

REMOVAL OF COPPER AND ZINC FROM WASTEWATER USING CHITOSAN

A Thesis Submitted in Partial Fulfilment for the Award of the Degree

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In
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CERTIFICATE

This is to certify that the thesis titled “**Removal of Copper and Zinc from wastewater using Chitisan**”, submitted to the National Institute of Technology, Rourkela by **Garima Jain**, Roll No. **211CH1258** for the award of the degree of **Master of Technology** in Chemical Engineering, is a bona fide record of research work carried out by her under my supervision and guidance. The work documented in this thesis has not been submitted to any other University or Institute for award of any other degree.

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ABSTRACT

Heavy metals are one of the most toxic materials to the environment. Adsorption is the process which is used for the removal of heavy metals from wastewater. Many researches have been conducted to remove heavy metals using different materials. Various adsorbents have been used to remove different type of heavy metal ions from wastewater especially those that are harmful to mankind. Activated carbons, plant or lignocellulosic wastes, clays and biopolymers are the most common adsorbents used. For this research, chitosan was used as a adsorbent to remove copper and zinc from wastewater. Chitosan, a type of biopolymer, is a good adsorbent to remove the heavy metal ions from wastewater. The synthetic wastewater was prepared in the laboratory to conduct the experiments. Batch experiments were conducted to obtain the optimum conditions for copper and zinc. Effect of parameter like pH, adsorbent dose, contact time, temperature and initial metal ion concentration were also determined. The optimum conditions obtained were 360 min contact time, 200 mg adsorbent dose and pH 5 for copper and 180 min contact time, 200 mg adsorbent dose and pH 7 for zinc. Adsorption behavior could be described using the Langmuir, Freundlich and Temkin isotherm model. Adsorption data was well fitted in Langmuir isotherm model for both metals. The maximum adsorption capacity was found to be 89% for copper and 96.97% for zinc. The kinetics of adsorption could describe using pseudo first order and pseudo second order kinetic model. In all cases the kinetics follows the pseudo second order rate equation. The negative values of ΔG^0 and ΔH^0 indicate that the process was thermodynamically spontaneous and exothermic in nature.

Keywords: Chitosan, Adsorption, Heavy metal removal, Adsorption Isotherm, Adsorption Kinetics

CHAPTER 1

INTRODUCTION

1.1 PROBLEM STATEMENT

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substance in aquatic environment. Industrial wastewater contains higher amount of heavy metals that can pollute the water when it is discharged to the nature. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Heavy metals are the elements that have more than 5 times the specific gravity than that of water. Heavy metals are one of the most toxic types of water pollutants. At least 20 metals are considered to be toxic and approximately half of these metals are emitted to the environment in quantities that are risky to the surroundings, additionally to the human health.

Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc (Srivastava and Majumder, 2008). These industries discharge heavy metals and wastewater directly or indirectly into the environment especially in developing countries. Due to their toxicity and non- biodegradability, they tend to accumulate in living organism. Therefore they cause numerous diseases and disorders. Zinc, copper, nickel, mercury, cadmium, lead and chromium are considered as toxic metals of particular concern in wastewater treatment. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water.

Copper as an essential element plays an important role in all living organisms. It also widely used in industries such as high electrical and thermal conductivity, good corrosion resistance, ready availability, high recyclability and attractive appearance (P. Saha et al., 2008). Copper(II) is one of the heavy metals most toxic to the living organisms and it is one of more widespread heavy metal contaminants of the environment. Extensive intake of Cu can causes hemolysis, hepatotoxic and nephro toxic affects vomiting, cramps, convulsions, or even death (Ozar et al., 2007).

Zinc is a bluish white metal with an atomic weight of 65.37. Zinc is chemically active and alloys readily with other metals. It is used in many industries for preparing large number of zinc alloys and compounds. The excessive intake of zinc may cause toxic effects such as carcinogenesis, mutagenesis and teratogenesis as a result of bioaccumulation (Nriagu, 1980).

