It was observed that adsorption capacity is strictly pH dependent and increases with increase in pH. At various pH values (4-6), the adsorption equilibrium and kinetics were studied. The adsorption process was found to be fast and a time span of 3 hours was needed for equilibrium to reach. It was observed that maximum adsorption capacity of the biosorbent was achieved at pH values of 4 to 6 and was found to be 0.40, 0.41 and 0.43 mmol g⁻¹ respectively. Different kinetic models i.e. intraparticle diffusion, Elovich, pseudo-first and pseudo-second-order equations were used to analyze the kinetic data while the equilibrium data were fitted into Redlich-Peterson, Sips, Freundlich and Langmuir isotherm models. Non-linear regression was applied for data fitness and was confirmed by using five error analysis methods. The equilibrium data followed Sips model while the kinetic data was well described by Elovich equation.

Memon et al., (15) used treated and untreated sawdust obtained from cedrus deodar wood for the preconcentration/removal of Cd(II) from water samples. It was observed that about 97% removal has taken place within 8 min. It was found that pH affects the binding

of metal ions and maximum adsorption was achieved in the pH range of 4 to 8. Two distinct pK_a values of sawdust were obtained from potentiometric titrations; the first has similar value to carboxylic group (3.3-4.8) while the other is similar to amines group (8.53-10.2) with the densities of 1.99×10^{-4} and 7.94×10^{-5} respectively. Desorption of the binded Cd(II) was carried out with 5 mL of 0.1 mol L^{-1} HCl solution. The adsorbent gave an enrichment factor of 120 with a detection limit of 0.016 g mL^{-1} . At various temperatures, the partitioning behavior of the system was described by using D-R and Langmuir isotherms. The removal of Cd(II) was also studied considering thermodynamic and kinetic behavior of sawdust.

Li et al., (16) investigated sawdust and modified peanut as adsorbents for the removal of Cu(II), Cr(III) and Pb(II) from water samples. The kinetic data showed that the adsorption of these metals on the biosorbents (sawdust and modified peanut husk) is not controlled by intraparticle diffusion rather it can be described by second-order equation and adsorption might be rate limiting step. Both Freundlich and Langmuir isotherms were applied to the equilibrium data and were found best choices to explain the adsorption data.

Sciban et al., (17) reported the use of poplar wood sawdust for the removal of Cd(II), Zn(II) and Cu(II) from electroplating wastewaters. The adsorption data fit into the Freundlich, BET, Langmuir and competitive Langmuir isotherms. The solid correspondence between experimental data and BET equation confirmed the multilayer adsorption. Cu(II) was preferentially adsorbed than Zn(II) and Cd(II) from wastewater while the adsorption of Cd(II) from wastewater was significantly lower than model water. This showed that the presence of other ions compete Cd(II) for adsorbent.

Qi and Aldrich (18) investigated the binding efficiency of the tobacco dust, a lignocellulosic agricultural waste. It was observed that heavy metals such as Ni(II), Zn(II), Cd(II), Cu(II) and Pb(II) were strongly binded by tobacco dust with a maximum loading capacity of 24.5, 25.1, 29.6, 36.0 and 39.6 mg of the metal per gram of sorbent respectively. A dilute HCl solution; efficiently desorbed the loaded heavy metals from the biosorbent. Over a wide range of pH ($\text{pH} > 2$) the tobacco dust is negatively charged as indicated from the measurement of surface acidity and Zeta potential, with a high OH^-

adsorption capacity and a strong surface acidity. It has been suggested from the changes in the surface morphology of the tobacco dust that the sorption of heavy metal ions on the tobacco could be associated with changes in the surface properties of the dust particles as visualized by atomic force microscopy. Some of the structures on the surface of particles were lost with leaching in the acid metal ion solution, which bring these changes on the surface. Nevertheless, the tobacco dust subjected to biosorption has no significant change in the chemical structure as revealed by Fourier transform infrared spectroscopy (FT-IR). Metal -H ion exchange or metal ion surface complexation adsorption or both were responsible for the uptake of heavy metal ions on the tobacco dust.

Schiewer and Patil (19) reported an inexpensive biomass; citrus peels for the removal of toxic heavy metals from industrial samples. The Langmuir sorption capacities of the orange peels, lemon peels and lemon-based protonated pectin peels (PPP) were evaluated and were found to be in the range of 0.7-1.2 mequiv. g^{-1} (39-67 mg g^{-1}) for Cd(II) per dry weight of biosorbent. A continuous pK_a spectrum approach was used to interpret the potentiometric titration. Four acidic sites were showed from continuous pK_a spectrum method with pK_a values of 3.8, 6.4, 8.4, 10.7 and a total site quantity of 1.14 mequiv. g^{-1} . An unusual shape with two plateau values was observed from the sorption isotherms of untreated citrus peels. On comparison with untreated peels, the protonated pectin peels showed a typical Langmuir model with a higher sorption capacity. The binding of the metal ions was decreased at low pH owing to increased competition by protons to the sites of biomass and this was demonstrated by pH-sensitive isotherm equations. It was sufficient to consider only one binding site with pK_a 3.8 and a quantity of 1.14 mequiv. g^{-1} instead of assuming four binding sites. The metal binding constant determined at various pH was used to predict accurately the metal uptake at one pH. The sorption isotherm shape was well described by 1:1 stoichiometry model than those of 1:2 stoichiometry. The 1:1 stoichiometry reduced to the Langmuir model for a constant pH.

Balaria and Schiewer (20) investigated the removal of Pb(II) from industrial wastewater using citrus peels; a cheap and an effective biomass. It was observed that the presence of biopolymer pectin on these peels was responsible for the binding of metal ions in solution. For the preparation of commercial biosorbents from citrus peels waste, it may

be useful to know the chemistry behind these interactions. In order to see the mechanistic evidence about the binding of lead by low and highly methoxylated citrus peels, the present study was carried out. The negative charges of these biopolymers were contributed by carboxyl groups as shown from potentiometric titrations, which were also supported by variability study of pH. The second-order kinetic model well fitted to the kinetic data obtained from the biosorption of Pb(II) on both low and high-methoxylated pectins, proposing that two monoprotic functional groups were binded with only one divalent metal ion. The carboxylic acid groups of the citrus pectin were the active contributors in Pb(II) binding as confirmed from the results of Fourier transform infrared spectroscopy (FT-IR).

Krishnani et al., (21) reported the removal of various heavy metals in single and mixed solutions as a function of pH and concentration of metal by using a biomatrix obtained from rice husk, a waste of lignocellulosic from agro-industry. The binding of metal by the functional groups was confirmed by Fourier transform infrared spectroscopy and scanning electron microscopy. A variety of experimental approaches were used to confirm the calcium and magnesium present in the biomatrix, in the ion exchange mechanism. The Langmuir isotherm was used to calculate maximum adsorption capacity and was found to be in increasing order as (mmol g^{-1}): Ni (0.094), Zn (0.124), Cd (0.149), Mn (0.151), Co (0.162), Cu (0.172), Hg (0.18), and Pb (0.28). At pH 2, the sorption capacity of Cr(III) onto biomatrix was found to be 1.0 mmol g^{-1} . X-ray photoelectron spectroscopy was used to determine the speciation of Hg, Cd and Cr adsorbed on the biomatrix. On comparison with former reported sorbents, the studied biomatrix has higher or comparable adsorption capacity.

Asadi et al., (22) reported the removal of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) by using sawdust and rice hull modified with heat, NaOH and HCl. The adsorption was found to be pH dependent and increased with initial metal concentration. Cd(II) and Pb(II) showed maximum adsorption at pH 5 while Cu(II), Zn(II) and Ni(II) showed the following orders: $\text{Cu} > \text{Zn} > \text{Ni}$ respectively. On comparison with sawdust, the rice hull has higher sorption capacity. The order of sorption capacities of the modified adsorbents were found to be $\text{base} > \text{heat} > \text{natural} > \text{acid}$. The adsorption data followed both Langmuir and

Freundlich models. The result obtained using suspensions, wastewaters and synthetic solutions was almost the same in the column experiments. Positive recovery was obtained with both HCl and water. The removal ability of the natural sorbents was comparable with commercial adsorbents.

Gode et al., (23) investigated the adsorption of Cr(VI) on treated and untreated sawdust of Turkish red pine tree (*pinus nigra*) from aqueous solutions. Different parameters affecting the adsorption like pH, concentration of modifier, mass of adsorbent and concentration of Cr(VI) were investigated. It was observed that the adsorption equilibrium data followed Freundlich model. Maximum removal of Cr(VI) was achieved at pH 3 within 120 min. It inferred from the experimental results that ion exchange and chelation are responsible for binding of metal ions to the sawdust. The percent removal of tartaric acid modified sawdust, base extracted sawdust and untreated sawdust at pH 3 was found to be 87.7%, 70.6% and 55.2% respectively. Maximum loading capacities for sawdust samples were found to be in the range of 8.3 to 22.6 mg g⁻¹.

Li et al., (24) reported the adsorption of Cd(II), Zn(II), Ni(II) and Co(II) from aqueous solution using chemically treated orange peel cellulose. The biosorbent properties were studied with respect to the influences of various chemical modifications like different acids (H₃PO₄, H₂C₂O₄, C₆H₆O₇) modification after saponification with NaOH and different alkalis saponification (Ca (OH)₂, NH₄OH and NaOH). FT-IR spectra indicate that the presences of various functional groups on the adsorbent are responsible for the binding of metal ions in aqueous solution. Maximum loading capacities of the SOA, SCA, SPA and SPA were evaluated for Cd(II), Zn(II), Co(II) and Ni(II) and were found to be 1.13, 1.21, 1.23 and 1.28 mol kg⁻¹ and on comparison with raw orange peel these were increased by 130, 60, 178 and 95% respectively. The biosorption of metal ions was studied as a function of solid/liquid ratio, shaking time, initial concentration of metal ions and pH of the solution. Lagergren first-order kinetics model was followed by kinetic data and biosorption equilibriums were attained in 60 min. The equilibrium data of all metal ions followed Freundlich and Langmuir models with regression coefficient R² > 0.95. Various concentrations of HCl were used for elution of adsorbed metal ions.

Dundar et al., (25) reported the removal of Cu(II) using litter of natural trembling poplar (*Populus tremula*) forest (LNTPF) in batch analysis. The effects of various parameters like temperature, agitating speed, particle size, pH, concentration of adsorbent and initial concentration of Cu(II) on sorption capacity of LNTPF were studied. It was observed that the sorption efficiency of LNTPF increases with increase in temperature, concentration of adsorbent, agitating speed, pH and with a decrease in initial Cu(II) concentration and particle size. Approximately 94% of the Cu(II) was removed within 5 min, showing that the adsorption process is very fast and about 30 min was sufficient for complete equilibration. The kinetic data were analyzed by pseudo-first and pseudo-second-order models and was found that kinetic data followed pseudo-second-order kinetic model. The biosorption mechanism was represented by EPR studies combined with FT-IR spectroscopy. The endothermic and spontaneous nature of the biosorption process was revealed from thermodynamic parameters like ΔG , ΔH and ΔS . The Langmuir model showed best fit into equilibrium data. It may be concluded that LNTPF might be used as an efficient and a cost effective biosorbent for the removal of Cu(II) from wastewater samples.

Mata et al., (26) reported sugar-beet pectin gels as a biosorbent for the treatment of wastewater contaminated by heavy metals. The biosorption and desorption of Cd(II), Pb(II) and Cu(II) were carried out in batch analysis using sugar-beet pectin hydro- and xerogels. The pectin was extracted and demethylated from the sugar-beet pulp, agricultural waste and were gelled in the presence of CaCl_2 . The hydro- and xerogels pectin beads being stable were found to be suitable for biosorption of heavy metals in various conditions. The Langmuir isotherm model and pseudo-2nd -order were fitted well into biosorption data and the corresponding parameters were obtained. In order to determine the possible binding mechanisms, the untreated and treated beads were characterized using SEM and FT-IR. Complexation or chelation with carbonyl groups and ion exchange with calcium of gel structure were responsible for binding. The metal cations substitute the calcium in the gels matrix as indicated by scanning electron microscopy. The regeneration of the gel was carried out with 0.1 M HNO_3 which recovered all the adsorbed metal and was considered as better eluent than H_2SO_4 and

HCl. It may be concluded that sugar-beet pectins is a suitable choice for the treatment and recovery of Cd(II), Pb(II) and Cu(II) from water samples.

Schiewer and Balaria (27) reported the uptake of Pb(II) using a pectin-rich byproduct of the fruit juice industry obtained after treatment of orange peels. Protonated peels has significantly higher negative surface as compared to original peels, with acidic groups around pH 4, 6 and 10 as confirmed by potentiometric titrations. Peels of orange have similar FT-IR spectra to those of pectin. After binding of Pb(II), the peak of carboxylic group shifted from 1636 to 1645 cm^{-1} which indicates that carboxylic group involved in Pb(II) binding. Equilibrium was established in 30 to 120 min depending upon the size of particles. The data showed that the model for first-order was inferior to those of second- or third-order. The smaller particles have much higher rate constants while particles of all sizes have similar capacities. At low sorbent dosages, the binding of Pb(II) was reduced by competing co-ions, on increase in ionic strength or decrease in pH, while the removal remains above 90% at high sorbent dosages. The uptake of Pb(II) was found to be 2 mmol g^{-1} at 300 ppm (40% of the dry weight). Citrus peels may be used as efficient biosorbents for industrial applications due to high stability, favorable kinetics and high uptake capacity.

Akar et al., (28) studied the removal of Ni(II) from synthetic and real samples of water utilizing the waste biomass entrapped in silica-gel matrix in batch and dynamic flow modes. The influence of solution pH, contact time, S/L ratio and initial concentration of nickel ion on biosorption were studied in batch system. The immobilized biosorbent was negatively charged in the pH range of 3.0-8.0 as exhibited from the measurement of Zeta potential. The biosorption capacity possessed by immobilized biomass was relatively high (98.01 mg g^{-1}) and it has been observed that biosorption equilibrium was established in a short interval of time (5 min). The Freundlich, Langmuir and Dubinin-Radushkevich isotherm models were fitted to the equilibrium data. The changes occurred on the surface structure of the waste biomass after immobilization and biosorption of Ni(II) and these charges in surface were screened by scanning electron microscopy. Fourier transform infrared spectroscopy was used for the confirmation of sorbent-sorbate interactions. In a continuous mode, the applicability of sorbent system was investigated and the effect of

various parameters such as biosorbent dosage, column size and flow rate on biosorption was investigated in column studies. The removal of Ni(II) from industrial wastewater was carried out successfully in dynamic flow mode using the proposed sorbent system. It was seen from the results that for the removal of Ni(II) from synthetic and real samples, the silica-immobilized waste biomass was an efficient and inexpensive sorbent.

Gupta et al., (29) reported the removal of Ni(II) and Cu(II), both as a pure ion and from their binary mixture in the concentration range of 5-100 mg L⁻¹ under dynamic and equilibrium conditions using Irish moss peat; an economical and operational adsorbent. The effect of pH on adsorption of both Ni(II) and Cu(II) was studied by changing the pH of the solution from 2-8. It was observed that pH of the solution strongly affects the adsorption of Ni(II) and Cu(II) on peat. Two-sites Langmuir adsorption isotherm was best fitted to the adsorption data at a temperature of 298 K, pH 4.0 and 4.5 and initial concentration for both Ni(II) and Cu(II) was 100 mg L⁻¹. The maximum adsorption capacity of peat was calculated to be 14.5 mg g⁻¹ for Ni(II) and 17.6 mg g⁻¹ for Cu(II) respectively. The breakthrough data were obtained for both pure component and binary mixture of Ni(II) and Cu(II) from the column experiments. The adsorbed nickel and copper were desorbed completely from the bed with 2.0 mM EDTA solution.

Kaiser et al., (30) investigated *Ficus religiosa* leaves (FRLs) as biosorbent in powder and immobilized form for the removal of Pb(II). The biosorption experiments were studied in batch system to determine optimum pH, equilibrium time, temperature and biosorption capacity. At optimum pH (4), the maximum biosorption capacity was observed to be 37.45 mg g⁻¹. The biosorption capacity was affected by rise in temperature from 20-40 °C and maximum removal of the Pb(II) was achieved at 25 °C. The experimental data were used to determine thermodynamic parameters. The equilibrium data obtained from the biosorption of Pb(II) were described using Freundlich and Langmuir models and was found that experimental data followed Langmuir model with correlation coefficient of 0.97. The Lagergren pseudo-2nd -order model was a suitable choice to describe the biosorption kinetics. The immobilization of the biomass (FRLs) was carried out in polysulfone matrix for continuous biosorption experiments. At various pH, bed depth and flow rates, the breakthrough curves were examined. The experimental data were

described by using Thomas model and bed depth service time (BDST). Desorption of the Pb(II) from biomass was carried out with a solution of 0.05 M HNO₃. The major removal mechanism was possibly being the ion exchange as shown from the releasing of Na, Mg and Ca ions during Pb(II) biosorption.

Ahmad et al., (31) described the adsorption of Pb(II) and Cu(II) from water samples using Meranti tree sawdust in batch systems. The influences of adsorbent dose, contact time and solution pH on equilibrium adsorption level were studied. The most common isotherms like Freundlich and Langmuir were used to determine the sorption equilibrium data of Pb(II) and Cu(II). The effect of temperature on biosorption of Pb(II) and Cu(II) on adsorbent was also studied and thermodynamic parameters such as entropy, enthalpy and free energy changes were evaluated which showed endothermic nature of the biosorption process.

Bozic et al., (32) used the sawdust of poplar, linden and beech trees for the removal of heavy metal ions from synthetic solutions. It was observed that the adsorption process strictly depend upon the pH, contact time, initial concentration of metal ions, type of ions and concentration of sawdust in suspension. Equilibrium was established in less than 20 min due to rapid kinetics of the adsorption process. The Langmuir model well fitted into adsorption equilibrium data. It was assumed that alkali-earth metals were substituted by protons and heavy metal ions thus confirming that adsorption process follows ion exchange mechanism. Adsorption capacity decreased with decreasing the initial pH of the solution and at a pH close to one, a zero value was achieved. For all type of investigated sawdust, maximum adsorption capacity (7-8 mg g⁻¹ of sawdust) was achieved in the pH range of 3.5-5.0. The biosorption process was strictly affected by concentration of sawdust and initial concentration of metal ions. The adsorption behavior was not affected by the particle size of the adsorbent. The adsorbent showed higher degree of adsorption for Cu(II) (80%) than Fe(II) (10%).

Jeon and Kim (33) reported the removal of Pb(II) by using sawdust chemically treated with phosphoric acid (85%) and maximum loading capacity (1.45 mmol Pb g⁻¹ dry mass) was achieved at pH 4. The energy dispersive X-ray (EDX) was used to analyze the component of phosphorylated sawdust and the increase of phosphate groups was

confirmed. At low temperature (10 °C), the loading capacity of the phosphorylated sawdust was high and about 98% Pb(II) was removed with 0.04 g of treated sawdust. Equilibrium for the Pb(II) was established mostly within 40 min.

Kaczala et al., (34) employed untreated sawdust of *Pinus sylvestris* for the removal of Pb(II) and V(II) from industrial wastewater after settling/sedimentation phase. The effects of different factors such as contact time, initial pH and mass of adsorbent on the biosorption were studied. The release of metal ions from sawdust was investigated as a function of pH. The adsorption data followed pseudo-second-order kinetic and obeyed Freundlich isotherm model. An increase in sorption efficiency was observed from 32 to 99% for Pb(II) and from 43 to 95% for V(II) when the initial pH was decreased from 7.4 to 4.0. The removal of V(II) was dependent on adsorbent dose in contrast to Pb(II) which was found to be independent from the adsorbent dose.

Lu et al., (35) chemically modified the orange peel cellulose biosorbent using 0.6 mol L⁻¹ citric acid at 80 °C after 0.1 mol L⁻¹ NaOH saponification in order to evaluate the mechanism of the adsorption of Cu(II) from chloride solutions. Fourier transform infrared spectroscopy and elemental analysis was used to characterize the raw orange peel and chemically modified biosorbents. The pH of zero charge, basic and acidic sites were also determined. The extent of the removal of Cu(II) were investigated as a function of solid/liquid ratio, pH of the solution, contact time and initial Cu(II) concentration. The adsorption data fitted well into the model obtained by the combination of Langmuir and Freundlich (L-F) isotherms. The chemically treated orange peel showed maximum adsorption capacity of 1.22 mol kg⁻¹ for Cu(II) and thus can be used as an efficient and cost effective biosorbent for the removal of Cu(II).

Lugo-Lugo et al., (36) studied the use of natural, formaldehyde-treated and copolymer-grafted orange peel biosorbents for the removal of Pb(II) from wastewater. The maximum adsorption of lead was observed at pH 5. The sorption capacity reached 99% in 10 min for natural and treated biosorbents while for grafted material it reached in 20 min. The adsorption on treated biomass followed pseudo-first-order equation with maximum adsorption capacity of 46.61 mg g⁻¹ for an initial concentration of 150 mg L⁻¹. The energy dispersive X-ray study showed that metal adsorption occurs on the surface.

The surface of the adsorbent was found to be rough by scanning electronic microscopy. The presence of $-NH_2$, $-COOH$ and $-OH$ groups were confirmed by Fourier transforms infrared spectroscopy which are the main groups on the surface involved in metal binding. A mass reduction of 80% was observed at 600 °C using thermogravimetric analysis.

Ning-chuan et al., (37) reported the orange peel chemically treated with $CaCl_2$ and $NaOH$ for the removal of $Cu(II)$. The adsorption of $Cu(II)$ was studied as a function of pH, contact time, temperature and initial metal concentration. Vant's Hoff equation was used to determine thermodynamic parameters like entropy (ΔS°), enthalpy (ΔH°) and free energy (ΔG°). It was observed that at optimum conditions the adsorption of $Cu(II)$ onto chemically modified orange peel is exothermic, spontaneous and feasible in nature. The equilibrium data obeyed Langmuir model and the maximum adsorption capacity was found to be 72.73 mg g^{-1} . Pseudo-second-order model showed best fit into kinetic data. It was found that the biosorption of $Cu(II)$ decreases with increase in temperature from 16 to 60 °C. The regeneration of the loaded biomass was carried out with HCl solution for further use with a little loss of biosorption capacity.

Rahman and Islam (38) studied the influences of various parameters like initial $Cu(II)$ concentration, biomass concentration, contact time and pH on biosorption of $Cu(II)$ onto sawdust of maple wood. The removal of metal ions increases with an increase in adsorbent concentration with a constant concentration of $Cu(II)$ in batch experiments. It was observed that an increase in initial concentration of $Cu(II)$ resulted in an increase in metal loading capacity per unit of weight of sorbent for a constant sorbent dose. The isotherms and isotherm constants were described by applying Freundlich and Langmuir models and were observed that isotherm constants varied with pH. Maximum loading capacity of the sawdust of maple wood was achieved at pH 6.0 and was found to be 9.51 mg g^{-1} .

Marin et al., (39) investigated the ability of orange waste biomass for the removal of $Cr(III)$ from wastewater samples. Different factors affecting the adsorption capacity like pH of the solution, adsorbent dose and particle size were investigated. It was observed that percentage of the metal removal increased with increase in pH and adsorbent dosage.

It was also noted that sorption capacity is independent of the particle size. The adsorption of Cr(III) onto orange waste was found to be a slow process taking three days for the equilibrium to be established. Kinetic studies showed that adsorption process followed pseudo-second-order model. Maximum adsorption capacity increased from 0.57 to 1.44 mmol g⁻¹ when pH was varied from 3 to 5, using Sips model and the equilibrium data were well described by of Sips model with Redlich-Peterson equation. The adsorbent was successfully used for the removal of Cr(III) in continuous mode and BDST model was used to represent the breakthrough curves. The adsorption capacity in batch mode was higher than continuous mode due to slow kinetics of Cr(III) adsorption onto orange waste.

Zakaria et al., (40) reported untreated local rubber wood sawdust (RWS) for the removal of Cr(VI) under a bench-scale shaking condition. Various parameters like temperature, pH, adsorbent dosage, eluting agent and initial Cr(VI) concentrations were investigated. It was observed that at pH less than 2 and initial Cr(VI) concentration of 100 mg L⁻¹, complete removal of Cr(VI) was achieved when the RWS dosage of greater than 1.5 % (w/v) was employed. The removal capacity of Cr(VI) decreased with increase in pH (3-9) and initial Cr(VI) concentrations (200-500 mg L⁻¹) as described by point of zero charge (pH_{pzc}) of 4.90. The recovery of Cr(VI) from RWS was rapid when 1 mol L⁻¹ HCl was used. The removal of Cr(VI) by RWS was found to be endothermic and non-spontaneous process having positive entropy.

Yan et al., (41) studied fresh tissues of *Myriophyllum spicatum* (*M. spicatum*) for the biosorption of Pb(II) and the effects of Zn(II) and Cu(II) on the biosorption of Pb(II) were measured in batch analyses. At various pH values and initial concentration of metal ions, the biosorption of Pb(II) was studied for single, binary and ternary solutions. It was observed that the biosorption capacity increases with increase in pH values from 2.0-6.0. The biosorption of Pb(II) was adversely affected by the presence of both Zn(II) and Cu(II). The three isotherm models: Freundlich, Sips and Langmuir were fitted to the experimental data and were found that only Sips model shows best fit for the experimental data. With increase in concentration of copper ions, the biosorption of Pb(II) decreased in Pb-Cu binary system and the competitive model of Langmuir well

fitted into biosorption equilibrium data obtained from the binary metal solutions. It may be concluded that biosorbent (*M. spicatum*) has no preference of Pb(II) over Cu(II) during biosorption of these metals on *M. spicatum* in binary solutions. The interaction between Pb(II) and *M. spicatum* was characterized using Fourier transform infrared (FT-IR) spectroscopy. The results show that the biosorption of Pb(II) was take place due to the presence of carbonyl, hydroxyl and carboxyl groups on the biomass.

Lawal et al., (42) reported seed husk of *Calophyllum inophyllum* (*C. inophyllum*) for the removal of Pb(II) from industrial samples. The influence of pH, contact time, temperature and initial concentration of metal ions on biosorption equilibrium, kinetics and thermodynamics were studied. As the initial concentration of metal ions increases, an increase in metal uptake was also observed. The pH of solution was optimized as 4 with maximum loading capacity of 4.86 mg g^{-1} and 97.2% removal of Pb(II). On comparison with Freundlich model ($R^2 = 0.7984$) and Temkin model ($R^2 = 0.8761$), the Langmuir isotherm model showed best fit into biosorption data of Pb(II) with high correlation coefficient ($R^2 = 0.9531$). The Lagergren pseudo-1st- and pseudo-2nd-order model were fitted into biosorption kinetics and was found that kinetic data shows best fit in pseudo-2nd -order kinetic model. The biosorption thermodynamic studies were conducted to determine the thermodynamic parameters such as standard entropy (ΔS), standard enthalpy (ΔH) and Gibbs free energy (ΔG). The endothermic and spontaneous nature of the biosorption of metal ions onto *C. inophyllum* was shown from these results. The biosorption of the Pb(II) take place as due to hydroxyl, amine and carboxyl groups as shown by Fourier transform infrared (FT-IR) spectroscopy.

Garcia-Rosales and Colin-Cruz (43) reported *Zea mays* (*Z. mays*) stalk sponge for the biosorption of Pb(II) from wastewater samples. At optimum pH of 6 ± 0.2 , the influence of concentration of metal ions and contact time on equilibrium and kinetics of biosorption of Pb(II) was studied. The sorption energetics of Pb(II) by *Z. mays* stalk sponge was described by using Freundlich model and the maximum loading capacity of Pb(II) was found to be 80 mg g^{-1} . Pseudo-1st and pseudo-2nd order kinetic models were fitted into biosorption kinetic studies for Pb(II) and the kinetic parameters were calculated. These models showed that pseudo-2nd-order kinetic model best fit into sorption kinetic of Pb(II)

on *Z. mays* with high correlation coefficient (0.9998). It can be observed that biosorption capacity strictly depends upon pH and *Z. mays* stalk sponge was found to be an effective biomass for the removal of Pb(II).

Moussaavi and Barikbin (44) investigated the removal of Cr(VI) from contaminated water using Pistachio hull powder (PHP). The biosorption of the Cr(VI) were conducted under the influence of pH (2-8), contact time (1-60 min), temperature (5-50 °C), concentration of PHP (0.5-8 g L⁻¹) and Cr(VI) concentration (50-200 mg L⁻¹). Approximately 99% of the Cr(VI) was adsorbed on PHP from solutions containing 50-200 mg L⁻¹ of Cr(VI) after equilibrated for 60 min with a concentration of adsorbent of 5 g L⁻¹. An increase in temperature from 5 to 40 °C caused an increase in percent adsorption of Cr(VI). The Langmuir and pseudo-2nd -order models showed best fit into equilibrium and kinetic data respectively. The Langmuir model was used to evaluate the maximum adsorption capacity and was found to be 116.3 mg g⁻¹ for Cr(VI) onto PHP. The removal of Cr(VI) from industrial water was carried out to analyze the sorption ability of the PHP. A decrease in concentration of the Cr(VI) from 25 mg L⁻¹ to less than 0.05 mg L⁻¹ was seen using 2 g L⁻¹ PHP after being equilibrated for 30 min. It may be concluded from these studies that treatment of industrial wastewaters containing Cr(VI) using PHP is a simple and reasonable process.

Reddy et al., (45) used *Moringa Oleifera* leaves (MOL) after chemical modification with base and citric acid (CAMOL) for removal of Pb(II) from water samples. The biosorbent was characterized by FT-IR, SEM and elemental studies. The biosorption studies were performed as a function of temperature, equilibration time, initial metal concentration, sorbent amount, and pH of the solution. Three adsorption kinetic models: pseudo-1st, pseudo-2nd and intraparticle diffusion were used to analyze the biosorption kinetic data. The Freundlich, Langmuir, Temkin and Dubinin-Radushkevick isotherm models were used to find out the biosorption equilibrium data. The equilibrium data at a temperature of 313 K was well fitted in Langmuir model with maximum loading capacity of 209.54 mg g⁻¹. The endothermic, spontaneous and the feasible nature of the biosorption of Pb(II) onto CAMOL was observed from the thermodynamic factors such as ΔG° , ΔH° and ΔS° in the temperature range of 293-313 K. Biosorbent was regenerated with dilute HCl

solution to make it fit for further adsorption studies. The biosorption of Pb(II) was not affected by the presence of some common metal ions like Na^+ , K^+ , Ca^{2+} and Mg^{2+} . It may be concluded from these results that the removal of lead from wastewater was successfully accomplished with CAMOL biomass.

Sha et al., (46) investigated the adsorption behavior of five heavy metals (Ni(II), Cd(II), Zn(II), Pb(II) and Cu(II)) on orange peel xanthate. The orange peel xanthate was prepared and characterized using TG analysis, Zeta potential and FT-IR studies. Different factors such as adsorption time, equilibrium pH, and initial metal ion concentration affecting the adsorption process were investigated. Maximum adsorption capacities of Ni(II), Cd(II), Zn(II), Pb(II) and Cu(II) were found to be 15.45, 76.57, 49.85, 218.34 and 77.60 mg g^{-1} respectively. The adsorption data followed Langmuir model for all five investigated metals. Equilibrium was established within 20 min and the kinetic data obeyed pseudo-second-order equation. A complexation mechanism was suggested for the adsorption process.

Liang et al., (47) converted orange peel (OP) into two novel adsorbents: KOP (K^+ type orange peel adsorbent) and MgOP (Mg^{2+} type orange peel adsorbent) and were characterized by using SEM and FT-IR. The influences various parameters like metal ion concentration, contact time, pH of the solution and solid/liquid ratio were investigated for the biosorption of Cu(II). Different isotherms models like Dubinin-Redushkevich, Langmuir and Freundlich were used to analyze the equilibrium data and it was found that Langmuir model was the best choice to describe the adsorption of Cu(II) by both KOP and MgOP. Maximum adsorption capacity for Cu(II) onto KOP and MgOP was found to be 59.77 and 40.37 mg g^{-1} respectively. An increase in contact time lead to an increase in Cu(II) adsorption and equilibrium was achieved within 20 min. Four different kinetic models: intraparticle diffusion, Elovich equation, pseudo-first and pseudo-second-order were used to examine the kinetic data and were found that kinetic data followed pseudo-second-order equation. It was observed from thermodynamic studies that adsorption of Cu(II) by KOP and MgOP is exothermic and spontaneous in nature.

Ning-chuan et al., (48) chemically modified orange peel with NaOH and investigated its use for the adsorption of Cu(II). Scanning electron microscopy, surface area analyzer and

infrared spectroscopy were used to characterize the adsorbent. The zeta potentials and the total negative charges on the surface of the adsorbent were determined. The influences of the different parameters like temperature, concentration of adsorbent and pH of the solution on the kinetic and equilibrium biosorption were investigated in batch systems. The adsorbent was applied in column mode to study its practical applicability and the breakthrough curves were obtained. The adsorption followed pseudo-second-order kinetics and the equilibrium data best fitted into both Freundlich and Langmuir models. Maximum sorption capacity for Cu(II) according to Langmuir equation was found to be 50.25 mg g^{-1} at pH 5.3. The results showed that adsorption capacity increased by chemical modification of the adsorbent with NaOH.

Ofomaja (49) investigated sawdust of the mansonia wood for the removal of Pb(II). The experimental data completely followed pseudo-second-order kinetics while first 5 min of the biosorption process followed pseudo-first-order kinetics. The importance of ion-exchange during first 5 min was indicated by similar values of pseudo-first-order rate constant (K_1) and ion-exchange constant (S). It was observed that pore and film diffusion was decreased with Pb(II) concentration while the intraparticle diffusion rate increased. The initial biosorption was intermediate as indicated by initial biosorption factor (R_i). The significance of ion-exchange during biosorption process was confirmed by an increase in ion-exchange phenomenon and a decrease in amount of Pb(II) removed. It was found that intraparticle diffusion rate increased with increase in temperature while a decrease was observed in pore and film diffusion. The highest value of pseudo-second-order kinetics and activation energy of film diffusion indicates that the overall rate of biosorption process was controlled by active participation of ion-exchange from pseudo-second-order model and film diffusion.

Semerjian (50) studied the adsorption of Cd(II) from wastewater samples using untreated sawdust of *Pinus halepensis*. The sorption efficiency was investigated in batch systems as a function of metal concentration, adsorbent dose, pH and contact time. Maximum adsorption of Cd(II) was achieved at pH 9.0. Equilibrium was established in 10-20 min when the concentration of Cd(II) was in the range of $1\text{-}50 \text{ mg L}^{-1}$. The complete removal of the Cd(II) was achieved with 10 g L^{-1} of adsorbent from a solution containing 5 mg L^{-1}

Cd(II) within 30 min. The percent removal of Cd(II) decreased from 100 to 87% with increase in Cd(II) concentration while the adsorption capacity increased from 0.11 to 5.36 mg g⁻¹. The Freundlich isotherm was the best choice to describe the equilibrium data with a correlation coefficient (R^2) of 0.960. Pseudo-second-order model was followed by the kinetic data.

Vinodhini and Das (51) used sawdust of neem wood to remove Cr(VI) from tannery wastewater in a fixed bed column. The influences of different parameters like flow rate (5-15 mL min⁻¹) and bed depth (5-15 cm) on the biosorption of Cr(VI) were investigated. The experimental data followed the bed depth service time model (BDST) and the adsorption capacity was found to be 33,009.9 mg g⁻¹ using this model. Elution was carried out with 2.0 N NaOH solutions after adsorption to regenerate the column. The recovery of Cr(VI) was not reached to 100% in each cycle due to the reduction of adsorbed Cr(VI) to Cr(III) in the surface of biosorbent. The effect of co-ions on the adsorption of Cr(VI) was carried out in column mode and it was observed that the presence of these ions decreased the exhaustion time and breakthrough curves of the column. In order to achieve the standard value (0.1 mg L⁻¹) of the Cr(VI), established by the Central Pollution Control Board (CPCB), about 3.75 L of tannery effluent were treated in three biosorption cycles. It was observed that sawdust of neem wood can be used as a low cost and efficient biosorbent for the removal of Cr(VI) from tannery effluents.

Schiewer and Iqbal (52) studied the removal of heavy metals from wastewater by using citrus peels. The role of pectin in metal binding was evaluated by comparing the sorption properties of native orange peels, citrus peels, depectinated peels, protonated peels and extracted pectic acid. The equilibrium was established in one hour as indicated by kinetic data. On comparison with second-order model, the first-order model was the best choice to describe the kinetic data. Two acidic sites with pK_a values of 4 (carboxyl) and 10.5 (hydroxyl) were shown by titrations. A two-site model was applied to determine the pH dependent surface charge. Both Freundlich and Langmuir models were fitted well into sorption data by assuming a 1: 2 binding stoichiometry. The maximum binding capacities of the studied biosorbents were found in the following order: pectic acid (2.9 mequi. g⁻¹)

> protonated peels and native peels > depectinated peels ($1.7 \text{ mequi. g}^{-1}$), which show the role of pectin in metal binding by citrus peels. It was found that depectinated peels were still good adsorbents as depectination did not completely remove the carboxyl groups that were involved in metal binding. The presence of hydroxyl and carboxyl groups and their involvement in metal binding was confirmed by FT-IR spectra in all studied materials.

Pereira et al., (53) reported the removal of Zn(II) from aqueous solutions and electroplating wastewater using chemically treated wood sawdust of *Manilkara sp.* and chemically treated sugarcane bagasse. Firstly, a modifying agent, the ethylenediaminetetraacetic dianhydride (EDTAD) was used to introduce amine and carboxyl groups into wood sawdust and sugarcane bagasse. Infrared spectroscopy (IR) and CHN were used to characterize the newly synthesized biosorbents: modified wood sawdust (ES) and modified sugarcane bagasse (EB). Secondly the adsorption capacity of Zn(II) by ES and EB was evaluated using aqueous single metal solutions and real electroplating wastewater and the concentrations of the Zn(II) was determined using inductively coupled plasma (ICP-OES) and direct titration with EDTA. The Langmuir model was used to develop the adsorption isotherms. The maximum adsorption capacities of Zn(II) were found to be 80 mg g^{-1} and 105 mg g^{-1} for aqueous solutions while these values were found to be 47 mg g^{-1} and 45 mg g^{-1} for industrial wastewater for ES and EB respectively. It was observed that the presence of other competing cations and /or interfering ions, mostly Ca^{2+} and Cl^- in the wastewater reduced the removal of Zn(II) from wastewater than spiked samples of Zn(II).

Marin et al., (54) investigated the roles of three major functional groups like carboxyl, hydroxyl and amine in the orange waste for the removal of Cr(III), Cd(II) and Zn(II). The contribution of these functional groups in metal binding was determined by blocking these groups with chemical treatment of the biosorbent. The chemical modification of the biosorbent was investigated by solid state carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. The decrease in metal adsorption capacity of the chemically treated biosorbent was determined in batch experiments. The metal binding capacity was reduced by blocking of COOH groups

through chemical esterification. However, the metal removal ability of the orange waste was not significantly changed with methylation and acetylation.

Witek-Krowiak et al., (55) reported peanut shell for the removal of Cr(III) and Cu(II) from wastewater samples. The operational conditions for biosorption like the effects of temperature, initial pH and initial concentration of biomass were optimized for each metal. Kinetic parameters were determined by correlation of experimental data with four kinetic models namely Elovich equation, power function equation, pseudo-first and pseudo-second-order. The biosorption equilibrium was described by using four well known adsorption isotherms. Freundlich and Langmuir (two-parameter models) and Redlich-Peterson and Sip (three-parameter models) were applied to the experimental data, which showed that the biosorbent possess high adsorption capacity and affinity for Cr(III) and Cu(II). The monolayer adsorption capacities for Cr(III) and Cu(II) were found to be 27.86 mg g^{-1} and 25.39 mg g^{-1} respectively. It was concluded that peanut shell can be used as an alternative cost effective biosorbent to remove the heavy metals from aqueous solutions.

Feng et al., (56) reported the biosorption kinetic, equilibrium and thermodynamic of Ni(II), Pb(II) and Cd(II) from aqueous solutions using grafted copolymerization modified orange peel (OPAA). The biosorption of metal ions onto OPAA was described by applying Freundlich and Langmuir isotherm models. The biosorption studies were carried out as a function of contact time and pH of the solution. The equilibrium data fitted well into Langmuir model showing sorption capacities of 162.6, 476.1 and 293.3 mg g^{-1} for Ni(II), Pb(II) and Cd(II) respectively. The biosorption capacity of the treated orange peel increased 16.5-, 4.2- and 4.6-times as compare to untreated orange peel for Ni(II), Pb(II) and Cd(II) respectively. Pseudo-second-order model fitted well into kinetic data of Ni(II), Pb(II) and Cd(II). The biosorption was found to be spontaneous in nature as indicated by negative values of free energy change (G) for all studied metal ions. The involvement of the hydroxyl and carboxyl groups in metal binding was indicated by FT-IR studies. A solution of 0.05 mol L^{-1} HCl was used to desorb Ni(II), Pb(II) and Cd(II) from the biosorbent.

References

1. N. Chubar, J. R. Carvalho, M. J. N. Correia, "Heavy metals biosorption on cork biomass: effect of the pre-treatment", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 238, 51–58 (2004).
2. F. Pagnanelli, S. Mainelli, S. D. Angelis, L. Toro, "Biosorption of protons and heavy metals onto olive pomace: Modelling of competition effects", *Water Research*, 39, 1639–1651 (2005).
3. R. Han, J. Zhang, W. Zou, J. Shi, H. Liu, "Equilibrium biosorption isotherm for lead ion on chaff", *Journal of Hazardous Materials B*, 125, 266–271 (2005).
4. Z. Al-Qodah, "Biosorption of heavy metal ions from aqueous solutions by activated sludge", *Desalination*, 196, 164–176 (2006).
5. R. Han, J. Zhang, W. Zou, H. Xiao, J. Shi, H. Liu, "Biosorption of copper(II) and lead(II) from aqueous solution by chaff in a fixed-bed column", *Journal of Hazardous Materials B*, 133, 262–268 (2006).
6. M. H. Kalavathy, T. Karthikeyan, S. Rajgopal, L. R. Miranda, "Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4 -activated rubber wood sawdust", *Journal of Colloid and Interface Science*, 292, 354–362 (2005).
7. F. N. Acar, Z. Eren, "Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions", *Journal of Hazardous Materials B*, 137, 909–914 (2006).
8. S. S. Baral, S. N. Das, P. Rath, "Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust", *Biochemical Engineering Journal*, 31, 216–222 (2006).
9. M. Sciban, M. Klasnja, B. Skrbic, "Modified softwood sawdust as adsorbent of heavy metal ions from water", *Journal of Hazardous Materials B*, 136, 266–271 (2006).
10. Z. Xuan, Y. Tang, X. Li, Y. Liu, F. Luo, "Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel", *Biochemical Engineering Journal*, 31, 160–164 (2006).

11. M. E. Argun, S. Dursun, C. Ozdemir, M. Karatas, "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics", *Journal of Hazardous Materials*, 141, 77–85 (2007).
12. M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, "Copper biosorption from aqueous solutions by sour orange residue", *Journal of Hazardous Materials*, 149, 269–274 (2007).
13. X. Li, Y. Tang, Z. Xuan, Y. Liu, F. Luo, "Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution", *Separation and Purification Technology*, 55, 69–75 (2007).
14. A. B. Perez-Marin, V. M. Zapata, J. F. Ortuno, M. Aguilar, J. Saez, M. Llorens, "Removal of cadmium from aqueous solutions by adsorption onto orange waste", *Journal of Hazardous Materials B*, 139, 122–131 (2007).
15. S. Q. Memon, N. Memon, S. W. Shah, M. Y. Khuhawar, M. I. Bhangar, "Sawdust—A green and economical sorbent for the removal of cadmium(II) ions", *Journal of Hazardous Materials B*, 139, 116–121 (2007).
16. Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, "Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk", *Journal of Hazardous Materials*, 141, 163–167 (2007).
17. M. Sciban, B. Radetic, Z. Kevresan, M. Klasnja, "Adsorption of heavy metals from electroplating wastewater by wood sawdust", *Bioresource Technology*, 98, 402–409 (2007).
18. B. C. Qi, C. Aldrich, "Biosorption of heavy metals from aqueous solutions with tobacco dust", *Bioresource Technology*, 99, 5595–5601 (2008).
19. S. Schiewer, S. B. Patil, "Modeling the effect of pH on biosorption of heavy metals by citrus peels", *Journal of Hazardous Materials*, 157, 8–17 (2008).
20. A. Balaria, S. Schiewer, "Assessment of biosorption mechanism for Pb binding by citrus pectin", *Separation and Purification Technology*, 63, 577–581 (2008).
21. K. K. Krishnani, X. Meng, C. Christodoulatos, V. M. Boddu, "Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk", *Journal of Hazardous Materials*, 153, 1222–1234 (2008).

22. F. Asadi, H. Shariatmadari, N. Mirghaffari, "Modification of rice hull and sawdust sorptive characteristics for removal of heavy metals from synthetic solutions and wastewater", *Journal of Hazardous Materials*, 154, 451–458 (2008).
23. F. Gode, E. D. Atalay, E. Pehlivan, "Removal of Cr(VI) from aqueous solutions using modified red pine sawdust", *Journal of Hazardous Materials*, 152, 1201–1207 (2008).
24. X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, "Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 317, 512–521 (2008).
25. M. Dundar, C. Nuhoglu, Y. Nuhoglu, "Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest", *Journal of Hazardous Materials*, 151, 86–95 (2008).
26. Y. N. Mata, M. L. Blazquez, A. Ballester, F. Gonzalez, J. A. Munoz, "Sugar-beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics", *Chemical Engineering Journal*, 150, 289–301 (2009).
27. S. Schiewer, A. Balaria, "Biosorption of Pb^{2+} by original and protonated citrus peels: Equilibrium, kinetics and mechanism", *Chemical Engineering Journal*, 146, 211–219 (2009).
28. T. Akar, Z. Kaynak, S. Ulusoy, D. Yuvaci, G. Ozsari, S. T. Akar, "Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode", *Journal of Hazardous Materials*, 163, 1134–1141 (2009).
29. B. S. Gupta, M. Curran, S. Hasan, T. K. Ghosh, "Adsorption characteristics of Cu and Ni on Irish peat moss", *Journal of Environmental Management*, 90, 954–960 (2009).
30. S. Qaiser, A. R. Saleemi, M. Umar, "Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: Batch and column study", *Journal of Hazardous Materials*, 166, 998–1005 (2009).

31. A. Ahmad, M. Rafatullah, O. Sulaiman, M. H. Ibrahim, Y. Y. Chii, B. M. Siddique, "Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood", *Desalination*, 247, 636–646 (2009).
32. D. Bozic, V. Stankovic, M. Gorgievski, G. Bogdanovic, R. Kovacevic, "Adsorption of heavy metal ions by sawdust of deciduous trees", *Journal of Hazardous Materials*, 171, 684–692 (2009).
33. C. Jeon, J. H. Kim, "Removal of lead ions using phosphorylated sawdust", *Journal of Industrial and Engineering Chemistry*, 15, 910–913 (2009).
34. F. Kaczala, M. Marques, W. Hogland, "Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto *Pinus sylvestris* sawdust", *Bioresource Technology*, 100, 235–243 (2009).
35. D. Lu, Q. Cao, X. Li, X. Cao, F. Luo, W. Shao, "Kinetics and equilibrium of Cu(II) adsorption onto chemically modified orange peel cellulose biosorbents", *Hydrometallurgy*, 95, 145–152 (2009).
36. V. Lugo-Lugo, S. Hernandez-Lopez, C. Barrera-Diaz, F. Urena-Nunez, B. Bilyeu, "A comparative study of natural, formaldehyde-treated and copolymer-grafted orange peel for Pb(II) adsorption under batch and continuous mode", *Journal of Hazardous Materials*, 161, 1255–1264 (2009).
37. F. Ning-chuan, G. Xue-yi, L. Sha, "Kinetic and thermodynamic studies on biosorption of Cu(II) by chemically modified orange peel", *Transactions of Nonferrous Metals Society of China*, 19, 1365–1370 (2009).
38. M. S. Rahman, M. R. Islam, "Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust", *Chemical Engineering Journal*, 149, 273–280 (2009).
39. A. B. P. Marin, M. I. Aguilar, V. F. Meseguer, J. F. Ortuno, J. Saez, M. Llorens, "Biosorption of chromium(III) by orange (*Citrus cinensis*) waste: Batch and continuous studies", *Chemical Engineering Journal*, 155, 199–206 (2009).
40. Z. A. Zakaria, M. Suratman, N. Mohammed, W. A. Ahmad, "Chromium(VI) removal from aqueous solution by untreated rubber wood sawdust", *Desalination*, 244, 109–121 (2009).

41. C. Yan, G. Li, P. Xue, Q. Wei, Q. Li, "Competitive effect of Cu(II) and Zn(II) on the biosorption of lead(II) by *Myriophyllum spicatum*", *Journal of Hazardous Materials*, 179, 721–728 (2010).
42. O. S. Lawal, A. R. Sanni, I. A. Ajayi, O. O. Rabi, "Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*", *Journal of Hazardous Materials*, 177, 829–835 (2010).
43. G. Garcia-Rosales, A. Colin-Cruz, "Biosorption of lead by maize (*Zea mays*) stalk sponge", *Journal of Environmental Management*, 91, 2079–2086 (2010).
44. G. Moussavi, B. Barikbin, "Biosorption of chromium(VI) from industrial wastewater onto pistachio hull waste biomass", *Chemical Engineering Journal*, 162, 893–900 (2010).
45. D. H. K. Reddy, Y. Harinath, K. Seshiah, A. V. R. Reddy, "Biosorption of Pb(II) from aqueous solutions using chemically modified *Moringa oleifera* tree leaves", *Chemical Engineering Journal*, 162, 626–634 (2010).
46. L. Sha, G. Xue-yi, F. Ning-chuan, T. Qing-hua, "Effective removal of heavy metals from aqueous solutions by orange peels xanthate", *Transactions of Nonferrous Metals Society of China*, 20, 8187–8191 (2010).
47. S. Liang, X. Guo, N. Feng, Q. Tian, "Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by $\text{Mg}^{2+}/\text{K}^{+}$ type orange peel adsorbents", *Journal of Hazardous Materials*, 174, 756–762 (2010).
48. F. Ning-chuan, G. Xue-yi, L. Sha, "Enhanced Cu(II) adsorption by orange peel modified with sodium hydroxide", *Transactions of Nonferrous Metals Society of China*, 19, 8146–8152 (2010).
49. A. E. Ofomaja, "Intraparticle diffusion process for lead(II) biosorption onto *mansonia* wood sawdust", *Bioresource Technology*, 101, 5868–5876 (2010).
50. L. Semerjian, "Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust", *Journal of Hazardous Materials*, 173, 236–242 (2010).
51. V. Vinodhini, N. Das, "Packed bed column studies on Cr(VI) removal from tannery wastewater by neem sawdust", *Desalination*, 264, 9–14 (2010).

52. S. Schiewer, M. Iqbal, "The role of pectin in Cd binding by orange peel biosorbents: A comparison of peels, depectinated peels and pectic acid", *Journal of Hazardous Materials*, 177, 899–907 (2010).
53. F. V. Pereira, L. V. A. Gurgel, L. F. Gil, "Removal of Zn^{2+} from aqueous single metal solutions and electroplating wastewater with wood sawdust and sugarcane bagasse modified with EDTA dianhydride (EDTAD)", *Journal of Hazardous Materials*, 176, 856–863 (2010).
54. A. B. P. Marin, J. F. Ortuno, M. I. Aguilar, V. F. Meseguer, J. Saez, M. Llorens, "Use of chemical modification to determine the binding of Cd(II), Zn(II) and Cr(III) ions by orange waste", *Biochemical Engineering Journal*, 53, 2–6 (2010).
55. A. Witek-Krowiak, R. G. Szafran, S. Modelski, "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent", *Desalination*, 265, 126–134 (2011).
56. N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, "Biosorption of heavy metals from aqueous solutions by chemically modified orange peel", *Journal of Hazardous Materials*, 185, 49–54 (2011).

EXPERIMENTAL

3.1. Experimental

3.1.1. Collection and preparation of sorbents

A variety of biosorbents were selected for our studies. These include sawdust, waste tea leaves and orange peels. A brief description of collection and preparation of these biosorbents is given below:

3.1.1.1. Sawdust

Sawdust of mulberry wood was collected from a local saw mill in bulk and the big particles of wood were separated manually. Then it was passed through sieve of 355 μm mesh size to obtain uniform size of the sawdust. A weighed amount of this uniform sized sawdust (10 g) was transferred in a beaker (250 mL) and added 100 mL distilled water and continued distilled water addition up to 200 mL to completely soak the sawdust in beaker. When sawdust completely settled down then decanted the distilled water and repeated this process for several times until the decanted water become cleared. Sawdust was then filtered through ordinary filter paper and washed again with distilled water to remove completely the dust particles. Cleaned and decolorized sawdust was dried in an oven till constant weight and stored in an air tight bottle for further use.

3.1.1.2. Waste tea leaves

Waste tea leaves were collected in bulk from local tea making shops and were dried. These were crushed and powdered with pestle in a mortar. The powdered leaves were sieved to obtain a particle size under 355 μm . A weighed amount of uniform sized waste tea leave (10 g) was transferred in a beaker (250 mL) and added 100 mL of 0.4% formaldehyde and kept overnight. After overnight keeping the solution was decanted and added distilled water. The decantation process was continued until the distilled water become cleared. The waste tea leave obtained after decantation were filtered through ordinary filter paper and washed again with distilled water. After filtration, the cleared and decolorized waste tea leaves were dried in an oven till constant weight and stored in an air tight bottle for further use.

3.1.1.3. Orange peels (OP)

Orange peels were collected from juice shops and washed with distilled water to remove the dirt particles. These peels were cut into small pieces with scissors and kept for several days in sun light. The dried peels were grinded using a grinder. The big particles were separated manually and crushed with pestle in a mortar. Then these peels were sieved to obtain a particle size under 355 μm . A weighed amount of these uniform sized peels (10 g) was transferred in a beaker (250 mL) and added 100 mL distilled water and continued water addition up to 200 mL to completely soak the peels in the beaker. When orange peels were completely settled down then decanted the distilled water and repeated this process for several times until the decanted water become cleared. Orange peels were then filtered through ordinary filter paper and washed again with distilled water to completely remove the dust particles. Cleaned and decolorized orange peels were dried in an oven till constant weight and stored in an air tight bottle for further use.

3.1.2. Carbonization of sorbents

3.1.2.1. Sawdust carbon (SDC)

A weighed amount of uniform particle sized sawdust (20 g) was loaded in an indigenously designed Pyrex vertical tubular glass reactor placed in a tubular furnace and heated in the reactor at 100 $^{\circ}\text{C}$ for one hour. The temperature was then increased at the rate of 10 $^{\circ}\text{C}$ after every hour and kept at 250 $^{\circ}\text{C}$ for three hours for complete conversion of sawdust into carbon. A known amount of this carbon (10 g) was transferred in a beaker (250 mL) and added 100 mL distilled water to it and continued adding water to it up to 200 mL to completely soak the carbon in beaker. When the carbon completely settled down then decanted the distilled water and repeated this process for several times until the decanted water become cleared. Carbon was then filtered through ordinary filter paper and washed again with distilled water. Cleaned and decolorized carbon was dried in an oven to get a constant weight and stored in an air tight bottle for further use.

3.1.2.2. Carbonized orange peel (COP)

Carbonization of the orange peel was done using the same procedure as for sawdust mentioned before.

3.1.3. Chemical treatment of sorbents

In order to enhance the sorption ability of these sorbents, it was necessary to modify its surface by chemical treatment. Therefore sawdust, sawdust carbon and orange peel were modified by chemical treatment before use for adsorption.

3.1.3.1. Chemical treatment of sawdust

A known amount of uniform particle sized sawdust (10 g) obtained in the previous step was transferred in to a beaker (250 mL) and added to it 200 mL of 1.0 M HCl. The mixture was kept overnight. The superficial solution was then decanted and added 100 mL distilled water and again decanted. The solution was decanted after each addition of distilled water and repeated this process until the decanted water become cleared. Sawdust was then filtered through ordinary filter paper and washed again with distilled water. Cleaned and decolorized sawdust was dried in an oven till constant weight and stored in an air tight bottle for further use.

3.1.3.2. Chemical treatment of sawdust carbon

A known amount (10 g) of uniform particle sized sawdust carbon (SDC) was transferred in three separate beakers and added to each beaker 200 mL of 1.0 M NaOH, HCl, and H₂SO₄. The mixtures were kept overnight. The superficial solutions were then decanted and added to it 200 mL of distilled water. The distilled water was again decanted and the process was repeated until the decanted water become cleared. Sawdust carbon was then filtered through ordinary filter paper and washed again with distilled water. Cleaned and decolorized sawdust carbon was dried in an oven till constant weight and stored in an air tight bottle for further use.

Similarly, a weighed amount (10 g) of HCl and H₂SO₄ treated sawdust carbon were transferred in to separate beakers and added to it 200 mL of 1.0 M NaOH solution to each

flask and kept overnight. The superficial solutions were then decanted and added 200 mL of distilled water. The distilled water was again decanted and the process was repeated until the decanted water become cleared. Sawdust carbon was then filtered through ordinary filter paper and washed again with distilled water. Cleaned and decolorized sawdust carbon obtained was dried in an oven till constant weight and stored in an air tight bottle for further use.

3.1.3.3. Chemical treatment of orange peels

A known amount of uniform particle sized orange peels (10 g) obtained in the previous step were transferred in to a beaker (250 mL) and added to it 200 mL of 1.0 M HCl. The mixture was kept overnight. The superficial solution was then decanted and added 100 mL distilled water and again decanted. The solution was decanted after each addition of distilled water and repeated this process until the decanted water become cleared. The orange peels were then filtered through ordinary filter paper and washed again with distilled water. Cleaned and decolorized orange peels were dried in an oven to get a constant weight and stored in an air tight bottle for further use. The resulting sorbent was designated as acid treated orange peel (AOP).

3.1.4. Collection of water samples

Water samples were collected from the surface water of river Badabera, Peshawar and river Swat, Pakistan. These samples were filtered before sorption procedures to remove suspended particles. Tap water samples were collected from our research laboratory of Peshawar University and used without any pretreatment.

3.1.5. Characterization of sorbents

The sorbents and their carbonized products were characterized before and after chemical treatments. Various techniques like FT-IR, SEM and EDX were used to ascertain the presence of various functional groups, porosity and elemental composition of these materials.

3.1.5.1. Characterization using FT-IR

FT-IR spectra of the sorbents were obtained by using NICOLET 380-FT-IR, Thermoscientific, UK, Fourier Transform Infrared Spectrophotometer along with OMNIC XP software and computer control disc (ZnSe) unit. The FT-IR spectra of the samples were recorded in the region of 400-4000 cm^{-1} .

3.1.5.2. Characterization by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX)

The morphologies of the sorbent particles were analyzed using scanning electron microscope (SEM-Model-JSM-5910, Japan JEOL) at Centralized Resource Laboratory, Department of Physics, University of Peshawar. For this purpose the sorbents particles were mounted on the brass discs (1.15 cm $\times$ 0.9 cm) and automatically analyzed using computer software. The elemental analyses were performed using dispersive x-ray (EDX-INCA 200 Oxford Instruments UK).

3.1.5.3. Surface area analysis

BET- N_2 adsorption experiments were conducted manometrically at -196 $^{\circ}\text{C}$ using Quantachrome NOVA 2200e surface area & pore size analyzer. Before adsorption experiments, the sorbent samples were degassed at 120 $^{\circ}\text{C}$ for a period of 4 hours in nitrogen atmosphere. Surface area was obtained by applying the standard BET equation to the adsorption data in the relative pressure (P/P_0) range 0.05-0.35. The value of 0.81 g mL^{-1} and $16.2 \times 10^{-20} \text{ m}^2$ were used for the density of liquid nitrogen and the molecular area of the adsorbate nitrogen at -196 $^{\circ}\text{C}$ respectively. The pore size distribution was determined by DR-method using the NOVA Win2 data analysis software.

3.1.6. Determination of nickel, lead and cadmium using atomic absorption spectrophotometer

Instrument

Flame atomic absorption spectrophotometer (Perkin-Elmer model AA200) was used during this work.

Chemicals

All chemicals and reagents used in this work were of analytical reagent grade purity and were used as such without further purification. $1000 \mu\text{g mL}^{-1}$ atomic absorption standard (Merck, Darmstadt Germany) of nickel, lead and cadmium were used. Working standards were prepared fresh each day from suitable serial dilution of stock solution.

The recommended instrumental parameters used for analysis of these metals are given below in table 3.1.

Table 3.1: Recommended instrumental parameters for selected metals (Ni, Pb and Cd)

Metal	Wavelength (nm)	Spectral band width (nm)	Flame
Nickel	232.0	0.2	Air/Acetylene
Lead	283.3	0.7	Air/Acetylene
Cadmium	228.8	0.7	Air/Acetylene

Preparation of standard curves

Working standards of each metal were prepared from $1000 \mu\text{g mL}^{-1}$ atomic absorption standard (Merck, Darmstadt Germany) in the range of 2 to $10 \mu\text{g mL}^{-1}$ for each metal. The instrument automatically measured the concentration of each metal from the standard curve. Standard curves of these metals are shown in Fig. 3.1-3.3.

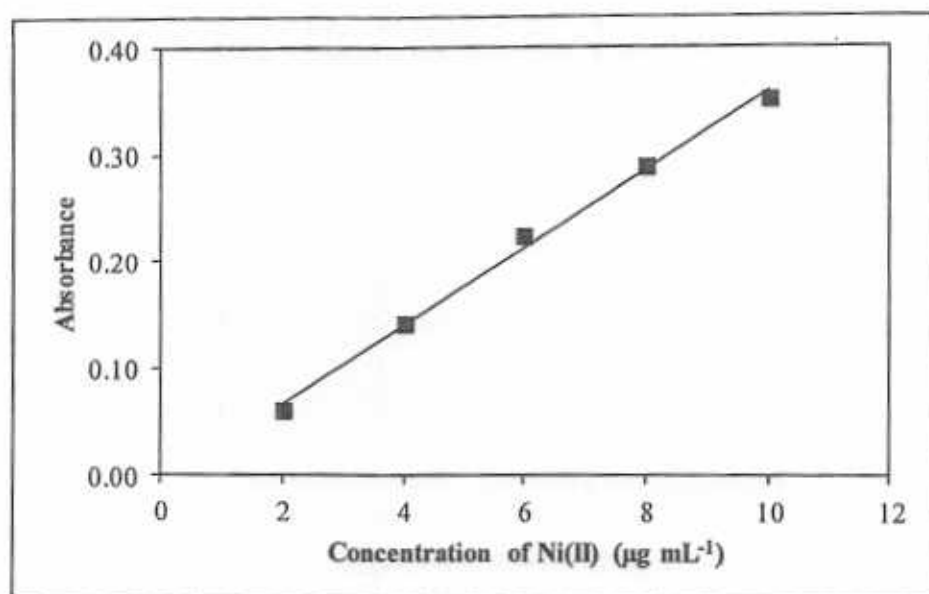


Figure 3.1: Standard curve for determination of Ni(II) using flame atomic absorption spectrophotometer

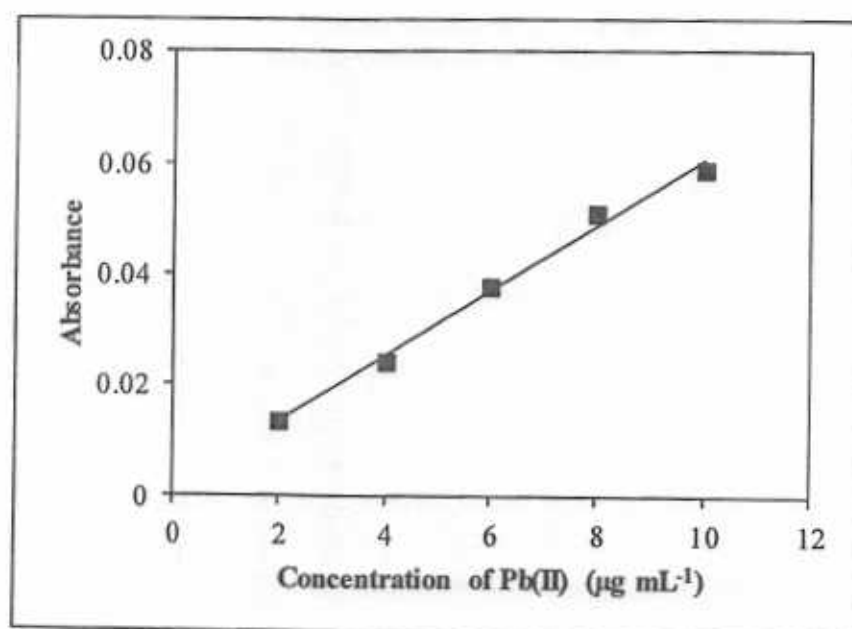


Figure 3.2: Standard curve for determination of Pb(II) using flame atomic absorption spectrophotometer

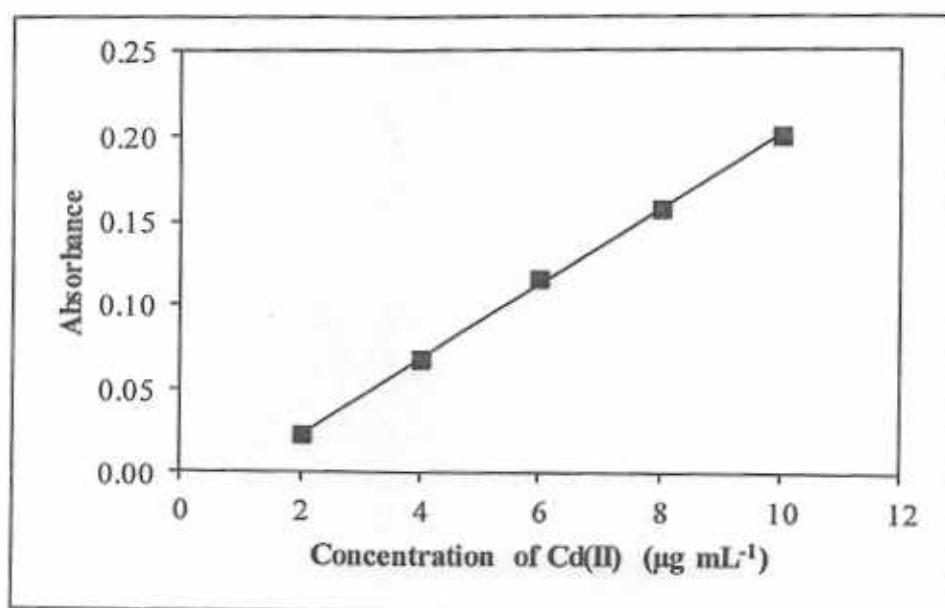


Figure 3.3: Standard curve for determination of Cd(II) using flame atomic absorption spectrophotometer

Procedure for determination of unadsorbed metal

After each experiment, the filtrate containing unadsorbed metal ions were transferred to 100 mL volumetric flask and diluted up to marks with distilled water. The solutions were analyzed for respective metal ions using atomic absorption spectrophotometer at optimum conditions. The concentration of each metal in the filtrate was calculated using standard curve constructed from the standard solutions.

3.1.7. Calculation of the amount of metal sorbed

The sorption capacity of metal ions (q_e) and percent sorption was calculated according to the following general equations:

$$q_e = \left[\frac{C_i - C_f}{m} \right] V$$

$$\% \text{ sorption} = \left[\frac{C_i - C_f}{C_i} \right] \times 100$$

Where q_e is the amount of metal ions adsorbed on the sorbent (mg g^{-1}), C_i and C_f represent the initial and equilibrium concentrations of metal ions, respectively; V is the volume of metal ions solution (mL) and m is the amount of sorbent (g).

Part A1: Investigation of adsorption behavior of Ni(II) using commercial and indigenous adsorbents

3.2. Experimental

Instruments

Atomic absorption spectrophotometer (Perkin Elmer model AA200), Digital balance (Model VB-302), Shaker (Gallenkamp, England), indigenously designed Pyrex vertical tubular glass reactor, Analog pH meter (Model-7020 Kent Industrial Measurement Limited Electronic Instrument LTD, Chertsey Surrey England) and Electrical Thermostatic water baths (Made in China) were used during this work.

Chemicals and reagents

All chemicals and reagents used in this work were of analytical reagent grade purity. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, H_3PO_4 , H_3BO_3 (BDH), NaOH, HNO_3 , H_2SO_4 , HCl, CH_3COOH , ethanol and acetone (Merck, Darmstadt Germany) were used for this work.

3.2.1. Solution preparation

Nickel solution ($1000 \mu\text{g mL}^{-1}$)

$1000 \mu\text{g mL}^{-1}$ nickel solution was prepared by dissolving 0.4 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water and diluted up to 100 mL. Working standards were prepared fresh from this solution by dilution.

Sodium hydroxide solution (1.0 M)

Sodium hydroxide solution was prepared by dissolving 20.0 g sodium hydroxide in distilled water and diluted up to 500 mL.

Hydrochloric acid solution (1.0 M)

Hydrochloric acid solution was prepared by adding 41.44 mL of conc. hydrochloric acid in distilled water and diluted up to 500 mL with distilled water.

Britton Robinson buffer solution

Britton Robinson buffer solution of pH 1-7 were prepared by mixing stock solutions of 0.4 M CH_3COOH , 0.4 M H_3PO_4 , 0.4 M H_3BO_3 and 0.2 M NaOH in different ratios for the adjustment of pH.

3.2.2. Sorption studies

3.2.2.1. The effect of pH on sorption of Ni(II) using silica gel, amberlite and sawdust

In order to optimize the pH of the solution a known amount of each sorbent (0.1 g) was taken in separate Erlenmeyer flasks (250 mL) and added 3 mL of Briton Robison buffer in the pH range of 1 to 7 by means of a pipette. Then $5 \mu\text{g mL}^{-1}$ of Ni(II) solution was added to it and diluted up to 20 mL with distilled water to completely soak the sorbents. The mixture was kept for 30 min for equilibration and filtered through ordinary filter paper. The experiments were conducted in triplicate for each pH. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of unadsorbed Ni(II) were determined using atomic absorption spectrophotometer.

3.2.2.2. The effect of contact time on sorption Ni(II) using silica gel, amberlite and sawdust

In order to observe the effect of contact time on the sorption process, a known amount of each sorbent (0.1 g) was taken in separate Erlenmeyer flasks (250 mL) and added to it 3 mL of Briton Robison buffer of pH 3 with the help a pipette. Then added $5 \mu\text{g mL}^{-1}$ of Ni(II) solution and diluted up to 20 mL to completely soak the sorbents. The mixture was allowed to equilibrate for contact time ranging from 10 to 60 min and then filtered through ordinary filter paper. Each experiment was performed in triplicate. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of unadsorbed Ni(II) were determined using atomic absorption spectrophotometer.

3.2.2.3. The effect of initial concentration of metal ions on sorption of Ni(II) using silica gel, amberlite and sawdust

For investigating the effect of initial metal ion concentration, known amount of each sorbent (0.1 g) was taken in separate Erlenmeyer flasks (250 mL). To this 3 mL of pH 3 Britton Robison buffer was added. This was followed by addition of Ni(II) and the amount of Ni(II) was varied in the range of 5 to 1000 $\mu\text{g mL}^{-1}$. Each solution was diluted up to 20 mL and allowed to equilibrate for 30 min. These were then filtered through ordinary filter paper. Each experiment was conducted in triplicate. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of unadsorbed Ni(II) were determined as mentioned before.

Similar optimization procedures were conducted for the columns studies but here each column (29 cm length and 1.0 cm diameter) was plugged with cotton/glass wool at the bottom and a small amount of cotton/glass wool was placed on the top to avoid the disturbance of sorbents. The rest of the procedure was the same as for batch method.

3.2.2.4. Desorption studies from silica gel, amberlite and sawdust

To regenerate the loaded sorbents and for complete elution of Ni(II) 30 mL of a variety of solvents like ethanol, acetone, NaCl (3 M), HCl (4 M) and HNO_3 (4 M) were used both for batch and column methods. For batch methods the loaded sorbents were poured into Erlenmeyer flasks and 30 mL of each solvent was added to it and kept for 30 min and then filtered. In case of column the eluent solutions were passed at 1.0 mL min^{-1} through the loaded columns. Each experiment was performed in triplicates. The eluates were then collected in 100 mL flasks and diluted up to marks with distilled water. The concentrations of the desorbed Ni(II) were determined in each flask as mentioned before.

3.2.2.5. Adsorption of Ni(II) using batch procedure at optimum conditions

Known amount of each sorbent (0.1 g) was taken in three separate Erlenmeyer flasks (250 mL) and adjusted the pH of the solid phase to pH 3 by soaking it in Britton Robinson buffer. To each beaker known volumes of Ni(II) solution from 100 $\mu\text{g mL}^{-1}$ diluted up to 20 mL was added and equilibrated for 60 min. The mixture was filtered and the filtrates

were diluted up to mark in 100 mL volumetric flasks. The experiments were performed in triplicate at optimum operational conditions. The concentrations of unadsorbed Ni(II) in filtrates were determined as mentioned before.

3.2.2.6. Adsorption of Ni(II) using column procedure at optimum conditions

Slurry of each sorbent (0.1 g) was made in distilled water and packed into three separate columns having 29 cm length and 1.0 cm diameter and plugged with cotton/glass wool at the bottom. To avoid the disturbance of sorbents a small amount of cotton/glass wool was placed on the top and these columns were rinsed with plenty of distilled water to remove any dirt particles present. The pH of each column was adjusted to pH 3 by passing through it Britton Robinson buffer and known volume of Ni(II) from $100 \mu\text{g mL}^{-1}$ was loaded to each column. Each experiment was performed in triplicates. The eluates were collected in 100 mL flasks, diluted up to marks and the concentrations of unadsorbed Ni(II) were determined as mentioned before.

Part A2: Investigation of adsorption behavior of Ni(II) using modified carbon derived from Mulberry wood sawdust

3.3. Experimental

Instruments

The same instruments were used as mentioned before.

Chemicals and reagents

The same chemicals and reagents were used as mentioned before.

3.3.1. Sorption studies

3.3.1.1. The effect of pH on sorption of Ni(II) using CSDC

Known amount of CSDC (0.1 g) was taken in Erlenmeyer flask (250 mL) and 3 mL of Briton Robison buffer solution in the pH range of 2 to 8 were added to it in order to optimize the pH of solutions. Then added $5 \mu\text{g mL}^{-1}$ of Ni(II) solution and diluted up to 20 mL. The mixture was kept for 30 min and filtered through ordinary filter paper. The experiments were performed in triplicate at each pH. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of Ni(II) were determined as mentioned before.

3.3.1.2. The effect of contact time on sorption of Ni(II) using CSDC

The effect of contact time on sorption process of Ni(II) on CSDC was investigated by taking a known amount of CSDC (0.1 g) in Erlenmeyer flasks (250 mL) and to this 3 mL of pH 7 Briton Robison buffer was added. This was followed by addition of $5 \mu\text{g mL}^{-1}$ of Ni(II) solution and diluted up to 20 mL. The contact time was varied from 30 to 90 min and the solutions were then filtered through ordinary filter paper. Each experiment was conducted in triplicates. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of unadsorbed Ni(II) were determined as mentioned before.

3.3.1.3. The effect of initial concentration of metal ions on sorption of Ni(II) using CSDC

In order to investigate the effect of initial metal ion concentrations on sorption of Ni(II) on CSDC a known amount of CSDC (0.1 g) was taken in Erlenmeyer flasks (250 mL) and to this was added 3 mL of pH 7 of Briton Robison buffer. This was followed by addition of Ni(II) solutions in the concentration range of 5 to 300 $\mu\text{g mL}^{-1}$ and diluted up to 20 mL to completely soak the sorbents. The mixture was kept for an optimum time (70 min) and filtered through ordinary filter paper. The experiments were performed in triplicate at optimum experimental conditions. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of unadsorbed Ni(II) were determined as mentioned before.

3.3.1.4. Adsorption of Ni(II) using batch procedure at optimum conditions

Known amount of CSDC (0.1 g) was taken in Erlenmeyer flask (250 mL) and adjusted the pH of the solid phase to pH 7 by soaking it in Britton Robinson buffer. This was followed by addition of known volumes of Ni(II) solution from 5 $\mu\text{g mL}^{-1}$ diluted up to 20 mL and equilibrated for 70 min. The mixture was filtered and the filtrates were diluted up to mark in 100 mL volumetric flasks. The experiments were performed in triplicate at optimum operational conditions. The concentrations of unadsorbed Ni(II) in filtrates were determined as mentioned before.

Part A3: Investigation of adsorption behavior of Ni(II) using waste tea leaves

3.4. Experimental

Instruments

The same instruments were used as mentioned before.

Chemicals

The same chemicals were used as mentioned before.

3.4.1. Sorption studies

3.4.1.1. The effect of pH on sorption of Ni(II) using waste tea leaves

For investigating optimum pH for sorption, a fixed amount of waste tea leaves (0.05 g) were taken in separate Erlenmeyer flasks (250 mL) and added to it 3 mL of Briton Robinson buffer in the pH range of 3 to 8, followed by addition of $5 \mu\text{g mL}^{-1}$ Ni(II) solutions and diluted up to 10 mL for complete soaking of the sorbent. The mixture was equilibrated for 30 min and filtered with ordinary filter paper. Filtrates were transferred to 100 mL volumetric flasks and diluted up to marks with distilled water. Each experiment was conducted in triplicates at each pH. The residual concentrations of Ni(II) in filtrates were determined as mentioned before.

3.4.1.2. The effect of sorbent dose on sorption of Ni(II) using waste tea leaves

The effect of sorbent dose on sorption of Ni(II) using waste tea leaves was evaluated by varying the amount of sorbent in the range of 0.03 to 0.15 g in Erlenmeyer flasks (250 mL). pH was adjusted to pH 7 (optimum) with Briton Robinson buffer, followed by addition of $5 \mu\text{g mL}^{-1}$ of Ni(II) solution and diluted up to 10 mL. The mixture was kept for 30 min to equilibrate and filtered through ordinary filter paper. Each experiment was performed in triplicates. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of unadsorbed Ni(II) was determined as mentioned before.