Many treatment processes that have been used to remove heavy metals from wastewater include precipitation and coagulation, ion exchange, electro dialysis, membrane filtration, flotation, reverse osmosis, and adsorption (Fenglain et al., 2011). Most of these processes are suffer from high cost. Adsorption is used many industries for water purification due to its low cost and applicability on large scale. Adsorption is commonly being done using activated carbon which adsorbs dissolved organic substances in the water treatment (Pope, 1996). To avoid the high cost of activated carbon many low-cost adsorbents have been used and tested to remove heavy metal ions. Different adsorbents have been used include rice husk ash (Srivastava et al., 2006), wood sawdust Modified Sugarcane Bagasse (Pereira, et al., 2009), modified flax shive (El-Shafey et al., 2002), waste biomass, waste activated sludge (Norton et al., 2004), and Lignite (Pentari, et al., 2009), chitosan (Shafaei et al., 2007). There are so many adsorbents have been used still new adsorbents are developed due to the increasing demand for treatment of industrial wastewater.

Recently, a number of studies were carried out on low cost adsorbents for removal of heavy metals from natural resources. One of such kind is the waste produced from fishery waste was used in the present study. Chitosan is a low cost adsorbent which is biodegradable and biocompatible polymer and it is produced by deacetylation of chitin (Ashraf et al., 2007).

Chitosan is a unique basic polysaccharide and partially deacetylated polymer of glucosamine obtained after alkaline deacetylation of the chitin (Guibal et al., 2001). It consists of mainly of β -(1-4-2- acetamido-2-deoxy-D-glucose) units and is the second most abundant biopolymer on earth after cellulose. It is widely distributed in crustacean shells and cell walls of fungus (Dutta et al., 2004, Mathur et al., 1990). Chitosan is soluble in dilute acids. The solubilisation occurs by the protonation of the $-\text{NH}_2$ function on the C-2 position of the D-glucosamine repeat unit, where the polysaccharide is converted to a polyelectrolyte in acidic media (Ramya et al., 2011). Chitosan is the only natural cationic polymer and thus it is used in many applications for the wastewater treatment. There are few review articles on the

potential applications of chitosan for pharmaceutical, veterinary medicine, and biomedicines are available in literature.

1.2 OBJECTIVE

The overall objective of this study was to investigate that the heavy metals removal from wastewater by adsorption using chitosan. The specific objectives are as follows:

- 1) To examine the effectiveness of chitosan for the adsorption of Cu and Zn from wastewater through
 - Adsorption isotherms studies
 - Adsorption kinetics studies
- 2) To examine effect of the following factors on the removal of Cu and Zn by adsorption on chitosan:
 - Effect of pH
 - Effect of adsorption doses
 - Effect of contact time
 - Effect of temperature
- 3) To examine the thermodynamic parameter of Cu and Zn by adsorption

1.3 SCOPE OF STUDY

The scope of this study is to test wastewater for the removal of copper and zinc using chitosan as an adsorbent. The wastewater was prepared in lab artificially. Batch studies were conducted using synthetic zinc and copper solution. The influence of pH, contact time, initial metal ion concentration, temperature and adsorbent concentration were investigated to optimize the conditions for maximum zinc and copper removal. The experimental data obtained were calculated and fitted using adsorption isotherms, various kinetic models and thermodynamic studies were conducted. Water quality analysis of the heavy metals was done using Atomic Adsorption Spectrophotometer.

1.4 ORGANIZATION OF THESIS

The thesis is divided into the following chapters:

Chapter 1 represents the background of the thesis research and the necessity of this project.

Chapter 2 describes the literatures based on the present work explaining the heavy metal pollution and their removal techniques. In this chapter influence of different parameters on adsorption using various adsorbents is also discussed. Many researchers studied the adsorption of heavy metals from wastewater using various adsorbents like activated carbon, rice husk, saw dust, charcoal and chitosan etc. Hence, in present study chitosan is used to remove the heavy metal from wastewater.

Chapter 3 presents the methodology employed to achieve the objectives of the thesis. It discusses the experiment that was conducted. It consists of procedures of experiment, equipment & apparatus used in experiment, and other relevant information that was used for conducting the experiments.