3.4.1.3. The effect of contact time on sorption of Ni(II) using waste tea leaves

The effect of contact time on sorption of Ni(II) on waste tea leave was evaluated by taking known amount of waste tea leaves (0.13 g) in Erlenmeyer flasks (250 mL) and added 3 mL of pH 7 Briton Robinson buffer (optimized) to it. Then to each flask $5 \mu\text{g mL}^{-1}$ Ni(II) solution was added and diluted up to 10 mL. The equilibration time was varied from 30 to 100 min and sorbent was separated by filtration. Each filtrate was transferred into 100 mL volumetric flasks and diluted up to marks with distilled water. Each experiment was performed in triplicates. The residual concentrations of Ni(II) were determined as mentioned before.

3.4.1.4. The effect of shaking time on sorption of Ni(II) using waste tea leaves

In order to observe the effect of shaking time of the reaction mixture on the sorption of Ni(II) on waste tea leaves, known amount of waste tea leaves (0.13 g) were taken in Erlenmeyer flask (250 mL). To this 3 mL of pH 7 Briton Robinson buffer were added, followed by addition of $5 \mu\text{g mL}^{-1}$ Ni(II) solution into each flask and diluted up to 10 mL for complete soaking of the sorbent. The flask contents were shaken and the shaking time was varied from 30 to 90 min at 60 rpm. The sorbent was separated through filtration and filtrates were transferred into 100 mL volumetric flasks and diluted up to marks. Each experiment was conducted in triplicates. The concentrations of Ni(II) in filtrates were determined as mentioned before.

3.4.1.5. The effect of initial concentration of metal ions on sorption of Ni(II) using waste tea leaves

The effect of initial concentration of metal ions on the sorption of Ni(II) was investigated by taking fixed amount of waste tea leaves (0.13 g) in separate Erlenmeyer flasks (250 mL) and adjusted the solution pH to optimum value i.e. 7.0. Then added Ni(II) solutions in the concentration range of 1 to $200 \mu\text{g mL}^{-1}$ and diluted up to 10 mL for complete soaking of sorbent. The content of the flasks were shaken for 90 min (optimized). The sorbent was separated by filtration and filtrates were diluted up to marks in 100 mL volumetric flasks. Each experiment was performed in triplicates and the concentration of Ni(II) was determined as mentioned before.

3.4.1.6. The effect of temperature on sorption of Ni(II) using waste tea leaves

For investigating the effect of temperature on sorption of Ni(II) on waste tea leaves, known amount (0.13 g) was taken in Erlenmeyer flask and 3 mL of pH 7 Briton Robinson buffer were added, followed by addition of $5 \mu\text{g mL}^{-1}$ Ni(II) solutions into each flask and diluted up to 10 mL for complete soaking of the sorbent. The reaction mixtures were equilibrated for 30 min on water bath at temperature varying to the range of 30 to 90 °C. Each experiment was conducted in triplicates. The sorbents were separated by filtration and the filtrates were diluted up to marks in 100 mL volumetric flasks and the residual concentrations of Ni(II) in the filtrates were determined as mentioned before.

Part B: Investigation of adsorption behavior of Pb(II) using acid treated orange peel and carbonized orange peel

3.5. Experimental

Instruments

The same instruments were used as mentioned before.

Chemicals and reagents

All chemicals and reagents used in this work were of analytical reagent grade purity. 1000 $\mu\text{g mL}^{-1}$ lead standard solution (Merck, Darmstadt Germany) was used. Working standards were prepared from suitable serial dilution of stock solution. Acetate buffer was used for the adjustment of pH of solutions.

3.5.1. Sorption studies

3.5.1.1. The effect of pH on sorption of Pb(II) using AOP and COP

In order to check the effect of solution pH on sorption of Pb(II) on AOP and COP, known amount of each sorbent (0.01 g) was taken in separate Erlenmeyer flasks (250 mL) and added 3 mL of acetate buffer of different pH ranging from 3 - 7 to adjust the pH of the solution. This was followed by addition of 50 $\mu\text{g mL}^{-1}$ of Pb(II) solution and diluted up to 10 mL. The mixture was kept for 30 min for equilibration and filtered through ordinary filter paper. Each experiment was conducted in triplicate basis for each pH. The filtrates were diluted up to mark in 100 mL flasks and the concentrations of Pb(II) were determined as mentioned before.

3.5.1.2. The effect of contact time on sorption of Pb(II) using AOP and COP

The effect of contact time on sorption of Pb(II) on AOP and COP was evaluated by taking known amount of each sorbent (0.01 g) in separate Erlenmeyer flasks (250 mL) and pH was adjusted with acetate buffer to pH 6.0 in case of AOP (optimum) while it was adjusted to pH 5.50 in case of COP (optimum). This was followed by addition of 50 μg

mL^{-1} of Pb(II) solution and diluted up to 10 mL. The mixture was kept for varied contact time ranging from 10 to 120 min and filtered through ordinary filter paper. Each experiment was performed in triplicates. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of Pb(II) were determined as mentioned before.

3.5.1.3. The effect of shaking time on sorption of Pb(II) using AOP and COP

For investigating the effect of shaking of the reaction mixture on the sorption of Pb(II) on AOP and COP, known amount of each sorbent (0.01 g) was taken in separate Erlenmeyer flasks (250 mL) and pH was adjusted with acetate buffer to pH 6.0 in case of AOP (optimum) while it was adjusted to pH 5.50 in case of COP (optimum). This was followed by addition of $50 \mu\text{g mL}^{-1}$ of Pb(II) solution and diluted up to 10 mL. The reaction mixture was shaken on a shaker and the shaking time was varied from 10 to 80 min at 60 rpm. The experiment was conducted in triplicate at each interval of times. The sorbent was separated by filtration and the filtrates were diluted up to marks in 100 mL volumetric flasks. The residual concentration of Pb(II) in the filtrates was determined as mentioned before.

3.5.1.4. The effect of sorbent dose on sorption of Pb(II) using AOP and COP

For investigating the effect of sorbent dose on sorption of Pb(II), amount of each sorbent in the range of 0.004 to 0.018 g was taken in separate Erlenmeyer flasks (250 mL) and pH of each flask was adjusted to optimum pH with acetate buffer of pH 6.0 in case of AOP and pH 5.50 in case of COP. This was followed by adding $50 \mu\text{g mL}^{-1}$ of Pb(II) solution and diluted up to 10 mL. The mixture was kept for 30 min to equilibrate and filtered through ordinary filter paper. Each experiment was performed in triplicates. The filtrates were diluted up to marks in 100 mL flasks and the concentrations of Pb(II) were determined as mentioned before.

3.5.1.5. The effect of initial concentration of metal ions on sorption of Pb(II) using AOP and COP

For investigating the effect of initial metal ion concentration on sorption behavior of Pb(II) on AOP and COP, known amount of each sorbent (0.012 g) was taken in separate

Erlenmeyer flasks (250 mL). Optimum pH for each sorbent (pH 6 for AOP and pH 5.5 for COP) was adjusting by adding 3 mL of acetate buffer to each flask. This was followed by addition of Pb(II) solution and the concentration of Pb(II) was varied from 50 to 250 $\mu\text{g mL}^{-1}$. The content of each flask was diluted to 10 mL. The reaction mixture was shaken on a shaker for complete equilibration for one hour at 60 rpm. The experiments were performed in triplicate for each concentration. The sorbent was separated by filtration and the filtrates were diluted up to marks in 100 mL volumetric flasks. The residual concentrations of Pb(II) in the filtrates were determined as mentioned before.

3.5.1.6. The effect of temperature on sorption of Pb(II) using AOP and COP

For evaluation of the effect of temperature on the sorption of Pb(II) on AOP and COP, known amount of each sorbent (0.012 g) was taken in separate Erlenmeyer flasks (250 mL). The pH was adjusted to optimum for each sorbent by addition of 3 mL acetate buffer solution. This was followed by adding 50 $\mu\text{g mL}^{-1}$ of Pb(II) solution and diluted up to 10 mL. The reaction mixtures were kept for 30 min on water bath and the temperature of the water bath was varied in the range of 30 to 90 °C. Each experiment was conducted in triplicates. The sorbents were separated by filtration and the filtrates were diluted up to marks in 100 mL volumetric flasks and the residual concentrations of Pb(II) in the filtrates were determined as mentioned before.

3.5.1.7. The effect of interfering ions on sorption of Pb(II) using AOP and COP

The effect of some common interfering ions i.e. alkali and alkaline earth metals (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) was investigated on the sorption of Pb(II). For this a known amount of each sorbent (0.012 g) was taken in separate Erlenmeyer flasks (250 mL). The pH was adjusted to optimum for each sorbent by addition of 3 mL acetate buffer solution. This was followed by adding 50 $\mu\text{g mL}^{-1}$ of Pb(II) solution and diluted up to 10 mL. The interfering ions were added in the range of 200 to 1400 μg from their standard solutions and the reaction mixtures were kept for 30 min. The experiments were carried out in triplicates. The sorbents were separated by filtration and the filtrates were diluted up to

marks in 100 mL volumetric flasks and the residual concentrations of Pb(II) in the filtrates were determined as mentioned before.

3.5.1.8. Desorption studies from AOP and COP

For preconcentration and regeneration of the sorbents, efficient desorption is required. For this purpose, desorption was carried out with a variety of solvents. The loaded sorbents were equilibrated in separate Erlenmeyer flask (250 mL) with 10 mL of 1.0 M different solvents like HCl, HNO₃, CH₃COOH, H₂SO₄, NaOH, NH₃ and NaCl. The solutions were equilibrated for 30 min. Each experiment was performed in triplicates. The mixtures were filtered and the filtrates were diluted up to marks in 100 mL volumetric flasks. The desorbed Pb(II) was determined as mention before.

For investigating the effect of concentration of HNO₃ on desorption of Pb(II), the loaded sorbents were equilibrated in separate Erlenmeyer flask (250 mL) with 10 mL of HNO₃ and the concentration of HNO₃ was varied from 1.0 to 3.0 M. The solutions were equilibrated for 30 min. Each experiment was performed in triplicates. The mixtures were filtered and the filtrates were diluted up to marks in 100 mL volumetric flasks. The desorbed Pb(II) was determined as mention before.

Similarly, for investigating the effect of volume of 1.5 M HNO₃ on desorption of Pb(II), the loaded sorbents were equilibrated in separate Erlenmeyer flask (250 mL) with 1.5 M HNO₃ by varying the volumes of HNO₃ in the range of 10 to 30 mL. The solutions were equilibrated for 30 min. Each experiment was performed in triplicates. The mixtures were filtered and the filtrates were diluted up to marks in 100 mL volumetric flasks. The desorbed Pb(II) was determined as mention before.

3.5.1.9. Sorption of Pb(II) on AOP and COP at optimum conditions

For sorption of Pb(II) on AOP and COP at optimum conditions, known weight (0.012 g) of each sorbent was taken in separate Erlenmeyer flasks (250 mL). To each flask, 5 mL of 100 µg mL⁻¹ of Pb(II) solution was added. pH of each solution was adjusted by addition of 3 mL of pH 6 acetate buffer. The reaction mixtures were equilibrated on a shaker for complete equilibration for one hour at 60 rpm. Each experiment was conducted

in triplicates. The sorbents were separated by filtration and the unadsorbed Pb(II) was determined as mentioned before.

Part C: Investigation of adsorption behavior of Cd(II) using chemically treated mulberry wood sawdust (CTSD)

3.6. Experimental

Instruments

The same instruments were used as mentioned before.

Chemicals and reagents

All chemicals and reagents used in this work were of analytical reagent grade purity. 1000 $\mu\text{g mL}^{-1}$ cadmium standard solution (Merck, Darmstadt Germany) was used. Working standards were prepared from suitable serial dilution of stock solution. Briton Robinson buffer was used for the adjustment of pH.

3.6.1. Sorption studies

3.6.1.1. The effect of pH on sorption of Cd(II) using CTSD

For investigating optimum pH for solution, a fixed amount of CTSD (0.1 g) were taken in Erlenmeyer flasks (250 mL) and added 3 mL of Briton Robinson buffer in the pH range of 1 to 7, followed by addition of 5 $\mu\text{g mL}^{-1}$ Cd(II) solutions and diluted up to 20 mL for complete soaking of the sorbent. The mixture was equilibrated for 30 min and filtered with ordinary filter paper. Filtrates were transferred to 100 mL volumetric flasks and diluted up to marks with distilled water. Each experiment was conducted in triplicates at each pH. The residual concentrations of Cd(II) in filtrates were determined as mentioned before.

3.6.1.2. The effect of contact time on sorption Cd(II) using CTSD

The effect of contact time on sorption of Cd(II) on CTSD was evaluated by taking known amount of CTSD (0.1 g) in Erlenmeyer flasks (250 mL) and added 3 mL of pH 6 Briton Robinson buffer (optimized) to it. Then to each flask 5 $\mu\text{g mL}^{-1}$ Cd(II) solution was added and diluted up to 20 mL. The equilibration time was varied from 10 to 60 min and

sorbent was separated by filtration. Each filtrate was transferred into 100 mL volumetric flasks and diluted up to marks with distilled water. Each experiment was performed in triplicates. The residual concentrations of Cd(II) were determined as mentioned before.

3.6.1.3. The effect of shaking time on sorption of Cd(II) using CTSD

In order to observe the effect of shaking of the reaction mixture on the sorption of Cd(II) on CTSD, known amount of CTSD (0.1 g) was taken in Erlenmeyer flask (250 mL). To this 3 mL of pH 6 Briton Robinson buffer were added, followed by addition of $5 \mu\text{g mL}^{-1}$ Cd(II) solution into each flask and diluted up to 20 mL for complete soaking of the sorbent. The flask contents were shaken and the shaking time was varied from 10 to 60 min at 60 rpm. The sorbent was separated through filtration and filtrates were transferred into 100 mL volumetric flasks and diluted up to marks. Each experiment was conducted in triplicates. The concentrations of Cd(II) in filtrates were determined as mentioned before.

3.6.1.4. The effect of initial concentration of metal ions on sorption of Cd(II) using CTSD

The effect of initial concentration of metal ions on the sorption of Cd(II) was investigated by taking fixed amount of CTSD (0.1 g) in Erlenmeyer flasks (250 mL) and adjusted the solution pH to optimum value i.e. 6.0. Then added Cd(II) solutions in the concentration range of 35 to $130 \mu\text{g mL}^{-1}$ and diluted up to 20 mL for complete soaking of sorbent. The content of the flasks were shaken for 60 min (optimized). The sorbent was separated by filtration and filtrates were diluted up to marks in 100 mL volumetric flasks. Each experiment was performed in triplicates and the residual concentration of Cd(II) was determined as mentioned before.

3.6.1.5. The effect of interfering ions on sorption of Cd(II) using CTSD

The effect of some common interfering ions i.e. alkali and alkaline earth metals (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) was investigated on the sorption of Cd(II). For this a known amount of each sorbent (0.1 g) was taken in Erlenmeyer flasks (250 mL). The pH was adjusted to optimum for each sorbent by addition of 3 mL Briton Robinson buffer solution. This was

followed by adding $5 \mu\text{g mL}^{-1}$ of Cd(II) solution and diluted up to 20 mL. The interfering ions were added in the range of 20 to 1100 μg from their standard solutions and the reaction mixtures were kept for 30 min. The experiments were carried out in triplicates. The sorbents were separated by filtration and the filtrates were diluted up to marks in 100 mL volumetric flasks and the residual concentrations of Cd(II) in the filtrates were determined as mentioned before.

3.6.1.6. Adsorption of Cd(II) using column procedure at optimum conditions

Slurry of CTSD (0.1 g) was made in distilled water and packed into a column having 29 cm length and 1.0 cm diameter and plugged with cotton/glass wool at the bottom. To avoid the disturbance of sorbents a small amount of cotton/glass wool was placed on the top and these columns were rinsed with plenty of distilled water to remove any dirt particles present. The pH of each column was adjusted to pH 6 by passing through it Britton Robinson buffer and known volume of Cd(II) from $100 \mu\text{g mL}^{-1}$ was loaded to this column. Each experiment was performed in triplicates. The eluates were collected in 100 mL flasks, diluted up to marks and the concentrations of unadsorbed Cd(II) were determined as mentioned before.

3.6.1.7. Desorption studies from CTSD

For preconcentration and regeneration of the sorbents, efficient desorption is required. For this purpose, desorption was carried out with a variety of solvents. The loaded sorbents were equilibrated in separate Erlenmeyer flask (250 mL) with 20 mL of 1.0 M different solvents like HCl, HNO_3 , H_2SO_4 , NH_3 and NaCl. The solutions were equilibrated for 30 min. Each experiment was performed in triplicates. The mixtures were filtered and the filtrates were diluted up to marks in 100 mL volumetric flasks. The desorbed Cd(II) was determined as mention before.

Similarly, for investigating the effect of concentration of HCl on desorption of Cd(II), the loaded sorbents were equilibrated in separate Erlenmeyer flask (250 mL) with 20 mL of HCl and the concentration of HCl was varied from 1.0 to 3.0 M. The solutions were equilibrated for 30 min. Each experiment was performed in triplicates. The mixtures were

filtered and the filtrates were diluted up to marks in 100 mL volumetric flasks. The desorbed Cd(II) was determined as mention before.

RESULTS AND DISCUSSIONS

Part A1: Investigation of adsorption behavior of Ni(II) using commercial and indigenous adsorbents

4.1. Results and discussions

4.1.1. Characterization of the adsorbents

For having better understanding into functional groups available on the surface of sawdust the FT-IR spectra of the treated and untreated material was recorded and is shown in Fig. 4.1.1 and 4.1.2 respectively. On comparing the spectra it was clear that most of the ionizable groups present in the untreated material are absent in the chemically treated one and thus making greater surface area available for adsorption. The presence of peaks at 3323, 2359 and 1594 cm^{-1} in chemically treated sawdust confirm the presence of $-\text{OH}$, $\text{C}-\text{H}$ saturated and $\text{C}=\text{C}$ functional groups.

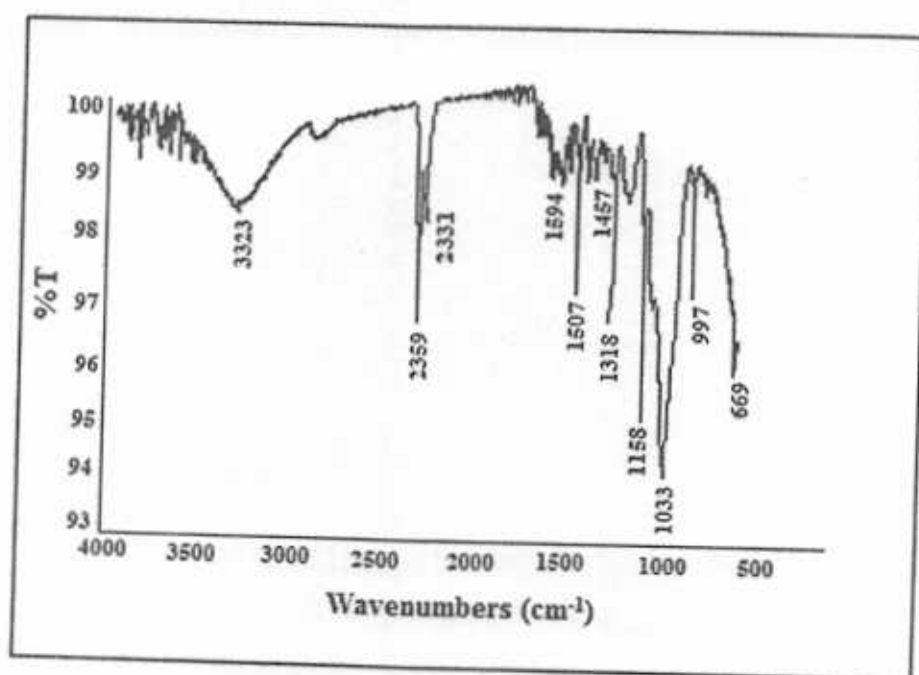


Figure 4.1.1: FT-IR spectra of untreated sawdust

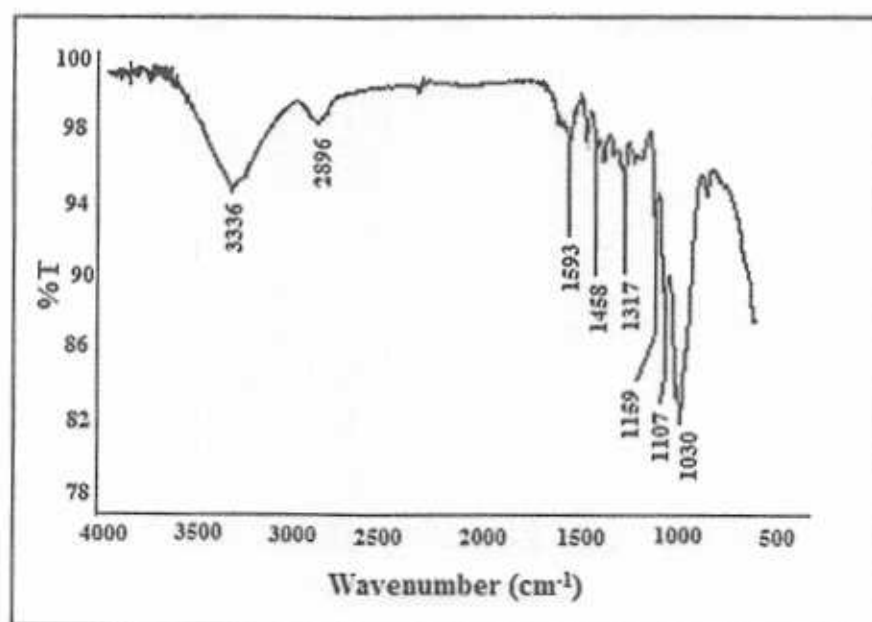


Figure 4.1.2: FT-IR spectra of treated sawdust

The morphology of the untreated and chemically treated sawdust was recorded by SEM photographs at 1000X and 2000X magnifications and the SEM images are shown in Fig. 4.1.3 and 4.1.4. On comparison, these figures show that the pore sizes of chemically treated sawdust are larger than the untreated one, thus making it more suitable for adsorption.

The results of Energy dispersive X-ray (EDX) studies are given in table 4.1.1. It was observed that the untreated sawdust contains calcium, carbon, and oxygen. It was also observed that calcium was removed after chemical treatment; the percentage of oxygen decreased and that of carbon increased indicating that chemical treatments improve the adsorption ability of the material.

The surface area of the CTSD was measured using nitrogen adsorption with Quantachrome Surface Area Pore Size Analyzer (NOVA 2200e). The specific surface area was calculated using Langmuir and BET isotherm equations. The micropore volume of the material was calculated by Dubinin-Radushkevich (DR) equation using the NOVA Win2 data analysis software and the results are given in table 4.1.2.

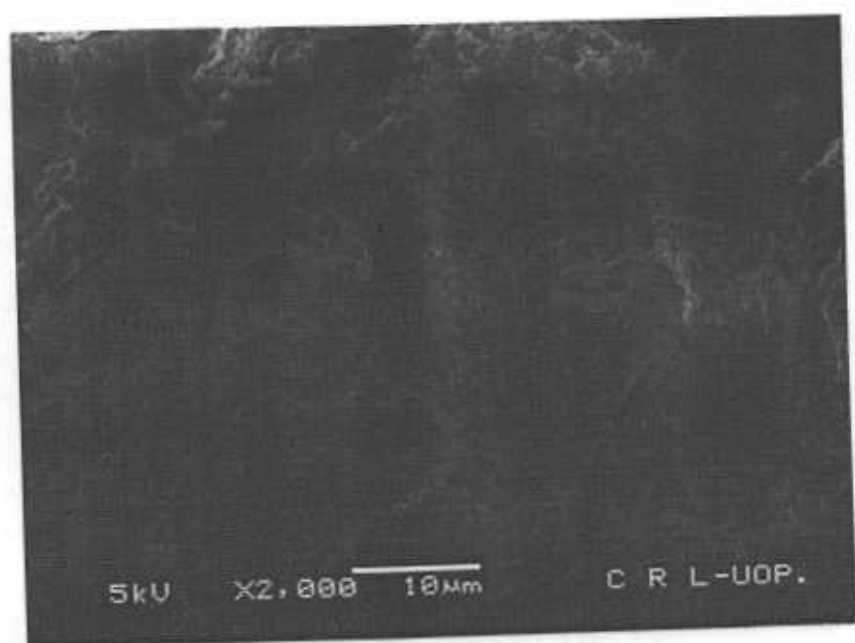


Figure 4.1.3: SEM of untreated sawdust

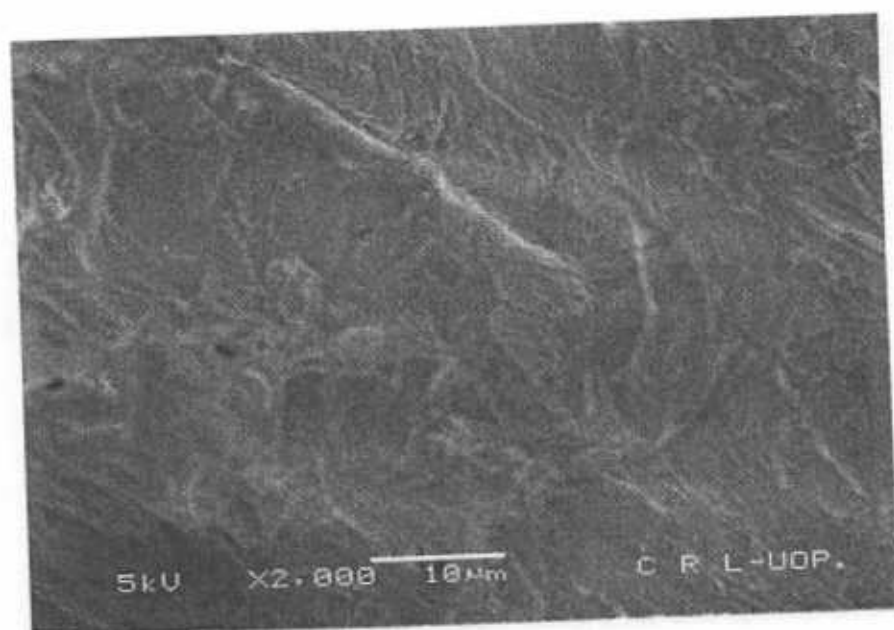


Figure 4.1.4: SEM of treated sawdust

Table 4.1.1: EDX elemental analysis of chemically treated and untreated sawdust

Sorbent	Element content (weight fraction %)		
	Carbon	Oxygen	Calcium
Chemically untreated sawdust	46.76	51.56	1.58
Chemically treated sawdust	51.62	48.38	0.00

Table 4.1.2: Characteristics of chemically treated sawdust (CTSD)

Characteristics	Methods		
	BET	DR-method	BJH- method
Surface area (m ² /g)	45.07	123.47	54.31
Average pore width (Å)	-	143.30	-
Micropore volume (cc/g)	-	0.04	-
Pore diameter (Å)	-	-	129.61
Pore volume (cc/g)	-	-	0.12

4.1.2. Sorption studies of Ni(II) using silica gel, amberlite and sawdust

4.1.2.1. Preliminary adsorption experiments

A known weight of washed (distilled water) and dried sawdust was taken in Erlenmeyer flasks (250 mL) and added to it a known concentration of Ni(II) solution. The contents of the flasks were kept for 30 min at room temperature for complete equilibration. The biosorbent was filtered and the filtrates were transferred into 100 mL volumetric flasks and diluted upto mark. The concentrations of unadsorbed Ni(II) were determined using atomic absorption spectrophotometer. The results showed good percent uptake and ensure the use of sawdust as a promising biosorbent for Ni(II) from aqueous solutions.

4.1.2.2. Optimization studies

After preliminary adsorption studies it was confirmed that Ni(II) can be removed from aqueous media using commercial and indigenous materials. For maximum adsorption, condition of pH, contact time and initial metal concentration were optimized and are discussed below:

4.1.2.2.1. The effect of pH on sorption of Ni(II) using silica gel, amberlite and sawdust

In the sorption processes of heavy metals pH is an important controlling parameter. For maximum uptake of Ni(II) on these sorbents, pH was varied from 1 to 7. The results are given in table 4.1.3 and shown in Fig. 4.1.5. It can be seen from the figure that binding of Ni(II) is strongly pH dependent and maximum sorption (98%) of Ni(II) was obtained at pH 3.0. The surface complexation theory explains that, as pH increases, the uptake of metal ions is also increased. It is due to the decrease in competition between proton and metal ions for sorption site on the surface of sorbents. However the removal of Ni(II) in the present case slightly decreased beyond pH 3.0, due to the formation of hydroxides of Ni(II). At pH 3, nickel is expected to be present in the free form as Ni(II) and the adoption would be mainly attributed to ion exchange mechanism that is by replacing the H^+ from phenolic and carboxylic groups of the sorbent by Ni(II). Adsorption in the case of silica gel and amberlite was independent of the pH.

Table 4.1.3: The effect of pH on sorption of Ni(II) from aqueous solution using silica gel, amberlite and sawdust

pH	% uptake of Ni(II)		
	Silica gel	Amberlite	Sawdust
1	34.000	94.400	82.000
2	43.500	95.800	69.000
3	94.000	96.000	87.000
4	93.600	96.400	84.000
5	93.600	94.600	83.000
6	93.400	94.000	82.000
7	93.200	94.000	79.000

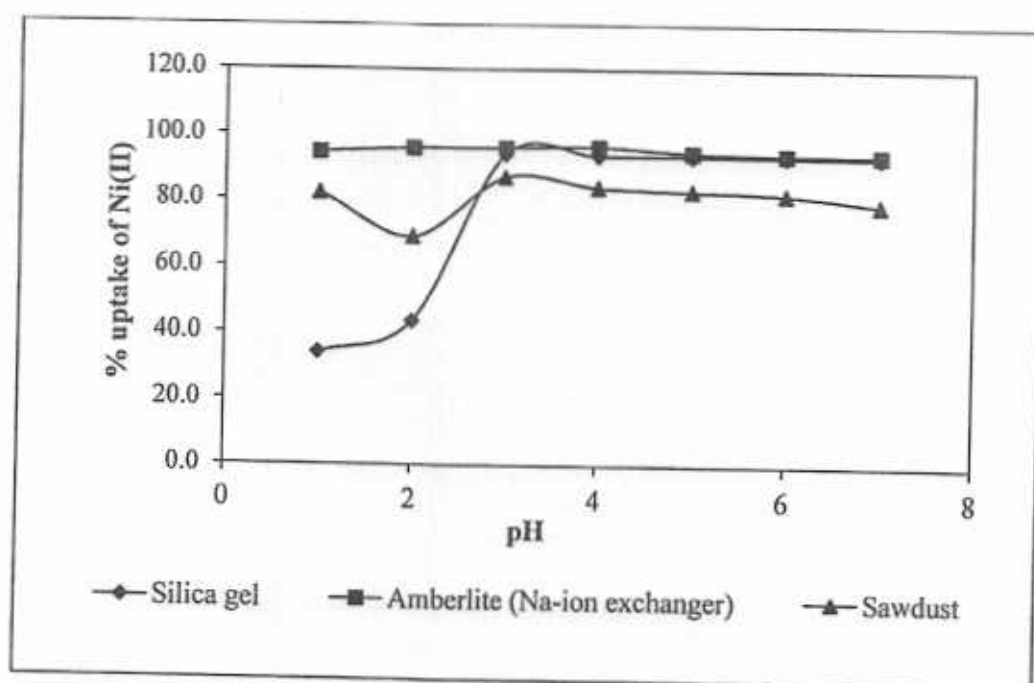


Figure 4.1.5: The effect of pH on sorption of Ni(II) from aqueous solution using silica gel, amberlite and sawdust (initial conc. $5 \mu\text{g mL}^{-1}$; contact time 30 min; volume of nickel solution 20 mL; sorbents dose 0.1 g)

4.1.2.2.2. The effect of contact time on sorption of Ni(II) using silica gel, amberlite and sawdust

Apart from the solution pH, contact time is also an important parameter affecting the sorption process. Therefore the effect of contact time on the sorption behavior of Ni(II) using three materials was investigated. Contact time was varied from 10 to 60 min using other parameter constant. The results are given in table 4.1.4 and shown in Fig. 4.1.6. Generally the sorption process is rapid at the start due to the availability of the sorption sites on biomass and as the sorption sites occupied then the sorption process becomes slow. A similar situation was also found in the sorption of Ni(II) on all three materials. It was observed that the uptake of Ni(II) is rapid for the first 10 min and increased from 50% to 95% in case of silica gel while in case of amberlite and sawdust the uptake of Ni(II) increased from 86% to 98 % in 60 min. Initially the sites on the sorbent are open and Ni(II) interacts with the sorption sites rapidly therefore the sorption rate is higher. The concentration gradient is also higher in the initial time between the bulk solution and the solid-liquid interface leading to higher sorption rate.

Table 4.1.4: The effect of contact time on sorption of Ni(II) using silica gel, amberlite and sawdust

Time (min)	% uptake of Ni(II)		
	Silica gel	Amberlite	Sawdust
10	50.000	97.600	86.560
20	60.000	97.200	87.670
30	75.000	97.000	88.750
40	87.500	96.600	89.450
50	92.500	96.600	90.520
60	95.000	96.600	90.780

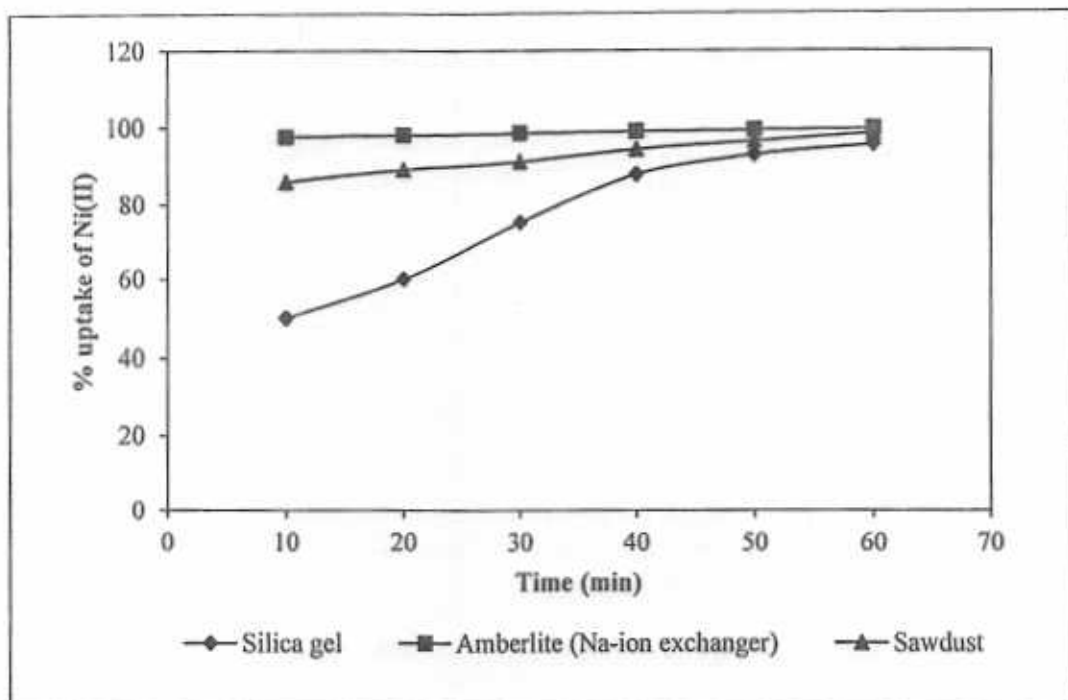


Figure 4.1.6: The effect of contact time on sorption of Ni(II) using silica gel, amberlite and sawdust (initial conc. $5 \mu\text{g mL}^{-1}$; contact time 10-60 min; volume of nickel solution 20 mL; sorbents dose 0.1 g)

4.1.2.2.3. Sorption isotherms of Ni(II) using silica gel, amberlite and sawdust

The sorption systems were designed by using sorption isotherm models. These models provide a relationship between the amount of Ni(II) sorbed on the sorbent and the concentration of Ni(II) in solution at equilibrium. The sorption isotherms of Ni(II) on sorbents were studied by the two most commonly used isotherms models Freundlich and Langmuir isotherms. The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surfaces and is expressed by the following equation:

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

The linear form of Freundlich equation is given below

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

Where K_F is the Freundlich sorption isotherm constant (mg g^{-1}), $1/n$ (g L^{-1}) is a measure of the sorption intensity and q_e is the amount sorbed (mg g^{-1}) and C_e is the equilibrium concentration ($\mu\text{g mL}^{-1}$).

The Langmuir isotherm is used for monolayer sorption on a homogeneous surface and is expressed by the following equation:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (3)$$

In a linear form, it is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (4)$$

Where C_e is the equilibrium concentration ($\mu\text{g mL}^{-1}$), q_e is the amount of solute sorbed per gram of sorbent; K_L and a_L are the Langmuir sorption isotherm constants and are related to the maximum capacity (L g^{-1}) and bonding strength (L mg^{-1}) respectively. The theoretical monolayer capacity is Q_0 and is numerically equal to $K_L a_L^{-1}$.

The Freundlich and Langmuir isotherms expression given in Equation 2 and 4 were used for analyzing equilibrium data. The value of K_F and n were calculated from the intercept and slope of the linear form of Freundlich isotherm respectively. The results are given in table 4.1.5 and shown in Fig. 4.1.7. The values of constant parameters of Freundlich isotherm are given in table 4.1.7. The values of n greater than unity indicate that Ni(II) is favorably sorbed by amberlite and sawdust. The nonlinear form of Freundlich isotherm is shown in Fig.4.1.7 which indicates that the sorption capacity increases with increase in initial metal concentrations.

The Langmuir isotherms model assumes the monolayer sorption of the adsorbate on a homogeneous surface of the adsorbent. The linear form of Langmuir isotherm model was obtained by plotting of C_e/q_e versus equilibrium concentration (C_e). The results are given in table 4.1.6 and shown in Fig. 4.1.8. The maximum sorption capacities for each material was calculated from this plot and were found to be 33.33 mg g⁻¹ for silica gel, 25.19 mg g⁻¹ for amberlite and 33.67 mg g⁻¹ for sawdust. A Langmuir isotherm for the sorption of Ni(II) on the three sorbents was plotted and is shown in Fig. 4.1.8. It can be seen from the table 4.1.7 that the correlation coefficient (> 0.950) of the Langmuir isotherm model higher than that of Freundlich suggesting that Langmuir model fits well into the experimental data. Table 4.1.7 also shows comparison of the sorption capacities and other constant parameters of silica gel, amberlite and sawdust used for the removal of Ni(II) from aqueous solutions. It can be seen that the sorption capacity of sawdust is higher than the other sorbents.

Table 4.1.5: Freundlich isotherm model for the sorption of Ni(II) using silica gel, amberlite and sawdust

Initial concentration (C _i) (µg mL ⁻¹)	Equilibrium concentration (C _e) (µg mL ⁻¹)			Sorption capacity (q _e) (mg g ⁻¹)		
	Silica gel	Amberlite	Sawdust	Silica gel	Amberlite	Sawdust
100	12.450	10.450	8.450	0.875	0.895	1.831
250	24.560	20.560	17.560	2.254	2.294	4.648
500	50.560	45.560	40.480	4.494	4.544	9.190
750	80.320	76.320	71.120	6.696	6.736	13.577
1000	119.340	115.340	109.570	8.806	8.846	17.808

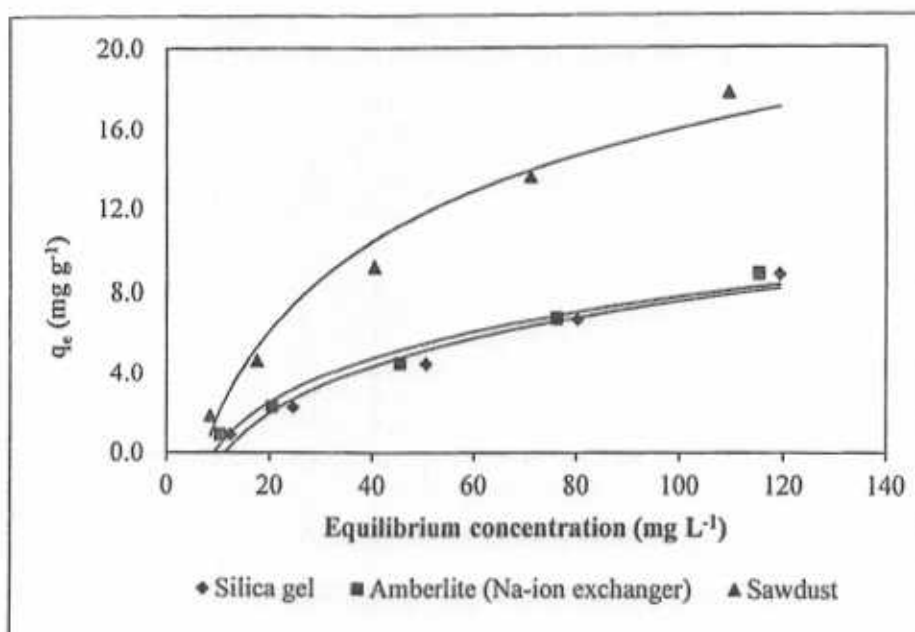


Figure 4.1.7: Freundlich isotherm model for the sorption of Ni(II) using silica gel, amberlite and sawdust (Initial concentration of Ni(II) 5-1000 $\mu\text{g mL}^{-1}$; pH 3.0; room temperature; sorbent dose 0.1 g; volume of Ni(II) solution 20 mL; contact time 30 min)

Table 4.1.6: Langmuir isotherm model for the sorption of Ni(II) using silica gel, amberlite and sawdust

Initial concentration (C _i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C _e) ($\mu\text{g mL}^{-1}$)			(C _e /q _e)		
	Silica gel	Amberlite	Sawdust	Silica gel	Amberlite	Sawdust
100	24.560	20.560	17.560	0.010	0.008	0.003
250	50.560	45.560	40.480	0.011	0.010	0.004
500	80.320	76.320	71.120	0.012	0.011	0.005
750	119.340	115.340	109.570	0.013	0.013	0.006

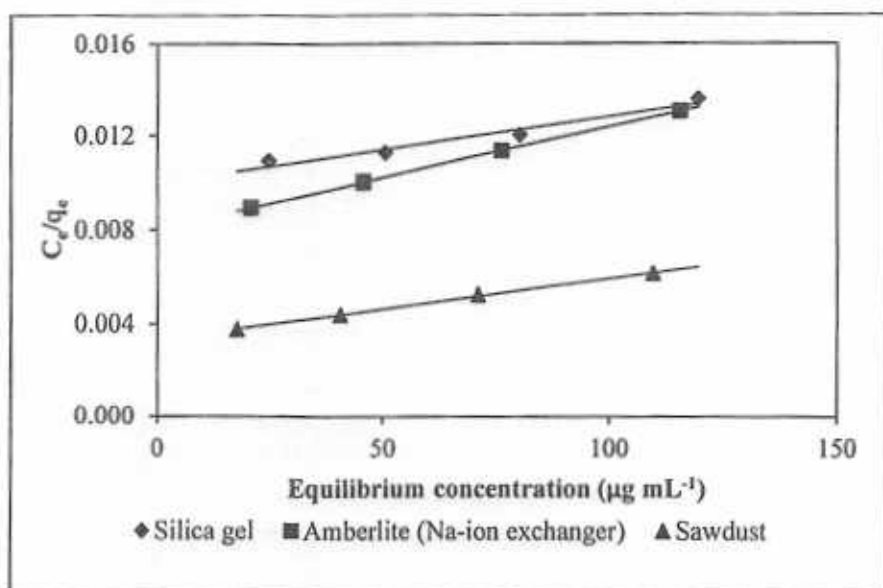


Figure 4.1.8: Langmuir isotherm model for the sorption of Ni(II) using silica gel, amberlite and sawdust (Initial concentration of Ni(II) 5-1000 $\mu\text{g mL}^{-1}$; pH 3.0; room temperature; sorbent dose 0.1 g; volume of Ni(II) solution 20 mL; contact time 30 min)

Table 4.1.7: Freundlich and Langmuir isotherm constants for the sorption of Ni(II) using silica gel, amberlite and sawdust

Sorbent	Freundlich model				Langmuir model			
	K_F (mg g ⁻¹)	n	1/n	R ²	a_L (L mg ⁻¹)	K_L (Lg ⁻¹)	Q_o (mg g ⁻¹)	R ²
Silica gel	0.076	0.987	1.013	0.9846	0.003	0.100	33.330	0.9571
Amberlite	0.115	1.068	0.936	0.9799	0.005	0.123	25.190	0.9999
Sawdust	0.329	1.146	0.871	0.9807	0.009	0.303	33.670	0.9987

4.1.2.2.4. Sorption kinetics of Ni(II) using silica gel, amberlite and sawdust

Four common kinetic models that are (i) pseudo-first-order (ii) pseudo-second-order (iii) intraparticle diffusion and (iv) Elovich equations were used for sorption kinetics of Ni(II) on silica gel, amberlite and sawdust. The model for pseudo-first-order is expressed as follow:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (5)$$

Where q_e is the amount of metal ion biosorbed (mg g^{-1}) at equilibrium, q_t is the amount of metal ions sorbed (mg g^{-1}) at any given time (min) and K_1 is the pseudo-first-order reaction rate constant for sorption (min^{-1}). The model for pseudo-second-order is as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (6)$$

Where q_e is the amount of metal ion sorbed (mg g^{-1}) at equilibrium, q_t is the amount of metal ions sorbed (mg g^{-1}) at any given time (min) and K_2 is the pseudo-second-order reaction rate constant for sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

A linear plot of time against $\log(q_e - q_t)$ was plotted for the determination of rate constant and sorption capacity for pseudo-first-order. The results are given in table 4.1.8 and shown in Fig. 4.1.9. The pseudo-second-order model is given in equation 5 and was obtained by plotting time (t) versus t/q_t . The results are given in table 4.1.9 and shown in Fig. 4.1.10. Similarly, the constant values of first order kinetics K_1 , q_e , R^2 and the second order kinetics K_2 , q_e and R^2 were calculated from the slope and intercept of each model respectively and are given in table 4.1.12. It was observed that the correlation coefficient values of the pseudo-second-order model are higher from the first order model in all

cases of sorbents. This suggests that the sorption might be controlled by second-order-model.

During sorption process, different steps occurs like in the first step sorbate (Ni) ions are transferred from aqueous media to the surface of sorbent (silica gel, amberlite or sawdust) while in second step the diffusion of sorbate ions into pores of sorbent taken place. There is a possibility that the controlling step is the transferring of sorbate from solution into pore of sorbent if the experiments are carried out in batch system with shaking of the reaction mixture. For checking of this possibility a graph of sorption capacity at time t (q_t) against square root of time ($t^{1/2}$) is plotted. The results are given in table 4.1.10 and shown in Fig. 4.1.11.

Intraparticle diffusion is a kinetic model which is related to the transporting of Ni(II) from its aqueous media to the pores of sorbent. This model is generally expressed by the following equation:

$$q_t = K_{int}t^{1/2} + C \quad (7)$$

Where C is the intercept and related to the thickness of the boundary layer and K_{int} ($\text{mol L}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion rate constant. The values of these constants are calculated directly from the intercept and slope of this graph and are given in table 4.1.12. Form Fig. 4.1.11 it can be seen that the plot of q_t versus $t^{1/2}$ is not passing through the origin which indicates that intraparticle diffusion is not the controlling step during sorption of Ni(II) on silica gel, amberlite and sawdust.

The Elovich kinetic equation is used to describe the kinetics of chemisorption on heterogeneous surfaces and is given as follows:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (8)$$

Where q_t is the amount of Ni(II) sorbed (mol L^{-1}) at time (t), α and β are known as the Elovich coefficients, α represents the initial sorption rate ($\text{mol L}^{-1} \text{min}^{-1}$) and β is related to the extent of surface coverage and activation energy for chemisorption (g min^{-1}) respectively. The Elovich coefficients were calculated from the linear plot of q_t versus $\ln t$. The results are given in table 4.1.11 and shown in Fig. 4.1.12. It might be shown from kinetic models that experimental data fitted well to the pseudo-second-order kinetic model with a high R^2 values for all three materials.

Table 4.1.8: First-order-kinetic model for Ni(II) sorption using silica gel, amberlite and sawdust

Time (min)	$\log (q_e - q_t)$		
	Silica gel	Amberlite	Sawdust
10	0.255	-0.795	0.380
20	0.146	-0.886	0.255
30	-0.096	-1.045	0.146
40	-0.522	-1.221	-0.096
50	-1.000	-1.522	-0.397

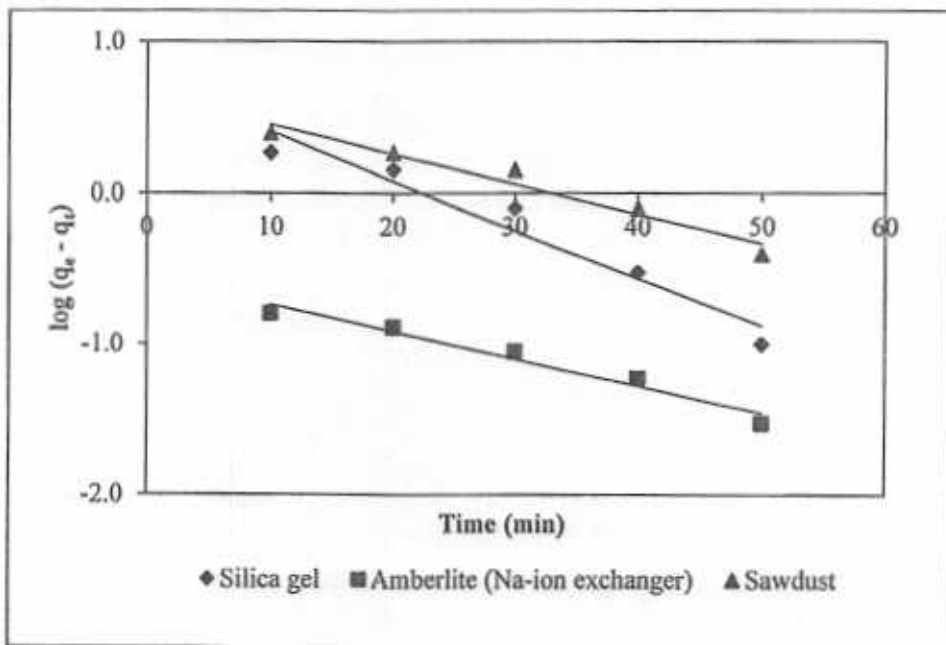


Figure 4.1.9: First-order-kinetic model for Ni(II) sorption using silica gel, amberlite and sawdust (Initial concentration of Ni(II) $5.0 \mu\text{g mL}^{-1}$; pH 3.0; room temperature; sorbent dose 0.1 g; volume of Ni(II) solution 20 mL)

Table 4.1.9: Pseudo second-order-kinetic model for Ni(II) sorption using silica gel, amberlite and sawdust

Time (min)	$t/q_t (\text{min g mg}^{-1})$		
	Silica gel	Amberlite	Sawdust
10	05.000	1.024	0.581
20	08.333	2.042	1.123
30	10.000	3.051	1.648
40	11.428	4.056	2.127
50	13.513	5.055	2.604

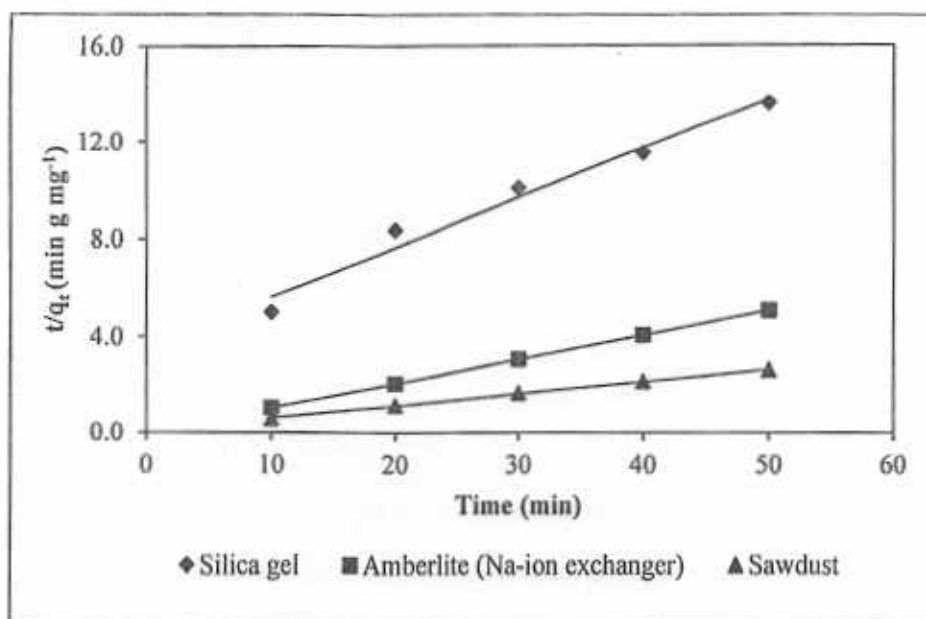


Figure 4.1.10: Second-order-kinetic model for Ni(II) sorption using silica gel, amberlite and sawdust (Initial concentration of Ni(II) $5.0 \mu\text{g mL}^{-1}$; pH 3.0; room temperature; sorbent dose 0.1 g; volume of Ni(II) solution 20 mL)

Table 4.1.10: Intraparticle diffusion mode for Ni(II) sorption using silica gel, amberlite and sawdust

$t^{1/2}$ (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)		
	Silica gel	Amberlite	Sawdust
3.162	2.000	9.760	17.200
4.472	2.400	9.790	17.800
5.477	3.000	9.830	18.200
6.324	3.500	9.860	18.800
7.071	3.700	9.890	19.200

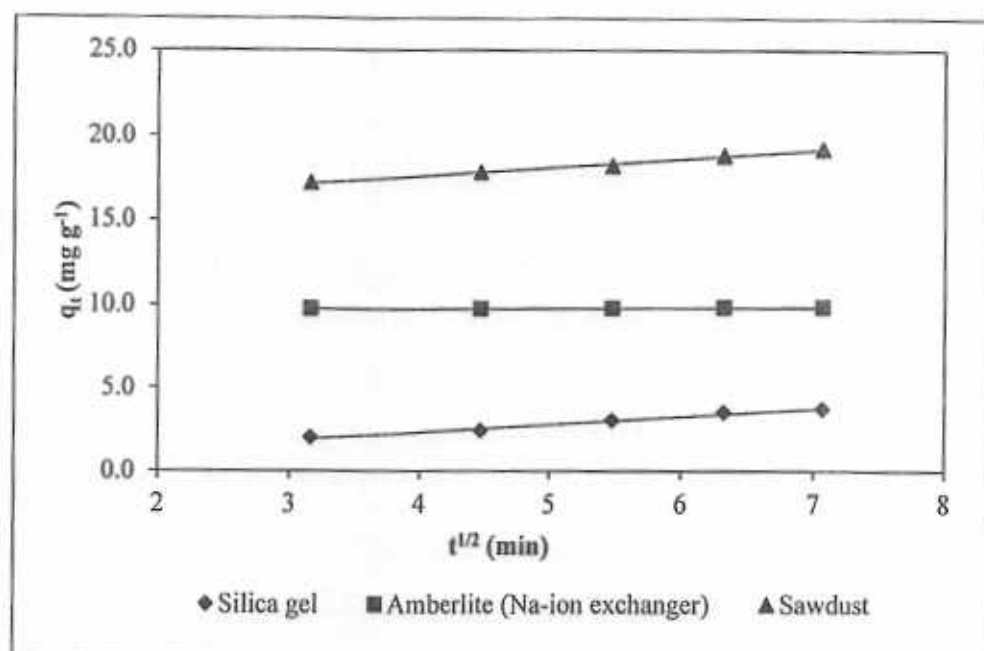


Figure 4.1.11: Intraparticle diffusion mode for Ni(II) sorption using silica gel, amberlite and sawdust (Initial concentration of Ni(II) $5.0 \mu\text{g mL}^{-1}$; pH 3.0; room temperature; sorbent dose 0.1 g; volume of Ni(II) solution 20 mL)

Table 4.1.11: Elovich equation for Ni(II) sorption using silica gel, amberlite and sawdust

Int (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)		
	Silica gel	Amberlite	Sawdust
2.302	2.000	9.760	17.200
2.995	2.400	9.790	17.800
3.401	3.000	9.830	18.200
3.688	3.500	9.860	18.800
3.912	3.700	9.890	19.200

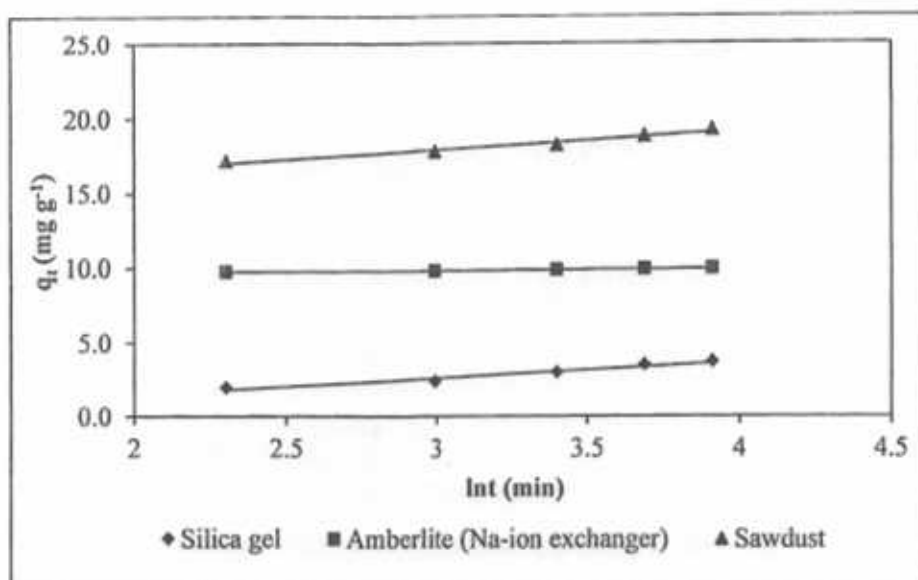


Figure 4.1.12: Elovich equation for Ni(II) sorption using silica gel, amberlite and sawdust (Initial concentration of Ni(II) $5.0 \mu\text{g mL}^{-1}$; pH 3.0; room temperature; sorbent dose 0.1 g volume of Ni(II) solution 20 mL)

Table 4.1.12: Kinetic parameters of Ni(II) sorption using silica gel, amberlite and sawdust

Sorbent	q_e (mg g ⁻¹) I_1 (exp)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic mode			Intraparticle diffusion model			Elovich model		
		K_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2	K_{int} (mg g ⁻¹ sec ^{1/2})	C	R^2	a (mg g ⁻¹ min ⁻¹)	β (g mg ⁻¹)	R^2
Silica gel	3.800	0.412	0.277	0.9570	0.011	4.970	0.9741	0.463	0.465	0.9824	0.594	0.904	0.9557
Amberlite	9.920	0.073	5.130	0.9427	0.431	9.921	1.000	0.034	9.647	0.9886	4.980E+50	12.46	0.9518
Sawdust	19.600	0.044	4.264	0.9525	0.025	19.802	0.9991	0.512	15.523	0.9903	1.410E+5	0.819	0.9587

4.1.2.2.5. Desorption study of Ni(II) from sawdust

Desorption of the retained Ni(II) from sawdust was investigated using 30 mL of different eluents like NaCl (3 M), HCl (4 M), HNO₃ (4 M) solutions, acetone and ethanol at optimum conditions and the results are given in table 4.1.13. The result shows that 30 mL of NaCl (3 M) solution is the best among the eluents investigated. Desorption studies were carried out under the same condition using the same elution volume. In batch method the effects of stirring time on desorption of Ni(II) from sawdust was also investigated and is shown in table 4.1.14. It was observed that with 40 minute stirring time almost 100% desorption was achieved.

Table 4.1.13: Comparison of different eluents for desorption of Ni(II)

Type of eluents	% Recovery
3M NaCl	65.370 ± 11.58
4M HCl	49.580 ± 5.12
4M HNO ₃	43.630 ± 2.85
Acetone	36.890 ± 2.15
Ethanol	62.300 ± 3.73

Table 4.1.14: Comparison of stirring time for desorption of Ni(II) using 30 mL 3M NaCl from sawdust

Stirring time (min)	% Recovery
30	96.180 ± 14.46
40	104.980 ± 11.20
50	85.400 ± 17.86

4.1.2.2.6. Application of the proposed method to real samples

The recovery of Ni(II) from mulberry sawdust after loading spiked taped water sample was checked and was found to be 97%. The method was successfully applied for preconcentration and determination of Ni(II) in the effluents of vegetable ghee industry and the result is given in table 4.1.15.

Table 4.1.15: Recovery test and determination of nickel in effluents of ghee industry using the proposed method

Sample	Ni(II) ($\mu\text{g mL}^{-1}$)		Recovery (%)
	Added	Found	
Ghee industry, Peshawar	0.0	0.094 ± 0.001	-
Tap water	1.0	0.970 ± 11.58	97.00

Part A2: Investigation of adsorption behavior of Ni(II) using modified carbon derived from Mulberry wood sawdust

4.2. Results and discussions

4.2.1. Characteristics of adsorbent

The IR spectrum of sawdust carbon (SDC) and chemically treated sawdust carbon (CSDC) were recorded and are shown in Fig. 4.2.1 and 4.2.2 respectively. A broad band in the region of high wave numbers (3359 cm^{-1}) shows the presence of -OH group on the surface of both types of carbons. A strong peak at 1574 cm^{-1} in CSDC and at 1578 cm^{-1} in SDC indicates the presence of stretching vibrations of $\text{C}-\text{C}$ of aromatic $\text{C}=\text{C}$ group, the peaks at 1211 cm^{-1} and 1031 cm^{-1} in CSDC and 1215 cm^{-1} in SDC are due to the presence of $\text{C}-\text{O}$ group.

The surface properties of both carbon samples were determined by N_2 adsorption method and the results are given in table 4.2.1. It can be seen from the table that surface area and average pore width of CSDC increased with chemical treatment.

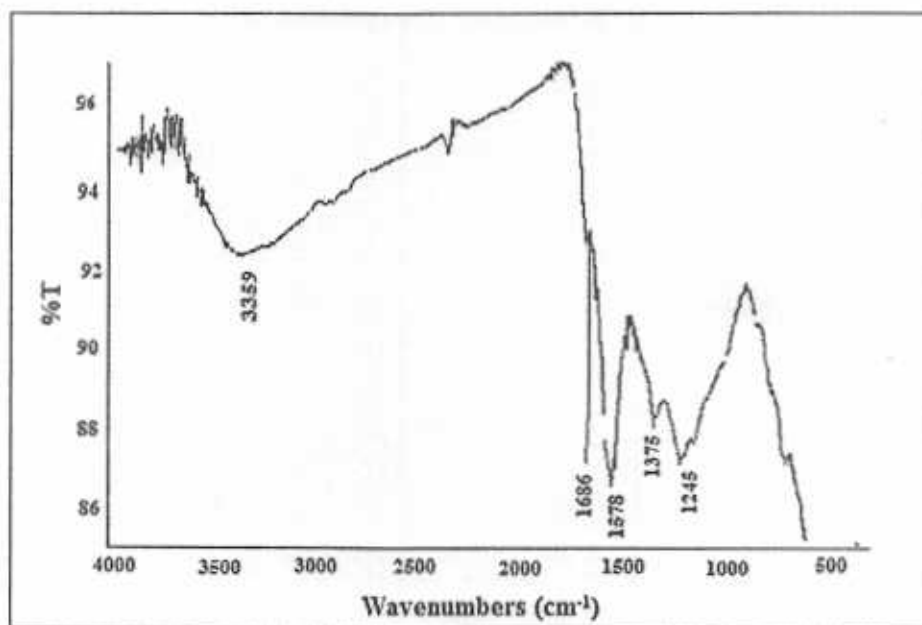


Figure 4.2.1: FT-IR spectrum of untreated SDC

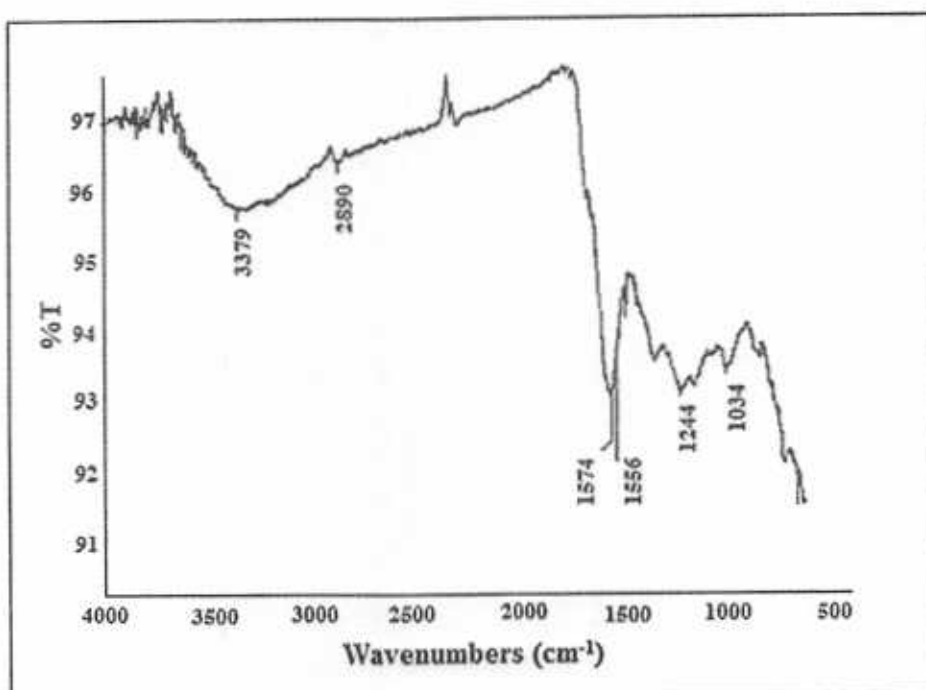


Figure 4.2.2: FT-IR spectrum of treated SDC

Table 4.2.1: Characterization of chemically treated and untreated sawdust carbon

Sorbent	Physical properties of SDC and CSDC			
	Surface area		DR method	
	BET ((m ² g ⁻¹)	Langmuir (m ² g ⁻¹)	Average pore width (Å)	Micropore volume (cm ³ g ⁻¹)
SDC	6.610	36.350	38.970	0.010
CSDC	11.940	66.540	55.080	0.020

The SEM image of CSDC and SDC were recorded and are shown in Fig. 4.2.3 and 4.2.4 respectively. The images show porous structure and the porous nature of adsorbent provide more adsorption sites from inner cavities to the sorbate. On carbonization of sawdust, the volatile components develop a high pressure which breaks down the cellular

structure and forms pores on the surface of carbon. With chemical treatment due to reaction more gases are released which produces hollows in the particles of carbon from which gas come out through small channels and forms hollow cylindrical shaped pores as shown in Fig. 4.2.4.

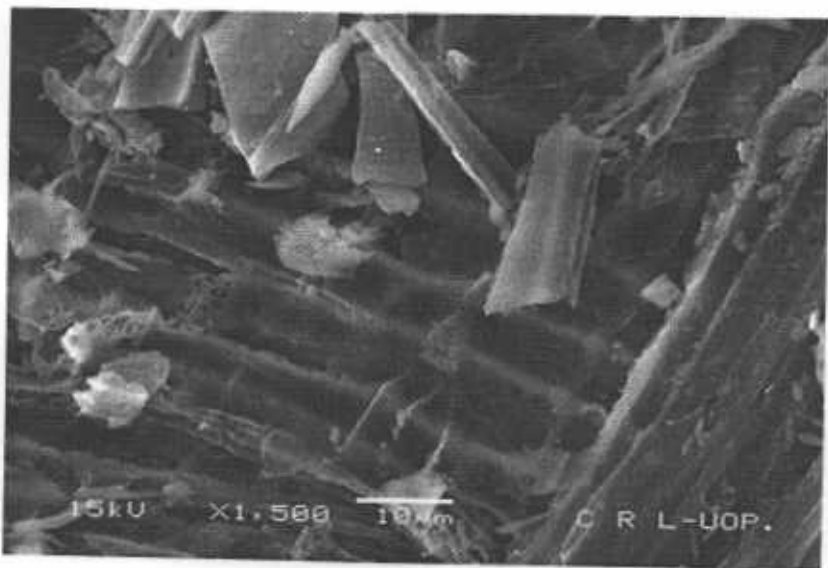


Figure 4.2.3: SEM of untreated SDC

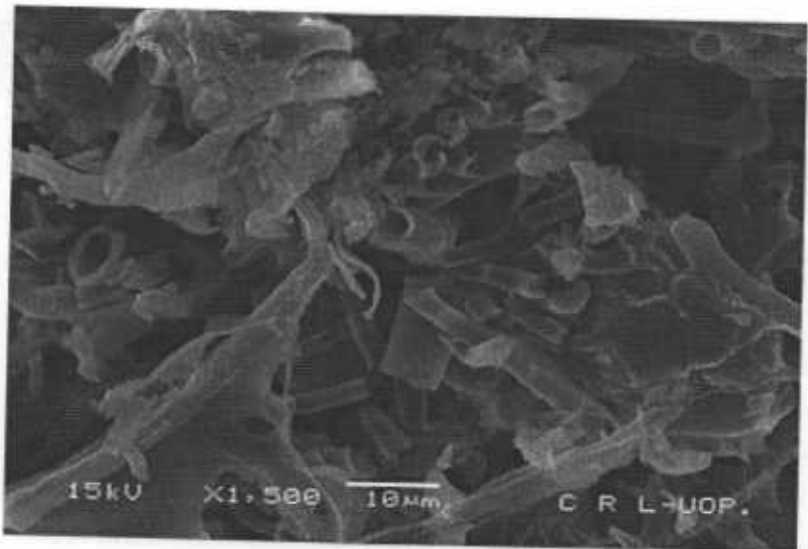


Figure 4.2.4: SEM of treated SDC

4.2.2. Activation of sawdust carbon (SDC)

In order to enhance the sorption ability of the SDC, various acids and bases were used. After treatment of SDC then the adsorption study of Ni(II) was carried out at neutral pH. The results are given in table 4.2.2 and shown in Fig. 4.2.5. The results reveal that NaOH treated sawdust carbon has the highest efficiency for the uptake of Ni(II) from aqueous solutions. Therefore 1.0 M NaOH has been selected for the chemical treatment of sawdust carbon.

Table 4.2.2: Comparison of different acids and bases used for activation of SDC

Activating agent (1.0 M)	% uptake of Ni(II)
NaOH	86.50
HCl	43.33
HNO ₃	38.20
H ₂ SO ₄	42.70
HCl/ NaOH	78.00
HNO ₃ / NaOH	79.50
H ₂ SO ₄ / NaOH	82.20

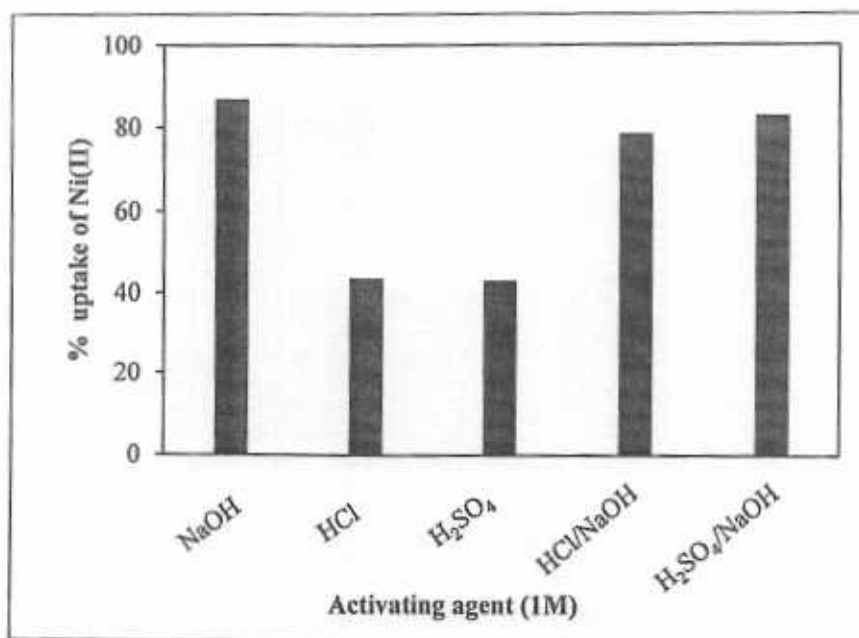


Figure 4.2.5: Comparison of different acids and bases used for activation of SDC (sorbent dose 0.1 g; contact time 70 min; volume of Ni(II) solution 20 mL; concentration of Ni(II) ion 5 $\mu\text{g mL}^{-1}$)

4.2.3. Sorption of Ni(II) using activated CSDC

4.2.3.1. Preliminary adsorption experiments

A known weight of washed (distilled water) and dried sawdust carbon was taken in Erlenmeyer flasks (250 mL) and added to it a known concentration of Ni(II) solution. The contents of the flasks were kept for 30 min at room temperature for complete equilibration. The biosorbent was filtered and the filtrates were transferred into 100 mL volumetric flasks and diluted upto mark. The concentrations of unadsorbed Ni(II) were determined using atomic absorption spectrophotometer. The results showed good percent uptake and ensure the use of sawdust carbon as a promising biosorbent for Ni(II) from aqueous solutions.

4.2.3.2. Optimization studies

The effects of various parameters like pH, contact time and initial metal concentration on sorption of Ni(II) using CSDC were investigated to obtain the optimum condition for maximum removal of Ni(II) from aqueous solutions. These are discussed below:

4.2.3.2.1. The effect of pH on sorption of Ni(II) using CSDC

The pH effect on the percent removal of Ni(II) from aqueous solution on CSDC was studied by varying pH of the solution in the range of pH 2.0-8.0. The results are given in table 4.2.3 and shown in Fig. 4.2.6. It was observed that the uptake of Ni(II) increased linearly with increasing pH from 2 to 5 and then up to pH 7 a small increase in uptake of Ni(II) was observed. At lower pH values the surface of carbon is mostly occupied by the hydronium ions (H_3O^+) which produces repulsion between the surface functional group and Ni(II). At relatively high pH more functional groups on the carbon surface become available for reaction with Ni(II). A decrease in uptake is observed above pH 7, which is due to the formation of Ni(II) hydroxides. Therefore pH 7 was chosen as optimum pH and further studies were carried out at pH 7.

Table 4.2.3: The effect of pH on sorption of Ni(II) using CSDC

pH	% uptake of Ni(II)
2	55.160
3	64.800
4	72.500
5	78.660
6	80.260
7	82.160
8	75.000

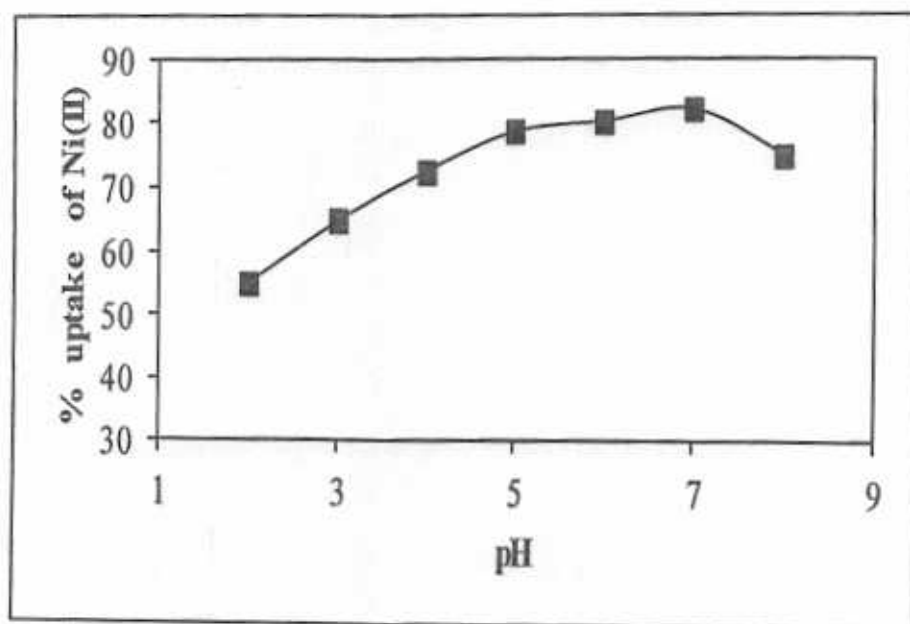


Figure 4.2.6: The effect of pH on sorption of Ni(II) using CSDC (sorbent dose 0.1g; contact time 70 min; volume of Ni(II) solution 20 mL; concentration of Ni(II) ion $5 \mu\text{g mL}^{-1}$)

4.2.3.2.2. The effect of contact time on sorption of Ni(II) using CSDC

The effect of contact time on the percent uptake of Ni(II) was studied from 30-90 min. The results are given in table 4.2.4 and shown in Fig. 4.2.7. It was observed that the uptake increases with increase in contact time from 30 min to 70 min and the equilibration established at 70 min with 83 % removal of Ni(II) from aqueous solution. Initially, the sorption sites are not saturated and available for metal binding. Therefore the sorption process is rapid and then become slow due to occupation of the sorption sites leading to slow or no adsorption beyond equilibrium time.