Chapter 4 presents the results and discussion that were obtained during the experimentations. This chapter emphasizes on obtaining optimal conditions that lead to the best conditions for the most efficient adsorption. It also describes the best model for adsorption like Langmuir, Freundlich and Temkin isotherm model in which the experimental data is well fitted.

Chapter 5 presents a conclusion to the thesis. It provides conclusions and recommendations. It highlights the results that were obtained from the thesis research.

CHAPTER 2

LITERATURE REVIEW

Removal of Heavy metals from the waste water is of most important because they not only contaminate the water bodies but are also toxic to the eco system. As the majority of the heavy metals are non-degradability and highly toxicity in nature (Tchobanoglous and Burton, 1991). Therefore their concentration have to be reduced to acceptable levels before discharging into the environment, or else these can pose a threat to the human as well as animal health.. Heavy metals such as lead, zinc, nickel, mercury, cadmium, copper, arsenic, cobalt, chromium, bismuth, ferrous etc. have been recognized as poisonous to environment and human health even present in traces. Which are originated mainly from metallurgical, metal finishing, mining, chemical manufacturing, battery manufacturing processed and in electroplating industries in considerable amounts.

2.1 COPPER AND ITS IMPORTANCE

Copper is an important engineering metal and it is widely used for various engineering purposes. It is used for making of alloys. It is also used in ceramic and pesticides. In many industries like electrical appliances, electrical, electronics, automotive, white goods etc. copper is used in manufacture of wires. It is also used in copper forming industries. Copper compounds are used in fungicides, algicides, insecticides, and wood preservatives. It is used in electroplating industry and manufacture of dye. Copper compounds are added to fertilizers and animal feed as a nutrient to support plant and animal growth (Landner & Linderstrom, 1999).

2.2 EMISSIONS OF COPPER

Copper enter into the environment through natural and anthropogenic sources. Air and water is contaminated by copper form mining, milling, electroplating industries, petroleum and refining melting plant. Copper is discharge into the industrial effluents of various industries like chloral-alkali, electroplating, paints and dyes, petroleum refining, fertilizers, mining and metallurgy, explosives, pesticides, iron and steel industries, burning of wood etc. due to the direct discharge of industrial and municipal waste water is polluted (Dara, 1993). The main source of pollution in copper industries are: Solis waste form mines, mine water and effluent

from water treatment plants, sulphur containing gases, electrolyte from electro-refining plant, acid sponge from sulphuric acid plant etc. (Bhatia, 2002).

2.3 ENVIRONMENTAL EFFECTS OF COPPER

Copper is regarded as one of the most basic toxic metals. The increase levels of copper in environment are posing a serious threat to mankind (Gustavo et al., 2007). It can cause harmful biochemical effects, toxicity and hazardous disease in human beings. Excessive intake of copper through air, water and food can cause harmful disease. Ingestion of 15-75 mg of copper can cause gastro-intestinal disorder. Excessive intake of copper can cause hemolysis, hepatotoxic and nephro toxic effects. Copper toxicity can cause irritation, corrosion, hepatic damage and central nervous system irritation followed by depression (Krishnamurthy and Vishwanathan, 1991). Prescribed limit for copper in drinking water is 0.05mg/L as per WHO norms and also 0.05 mg/L as per ISI prescribed limits, 1993(Shrivastava, 2009).

2.4 ZINC AND ITS IMPORTANCE

Zinc is a bluish-white metal. It is found in IIB group of the periodic table. It is brittle and crystalline at ordinary temperature. But it become ductile and malleable when heated at temperature ranges from 110⁰ to 115⁰C. It is tremendously reactive metal that will combine with oxygen and other non-metals and will react dilute acids to release hydrogen. Zinc metal and zinc alloys are very resistant to corrosion. Due to its extensive usage in electroplating, metal plating, chemical manufacturing industries, etc. the demand of zinc has been increasing globally.

Zinc is used in galvanization of steel to the manufacture of the negative plates in electrical batteries, preparation of alloys. Zinc is used in plastics, cosmetics, wallpaper, printing inks, photocopier paper etc. as a pigment. In the production of rubber it plays an important role as a catalyst during manufacture. Zinc oxide used in ointments for burns and skin protection. Zinc pyrithione used in anti-dandruff shampoos. Zinc chloride used in the manufacture of artificial silk. It is also used in printing and dyeing textiles.