Table 4.2.4: The effect of contact time on sorption of Ni(II) using CSDC

Time (min)	% uptake of Ni(II)
30	74.330
40	75.330
50	77.160
60	80.860
70	81.860
80	82.200
90	82.360

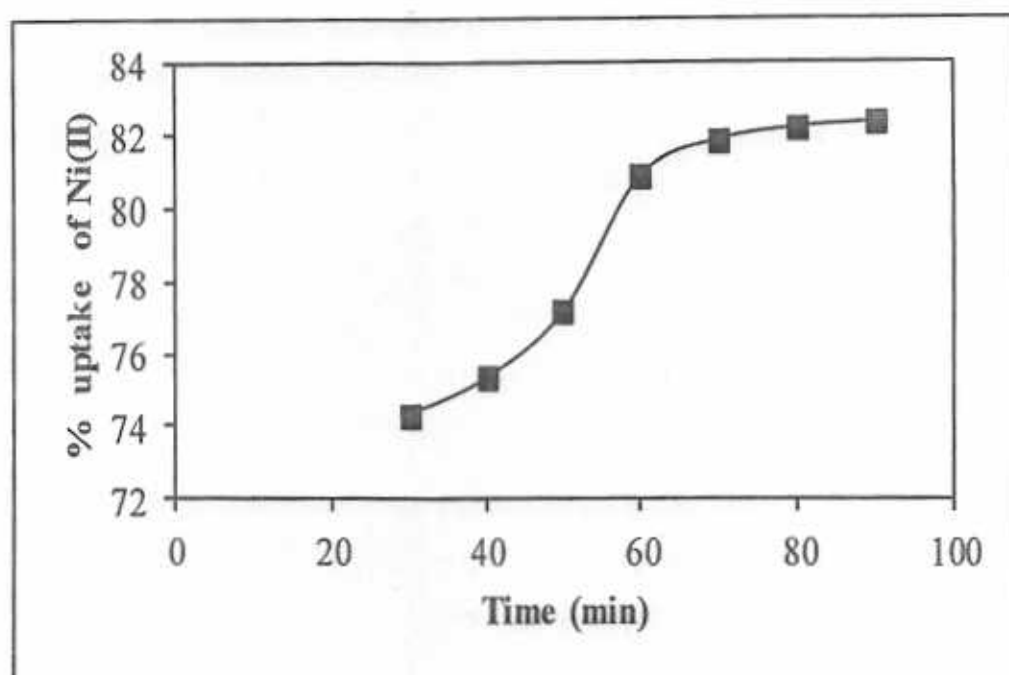


Figure 4.2.7: The effect of contact time on sorption of Ni(II) using CSDC (sorbent dose 0.1g; pH 7.0; volume of Ni(II) solution 20 mL; concentration of Ni(II) ion $5 \mu\text{g mL}^{-1}$)

4.2.3.2.3. Sorption isotherms of Ni(II) using CSDS

Both Freundlich and Langmuir sorption isotherms were applied to fit the data of sorption of Ni(II) on CSDC and the isotherms. The results are given in table 4.2.5 and 4.2.6 and shown in Fig. 4.2.8 and 4.2.9. The linear form of Freundlich and Langmuir equations were applied to evaluate the constant parameters and the values of these constants are given in table 4.2.7. The correlation coefficient value shows the fitness of the sorption data. The straight line (Fig. 4.2.8) shows that with increase in sorption capacity there is a decrease in average energy of sorption. The value of n is indication of favorable adsorption process. If this value is greater than unity then the process will be favorable. It was found that the value of n is greater than unity, suggesting that Ni(II) favorably sorbent by CSDC. Similarly, a linear graph is obtained by plotting C_e/q_e versus C_e (Fig. 4.2.9) and the constant parameters of the Langmuir model were calculated from the slope and intercept. These values are given in table 4.2.7. It was observed from table 4.2.7 that the maximum monolayer adsorption capacity (Q_0) is 100 mg g^{-1} . The data shows that both Freundlich and Langmuir isotherm models can be used to describe the sorption behavior of Ni(II) on CSDC.

Table 4.2.5: Freundlich isotherm for sorption of Ni(II) using CSDC

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)	Sorption capacity (q_e) (mg g^{-1})
5	0.263	0.014
25	1.380	0.072
250	38.250	0.847
300	54.500	0.982
750	139.250	2.443
1000	182.500	3.270

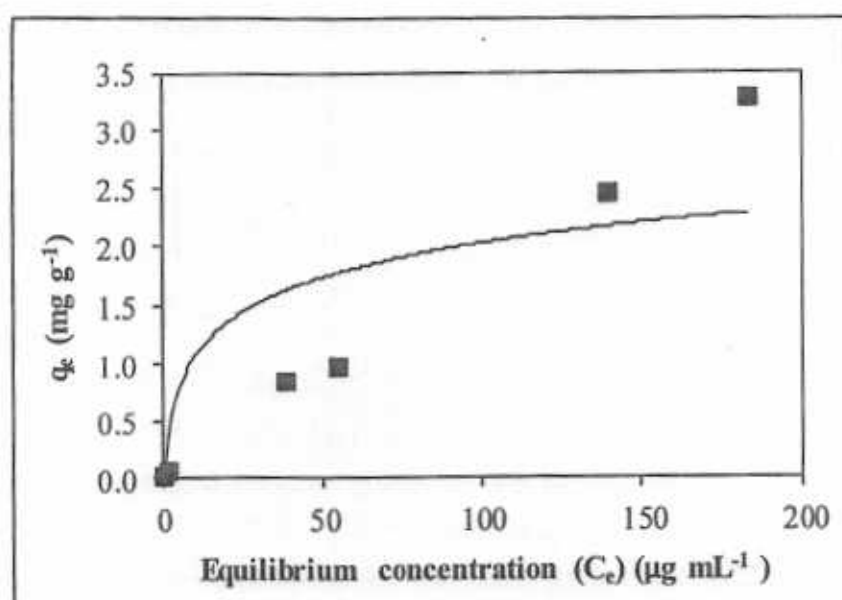


Figure 4.2.8: Freundlich isotherm for sorption of Ni(II) using CSDC (sorbent dose 0.1g; contact time 70 min; volume of Ni(II) solution 20 mL; pH 7.0; concentration of Ni(II) 5-1000 $\mu\text{g mL}^{-1}$)

Table 4.2.6: Langmuir sorption isotherm for sorption of Ni(II) using CSDC

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)	C_e/q_e
5	0.263	3.560×10^{-4}
25	1.380	3.810×10^{-4}
250	38.250	9.030×10^{-4}
300	54.500	1.109×10^{-3}

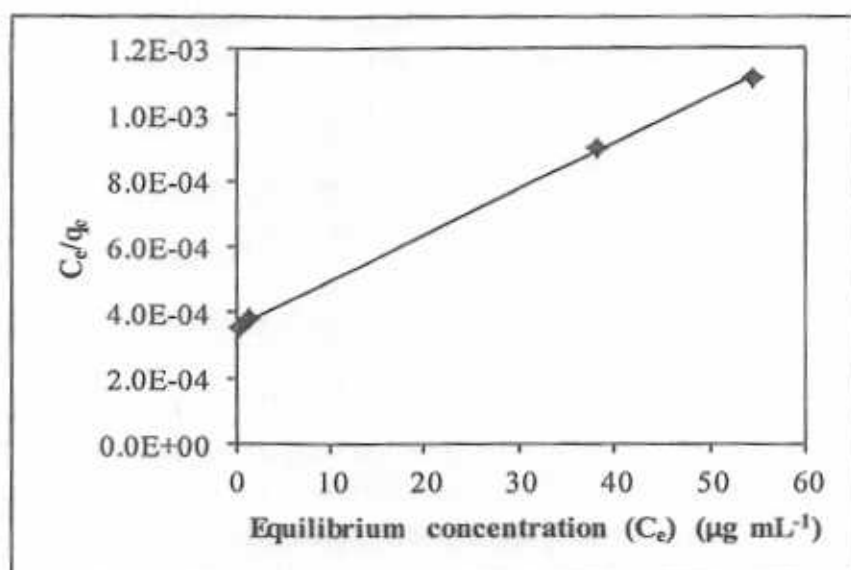


Figure 4.2.9: Langmuir sorption isotherm for sorption of Ni(II) using CSDC (sorbent dose 0.1g; contact time 70 min; volume of Ni(II) solution 20 mL; pH 7.0; concentration of Ni(II) 5-1000 $\mu\text{g mL}^{-1}$)

Table 4.2.7: Freundlich and Langmuir isotherm constants for the sorption of Ni(II) on CSDC

Parameter	Value
Freundlich isotherm	
$K_F (\text{mg g}^{-1})$	0.047
n	1.254
$1/n$	0.797
R^2	0.9960
Langmuir isotherm	
$a_L (\text{L mg}^{-1})$	0.025
$K_L (\text{L g}^{-1})$	2.500
$Q_o (\text{mg g}^{-1})$	100.000
R^2	0.9994

4.2.3.2.4. Kinetics of sorption of Ni(II) using CSDC

The sorption kinetics for the adsorption of Ni(II) on CSDC was investigated using Lagergren pseudo first order, pseudo second order, intraparticle diffusion and Elovich models.

For pseudo first-order and pseudo second-order kinetics of Ni(II) adsorption on CSDC plot of $\log (q_e - q_t)$ versus time (t) and t/q_t versus time (t) were plotted. The results are given in table 4.2.8 and 4.2.9 shown in Fig. 4.2.10 and 4.2.11 respectively. The values of rate constants of these models were calculated from the slope and intercept and are given in table 4.2.12. It was found that the correlation coefficient value ($R^2 = 0.9980$) of pseudo second order equation is greater than pseudo first-order, suggests that it best fitted into kinetic data as compared to the pseudo first order equation ($R^2 = 0.9270$).

Table 4.2.8: Pseudo-first-order kinetics of Ni(II) sorption using CSDC

Time (min)	$\log (q_e - q_t)$
30	0.205
40	0.148
50	0.017
60	-0.522
70	-1.000
80	-1.477

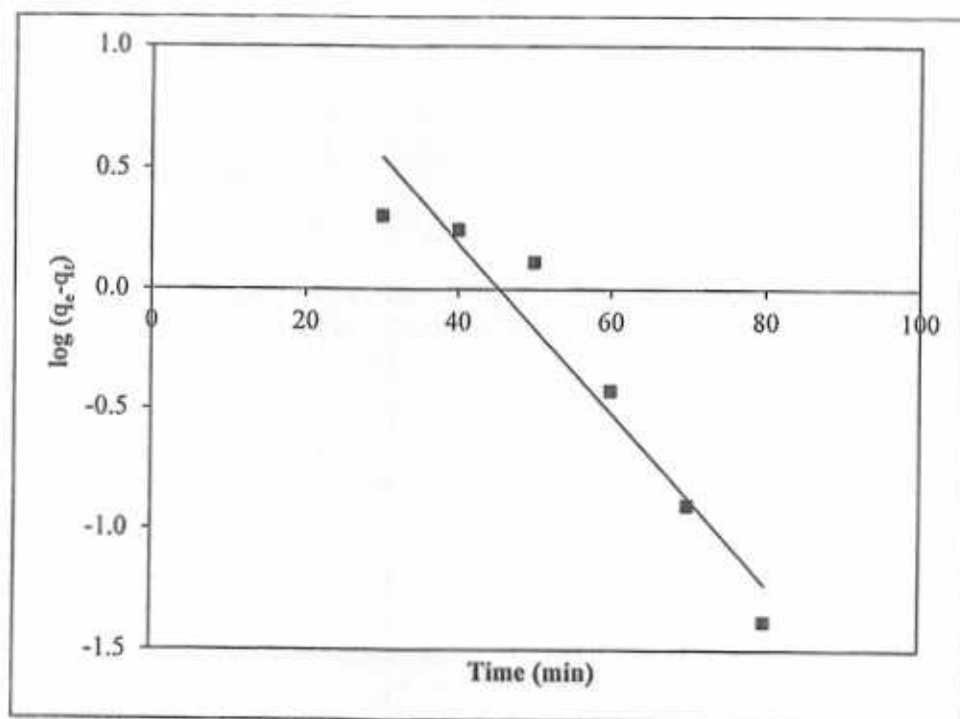


Figure 4.2.10: Pseudo-first-order kinetics of Ni(II) sorption using CSDC (sorbent dose 0.1g; initial concentration of Ni(II) 5 $\mu\text{g mL}^{-1}$; volume of Ni(II) solution 20 mL; pH 7.0)

Table 4.2.9: Pseudo-second-order kinetics of Ni(II) sorption using CSDC

Time (min)	t/q_t (min g mg ⁻¹)
30	2.017
40	2.654
50	3.239
60	3.709
70	4.275
80	4.866

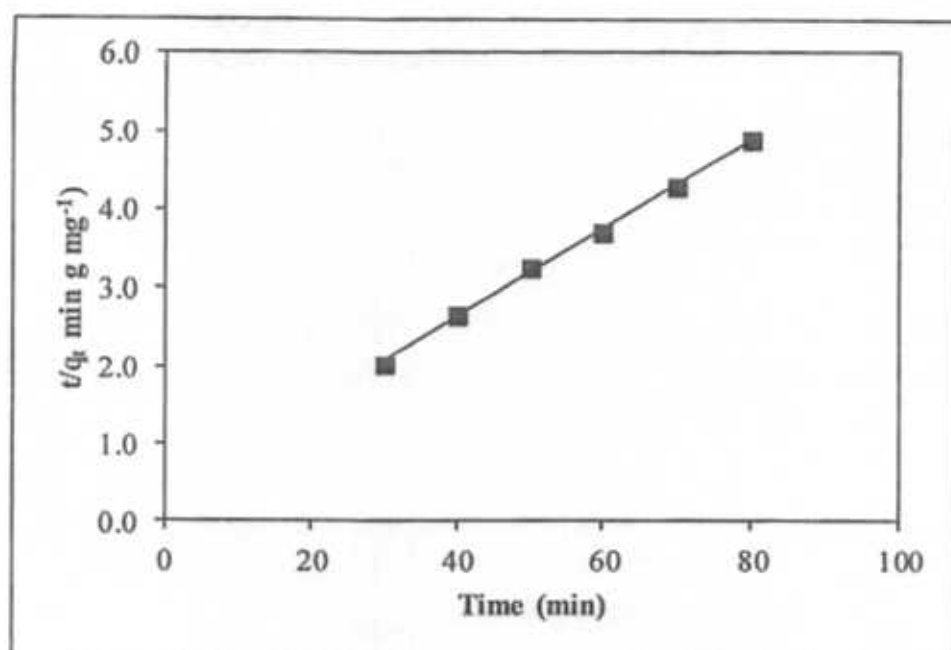


Figure 4.2.11: Pseudo-second-order kinetics of Ni(II) sorption using CSDC (sorbent dose 0.1g; Initial concentration of Ni(II) 5 $\mu\text{g mL}^{-1}$; volume of Ni(II) solution 20 mL; pH 7.0)

The kinetic data were also fitted in intraparticle diffusion model as in the previous case. The value of K_{int} ($\text{mg g}^{-1} \text{sec}^{1/2}$) was calculated from slope of the liner plot of q_t versus $t^{1/2}$. The results are given in table 4.2.10 and shown in Fig. 4.2.12. If the uptake of Ni(II) on CSDC is due to intraparticle diffusion then the plot should be linear and pass through the origin but Fig. 4.2.12 shows that line is not passing through the origin indicating that different kinetic processes are involved in controlling the uptake of Ni(II) on CSDC.

The Elovich coefficients were calculated from the slope and intercept of the linear plot of q_t versus $\ln t$. The results are given in table 4.2.11 and shown in Fig. 4.2.13. The experimental data fitted well to the pseudo-second- order kinetic model with a high R^2 value (> 0.99) and this is also confirmed by the closeness of experimental q_e value with calculated one.

Table 4.2.10: Intraparticle diffusion model of Ni(II) uptake using CSDC

$t^{1/2}$ (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)
5.477	14.866
6.324	15.066
7.071	15.433
7.745	16.173
8.366	16.373
8.944	16.440
9.486	16.473

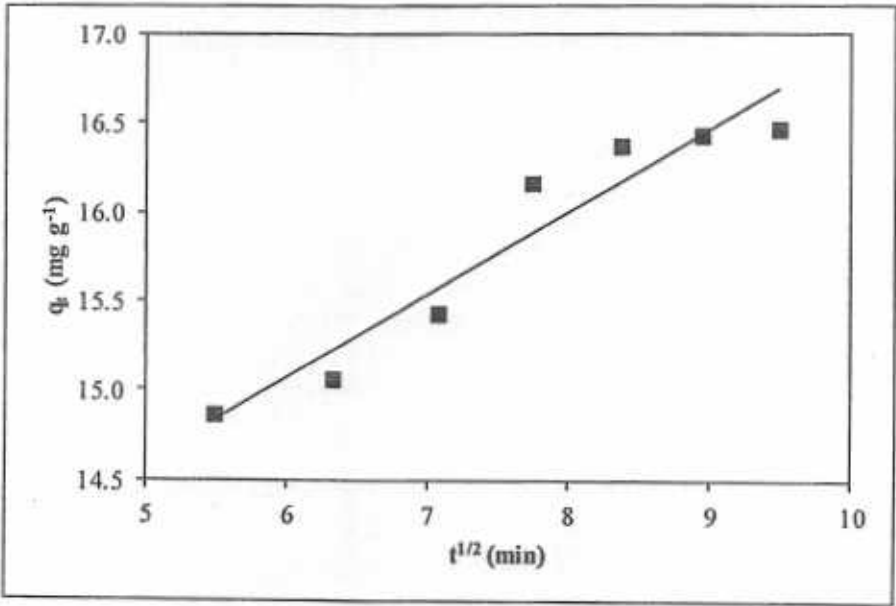


Figure 4.2.12: Intraparticle diffusion model of Ni(II) uptake using CSDC (sorbent dose 0.1g; initial concentration of Ni(II) ion 5 $\mu\text{g mL}^{-1}$ volume of Ni(II) ion solution 20 mL; pH 7.0)

Table 4.2.11: Elovich model of Ni(II) uptake using CSDC

Int (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)
3.401	14.866
3.688	15.066
3.912	15.433
4.094	16.173
4.248	16.373
4.382	16.440
4.499	16.473

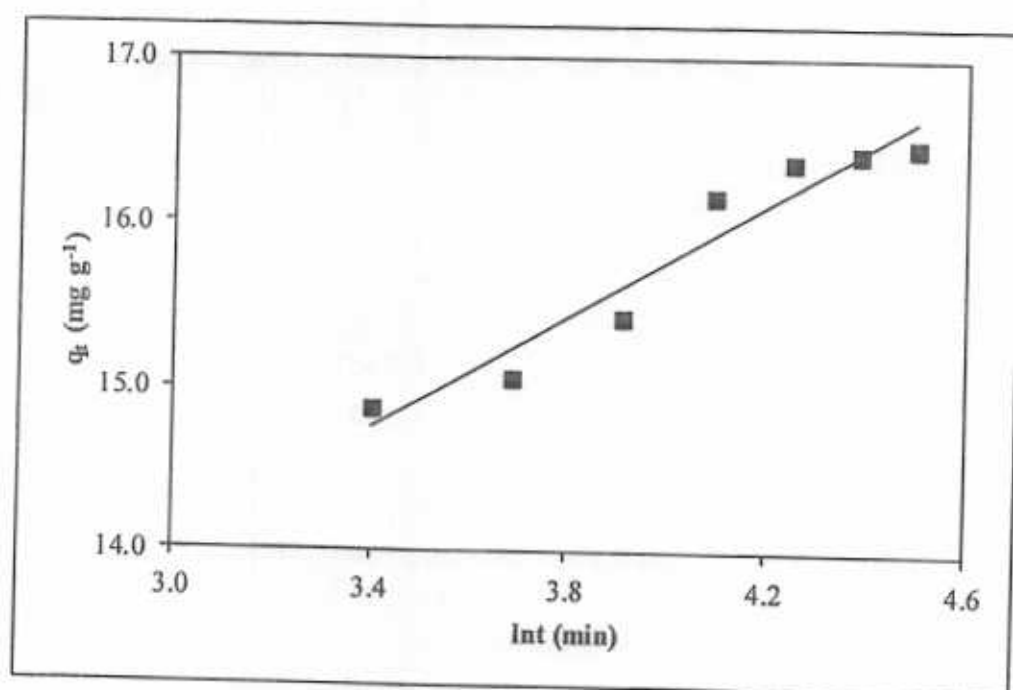


Figure 4.2.13: Elovich model of Ni(II) uptake using CSDC (sorbent dose 0.1g; initial concentration of Ni(II) 5 $\mu\text{g mL}^{-1}$; volume of Ni(II) solution 20 mL; pH 7.0)

Table 4.2.12: Kinetic parameters of Ni(II) sorption on CSD

Model	Parameters	Values
Pseudo-first order kinetics	q_e (mg g ⁻¹) (exp)	16.470
	k_1 (min ⁻¹)	0.081
	q_e (mg g ⁻¹)	40.450
	R^2	0.9270
Pseudo-second order kinetics		
	k_2 (g mg ⁻¹ min ⁻¹)	0.006
	q_e (mg g ⁻¹)	22.720
	R^2	0.9980
Intraparticle diffusion model		
	K_{int} (mg g ⁻¹ sec ^{1/2})	0.648
	C	12.302
	R^2	0.9430
Elovich model		
	α (mg g ⁻¹ min ⁻¹)	237.460
	β (g mg ⁻¹)	0.437
	R^2	0.9350

Part A3: Investigation of adsorption behavior of Ni(II) using waste tea leaves

4.3. Results and discussions

4.3.1. Characterization of waste tea leaves

In order to identify the functional groups of the treated and untreated waste tea leaves, FT-IR techniques was recorded in the frequency range from 600 to 4000 cm^{-1} and are shown in Fig. 4.3.1 and 4.3.2 respectively. The presence of peaks in all cases at 2924, 1734, 1610 and 1558 cm^{-1} in waste tea leaves confirm the presence of C - H saturated, C = O, C = N and C = C respectively. By comparing the IR spectra of all three materials, the functional group intensity was the same in water washed and formaldehyde (0.4%) treated. For further analysis formaldehyde treated waste tea leaves were used to avoid the interferences from color of tea extract.

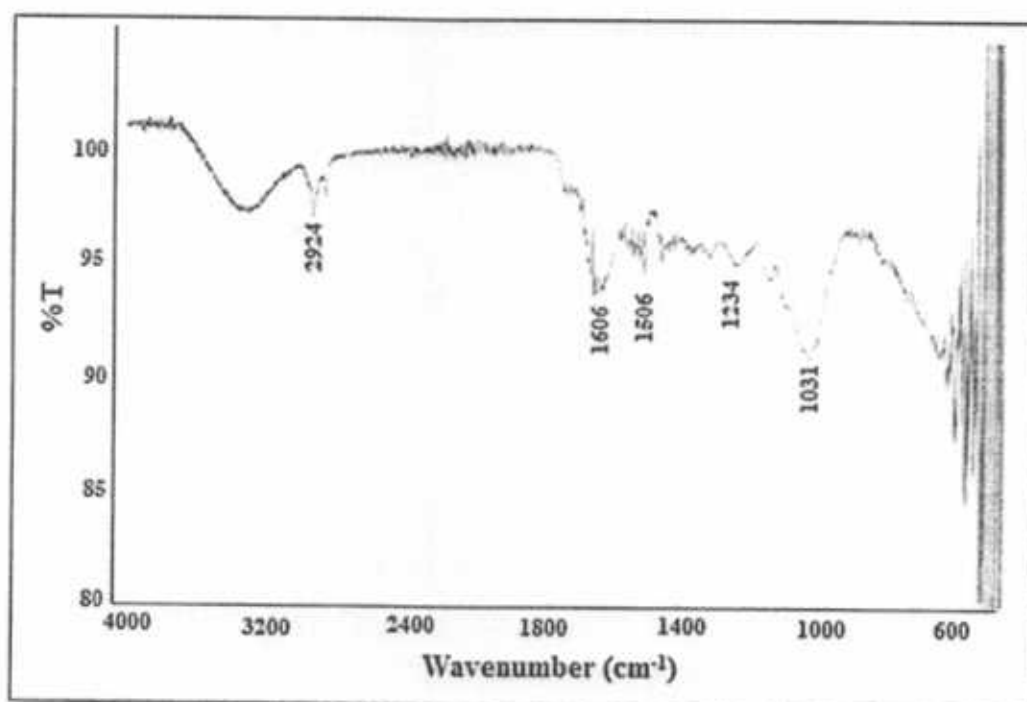


Figure 4.3.1: FT-IR spectrum of washed (distilled water) waste tea leaves

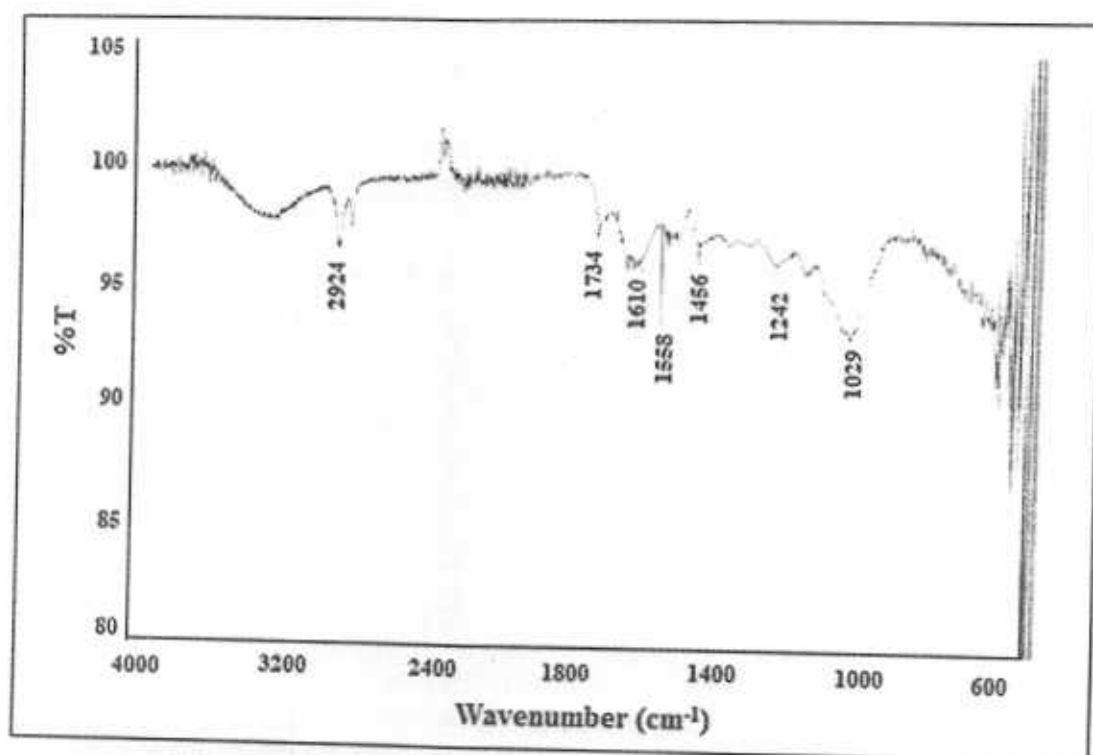


Figure 4.3.2: FT-IR spectrum of formaldehyde (0.4%) treated waste tea leaves

4.3.2. Sorption studies of Ni(II) using waste tea leaves

4.3.2.1. Preliminary adsorption experiments

A known weight of washed (distilled water) and dried waste tea leaves were taken in Erlenmeyer flasks (250 mL) and added to it a known concentration of Ni(II) solution. The contents of the flasks were kept for 30 min at room temperature for complete equilibration. The biosorbent was filtered and the filtrates were transferred into 100 mL volumetric flasks and diluted upto mark. The concentrations of unadsorbed Ni(II) were determined using atomic absorption spectrophotometer. The results showed good percent uptake and ensure the use of waste tea leaves as a promising biosorbent for Ni(II) from aqueous solutions.

4.3.2.2. Optimization studies

The sorption process of Ni(II) using waste tea leaves may be affected by various variables such as pH, contact time, sorbent dose, initial metal concentration and temperature. These are discussed below:

4.3.2.2.1. The effect of pH on sorption of Ni(II) using waste tea leaves

The effect of the solution pH on the sorption of Ni(II) on waste tea leaves was investigated. The pH was varied from 3.0 to 8.0. The results are given in table 4.3.1 and shown in Fig. 4.3.3. It can be observed from the plot of pH versus percent uptake that adsorption increases with increase in pH of the solution. The % uptake was found to increase from 11.2 % to 70.2 % with increase in pH from 3 to 7. At lower pH, the % uptake is lower due to H^+ ion present in the solutions, which compete with Ni(II) for active sites on the sorbent causing a decrease in the % uptake of Ni(II). At high pH the surface of tea leaves become negatively charged which leads to high uptake of Ni(II) through electrostatic attraction. It was observed that the sorption increased up to pH 7, where maximum sorption was achieved. Decrease in adsorption was observed beyond pH 7 due to formation of metal hydroxide. Therefore pH 7 was selected as optimum pH for adsorption of Ni(II) on waste tea leaves.

Table 4.3.1: The effect of pH on sorption of Ni(II) using waste tea leaves

pH	% uptake of Ni(II)
3	11.200
4	17.200
5	49.933
6	62.866
7	70.600
8	52.933

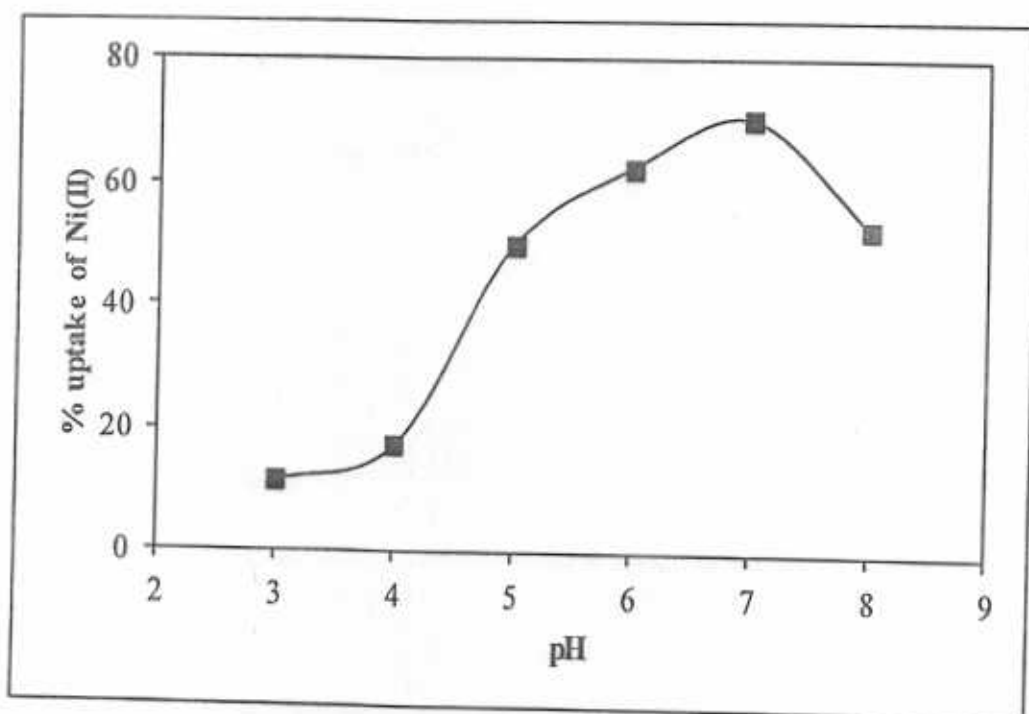


Figure 4.3.3: The effect of pH on sorption of Ni(II) using waste tea leaves (initial concentration of Ni(II) $5 \mu\text{g mL}^{-1}$; pH 3.0-8.0; sorbent dose 0.05 g; contact time 30 min; room temperature)

4.3.2.2.2. The effect of contact time on sorption of Ni(II) using waste tea leaves

The effect of contact time on the sorption of Ni(II) on waste tea leaves with shaking and without shaking was investigated. The contact time was varied from 30 to 100 min. The results are given in table 4.3.2 and shown in Fig 4.3.4. It can be seen from the figure that a steady increase in % uptake was observed with increase in contact time. Further it was noticed that in case when shaking was used greater uptake was observed for the same equilibration time in contrast to the case with no shaking. At 90 min contact time 82% uptake for Ni(II) was observed with shaking in contrast to 72% uptake without shaking.

Table 4.3.2: The effect of contact time on sorption of Ni(II) using waste tea leaves

Time (min)	% uptake of Ni(II)	
	without shaking	with shaking
30	50.533	60.866
40	55.266	64.200
50	58.933	67.866
60	62.400	71.733
70	65.200	74.466
80	68.466	78.533
90	72.066	80.866
100	73.266	82.133

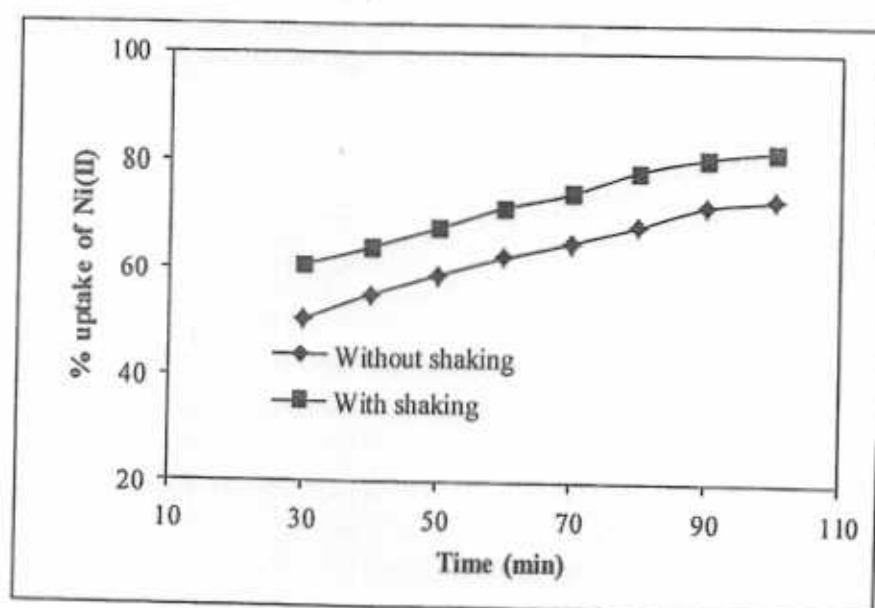


Figure 4.3.4: The effect of contact time on sorption of Ni(II) using waste tea leaves (initial concentration of Ni(II) $5 \mu\text{g mL}^{-1}$; pH 7.0; sorbent dose 0.05 g; contact time 30-100 min; room temperature)

4.3.2.2.3. The effect of sorbent dose on sorption of Ni(II) using waste tea leaves

The sorbent dose is an important factor which affects the sorption process. Generally, as the sorbent dose increases the sorption also increases due to availability of the sorption sites for metal ions binding. Therefore the effect of sorbent dose on sorption of Ni(II) was studied and the amount of sorbent was varied from 0.03 to 0.15 g. The results are given in table 4.3.3 and shown in Fig. 4.3.5. Initially, the sorption sites are occupied by available metal ions and no further sorption occur due to non-availability of sorption sites. As the sorbent dose increases from 0.03 to 0.15 g, the sites for sorption also increase and 100% uptake was achieved at 0.13 g of sorbent. Therefore further studies were carried out at this optimum sorbent dose.

Table 4.3.3: The effect of sorbent dose on sorption of Ni(II) using waste tea leaves

Sorbent dose (g)	% uptake of Ni(II)
0.03	93.600
0.05	95.266
0.07	97.533
0.09	98.600
0.11	99.400
0.13	100.000
0.15	100.000

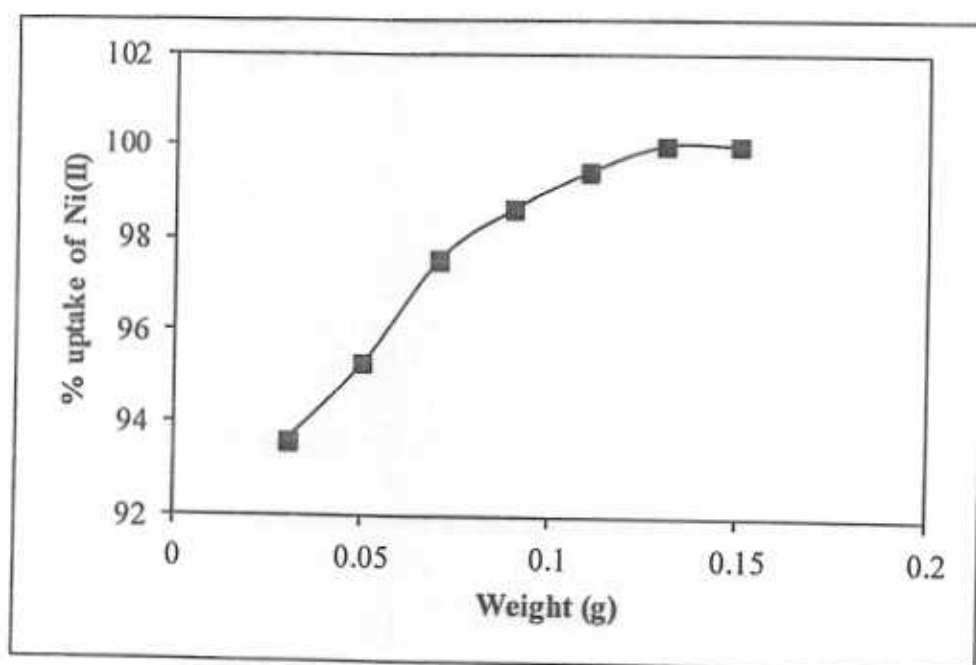


Figure 4.3.5: The effect of sorbent dose on sorption of Ni(II) using waste tea leaves (initial concentration of Ni(II) $5 \mu\text{g mL}^{-1}$; pH 7.0; sorbent dose 0.03-0.15 g; contact time 30 min; room temperature)

4.3.2.2.4. Sorption isotherms of Ni(II) using waste tea leaves

The sorption of Ni(II) on waste tea leaves was studied by two most commonly used isotherms; the Freundlich and Langmuir isotherm. The results are given in table 4.3.4 and 4.3.5 and shown in Fig. 4.3.6 and 4.3.7 respectively. The constant parameters of these isotherms were calculated from slope and intercept of the linear form of these equations and are given in table 4.3.6. The n value of the Freundlich model shows that Ni(II) is not sorbed favorably on waste tea leaves because it is less than unity. It may be concluded from these results that the sorption data of Ni(II) on waste tea leaves shows bit fit into Langmuir isotherm model due to high correlation coefficient ($R^2 = 0.9405$).