Zinc is also a metallic element, found in the body as divalent cations, which does not undergo metabolism. Zinc interacts electro-statically with anions (i.e. carbonate, hydroxides, and oxalate) and negatively charged moieties on macromolecules such as proteins. Zinc as well

form chelation complexes with amino acids and multidentate organic acids such as ethylenediaminetetraacetic acid. Zinc compounds are also used in the drug industry as ingredients in some common products, like vitamin supplements, sun blocks, diaper rash ointments, deodorants, athlete's foot preparations and poison ivy preparations, and antidandruff shampoos (ATSDR, 2005). Zinc occurs naturally in many foods. Even zinc is important for human health if a pregnant woman doesn't get enough amount of zinc, her babies may have birth defects.

2.5 EMISSIONS OF ZINC

Zinc is widely used in many industries such as paint, batteries, fertilizers and pesticides, galvanization, pigment, polymer stabilizers, fossil fuel and combustion, electroplating, paper and pulp, pharmaceutical, textile mills, mining industries, etc. these industries are the main source of zinc pollution. The waste generated from these industries directly discharge to the environment and the water is polluted with zinc due to the excessive amount of zinc (Harte et al., 1991).

Zinc is also available in some medicated shampoos contain zinc pyrithione to control dandruff. Residues of zinc from zinc-plated cold water tanks leach into tap water and are flushed away when water is used.

2.6 ENVIRONMENTAL EFFECTS OF ZINC

The excessive intake of zinc into the body through food, water or other dietary supplements can also affect human health. The recommended dietary allowances of zinc for man are 11mg/day and for women is 8mg/day (ATSRD, 2005). Beyond this limit it may cause many health problems like stomach cramps, nausea and vomiting. High level ingestion of zinc for several months can cause anaemia, damage the pancreas and decrease the levels of cholesterol. Ingesting low level of zinc compounds like zinc acetate and zinc chloride may cause skin irritation. Insufficient amount of zinc in diet can cause loss of appetite, decreased sense of taste and smell, decreased immune function, slow wound healing and skin sores.

2.7 CHITOSAN

Chitin is the second most abundant natural polysaccharide next to cellulose. It is found in the shells of crustaceans such as crab, shrimp as well as in exoskeleton of marine zooplankton

also have chitin in their wings. Chitin is found in the cell walls of yeast, mushrooms and fungi (Roberts, 1992).