Table 4.3.4: Freundlich isotherm for sorption of Ni(II) using waste tea leaves

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)	Sorption capacity (q_e) (mg g^{-1})
1	0.053	0.463
20	0.360	16.400
50	1.338	36.613
100	3.815	61.843
150	6.186	88.140

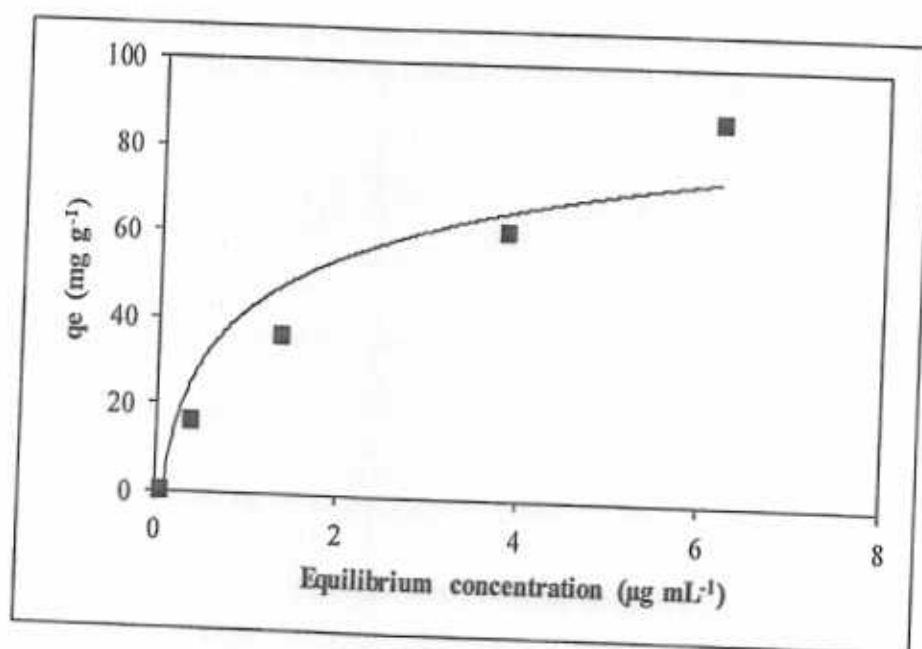


Figure 4.3.6: Freundlich isotherm for sorption of Ni(II) using waste tea leaves (initial concentration of Ni(II) 1-150 $\mu\text{g mL}^{-1}$; pH 7.0; sorbent dose 0.13 g; contact time 90 min; room temperature)

Table 4.3.5: Langmuir isotherm for sorption of Ni(II) using waste tea leaves

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)	C_e/q_e
20	0.360	2.195×10^{-2}
50	1.338	3.656×10^{-2}
100	3.815	6.169×10^{-2}
150	6.186	7.018×10^{-2}

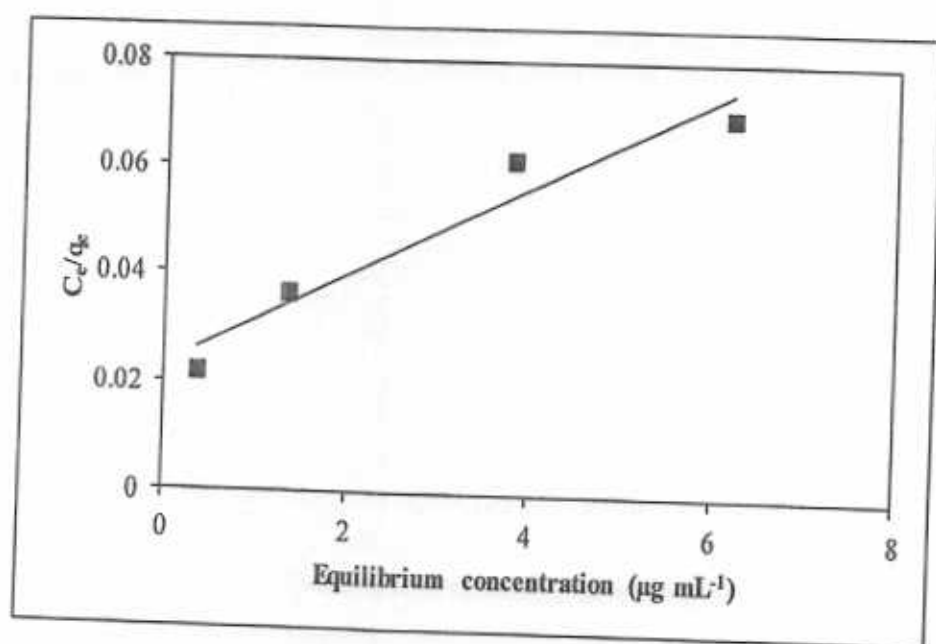


Figure 4.3.7: Langmuir isotherm for sorption of Ni(II) using waste tea leaves (initial concentration of Ni(II) 1-150 $\mu\text{g mL}^{-1}$; pH 7.0; sorbent dose 0.13 g; contact time 90 min; room temperature)

Table 4.3.6: Freundlich and Langmuir isotherm constants for the sorption of Ni(II) on waste tea leaves

Parameter	Value
Freundlich isotherm	
$K_F (\text{mg g}^{-1})$	19.220
n	0.946
$1/n$	1.056
R^2	0.9263
Langmuir isotherm	
$a_L (\text{L mg}^{-1})$	0.354
$K_L (\text{L g}^{-1})$	42.730
$Q_o (\text{mg g}^{-1})$	120.500
R^2	0.9405

4.3.2.2.5. Kinetics of sorption of Ni(II) on waste tea leaves

The rate constant for pseudo-first-order kinetics can be determined from slope of the linear plot of time against $\log (q_e - q_t)$ and the second-order rate constant $K_2 (\text{g mg}^{-1} \text{min}^{-1})$ can be calculated from the intercept of the plot time (t) against t/q_t . The results are given in table 4.3.7 and 4.3.8 and shown in Fig. 4.3.8 and 4.3.9 respectively. It was observed from the table 4.3.11 that the correlation value ($R^2 = 0.9946$) of pseudo-second-order model is greater than the pseudo-first-order model ($R^2 = 0.9856$). This suggests that the adsorption might be controlled by pseudo-second-order model.

Similarly, the kinetic data were also fitted in intraparticle diffusion model as in the previous case. The value of $K_{int} (\text{mg g}^{-1} \text{sec}^{1/2})$ was calculated from slope of the liner plot of q_t versus $t^{1/2}$. The results are given in table 4.3.9 and shown in Fig. 4.3.10. If the uptake of Ni(II) on waste tea leaves is due to intraparticle diffusion then the plot should be linear and pass through the origin but Fig. 4.3.10 shows that line is not passing

through the origin indicating that different kinetic processes are involved in controlling the uptake of Ni(II) on waste tea leaves.

The Elovich coefficients were calculated from the slope and intercept of the linear plot of q_t versus $\ln t$. The results are given in table 4.3.10 as shown in Fig. 4.3.11.

Table 4.3.7: Pseudo-first-order kinetics of Ni(II) uptake using waste tea leaves

Time (min)	$\log (q_e - q_t)$
30	0.327
40	0.253
50	0.154
60	0.017
70	-0.115

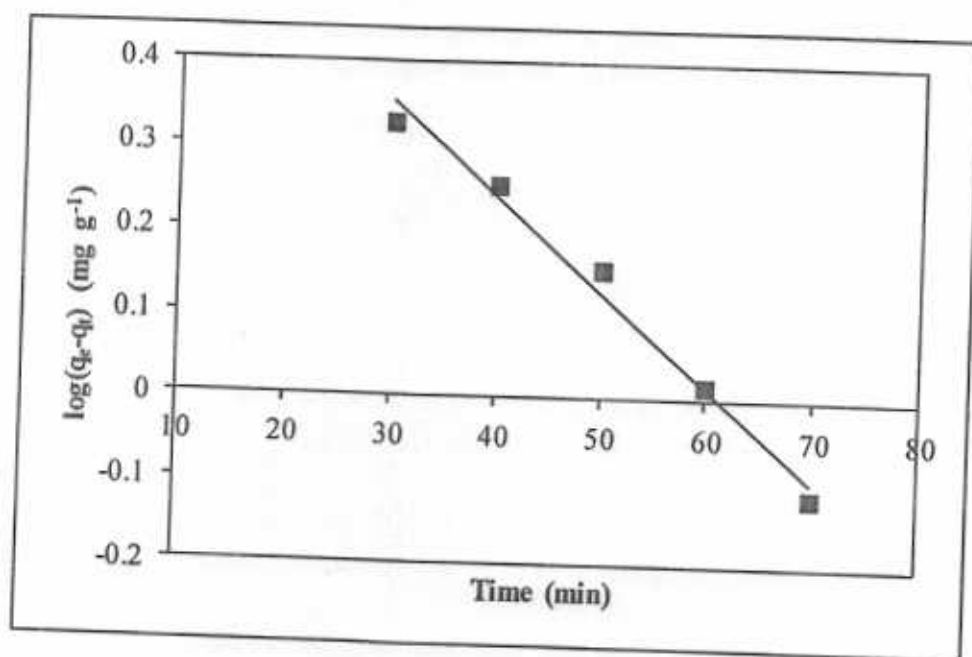


Figure 4.3.8: Pseudo-first-order kinetics of Ni(II) uptake using waste tea leaves (sorbent dose 0.13 g; initial concentration of Ni(II) $5 \mu\text{g mL}^{-1}$ volume of Ni(II) solution 10 mL; pH 7.0)

Table 4.3.8: Pseudo-second-order kinetics of Ni(II) uptake using waste tea leaves

Time (min)	t/q_t (min mg g ⁻¹)
30	4.928
40	6.230
50	7.367
60	8.364
70	9.400
80	10.186
90	11.129

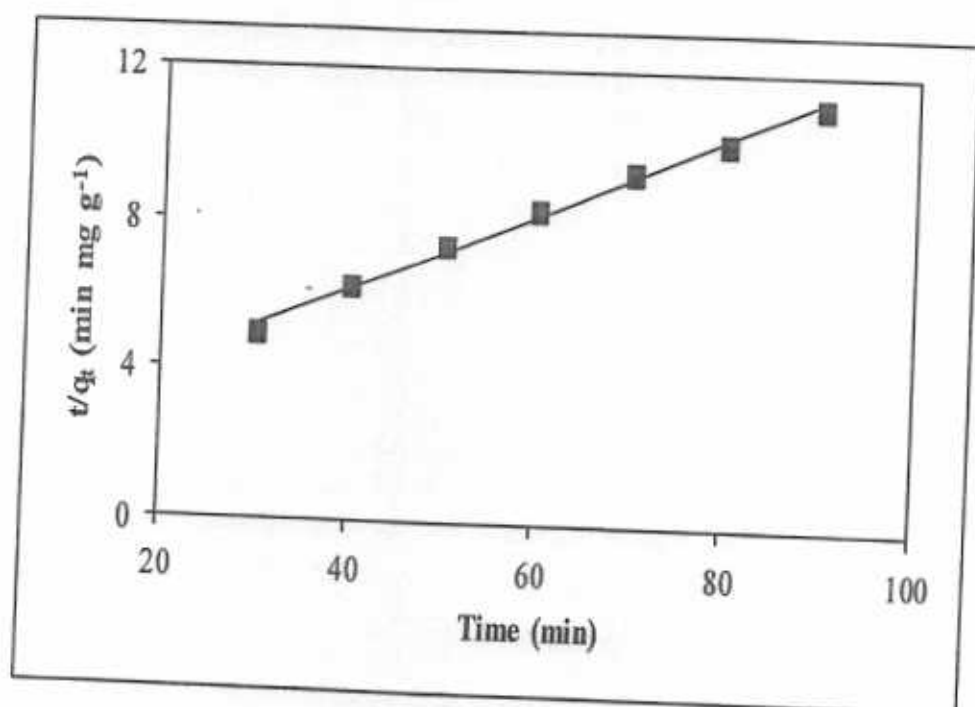


Figure 4.3.9: Pseudo-second-order kinetics of Ni(II) uptake using waste tea leaves (sorbent dose 0.13 g; Initial concentration of Ni(II) 5 µg mL⁻¹; volume of Ni(II) solution 10 mL; pH 7.0)

Table 4.3.9: Intraparticle diffusion model of Ni(II) uptake using waste tea leaves

$t^{1/2}$ (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)
5.477	4.928
6.324	6.230
7.071	7.367
7.745	8.364
8.366	9.400
8.944	10.186
9.486	11.129

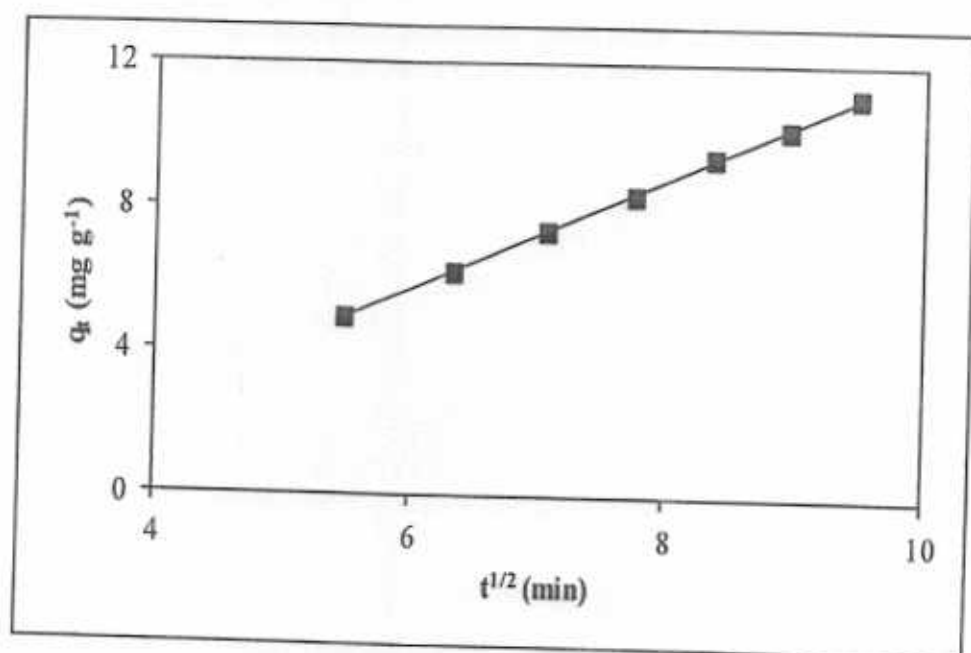


Figure 4.3.10: Intraparticle diffusion model of Ni(II) uptake using waste tea leaves (sorbent dose 0.13 g; Initial concentration of Ni(II) 5 μ g mL⁻¹; volume of Ni(II) solution 10 mL; pH 7.0)

Table 4.3.10: Elovich model of Ni(II) uptake using waste tea leaves

Int (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)
3.401	4.928
3.688	6.230
3.912	7.367
4.094	8.364
4.248	9.400
4.382	10.186
4.499	11.129

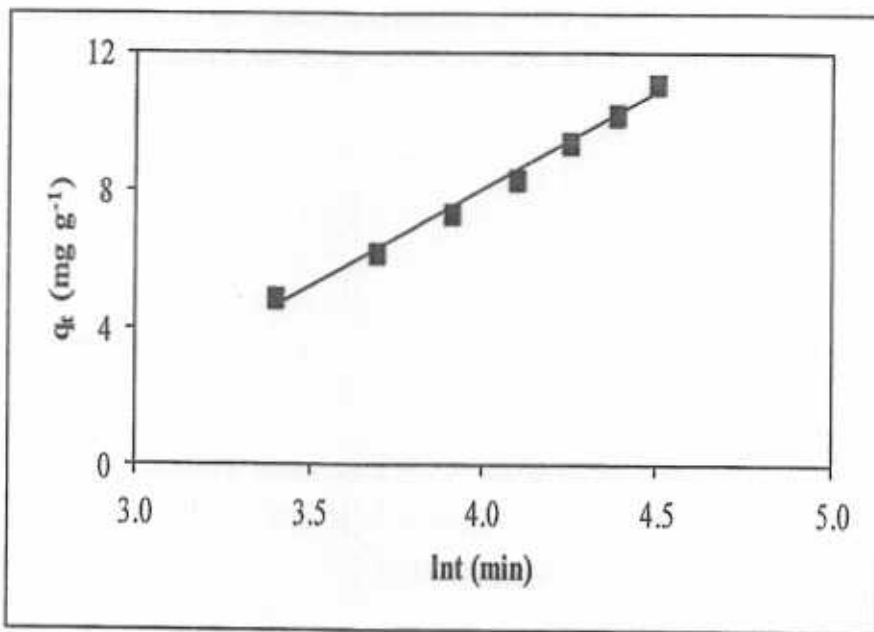


Figure 4.3.11: Elovich model of Ni(II) uptake using waste tea leaves (sorbent dose 0.13 g; initial concentration of Ni(II) 5 $\mu\text{g mL}^{-1}$; volume of Ni(II) solution 10 mL; pH 7.0)

Table 4.3.11: Kinetic parameters of Ni(II) sorption on waste tea leaves

Model	Parameters	Values
Pseudo-first order kinetics	q_e (mg g ⁻¹) (exp)	8.213
	k_1 (min ⁻¹)	0.026
	q_e (mg g ⁻¹)	4.880
	R^2	0.9856
Pseudo-second order kinetics		
	k_2 (g mg ⁻¹ min ⁻¹)	0.005
	q_e (mg g ⁻¹)	9.800
	R^2	0.9946
Intraparticle diffusion model		
	K_{int} (mg g ⁻¹ sec ^{1/2})	1.537
	C	-3.499
	R^2	0.9997
Elovich model		
	α (mg g ⁻¹ min ⁻¹)	4.390×10^{-35}
	β (g mg ⁻¹)	0.178
	R^2	0.9924

4.3.2.2.6. Thermodynamics of sorption of Ni(II) on waste tea leaves

The study of thermodynamic assumes that the energy in an isolated system cannot be lost or gained when the entropy change is the driving force. Thermodynamic parameters were calculated for determination of sorption process, to see if the sorption will occur spontaneously or not. The change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of sorption process was calculated by following equations:

$$K_D = \frac{q_e}{C_e} \quad (1)$$

$$\Delta G^\circ = -RT \ln K_D \quad (2)$$

$$\ln K_D = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

Where K_D is the distribution constant, q_e is the amount of metal ion sorbed (mg g^{-1}) at equilibrium and C_e is the equilibrium concentration ($\mu\text{g mL}^{-1}$).

The values of $\ln K_D$ were plotted against $1/T$. The results are given in table 4.3.12 and shown in Fig. 4.3.12. The values of K_D , ΔG° , ΔH° and ΔS° for sorption of Ni(II) on waste tea leaves were calculated using equation 1, 2 and 3 and are given in table 4.3.13. The negative value obtained for ΔH° indicated an exothermic sorption process. The positive value of ΔS° showed the affinity of waste tea leaves for Ni(II) whereas the negative value of ΔG° showed that the sorption process is spontaneous at the studied temperature range.

Table 4.3.12: Van't Hoff equation for estimation of thermodynamic parameters for Ni(II) sorption on waste tea leaves

$1/T \text{ (K}^{-1}\text{)}$	$\ln K_D$
3.195×10^{-3}	11.705
3.096×10^{-3}	11.587
3.003×10^{-3}	11.503
2.915×10^{-3}	11.045
2.833×10^{-3}	10.861
2.755×10^{-3}	10.461

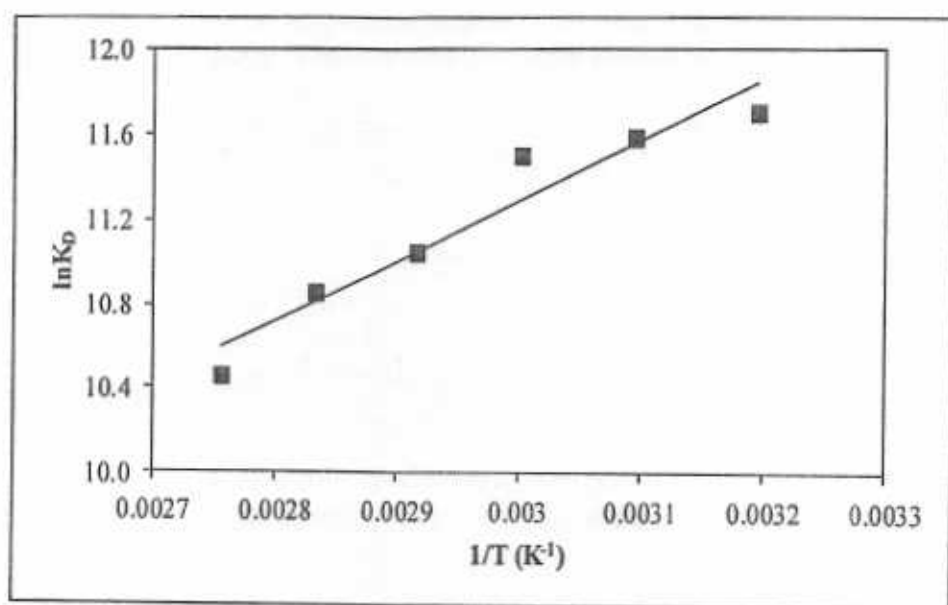


Figure 4.3.12: Plot of $\ln K_D$ versus $1/T$ for estimation of thermodynamic parameters for Ni(II) sorption on waste tea leaves (Initial concentration of Ni(II) $5 \mu\text{g mL}^{-1}$; pH 7.0; sorbent dose 0.13 g; volume of Ni(II) solution 10 mL)

Table 4.3.13: Thermodynamic parameters for the sorption of Ni(II) on waste tea leaves

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ K ⁻¹ mol ⁻¹)
313	-30.440	-23.680	0.022
323	-31.090	-	-
333	-31.830	-	-
343	-31.480	-	-
353	-31.870	-	-
363	-31.560	-	-

Part B: Investigation of adsorption behavior of Pb(II) using acid treated orange peels and carbonized orange peels

4.4. Results and discussions

4.4.1. Characteristics of acid treated orange peels (AOP) and carbonized orange peels (COP)

FT-IR spectra were recorded in order to identify the functional groups on the surface of AOP and COP. The results are given in Fig. 4.4.1 to 4.4.5. Fig 4.4.1 is the FT-IR spectrum of untreated orange peels which shows the presence of -OH, C - H stretching, COOH and C = C at 3327, 2810, 1645 and 1600 cm^{-1} respectively. The chemical treatment of orange peels made these groups more prominent as shown from the Fig. 4.4.2. The intensity of these groups become less after sorption Pb(II) on AOP as obvious from the Fig. 4.4.3, suggesting that these groups are involved in Pb(II) binding on AOP. These functional groups disappeared on the surface of carbonized orange peels after carbonation as shown in Fig. 4.4.4 and 4.4.5. This suggests that physical adsorption mechanism plays an important role in Pb(II) binding on carbonized orange peels.

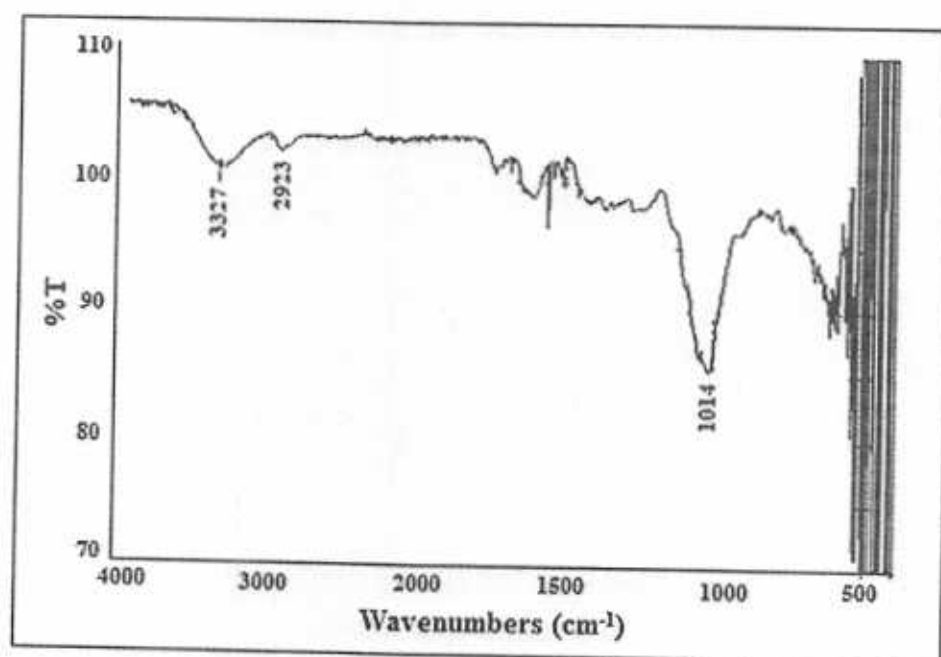


Figure 4.4.1: FT-IR spectrum of untreated orange peels

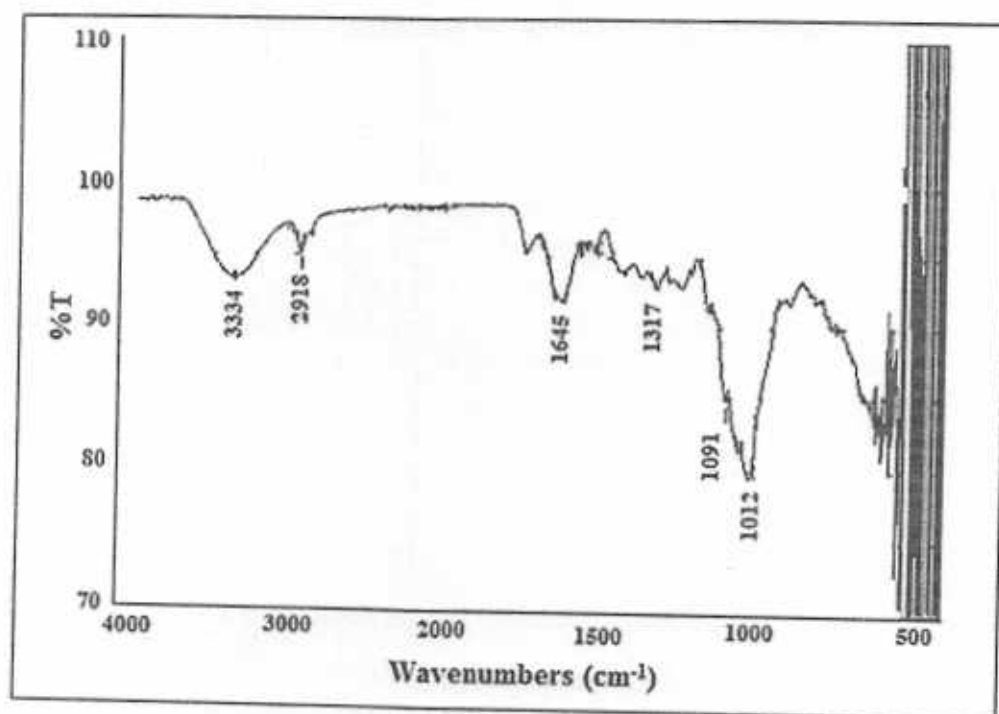


Figure 4.4.2: FT-IR spectrum of treated orange peels

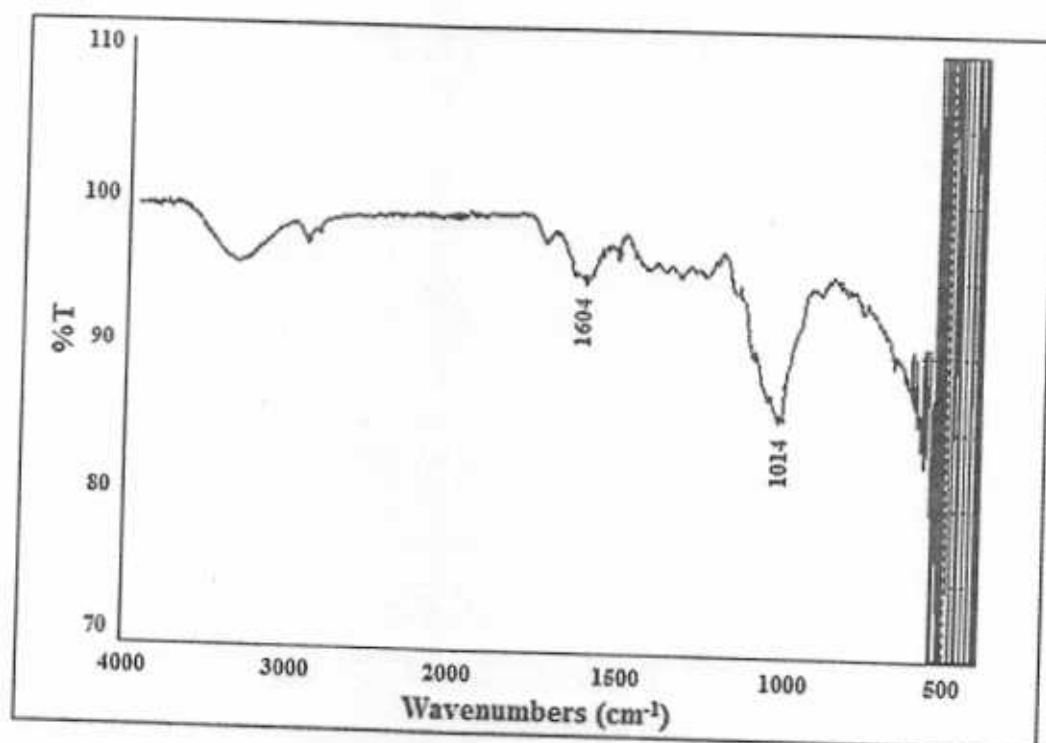


Figure 4.4.3: FT-IR spectrum of treated orange peels after adsorption of Pb(II)

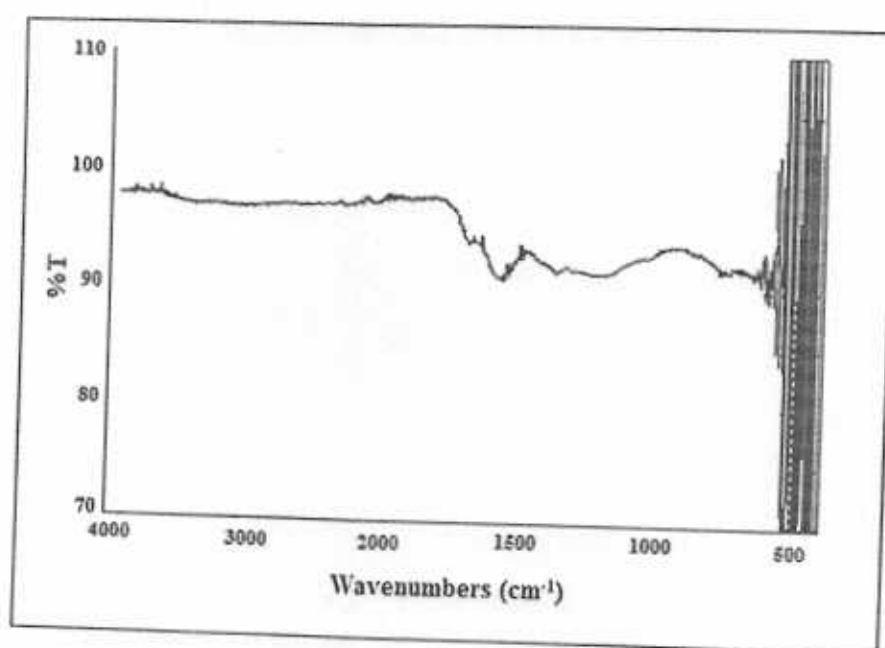


Figure 4.4.4: FT-IR spectrum of washed (dist. water) carbonized orange peels

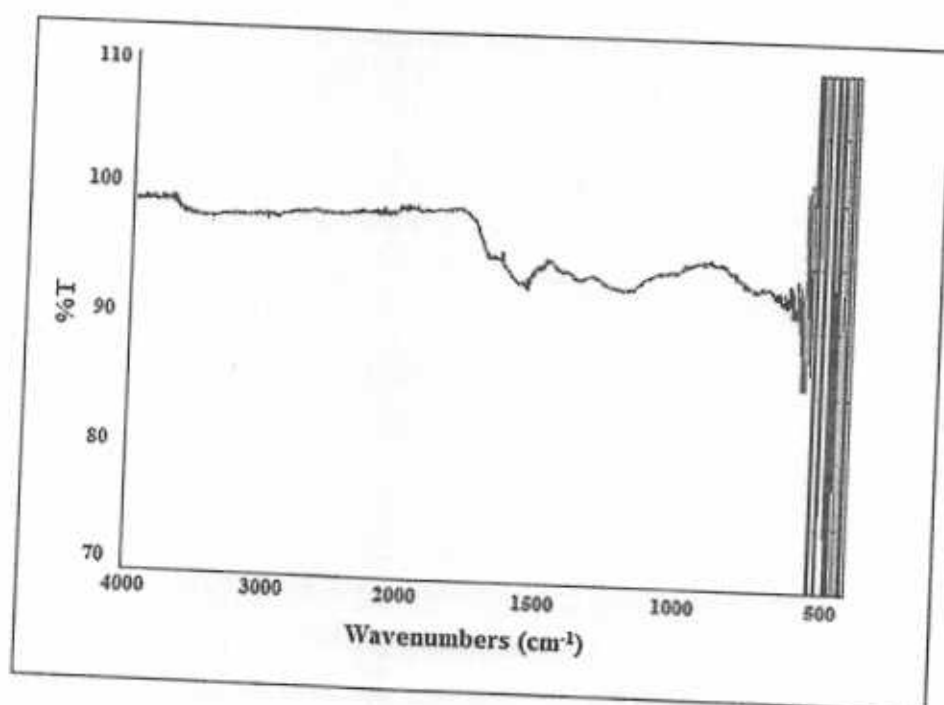


Figure 4.4.5: FT-IR spectrum of washed carbonized orange peels after adsorption of Pb(II)

4.4.2. Sorption studies of Pb(II) using AOP and COP

4.4.2.1. Preliminary adsorption experiments

A known weight of washed (distilled water) and dried orange peels and carbonized orange peels powder were taken in separate Erlenmeyer flasks (250 mL) and added to it a known concentration of Pb(II) solution. The contents of the flasks were kept for 30 min at room temperature for complete equilibration. The biosorbent was filtered and the filtrates were transferred into 100 mL volumetric flasks and diluted upto mark. The concentrations of unadsorbed Pb(II) were determined using atomic absorption spectrophotometer. The results showed good percent uptake and ensure the use of orange peels and carbonized orange peels as promising biosorbents for Pb(II) from aqueous solutions.

4.4.2.2. Optimization studies

After preliminary adsorption studies it was confirmed that Pb(II) can be removed from aqueous media using commercial and indigenous materials. For maximum adsorption condition of pH, contact time and initial metal concentration were optimized and are discussed below:

4.4.2.2.1. The effect of pH on sorption Pb(II) using AOP and COP

The effect of solution pH on sorption behavior of Pb(II) from aqueous solution using acid treated orange peels (AOP) and carbonized orange peels (COP) was investigated in the range of 3 to 7. The results are given in table 4.4.1 and shown in Fig. 4.4.6. It can be seen from the figure that increase in uptake of Pb(II) is observed in both cases with increase in pH up to 5.5 for COP and pH 6 for AOP. Beyond pH 5.5 there was no effect on the uptake in case of COP while in case of AOP a decrease in the uptake of Pb(II) was observed with increase in pH beyond 6. About 100% uptake was achieved at pH 5.5 for COP. At lower pH, the percent sorption is lower due to H^+ ion present in the solutions, which compete with Pb(II) for active sites on the sorbent causing a decrease in the percent sorption of Pb(II). At higher pH, the surface of the orange peel waste may

become negatively charged which results for higher sorption of Pb(II) through electrostatic attraction.

Table 4.4.1: The effect of pH on sorption of Pb(II) using AOP and COP

pH	% uptake of Pb(II)	
	OP	COP
3.0	45.180	30.913
3.5	54.100	48.893
4.0	56.140	58.033
4.5	63.320	74.126
5.0	71.810	91.033
5.5	80.690	100.000
6.0	94.790	100.000
6.5	89.920	100.000
7.0	57.240	100.000

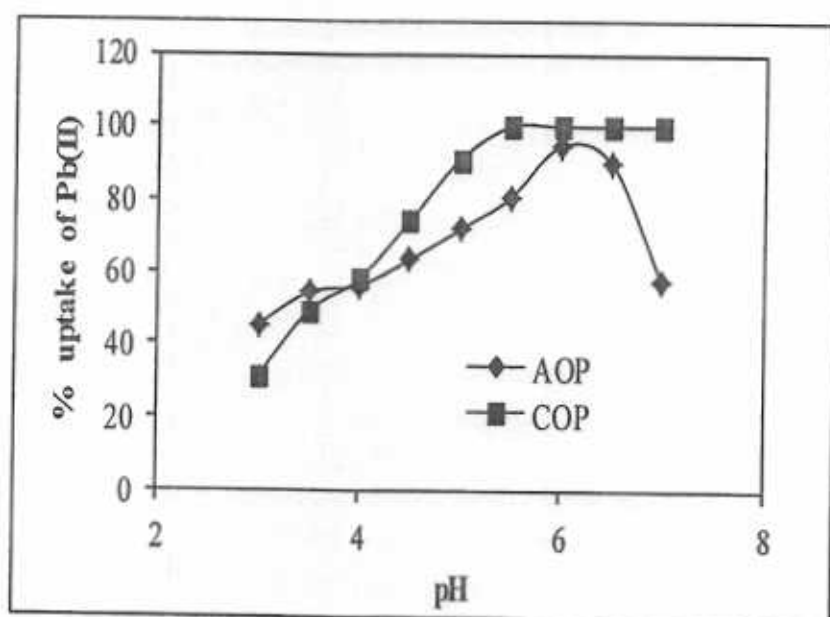


Figure 4.4.6: The effect of pH on sorption of Pb(II) using AOP and COP (Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 3-7.0; room temperature;

sorbent dose 10 mg; volume of Pb(II) solution 10 mL; contact time 30 min)

4.4.2.2.2. The effect of contact time on sorption of Pb(II) using AOP and COP

The effect of contact time with and without shaking on the percent sorption of Pb(II) on AOP and COP was investigated in the range of 10 to 120 min. The results are given in table 4.4.2 and shown in Fig. 4.4.7. It was observed that the uptake of Pb(II) is rapid for the first 10 min and increased from 57% to 100% in 90 min without shaking and from 73% to 100% with shaking in 60 min with AOP and in case COP with or without shaking the uptake reaches up to 100% within 80 min. Initially the sites on the biosorbent are open and Pb(II) interacts with the sorption sites rapidly therefore the sorption rate is higher. The concentration gradient is also higher in the initial time between the bulk solution and the solid-liquid interface leading to higher sorption rate. At 90 min contact time the maximum uptake of Pb(II) was observed with both AOP and COP.

Table 4.4.2: The effect of contact time on sorption of Pb(II) using AOP and COP

Time (min)	% uptake of Pb(II)			
	Without shaking (AOP)	With shaking (AOP)	Without shaking (COP)	With shaking (COP)
10	56.580	72.900	38.606	49.020
20	57.000	79.640	46.513	59.873
30	66.940	85.920	56.766	65.953
40	73.860	88.080	72.746	72.560
50	81.160	97.420	76.760	76.000
60	83.980	100.000	91.413	78.593
70	88.420	100.000	93.746	92.406
80	92.780	100.000	100.000	92.786
90	99.120	100.000	100.000	93.980
100	100.000	100.000	100.000	95.780
110	100.000	100.000	100.000	98.890
120	100.000	100.000	100.000	100.000

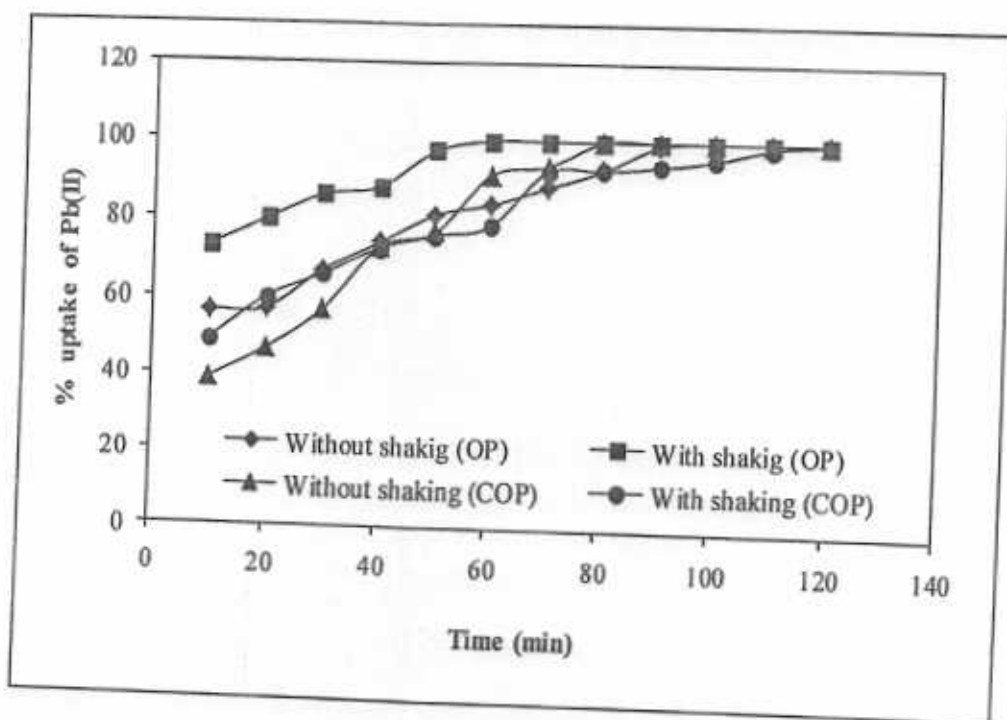


Figure 4.4.7: The effect of contact time on sorption of Pb(II) using AOP and COP (Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 10 mg; volume of Pb(II) solution 10 mL; contact time 10-120 min)

4.4.2.2.3. The effect of sorbent dose on sorption of Pb(II) using AOP and COP

The effect of sorbent dose of AOP and COP on the sorption behavior of Pb(II) was studied by varying amounts of sorbent in the range of 4 mg to 18 mg. The results are given in table 4.4.3 shown in Fig. 4.4.8. The sorption of Pb(II) increased from 60% to 100% with an increase in sorbent dose from 4 to 12 mg in both cases. It indicates that the equilibrium concentration in solution decreases with increasing dose of sorbent for a given initial concentration of Pb(II). This is due to the fact that for a constant initial concentration greater surface area becomes available due to increase in amount of sorbent.