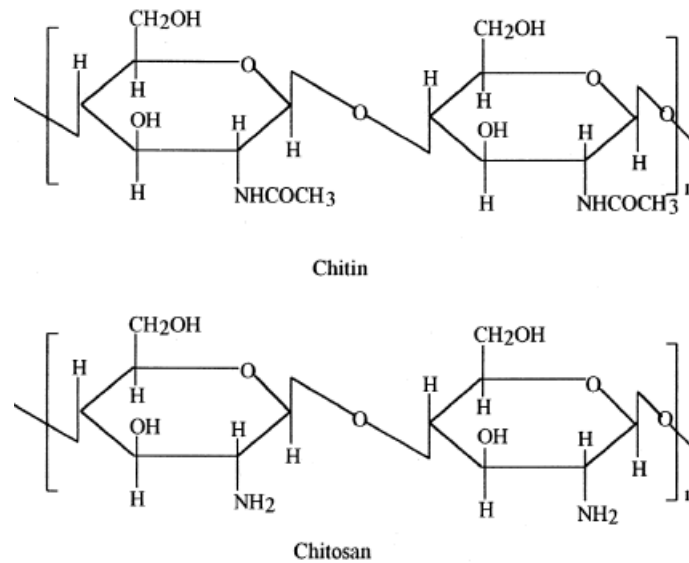


Figure 2.1: Structure of chitin and chitosan

Figure 2.1 shows the structure of chitin and chitosan. Since the biodegradation of chitin is very slow in crustacean shell waste, accumulation of large quantities of discards from processing of crustaceans has become a major problem in the seafood processing industry. So, it is important to recycle these by-products. These by-products could use in other industries for the treatment of wastewater. With the help of these by-products many problems can be solved such as solid waste disposal problem. But, chitin is an extremely insoluble material. The insolubility of chitin is a major problem that confronts the development of processes and uses of chitin (Rinaudo, 2006), and so far, very few large-scale industrial uses have been found. Chitin is a derivative of cellulose. Chitin is a long chain of N-acetyl-D-glucosamine units. Professor C. Rouget first discovered the chitosan in 1859. Chitosan is made by cooking chitin in alkali similar to the process for making soap. When it is cooked the glucosamine units are combining to form chitosan chains. Each glucosamine unit contains a free amino group. These groups can take a positive charge which gives chitosan an amazing property (Deans and Dixon, 1992). Commercially chitosan is produced by deacetylation of chitin. A common method for the synthesis of Chitosan is the deacetylation of chitin using sodium hydroxide in excess as a reagent and water as a solvent (Kumar et al., 2013). Chitosan is soluble in acid solutions and is chemically more versatile than chitin or cellulose. Chitosan is the only pseudo natural cationic polymer and it is used in many industrial applications for water treatment.

Chitin and chitosan are widely used for wastewater treatments in many industries that decrease the chemical oxygen demand and total nitrogen (Sudha, 2010). Chitosan has limited application of water treatment due to its low mechanical strength and flexible behaviour. On the other hand addition of synthetic polymers increases the properties of chitosan. Chitosan also has drawbacks like acidic solubility, low thermal and mechanical stability. To overcome these drawbacks, chitosan can be modified physically and chemically also (Shanmugapriya et al., 2011).

2.7.1 PROPERTIES OF CHITOSAN

Most of the polysaccharides like cellulose, dextran, pectin, agar etc. are neutral or acidic in nature. Chitin and chitosan are the naturally occurring polysaccharides. They have the unique properties include polyxysalt formation, ability to form films, optical structural characteristics and chelates metal ions (Larry, 1998). Chitin is highly hydrophobic in nature and it is insoluble in water and most organic solvents. Chitosan is soluble in hexafluoro-isopropanol, hexafluoroacetone, chloroalcohols in conjugation with aqueous solutions (Muzzarelli et al., 1984).

2.7.1.1 CHEMICAL PROPERTIES OF CHITOSAN

The chemical properties of chitosan are given below:

1. Reactive amino groups.
2. Chelates many transitional metal ions.
3. Linear polymine.
4. Reactive hydroxyl groups available (Dutta et al., 2004).

2.7.1.2 BIOLOGICAL PROPERTIES OF CHITOSAN

Biological properties of chitosan are as follows:

1. It is biocompatible
2. Regenerative effect on connective gum tissue.
3. It is hemostatic and fungistatic
4. It is antitumor
5. It is Anticholesteremic
6. It accelerates bone formation
7. Immunoadjuvant (Dutta et al., 2004)

2.7.2 APPLICATION OF CHITOSAN

Chitosan is widely used in different products and applications ranging from pharmaceutical and cosmetic products to water treatment and plant protection. Different properties are required in different industrial applications. Some of the important applications of chitosan are given below:

- Chitosan derivatives are used in three areas of cosmetics such as hair care, skin care and oral care.
- Used in shampoos, hair colorants, lotions, hair sprays and hair tonics.
- Used in many industries for wastewater treatment as adsorbent.
- Used in paper industry.
- Used in textile industry.
- Used in food processing industry.
- Used in photography as a fixing agent.
- Used in biomedical applications.

2.8 DIFFERENT TECHNIQUES FOR WASTE WATER TREATMENT

Chemical, biological and physical waste water treatment processes are currently the most commonly used methods of treating aqueous hazardous waste. Chemical treatment converted waste into less hazardous substance using various techniques such as flocculation, oxidation or reduction, ion exchange and chemical precipitation. Biological treatment uses microorganisms to degrade organic compounds in the waste stream. Physical treatment processes include gravity separation, phase change system, such as air and steam stripping of volatiles from liquid waste, and various filtration operations, including adsorption.

2.8.1 ADSORPTION

Adsorption is defined as the process where a solute is removed from the liquid phase through contact with a solid adsorbent which has a particular affinity for that particular solute (W. L. McCabe et al., 2005). The phenomenon of the enrichment of chemical substances at the surface of a solid is termed 'adsorption'. All adsorption processes mainly depend on solid-liquid equilibria and on mass transfer rates (Bing et al., 2009). The reverse of adsorption is referred to as 'Desorption'.

Most adsorbents are extremely porous materials, and adsorption takes place totally on the walls of the pores or at the particular sites inside the particle. Adsorption can take place as a result of variations in molecular weight, shape, or polarity which cause some molecules to be control strongly on the surface than others or because the pores are too tiny to admit the larger molecules. The overall adsorption rate is controlled by the rate of diffusion of solute within the capillary pores of the adsorbent and varies with root of the contact time with the adsorbent. The adsorption process may be batch, semi-batch and continuous. Batch operations are usually conducted when small amounts are to be treated. The equilibrium distribution depends on the contact time in batch operation (Mishra et al., 2008).

2.8.1.1 ADSORPTION OF COPPER

Adsorption plays an important role in processes like heterogeneous catalysis. The oldest known application of adsorption is purification. Water clarification is still accomplished by the use of adsorbents (Yadla et al., 2012).

Adsorption studies were carried out using a variety of adsorbents such as: Activated carbon, low cost adsorbents for biomass, waste sludge, rice husk, sugarcane bagasse, lignite, chitosan etc. Chitosan is widely used in the removal of heavy metals contamination. The crosslinked chitosan synthesized by the homogeneous reaction of chitosan in aqueous acetic acid solution with epichlorohydrin had been used to investigate the adsorptions of three metals of Cu (II), Zn (II), and Pb (II) ions in aqueous solution. The study showed the maximum peak at pH 7 (Chen et al., 2009).

M.W. Wana et al., (2010) investigated adsorption of Cu (II) by chitosan-coated sand (CCS) and the equilibrium studies were determined by the using both Langmuir and Freundlich isotherm models. He found that the maximum adsorption capacity was 8.18 mg/g. The equilibrium kinetic agreed very well with pseudo second order kinetics which indicated that adsorption was controlled by Chemisorption.

The cross-linked chitosan beads with glutaraldehyde have lower percentage of swelling and several enhanced physical properties. Chitosan beads, chitosan–GLA beads and chitosan–alginate beads correspond to the category of mesoporous. In this study, the capacity of chitosan beads, chitosan–GLA (glutaraldehyde) beads and chitosan–alginate beads were examined. Equilibrium data were fitted to non-linear Langmuir, Freundlich and Sips isotherms. Based on Langmuir isotherms, the maximum monolayer adsorption capacity for

chitosan beads, chitosan–GLA beads and chitosan–alginate beads are 64.62 mg/g, 31.20 mg/g, 19.51 mg/g and 67.66 mg/g, respectively. Chitosan–GLA beads showed a lower adsorption capacity due to the cross-linking which reduces the number of amino groups available for the uptake of Cu (II) ions. The pseudo-second order best describes the adsorption process, which assumes that chemisorptions are the rate controlling mechanism (W. Ngah and Fatinathan, 2008).

Schmuhl et al., (2001) studied the ability of chitosan as an adsorbent for Cu (II) ions in aqueous solution. The experiments were done as batch processes. Equilibrium studies were conducted on both cross-linked and non-cross-linked chitosan for both metals. He found the optimum pH was 3 to 5 for the removal of Cu (II). From the experimental data it was observed that the metal concentration for copper can be lowered by means of the batch process from 10 mg/L to 2.4 mg/L.

Chitosan with nylon 6 membranes was used as adsorbent to remove copper and cadmium ions from synthetic wastewater. Characterization of the synthesized membrane has been done with FTIR, XRD, TGA and SEM. The optimum pH for removal of Cd(II) and Cu(II) was found to be 5 using chitosan with nylon 6. The removal efficiency of copper increased in the pH range from 3 to 5. The optimum pH for copper was found to be 5. The removal efficiency of Cu⁺² ions onto chitosan increased rapidly with increase in contact time from 0-360 min and then reaches equilibrium after 360 min (N. Prakash et al., 2012).