Table 4.4.3: The effect of sorbent dose on sorption of Pb(II) using AOP and COP

Sorbent dose (mg)	% uptake of Pb(II)	
	AOP	COP
4	59.750	45.313
6	62.120	45.606
8	84.130	65.033
10	86.460	82.820
12	99.870	89.480
14	100.000	100.000
16	100.000	100.000
18	100.000	100.000

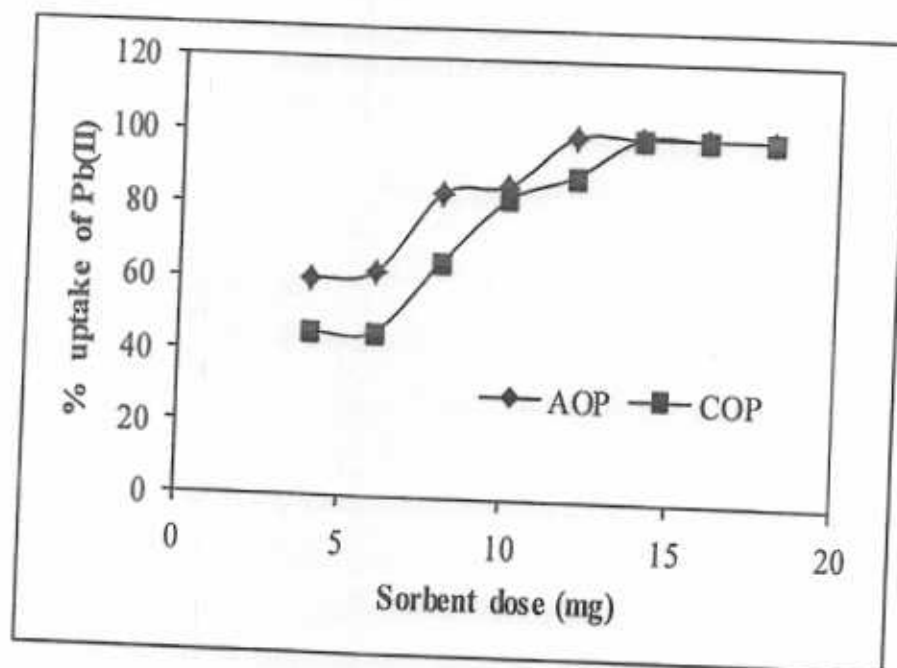


Figure 4.4.8: The effect of sorbent dose on sorption of Pb(II) using AOP and COP
(Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room

temperature; sorbent dose 10 mg; volume of Pb(II) solution 10 mL;
contact time 30 min)

4.4.2.2.4. Sorption isotherm for Pb(II) on AOP and COP

The most common two isotherm models i.e. Freundlich and Langmuir were used to analyze the equilibrium data of Pb(II) on AOP and COP. The results are given in table 4.4.4 and 4.4.5 and shown in Fig. 4.4.9 and 4.4.10 respectively. The Freundlich constants were calculated from the linear form of Freundlich isotherm equation and given in table 4.4.6. These values of n in both cases are greater than unity indicating that sorption of Pb(II) on AOP and COP is the favorable process.

The Langmuir isotherms model assumes the monolayer sorption over a homogeneous orange peel and carbonized orange peel sorbent at room temperature and the values of the monolayer adsorption capacities were calculated from the linear form of Langmuir equation and were found to be 1040 mg g^{-1} and 993.11 mg g^{-1} for AOP and COP respectively. The other constant parameters are given in table 4.4.6. Freundlich and Langmuir isotherms both best fitted the data for sorption of Pb(II) as shown in Fig. 4.4.9 and 4.4.10 respectively.

Table 4.4.4: Freundlich isotherm for sorption of Pb(II) using AOP and COP

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)		Sorption capacity (q_e) (mg g^{-1})	
	AOP	COP	AOP	COP
50	0.746	2.081	0.354	0.565
100	1.890	5.641	0.675	0.668
150	3.350	8.747	0.970	0.803
200	6.010	12.806	1.165	0.870
250	9.199	15.480	1.316	1.037

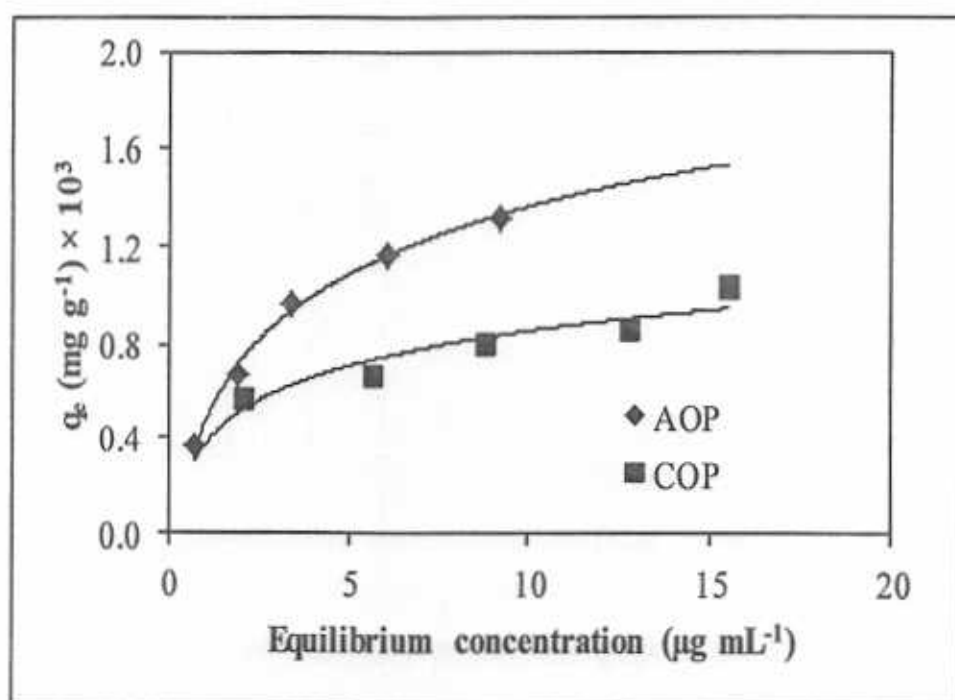


Figure 4.4.9: Freundlich isotherm for sorption of Pb(II) using AOP and COP (Initial concentration of Pb(II) 50-250 $\mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL; shaking time 60 min)

Table 4.4.5: Langmuir isotherm for sorption of Pb(II) using AOP and COP

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)		(C _e /q _e)	
	AOP	COP	AOP	COP
50	0.746	2.081	2.100	3.945
100	1.890	5.641	2.860	8.479
150	3.350	8.747	3.460	11.453
200	6.010	12.806	5.160	14.829
250	9.199	15.480	6.980	15.800

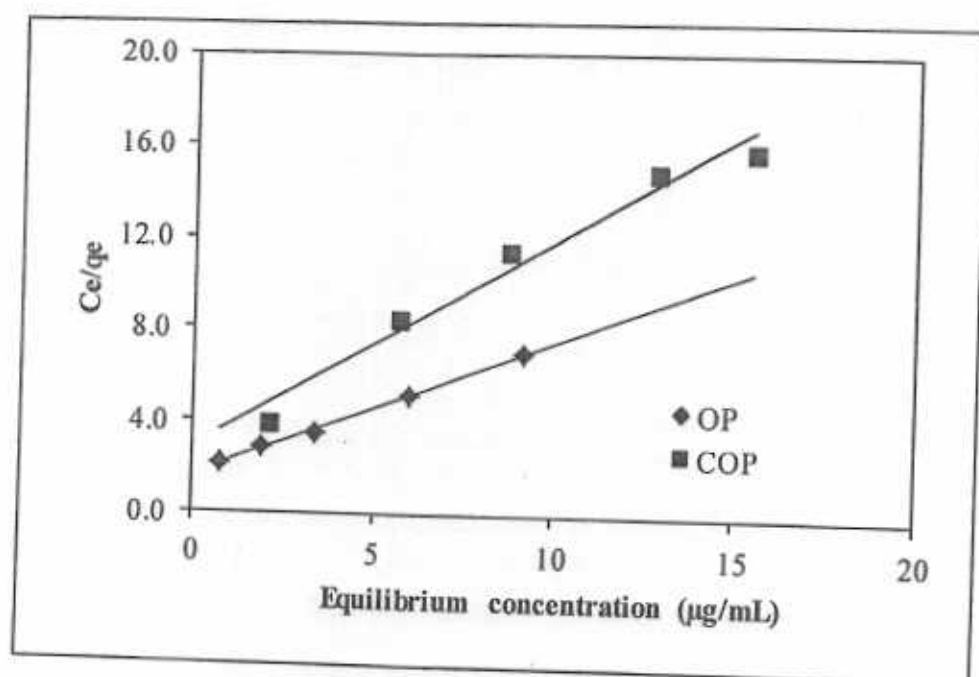


Figure 4.4.10: Langmuir isotherm for sorption of Pb(II) using AOP and COP (Initial concentration of Pb(II) 50-250 $\mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL; shaking time 60 min)

Table 4.4.6: Freundlich and Langmuir isotherm constants for the sorption of Pb(II) using AOP and COP

Sorbent	Freundlich model				Langmuir model			
	K_F (mg g ⁻¹)	n	1/n	R ²	a_L (L mg ⁻¹)	K_L (Lg ⁻¹)	Q_o (mg g ⁻¹)	R ²
AOP	0.453	1.900	0.525	0.9656	0.343	0.598	1040.000	0.9980
COP	0.334	2.510	0.397	0.9470	0.436	0.433	993.110	0.9580

4.4.2.2.5. Kinetics of sorption of Pb(II) on AOP and COP

The kinetic data of the Pb(II) were fitted into previously discussed four kinetic models. The rate constant for pseudo-first-order can be determined from the slope of linear plot of time against $\log (q_e - q_t)$ and the second order rate constant K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) for pseudo-second-order model can be determined from the intercept of the plot time (t) against t/q_t . The results are given in table 4.4.7 and 4.4.8 and shown in Fig. 4.4.11 and 4.4.12 respectively. It was observed from the table 4.4.11 that the value of correlation coefficient of the pseudo-second-order model is higher than the first order model in both cases of sorbents suggesting that the sorption might be controlled by second-order kinetics.

Table 4.4.7: Pseudo-first kinetics of Pb(II) sorption using AOP and COP

Time (min)	$\log (q_e - q_t)$	
	AOP	COP
10	2.257	5.487
20	2.253	5.427
30	2.139	5.334
40	2.037	5.134
50	1.894	5.065
60	1.824	4.632
70	1.683	4.495

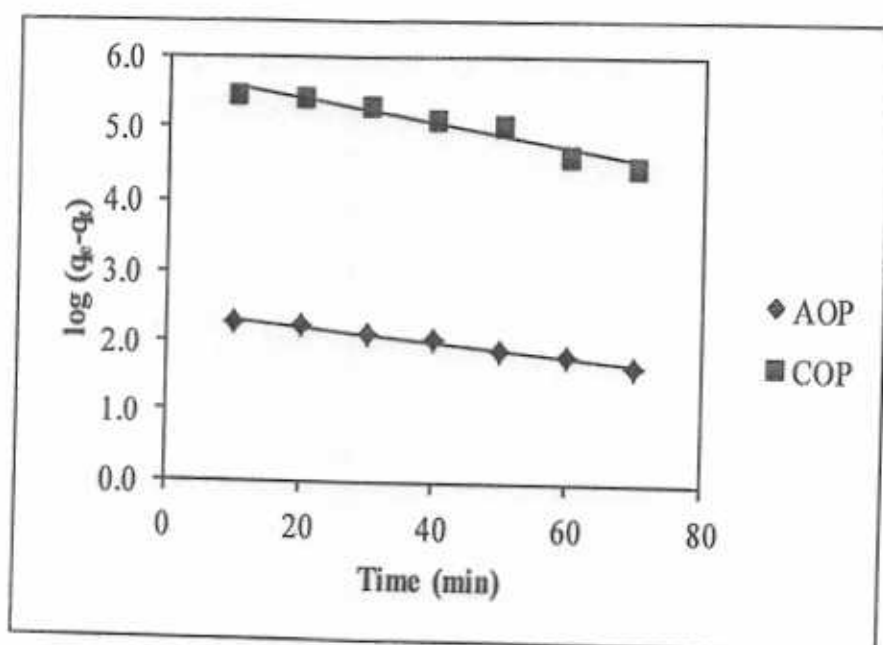


Figure 4.4.11: Pseudo-first kinetics of Pb(II) sorption using AOP and COP (Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL)

Table 4.4.8: Pseudo-second kinetics of Pb(II) sorption using AOP and COP

Time (min)	t/q_t (min g mg ⁻¹)	
	AOP	COP
10	0.042	0.051
20	0.084	0.085
30	0.107	0.105
40	0.129	0.109
50	0.147	0.130
60	0.171	0.131
70	0.189	0.149

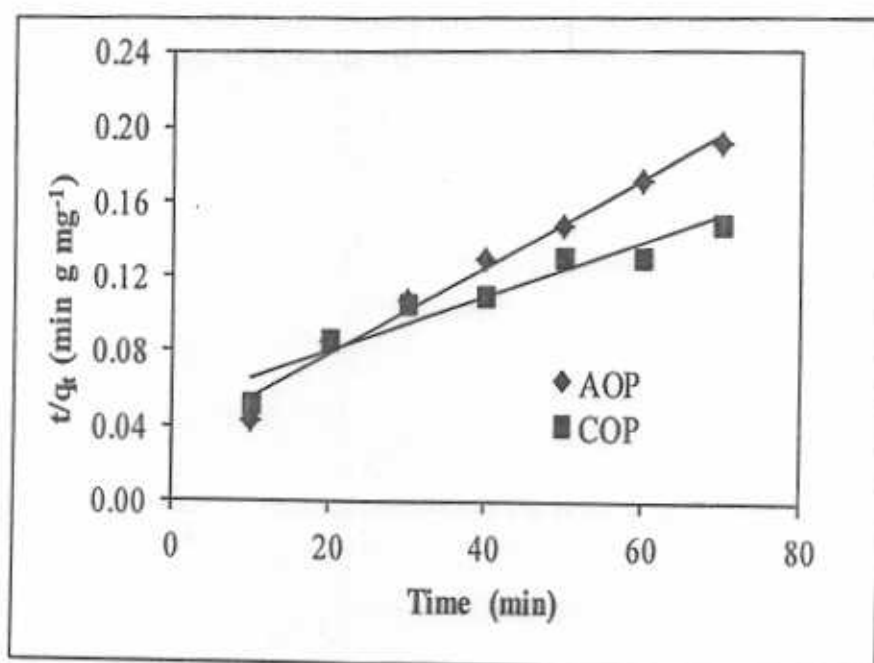


Figure 4.4.12: Pseudo-second kinetics of Pb(II) sorption using AOP and COP
 (Initial concentration of Pb(II) 50 $\mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL)

Similarly, the constant parameters of the intraparticle diffusion model were evaluated from the slope and intercept of plot q_t versus square root of time. The results are given in table 4.4.9 and shown in Fig. 4.4.13. The Fig. 4.4.13 shows that the plot of q_t versus $t^{1/2}$ is not passing through the origin indicating that intraparticle diffusion is not the controlling step during sorption of Pb(II) on AOP and COP.

The Elovich coefficients were calculated from slope and intercept of the plot of q_t versus $\ln t$. The results are given in table 4.4.10 and shown in Fig. 4.4.14. It can be seen from the table 4.4.11 that the correlation coefficient of the COP is greater than AOP indicating that kinetic data of Pb(II) on AOP follow the Elovich model.

Table 4.4.9: Intraparticle diffusion model of Pb(II) sorption using AOP and COP

$t^{1/2}$ (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)	
	AOP	COP
3.162	235.777	193.033
4.472	237.500	232.566
5.477	278.944	283.833
6.324	307.750	363.733
7.071	338.194	383.800
7.745	349.944	457.066
8.366	368.444	468.733

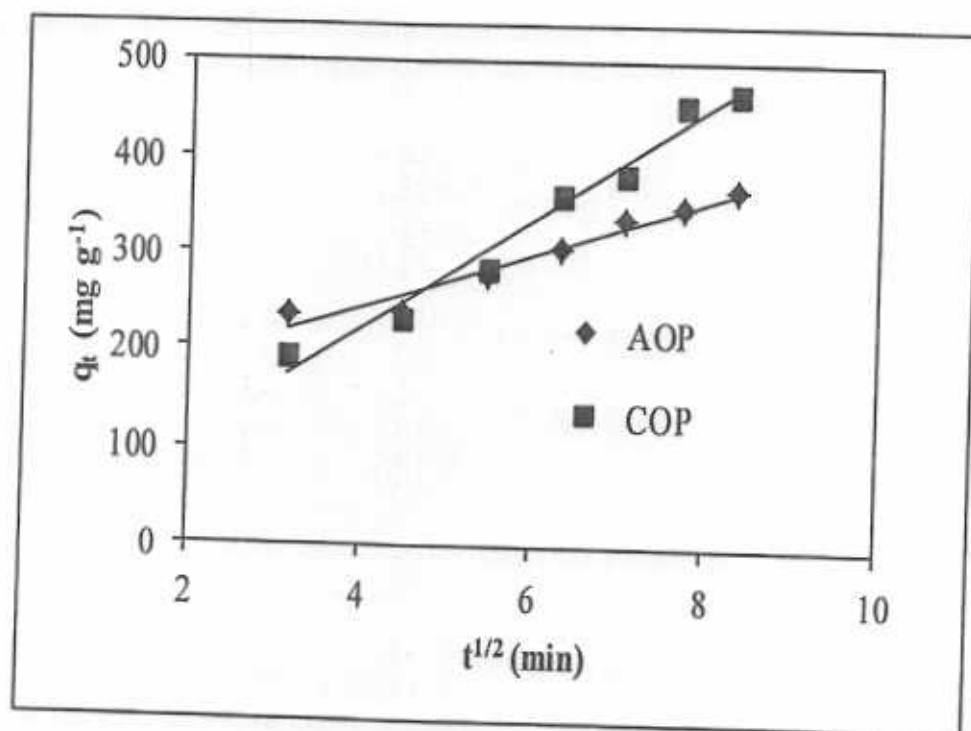


Figure 4.4.13: Intraparticle diffusion model of Pb(II) sorption using AOP and COP
 (Initial concentration of Pb(II) 50 µg mL⁻¹; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL)

Table 4.4.10: Elovich model of Pb(II) sorption using AOP and COP

Int (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)	
	AOP	COP
2.302	235.777	193.033
2.995	237.500	232.566
3.401	278.944	283.833
3.688	307.750	363.733
3.912	338.194	383.800
4.094	349.944	457.066
4.248	368.444	468.733

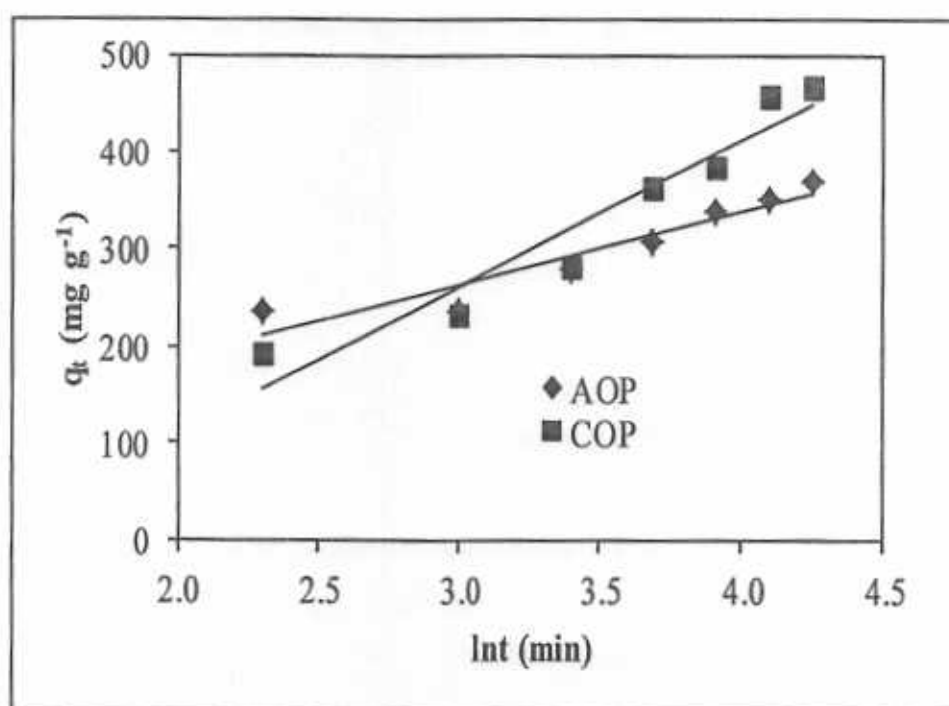


Figure 4.4.14: Elovich model of Pb(II) sorption using AOP and COP (Initial concentration of Pb(II) 50 $\mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL)

Table 4.4.11: Kinetic parameters of Pb(II) sorption using AOP and COP

Sorbent	q_e (mg g ⁻¹) I_1 (exp)	Pseudo-first- order kinetic model			Pseudo-second- order kinetic mode			Intraparticle diffusion model			Elovich model		
		K_1 (min ⁻¹)	q_e (mg g ⁻¹) I_1	R^2	K_2 (g mg ⁻¹ I ₁ min ⁻¹)	q_e (mg g ⁻¹)	R^2	K_{int} (mg g ⁻¹ sec ^{1/2})	C	R^2	α (mg g ⁻¹ min ⁻¹)	β (g mg ⁻¹)	R^2
AOP	368.444	0.023	260.610	0.9750	0.00013	500.000	0.9820	27.550	133.500	0.9080	129.540	0.013	0.8990
COP	468.733	0.039	592.920	0.9310	0.00002	1000.000	0.9490	52.290	14.140	0.9600	84.770	0.012	0.9500

4.4.2.2.6. Thermodynamics of sorption of Pb(II) on AOP and COP

Thermodynamic parameters like change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of sorption process were calculated using Van't Hoff equation as discussed earlier. A plot of $\ln K_D$ versus $1/T$ was constructed. The results are given in table 4.4.12 and shown in Fig. 4.4.15. The values of ΔH° and ΔS° were calculated from the slope and intercept of this plot and are given in table 4.4.13. The positive value obtained for ΔH° indicated an endothermic sorption process. The endothermic sorption process could be due to increase in the rate of diffusion and mobility of the Pb(II) from the external boundary layer into the internal pores of the sorbent due to increase in temperature. The positive value of ΔS° showed the affinity of AOP and COP for Pb(II) where as the negative value of ΔG° shows that sorption process is spontaneous at the studied temperature range.

Table 4.4.12: Van't Hoff equation for estimation of thermodynamic parameters for Pb(II) sorption using AOP and COP

$1/T \text{ (K}^{-1}\text{)}$	$\ln K_D$	
	AOP	COP
3.195×10^{-3}	12.130	12.006
3.096×10^{-3}	12.290	12.053
3.003×10^{-3}	12.900	12.371
2.915×10^{-3}	13.110	14.205

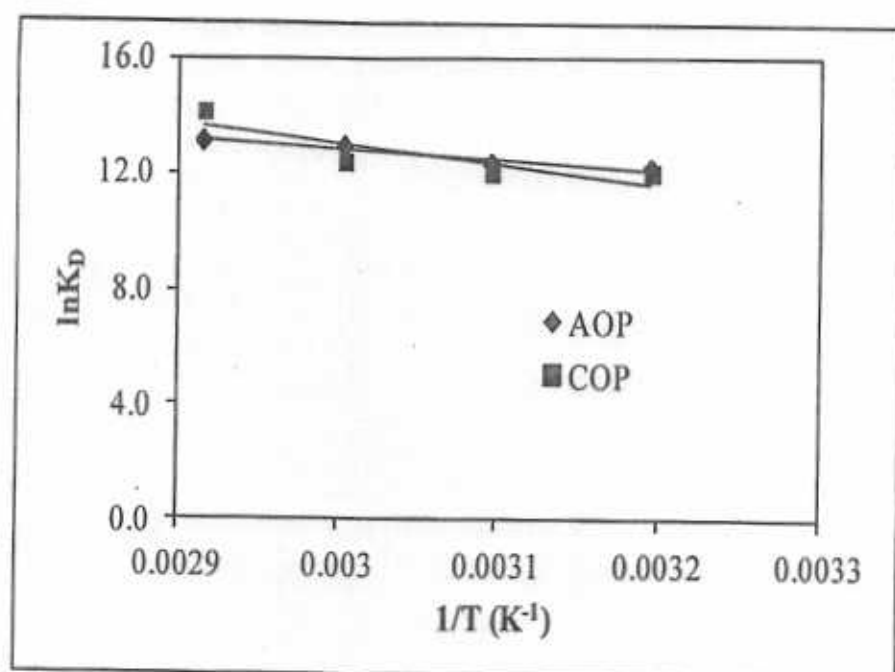


Figure 4.4.15: Plot of $\ln K_D$ versus $1/T$ for estimation of thermodynamic parameters for Pb(II) sorption using AOP and COP (Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 5.5 and 6.0; sorbent dose 12 mg; volume of Pb(II) solution 10 mL)

Table 4.4.13: Thermodynamic parameters for the sorption of Pb(II) using AOP and COP

sorbent	ΔG° (kJ mol ⁻¹)				ΔH° (kJ mol ⁻¹)	ΔS° (kJ K ⁻¹ mol ⁻¹)
	303 K	313 K	323 K	333 K		
AOP	-30.100	-31.560	-33.000	-35.710	31.630	0.201
COP	-30.240	-31.360	-33.220	-39.320	60.710	0.290

4.4.2.2.7. The effect of interfering ions on sorption behavior of Pb(II) using AOP and COP

The effect of some interfering ions relevant to wastewater e.g. alkali and alkaline earth metals, Na^+ , K^+ , Mg^{2+} and Ca^{2+} on the sorption of Pb(II) at optimum conditions was studied in the range of 200-1400 μg . The results are given in table 4.4.14 and shown in Fig. 4.4.16. It can be seen from the figure that the effect of interfering ions on the sorption of Pb(II) on AOP and COP is negligible. The values on the line show the percent uptake of Pb(II) when there is no addition of these interfering ions. The % uptake of Pb(II) is not affected by presence of interfering ions in both cases.

Table 4.4.14: The effect of interfering ions on sorption of Pb(II) using AOP and COP

Wt. of interfering ions (μg)	% uptake of Pb(II)	
	AOP	COP
0.000	78.940	93.450
200	76.270	94.432
400	77.090	95.653
600	76.340	98.733
800	77.730	100.000
1000	77.630	100.000
1200	77.800	100.000
1400	76.520	100.000

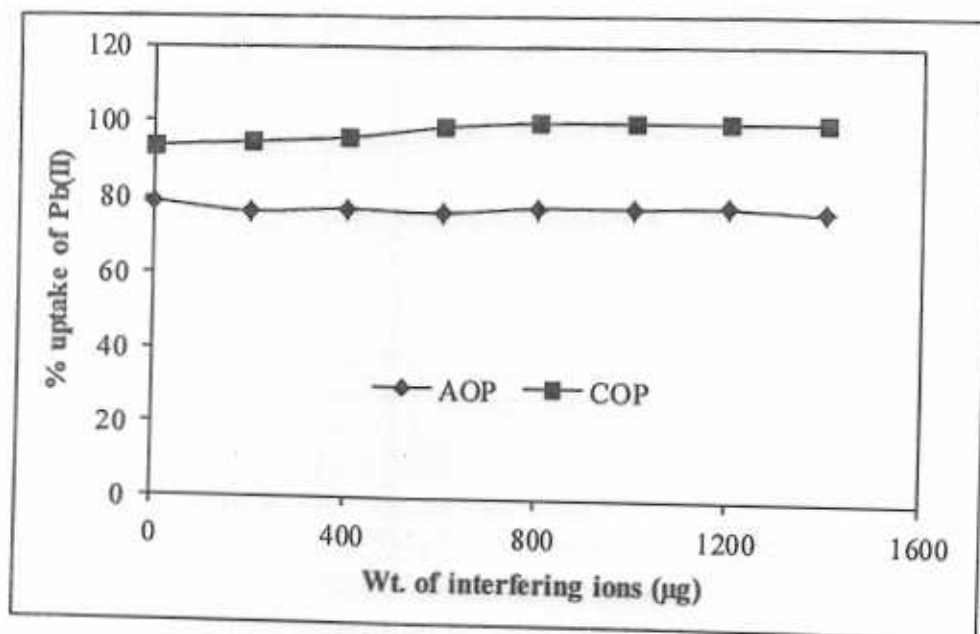


Figure 4.4.16: The effect of interfering ions on sorption of Pb(II) using AOP and COP (Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 5.5 and 6.0; room temperature; sorbent dose 12 mg; volume of Pb(II) solution 10 mL)

4.4.2.2.8. Percent recovery of Pb(II) after sorption

Desorption of the retained Pb(II) from AOP was investigated using 20 mL of different eluents like NaCl (1.0 M), HCl (1.0 M), HNO_3 (1.0 M), NaOH (1.0 M) and CH_3COOH (1.0 M) solutions at optimum conditions. The results are given in table 4.4.15 and shown in Fig.4.4.17. It can be seen from the results that maximum desorption was achieved with HNO_3 and therefore concentration of HNO_3 was then further optimized. The results are given in table 4.4.16 and shown in Fig. 4.4.18. It was found that maximum recovery of Pb(II) was achieved with 1.5 M HNO_3 solution. Desorption of Pb(II) from COP was also carried out with different desorbents but no recovery was observed. Therefore, only AOP was used for application of real samples.

Table 4.4.15: The effect of various eluents for desorption of Pb(II) from AOP

Eluent (1.0 M)	% Recovery
HCl	63.53
HNO ₃	65.66
NaOH	34.83
CH ₃ COOH	15.97
NaCl	9.98

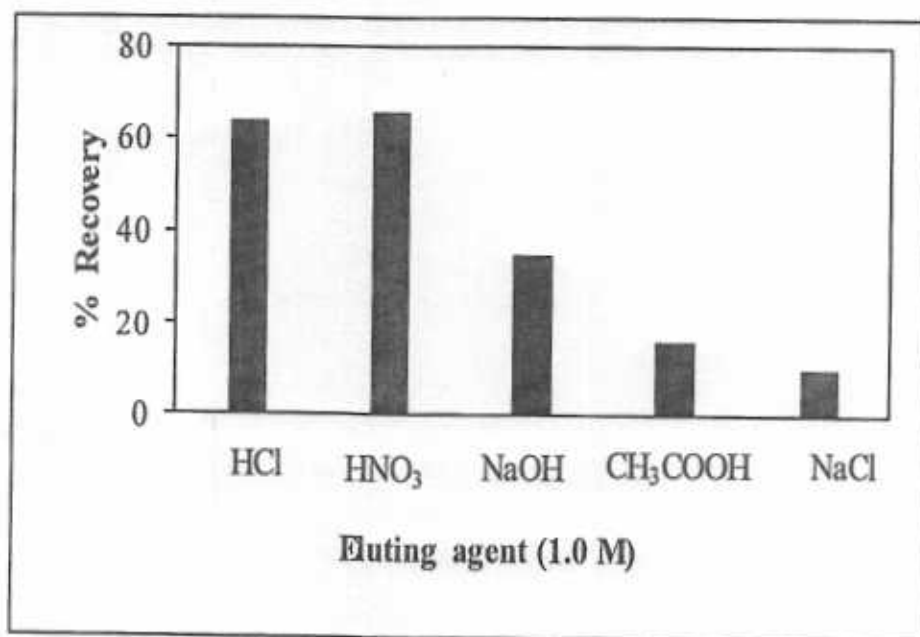


Figure 4.4.17: The effect of various eluents for desorption of Pb(II) from AOP
 (Initial concentration of Pb(II) 50 µg mL⁻¹; pH 6.0; room temperature; sorbent dose 12 mg, volume of Pb(II) solution 10 mL)

Table 4.4.16: The effect of concentration of HNO_3 for desorption of Pb(II) from AOP

Concentration of HN_3 (M)	% Recovery
1.0	65.660
1.5	74.740
2.0	73.330
2.5	63.820
3.0	50.200

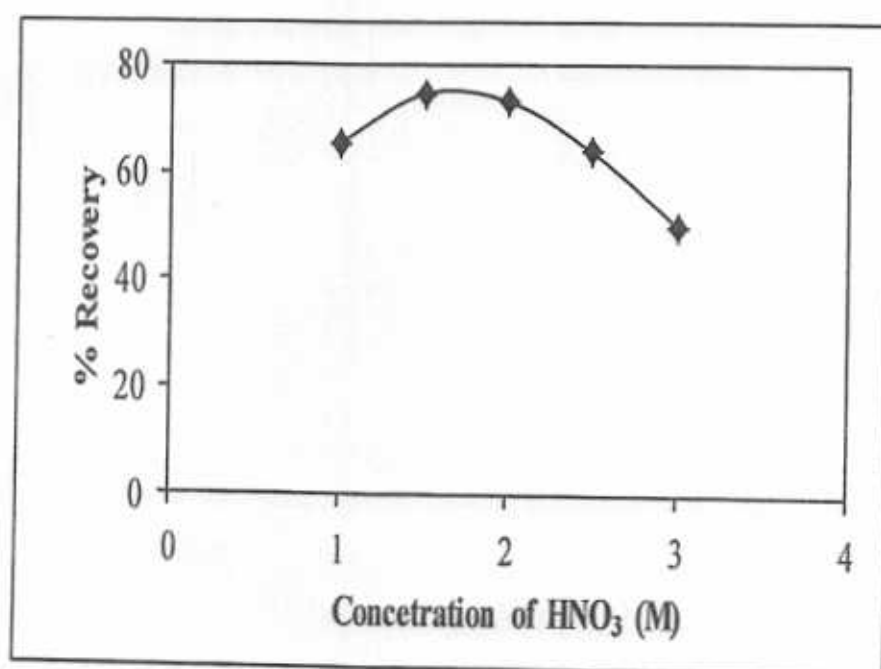


Figure 4.4.18: The effect of concentration of HNO_3 for desorption of Pb(II) from AOP (Initial concentration of Pb(II) $50 \mu\text{g mL}^{-1}$; pH 6.0; room temperature; sorbent dose 12 mg, volume of Pb(II) solution 10 mL)

4.4.2.2.9. Application of the proposed method to real samples

The proposed method was applied to the analysis of Pb(II) in tap water. Standard addition method was used for the analysis of Pb(II) in tap water. It can be seen from the table 4.4.17 that 100 percent recovery at lower concentration was achieved indicating the suitability of AOP as a biosorbent for preconcentration of Pb(II) from aqueous samples.

Table 4.4.17: Removal of Pb(II) from water samples using 1.5 M HNO₃

Pb(II) added (µg)	Pb(II) sorbed (µg)	Pb(II) found (µg)	% Recovery of Pb(II)
Tap water			
0.000	-	-	-
100	100	0.000	100.000
300	300	0.000	100.000
500	500	0.000	100.000

Part C: Investigation of adsorption behavior of Cd(II) using chemically treated sawdust (CTSD)

4.5. Results and discussions

4.5.1. Characterization of chemically treated sawdust (CTSD)

Scanning electron microscopy, energy dispersive x-rays and Fourier transform infrared were used for characterization of the chemically untreated and treated sawdust. The results of these techniques are discussed earlier.

4.5.2. Sorption studies of Cd(II) using chemically treated sawdust

4.5.2.1. Preliminary adsorption experiments

A known weight of washed (distilled water) and dried sawdust was taken in Erlenmeyer flasks (250 mL) and added to it a known concentration of Cd(II) solution. The content of the flasks were kept for 30 min at room temperature for complete equilibration. The biosorbent was filtered and the filtrates were transferred into 100 mL volumetric flasks and diluted upto mark. The concentrations of unadsorbed Cd(II) were determined using atomic absorption spectrophotometer. The results showed good percent uptake and ensure the use of sawdust as a promising biosorbent for Cd(II) from aqueous solutions.

4.5.2.2. Optimization studies

After preliminary adsorption studies it was confirmed that Cd(II) can be removed from aqueous solution using chemically treated sawdust. For maximum adsorption; various parameters like pH, contact time and initial metal concentrations were optimized and are discussed below:

4.5.2.2.1. The effect of pH on sorption of Cd(II) using CTSD

In the sorption processes of heavy metals pH is an important controlling parameter. For maximum uptake of Cd(II) on chemically treated sawdust (CTSD), pH was varied from 3 to 7. The results are given in table 4.5.1 and shown in Fig. 4.5.1. It can be seen from the

figure that binding of Cd(II) is strongly pH dependent and maximum sorption (58.50%) of Cd(II) was obtained at pH 6.0. The uptake of Cd(II) was lower in acidic pH because the surface became protonated in acidic pH which hindered the sorption process due to electrostatic repulsion. With increase in pH the hydronium ions concentration decreased and the active sites on the CTSD became dissociated and exchanged with Cd(II) in solution. Therefore pH 6 was selected as an optimum pH to ensure that there is no precipitation of Cd(II) as hydroxide.

Table 4.5.1: The effect of pH on sorption of Cd(II) using CTSD

pH	% uptake of Cd(II)
3	20.600
4	41.030
5	53.000
6	58.500
7	31.260

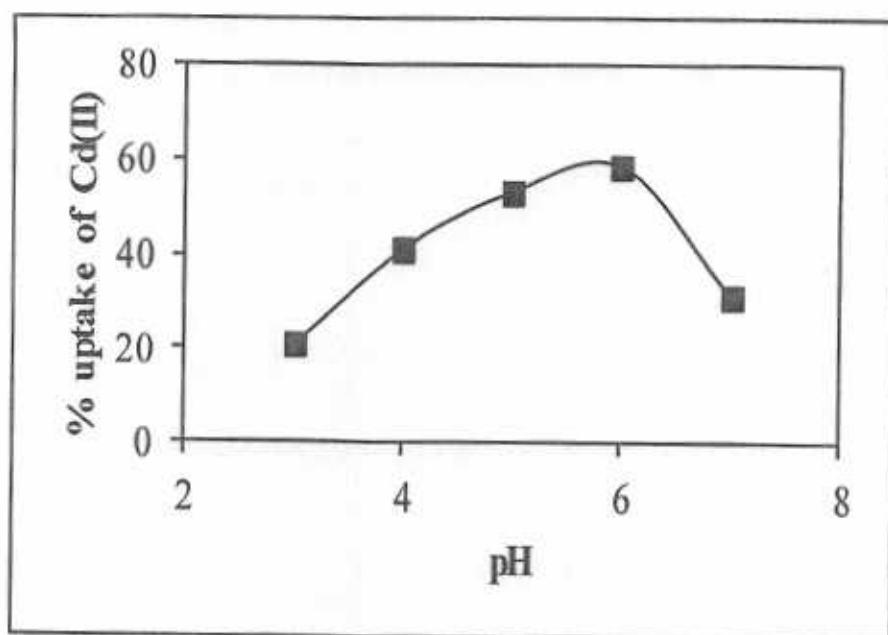


Figure 4.5.1: The effect of pH on sorption of Cd(II) using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; contact time 30 min; concentration of Cd(II) $5 \mu\text{g mL}^{-1}$)

4.5.2.2.2. The effect of contact time on sorption of Cd(II) using CTSD

In order to find out optimum contact time, the sorption of Cd(II) was carried out on CTSD at pH 6 with and without shaking. The results are given in table 4.5.2 and shown in Fig. 4.5.2. It can be seen that the sorption of Cd(II) increased with time and reached to a constant value at 50 min without shaking and at 30 min with shaking. The time required to reach at the state of equilibrium was termed equilibration time and the amount of Cd(II) sorbed at equilibration time showed the maximum sorption capacity of sorbent under these specific conditions. The increased sorption in the first 10 min was due to the availability of sites on the CTSD surface but with the increase in time the sites get occupied and the sorption became independent of time.

Table 4.5.2: The effect of contact time on sorption of Cd(II) using CTSD

Time (min)	% uptake of Cd(II)	
	Without shaking	With shaking
10	24.460	56.330
20	42.400	75.060
30	44.530	75.700
40	46.800	75.460
50	47.860	74.460
60	47.660	74.200

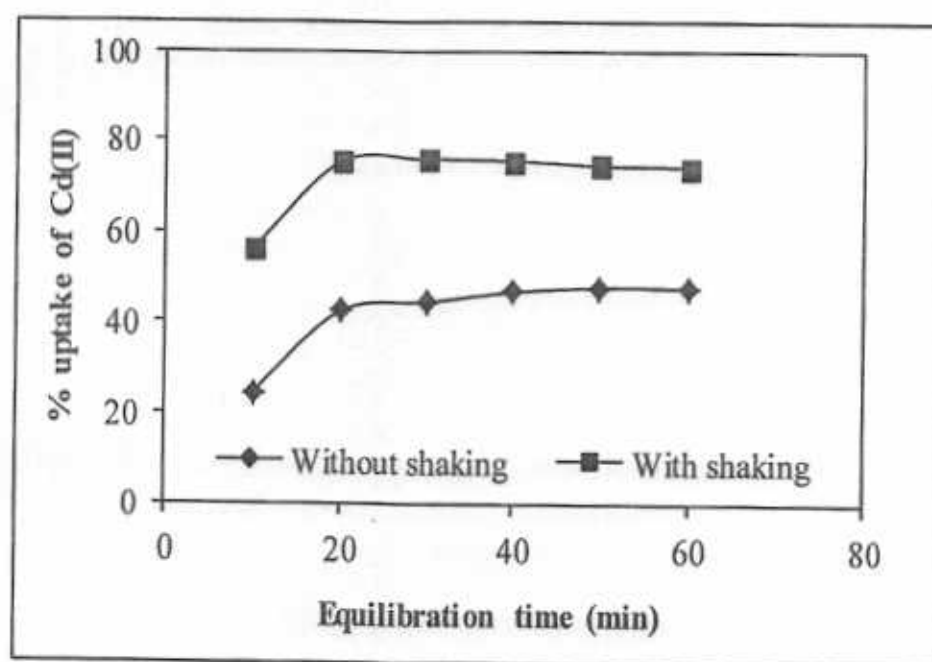


Figure 4.5.2: The effect of contact time on sorption of Cd(II) using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; pH 6; concentration of Cd(II) 5 $\mu\text{g mL}^{-1}$)

4.5.2.2.3. Sorption isotherms of Cd(II) using CTSD

The sorption equilibrium data of the Cd(II) on CTSD were analyzed using Langmuir and Freundlich isotherm models.

A linear plot of specific sorption of Cd(II) (C_e/q_e) on CTSD against the equilibrium concentration (C_e , $\mu\text{g mL}^{-1}$) was obtained. The results are given in table 4.5.3 and shown in Fig. 4.5.3. The constant Q_0 and K_L were determined from the slope and intercept of the Langmuir isotherm and are given in table 4.5.5. The high value of regression coefficient (R^2) indicates that Cd(II) sorbed by CTSD forms monolayer on the surface at room temperature. The monolayer capacity was calculated and found to be 403.73 mg g^{-1} .

The Freundlich isotherm was constructed by plotting of q_e against equilibrium concentration (C_e). The results are given in table 4.5.4 and shown in Fig. 4.5.4. The constants parameters of the Freundlich model were also calculated from the slope and intercept of the linear form of this model. These values are given in table 4.5.5. The equilibrium processes of Cd(II) on CTSD were explained by the Langmuir isotherm, therefore only the Langmuir isotherm model can be used to describe the sorption behavior of Cd(II) on CTSD.

Table 4.5.3: Langmuir isotherm for sorption of Cd(II) using CTSD

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)	C_e/q_e
35	0.008	0.062
45	0.102	0.608
60	0.223	1.030
90	0.464	1.490
130	1.280	3.410

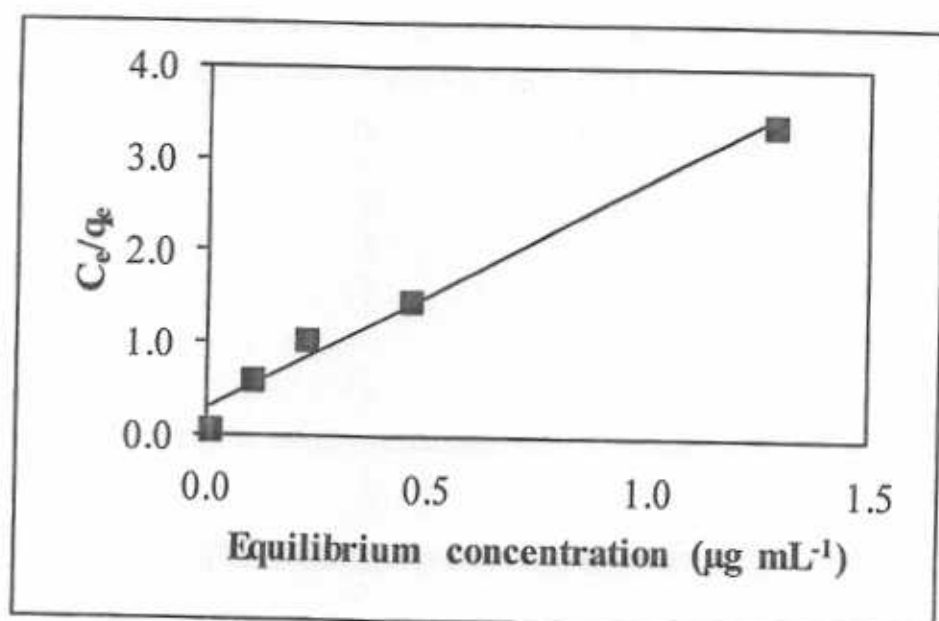


Figure 4.5.3: Langmuir isotherm for sorption of Cd(II) using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; initial Cd(II) concentration 35-130 $\mu\text{g mL}^{-1}$; pH 6; contact time 60 min)

Table 4.5.4: Freundlich isotherm for sorption of Cd(II) using CTSD

Initial concentration (C_i) ($\mu\text{g mL}^{-1}$)	Equilibrium concentration (C_e) ($\mu\text{g mL}^{-1}$)	Sorption capacity (q_e) (mg g^{-1})
35	0.008	139.133
45	0.102	169.800
60	0.223	217.667
90	0.464	313.533
130	1.280	391.733

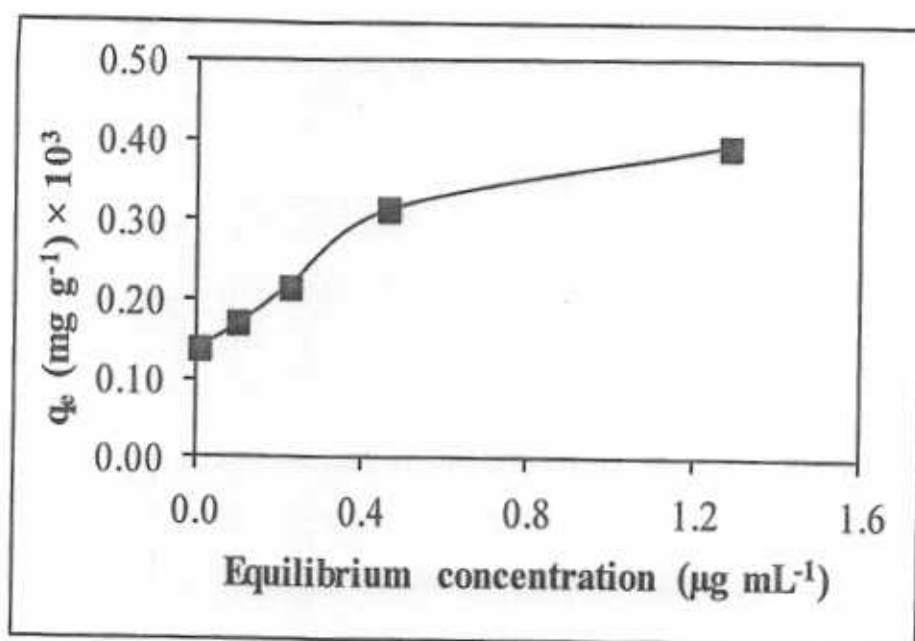


Figure 4.5.4: Freundlich isotherm for sorption of Cd(II) using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; initial Cd(II) concentration 35-130 $\mu\text{g mL}^{-1}$; pH 6; contact time 60 min)

Table 4.5.5: Langmuir and Freundlich isotherm constants for sorption of Cd(II) on CTSD

Parameter	Value
Langmuir isotherm	
$a_L (\text{L mg}^{-1})$	8.570
$K_L (\text{L g}^{-1})$	3.460
$Q_o (\text{mg g}^{-1})$	403.730
R^2	0.9983
Freundlich isotherm	
$K_F (\text{mg g}^{-1})$	0.334
N	4.830
$1/n$	0.208
R^2	0.8774

4.5.2.2.4. Kinetics of sorption of Cd(II) using CTSD

To study the kinetics of the sorption of Cd(II) on CTSD, the data were fitted in to four most common models as discussed earlier. A plot of $\log (q_e - q_t)$ versus (t) was constructed for pseudo-first-order. The results are given in table 4.5.6 and shown in Fig. 4.5.5. The value of the sorption rate constant of pseudo first-order (K_1) for Cd(II) sorption by CTSD was determined from the slope of this plot and is given in table 4.5.10.

Similarly, for calculating the values of q_e and K_2 a plot of t/q_t versus time (t) was constructed. The results are given in table 4.5.7 and shown in Fig. 4.5.6. The values of q_e and K_2 were determined from the intercept and slope of this plot and are given in table 4.5.10. The pseudo-second-order model better represented the sorption kinetics and shows that the overall rate of Cd(II) sorption process may be due to chemical sorption.

Table 4.5.6: Pseudo-first-order kinetics of Cd(II) sorption using CTSD

Time (min)	$\log (q_e - q_t)$
10	0.767
20	0.135
30	-0.079
40	-0.574

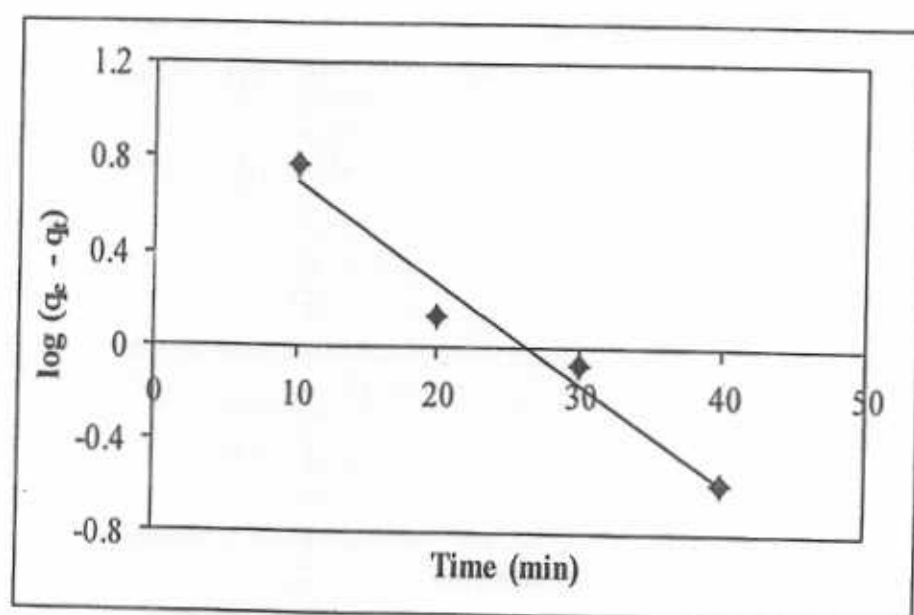


Figure 4.5.5: Pseudo-first-order kinetics of Cd(II) sorption using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; pH 6; concentration of Cd(II) $5 \mu\text{g mL}^{-1}$)

Table 4.5.7: Pseudo-second-order kinetics of Cd(II) sorption using CTSD

Time (min)	t/q_t (min g mg ⁻¹)
10	1.634
20	1.886
30	2.694
40	3.418

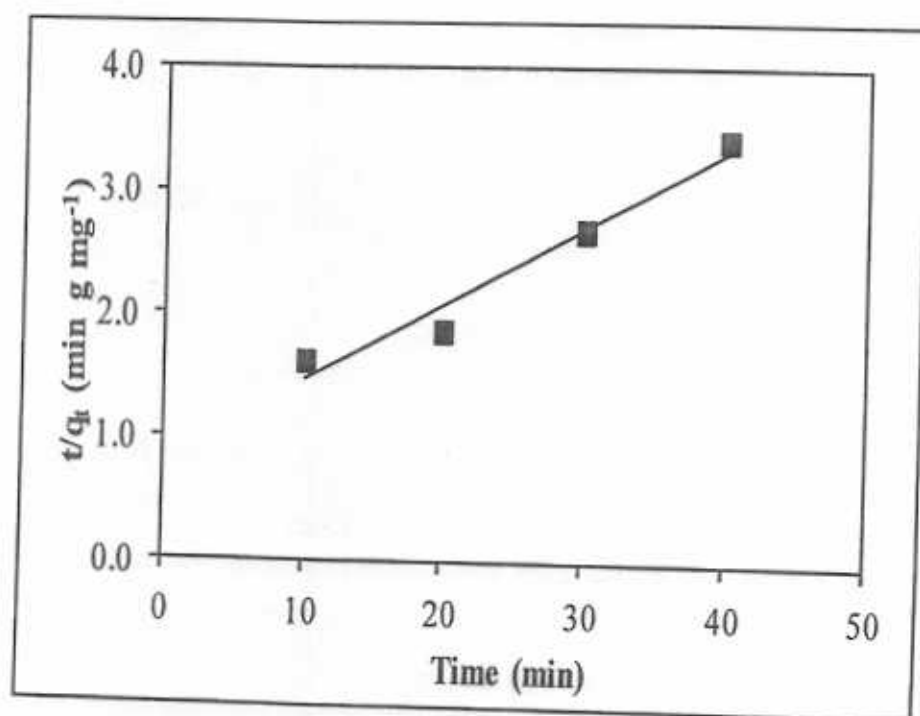


Figure 4.5.6: Pseudo-second-order kinetics of Cd(II) sorption using CTSD (sorbent dose 0.1g; volume of Cd(II) solution 20 mL; pH 6; concentration of Cd(II) 5 $\mu\text{g L}^{-1}$)

A plot of q_t against $t^{1/2}$ was constructed and the results are given in table 4.5.8 and shown in Fig. 4.5.7. The value of K_{int} ($\text{mg g}^{-1} \text{sec}^{1/2}$) was calculated from slope of this plot and is given in table 4.5.10. If intraparticle diffusion is involved in the sorption process then the plot of q_t against square root of time ($t^{1/2}$) should be linear and pass through the origin. In our case the line is not passing through the origin which indicates that some other kinetic processes is controlling the rate of sorption and all may be working simultaneously.

The Elovich coefficients were calculated from the linear plot of q_t versus $\ln t$. The results are given in table 4.5.9 and shown in Fig. 4.5.8. It was observed that the data obtained from experiments fitted well to the pseudo-second-order kinetic model with a high value of R^2 .

Table 4.5.8: Intraparticle diffusion model of Cd(II) sorption using CTSD

$t^{1/2}$ (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)
3.162	6.116
4.472	10.600
5.477	11.133
6.324	11.700

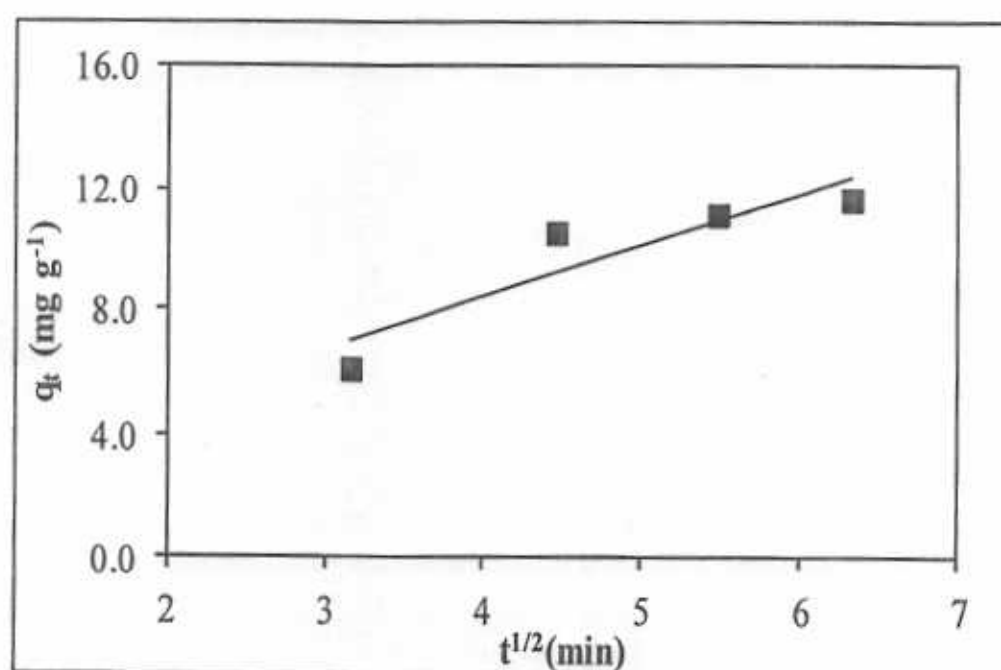


Figure 4.5.7: Intraparticle diffusion model of Cd(II) sorption using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; pH 6; concentration of Cd(II) 5 μ g mL⁻¹)

Table 4.5.9: Elovich model of Cd(II) sorption using CTSD

Int (min)	Sorption capacity at time (t) q_t (mg g ⁻¹)
2.302	6.116
2.995	10.600
3.401	11.133
3.688	11.700

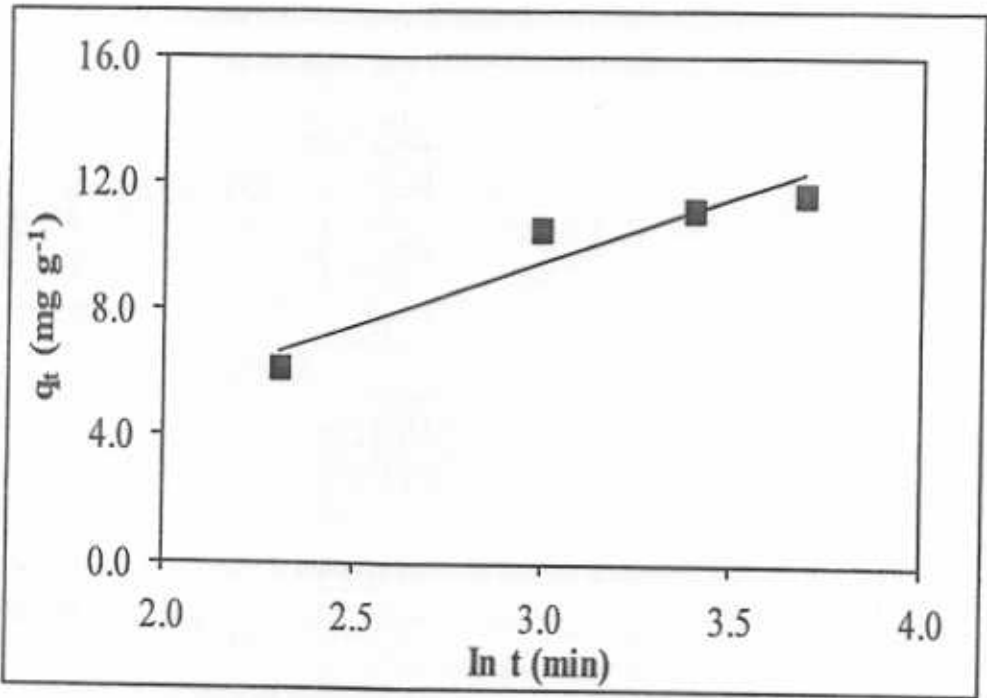


Figure 4.5.8: Elovich model of Cd(II) sorption using CTSD (sorbent dose 0.1g; volume of Cd(II) solution 20 mL; pH 6; concentration of Cd(II) 5 $\mu\text{g mL}^{-1}$)

Table 4.5.10: Kinetic parameters of Cd(II) sorption on CTSD

Model	Parameters	Values
Pseudo-first order kinetics	q_e (mg g ⁻¹) (exp)	11.700
	k_1 (min ⁻¹)	0.096
	q_e (mg g ⁻¹)	13.240
	R^2	0.9680
Pseudo-second order kinetics		
	k_2 (g mg ⁻¹ min ⁻¹)	0.004
	q_e (mg g ⁻¹)	16.390
	R^2	0.9887
Intraparticle diffusion model		
	K_{int} (mg g ⁻¹ sec ^{1/2})	1.717
	R^2	0.8380
	C	1.540
Elovich model		
	α (mg g ⁻¹ min ⁻¹)	7.650
	β (g mg ⁻¹)	0.247
	R^2	0.9020

4.5.2.2.5. The effect of interfering ions on the sorption behavior of Cd(II) using CTSD

The effect of some interfering ions relevant to wastewater e.g. alkali and alkaline earth metals (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) on the sorption of Cd(II) at optimum conditions was studied in the range of 60-1000 μg . The results are given in table 4.5.11 and shown in Fig. 4.5.9. It can be seen from the figure that the effect of interfering ions on the sorption

of Cd(II) on CTSD is negligible. The value on line shows the % uptake of Cd(II) without the present of these interfering ions.

Table 4.5.11: The effect of interfering ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) on sorption of Cd(II) using CTSD

Weight of interfering ions (μg)	% uptake of Cd(II)
0	75.145
60	75.019
80	75.001
100	75.243
200	75.780
400	76.214
600	76.670
800	77.234
1000	77.730

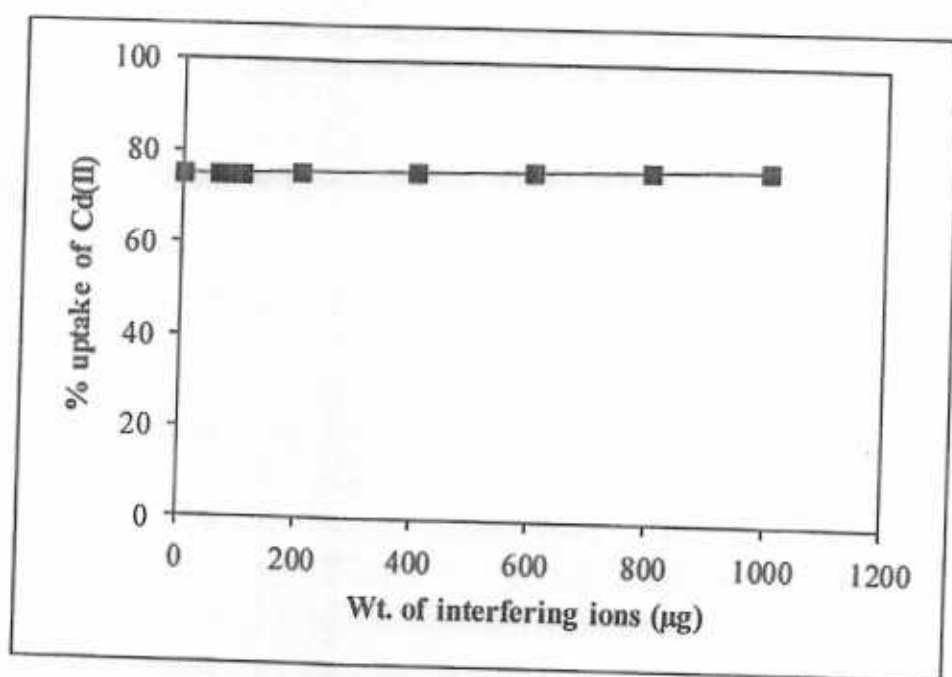


Figure 4.5.9: The effect of interfering ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) on sorption of Cd(II) using CTSD (sorbent dose 0.1 g; volume of Cd(II) solution

20 mL; pH 6; shaking time 30 min; concentration of Cd(II) $25 \mu\text{g mL}^{-1}$)

4.5.2.2.6. Percent recovery of Cd(II) after sorption

Desorption of the retained Cd(II) from CTSD was investigated using 20 mL of different eluents like NaCl (1.0 M), HCl (1.0 M), HNO_3 (1.0 M) and H_2SO_4 solutions at optimum conditions. The results are given in table 4.5.12 and shown in Fig.4.5.10. It can be seen from the results that maximum desorption was achieved with HCl and therefore concentration of HCl was then further optimized. The results are given in table 4.4.13 and shown in Fig. 4.5.11. It was found that maximum recovery (85.79%) of Cd(II) was obtained with 1.5 M HCl solution.

Table 4.5.12: Comparison of different eluents for desorption of Cd(II) from CTSD

Eluting agent (1.0 M)	% Recovery
NaCl	79.730
HCl	82.980
HNO_3	69.790
H_2SO_4	64.230

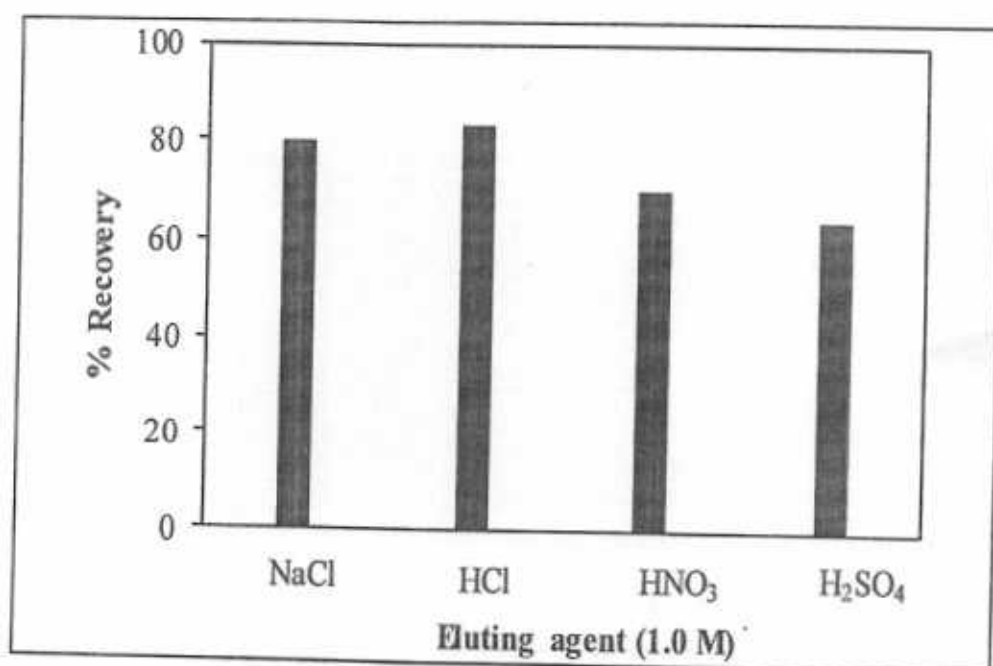


Figure 4.5.10: Comparison of different eluents for desorption of Cd(II) from CTSD
(sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; pH 6;
concentration of Cd(II) 25 $\mu\text{g mL}^{-1}$; volume of eluent 20 mL)

Table 4.5.13: Comparison of different concentrations of HCl for desorption of Cd(II) from CTSD

Concentration of HCl (M)	% Recovery
1.0	78.850
1.5	85.790
2.0	83.880
2.5	84.370
3.0	80.690

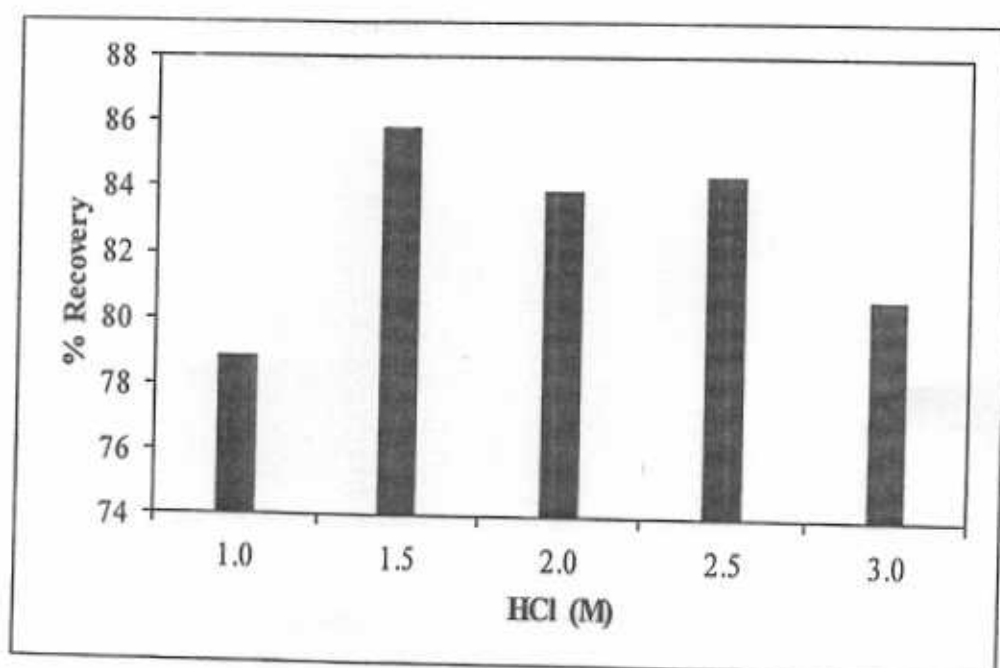


Figure 4.5.11: Comparison of different concentrations of HCl for desorption of Cd(II) from CTSD (sorbent dose 0.1 g; volume of Cd(II) solution 20 mL; pH 6; concentration of Cd(II) 25 $\mu\text{g mL}^{-1}$; volume of HCl 20 mL)

5.4.2.2.9. Application of the proposed method to real samples

The proposed method was applied to the analysis of Cd(II) in tap water and river water samples. Standard addition method was used for the analysis of Cd(II) in water samples. The results are given in table 4.5.3. It was observed that the recoveries of cadmium from real samples were in the range of 86.93-109.66%. These results show that the CTSD is a suitable biosorbent for solid phase extraction and determination of Cd(II) in environmental samples.

Table 4.5.14: Determination of Cd(II) in water samples

Cd(II) added (μg)	Cd(II) found (μg)	% Recovery
Tap water		
0.000	0.000	-
100	97.560 ± 5.20	97.560
300	284.430 ± 2.25	95.330
River Badabaira, Peshawar		
0.000	10.100 ± 3.04	-
100	86.930 ± 2.95	79.020
300	278.460 ± 13.00	89.820
River Swat, Charsadda		
0.000	0.000	-
100	107.960 ± 15.56	107.960
300	329.930 ± 11.39	109.660

CONCLUSIONS

Comparative studies for sorption of Ni(II) in batch and column methods were conducted using commercial sorbents amberlite, silica gel and indigenous material, mulberry wood sawdust. Optimum conditions such as solution pH, contact time, initial metal concentrations were investigated. The sorption of Ni(II) was found to be strictly pH dependent and maximum sorption (98%) was achieved at pH 3 for the three materials. Freundlich and Langmuir isotherm models were used for the representation of equilibrium data. The Langmuir model was shown to best fit into equilibrium data with high correlation coefficient ($R^2 > 0.95$) for all three materials. The maximum loading capacities (Q_0) of silica gel, amberlite and sawdust were found to be 33.3, 25.19 and 33.67 mg g⁻¹ respectively. Four sorption kinetic models: pseudo-first-, pseudo-second-order, intraparticle diffusion and Elovich model were used to analyze the kinetic data. It was observed that the sorption kinetic data fitted well into the pseudo-second-order-kinetic model ($R^2 > 0.97$) for all three materials. From the results it was concluded that the indigenous material is comparable with the expensive commercial materials for the removal of Ni(II) from aqueous solution and hence could be used for decontamination. The recovery study indicates that Ni(II) could be completely recovered from indigenous mulberry wood sawdust and therefore it could also be used for preconcentration of Ni(II) in trace determination.

Sawdust of the mulberry wood was converted into carbon using indigenously designed glass reactor. The sorption ability of the derived carbon was enhanced by chemical treatment with NaOH, HCl and H₂SO₄. The NaOH-activated sawdust carbon showed the best results. Chemically treated sawdust carbon (CSDC) and untreated sawdust carbon (SDC) were characterized using FT-IR, scanning electron microscopy and energy dispersive x-ray. The surface area of the CSDC and SDC were determined using surface area and pore size analyzer. Maximum % uptake of Ni(II) (86.50 %) was achieved at pH 7.0 after equilibration for 70 min. The batch sorption data were analyzed by Freundlich and Langmuir models and showed best fit into Langmuir model. The sorption data were also correlated with kinetic models like pseudo-first, pseudo-second order, intraparticle diffusion and Elovich. It was found that the data followed pseudo-second-order kinetic model with high regression coefficient ($R^2 > 0.99$). In the desorption process, percent recovery of Ni(II) from CSDC was low therefore it could be used only for the removal of Ni(II) from aqueous solutions.

The removal of Ni(II) from aqueous solutions was also investigated using waste tea leaves after washing with formaldehyde (0.4%). The effect of various parameters like temperature, pH, contact and shaking time, sorbent dose and initial metal concentration on sorption of Ni(II) using waste tea leaves were studied in batch experiments. The equilibrium data were fitted into Freundlich and Langmuir model and showed that the data followed Langmuir model. Maximum sorption capacity of the waste tea leaves for Ni(II) was evaluated from the Langmuir isotherm and was found to be 120.50 mg g^{-1} . Kinetic data were tested using the pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich equation. The kinetics of the sorption process was found to follow the pseudo-second-order kinetic model, suggesting that the sorption process was controlled by chemisorption. The plot of intraparticle diffusion model was not passing through the origin which indicates that more than one process affect the sorption phenomenon. Thermodynamic parameters such as standard entropy, free energy and enthalpy indicate that the sorption of Ni(II) on waste tea leaves is a spontaneous and exothermic process. The results showed that waste tea leaves have the potential to be used as a low cost sorbent for the removal of Ni(II) from aqueous solution.

A comparative sorption study of the Pb(II) was conducted using acid modified orange peels (AOP) and carbonized orange peels (COP) in batch modes. The sorption of Pb(II) on AOP and COP was found to be strictly pH dependent and maximum uptake (100%) was achieved at pH 6.0 and 5.5 respectively. The equilibrium data of Pb(II) were fitted into Freundlich and Langmuir models and was found that the data followed both models. Monolayer sorption capacities of AOP and COP were calculated using Langmuir isotherm and were found to be 1040 and 993.11 mg g^{-1} for Pb(II) respectively. Four common kinetic models: pseudo-first, pseudo-second-order, intraparticle diffusion and Elovich were used to analyze the kinetic data. On comparison, pseudo-second-order model was found to best fitted into kinetic data than other models. Thermodynamic parameters ΔG° , ΔH° and ΔS° were calculated using Van't Hoff equation which indicates that Pb(II) sorption on AOP and COP is spontaneous and endothermic process. The interferences effect of selected cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) on the sorption behavior of Pb(II) using AOP and COP were studied and no interferences effect of the studied cations on sorption of Pb(II) was found. Various eluents for recovery of Pb(II) after sorption were used and among them HNO_3 (1.5 M) was found to be the best eluent for recovery of Pb(II). The recovery study indicates that Pb(II) could be completely recovered from AOP and therefore it could be

used for preconcentration of Pb(II) in trace determination while COP was not regenerated and hence can be used only for the removal of Pb(II) from aqueous solutions.

Sawdust of the mulberry wood, after chemical treatment with hydrochloric acid (1.0 M) (CTSD) was used for the removal of Cd(II) from aqueous solution in batch systems. The sorption of Cd(II) was found to be pH dependent and maximum sorption was achieved at pH 6 with 30 min shaking. The sorption data were analyzed using Freundlich and Langmuir isotherms. The equilibrium data fitted best in the Langmuir isotherm and confirmed the monolayer sorption of Cd(II) on CTSD with sorption capacity of 403.73 mg g^{-1} . Pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich models were used to analyze the kinetic data. The data shows that pseudo-second-order model ($R^2 = 0.9887$) was the best choice among the kinetic models for description of sorption of Cd(II) on CTSD. The interferences effects of selected cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) on the sorption behavior of Cd(II) using the CTSD was studied and were found to have no effect on sorption of Cd(II) on CTSD. A variety of desorbents were used for the recovery of Cd(II) from loaded CTSD and maximum desorption of Cd(II) was achieved with 1.5 M HCl solution. From the results of sorption process of Cd(II), it may be concluded that mulberry wood sawdust is the best alternative to the expensive materials like ion exchange resins and activated carbon for the treatment of water and wastewater containing metal ions.