N. Prakash et al, 2012 conducted a study on the influence of clay on the adsorption of heavy metals like copper and cadmium on chitosan from simulated industrial wastewater. In this study chitosan–clay blend was prepared with ratio of (1:1), (1:2), and (2:1), and were used as membranes for the removal of copper and cadmium ions from synthetic industrial wastewater. The chemical parameters for quantities of adsorption of heavy metal contamination were done, and the kinetics of adsorption was also carried out. With increase in pH within the range of 3 to 5, the removal efficiency of copper also increased. The optimum pH for copper was found to be 5. The removal efficiency of Cu²⁺ ions on chitosan increased rapidly with increasing the contact time from 0 to 360 min and then reaches equilibrium after 360 min. (N. Prakash et al., 2012).

2.8.1.2 ADSORPTION OF ZINC

Due to the high cost of Activated carbon limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal. Karthikeyen et al., (2004) examined the removal of Zn (II) using chitosan. They found that an optimum contact period of six minutes was required for the maximum removal of zinc (II) by chitosan. The adsorption mechanism also depends upon the particle size of the adsorbent, pH of the medium and the presence of other anions like chlorides and nitrates. The optimum pH was found to be 7 and the equilibrium data was well fitted in Langmuir isotherm. Thermodynamic and equilibrium parameters showed that the adsorption process was endothermic and spontaneous in nature.

Guan et al., (2009) studied the feasibility of precipitation of heavy metal ion Mn(II) and Zn (II) by water-soluble chitosan. FT-IR analysis was also carried out between chitosan and metal ion. The optimum pH was found in the range from 5 to 9, there were three stages for different actions: precipitation of metal hydroxide and coprecipitation of metal hydroxide and chitosan–metal complex, chelation of chitosan for metal ion. The selective chelation of chitosan for Mn (II) and Zn (II) mixture solution was also studied. From the results it is clear that the chelation of chitosan for Mn (II) was prior to Zn (II) in multiple component solution. Zhu et al., (2012) investigated in single and ternary metal system the competitive adsorption of Pb(II), Cu(II) and Zn(II) onto a novel xanthate-modified magnetic chitosan (XMCS). In single system, equilibrium studies showed that the adsorption of Pb(II), Cu(II) and Zn(II) followed the Langmuir model and they found the maximum adsorption capacities were 76.9, 34.5 and 20.8 mg/g, respectively. In ternary system, they found the combined action of the metals to be antagonistic and the metal sorption followed the order of Pb(II) > Cu(II) > Zn(II). The Langmuir isotherm fitted the data of Pb(II) and Cu(II) well while the equilibrium data of Zn(II) was well fitted in the Freundlich model.

Sidhaarth et al., (2012) studied the applicability of Iron oxide nanoparticles for the selective removal of lead and zinc from aqueous solution and effluents. Nanoparticles were prepared by coprecipitation method and then characterized by X-Ray diffraction, Scanning electron microscopy and Atomic force microscopy. The size of the particle was determined as 18.14nm using scherrer formula. The adsorption was found to be dependent on the influencing parameters. Lead and zinc removal was found to be 89 and 95% with an initial

concentration of 300mg/l and 160mg/l with adsorbent dosage of 20mg/50ml and 25mg/100ml with a contact time of 10 and 40 minutes in the alkaline range of pH11 and pH13. The adsorption data were fitted to Langmuir, Freundlich and Temkin isotherms and kinetic constants were determined.

Bassi et al (2000) proved that in commercially available chitosan (chitosan flakes supplied by Sigma, with a DDA of 85%) the order of metal ion adsorption decreased as follows copper (1 mg/g) > lead (0.20 mg/g) > cadmium (0.13 mg/g) > zinc (0.06 mg/g) when starting with a 10 mg/L metal solution. The metal adsorption uptake was found to be pH-dependent, with a maximum between pH 6 and pH 7. Equilibrium studies correlated well with the Langmuir isotherm equation, with a maximum adsorption capacity of 11.7 mg/g for the zinc ions.

Vold et al., (2003) studied the selective adsorption of copper, zinc, cadmium and nickel on further deacetylated commercial chitosan and observed a high selectivity to copper compared to zinc, cadmium and nickel between a pH of 5 and 6.

Tanja Becker et al., (2000) studied the capacities for nickel (II), zinc (II) and cadmium (II) ions were investigated in aqueous nitrate, chloride and sulphate solutions at pH 6. The selectivity's been determined in mixtures of nickel (II), zinc (II), cadmium (II), magnesium (II) and calcium (II) and was recorded as a function of the pH value and the counter-ion. In sulphate solutions four chitosan derivatives show higher metal uptake than in solutions of nitrate or chloride.

Ding et al., (2006) studied the kinetics of Zn (II) ion on chitosan derivatives. He studied the adsorption capacities and rates of Zn (II) ions onto chitosan derivatives. He found that the adsorption isotherm data was well fitted in Langmuir and Freundlich isotherm model. He also found that the kinetic experimental data was well fitted in second order kinetic model, which says that the chemical adsorption is rate limiting step.

CHAPTER 3

MATERIAL & METHODS

3.1 CHEMICALS

All the chemicals used were of analytical reagent grade. Zinc sulphate heptahydrate and copper sulphite were used for preparation of stock solutions. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

3.2 INSTRUMENTATION

The list of the instruments used during the adsorption experiments and their functions are given in the Table 3.1

TABLE 3.1: List of Instruments

Instruments	Makers	Function
Analytical Balance	Sartorius	Weight Measurement
pH meter	EuTech Instruments	Measurement of pH
Ultra-pure water system	Sartorius	Preparation of the stock solution, throughout the experiment etc.
Atomic Absorption spectrophotometer	A Analyst 200, Perkin Elmer	Estimation of metal ion concentration
Shaker	Lab Companion model SI-300R	Batch adsorption studies of heavy metals
UV spectrophotometer	Jasco V-530	Estimation of metal ion concentration

3.3 STOCK SOLUTION PREPERATION

Stock solution of 10 mg/l Cu (II) ion is prepared dissolving copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). To do this 39.28 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is added in distilled water contained in 1000ml volumetric. Stock solution of 10 mg/l of Zn is prepared by dissolving zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). To do this 43.96 mg of Zinc sulphate heptahydrate solution is added to distilled water contained in 1000 ml volumetric flask. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

3.4 ADSORPTION EXPERIMENT

Batch adsorption experiments of copper and zinc were carry out to determined the adsorption capacity of chitosan at different metal concentrations ranging from 10 to 120 ppm and a fixed amount (50mg) of chitosan in order to calculate the adsorption constant using different isotherms. 50 mL of different concentration of copper (II) and zinc (II) solutions ranging from 10–120 ppm were used. The chitosan (50 g) was added to flasks and agitated at 25⁰C and 100 rpm for 360 min for copper and 180 min for zinc. The initial and final concentrations of the solutions were measured were determined by AAS at the maximum adsorption wavelength and the adsorption capacities of the adsorbent were calculated. After equilibrium was attained, the metal uptake capacity for each sample was calculated according to a mass balance on the metal ion using equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg L⁻¹), C_e is the equilibrium metal concentration (mg L⁻¹) and q_e is the metal quantity adsorbed at equilibrium (mg/g). Experiments were carried out at different initial pH values. The initial pH of the solution was adjusted with either HCl or NaOH. The percent removal of metals from the solution was calculated by the following equation.

$$\%removal = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 (mg/L) is the initial metal ion concentration and C_i (mg/L) is the final metal ion concentration in the solution.

3.5 ADSORPTION KINETICS

The kinetic study of adsorption in wastewater plays an important role because it affords important insight into the reaction pathways and into the mechanism of the reaction. Kinetic models have been proposed to explain the mechanism of a solute sorption from aqueous solution onto an adsorbent:

- Pseudo first order kinetic model.
- Pseudo second order kinetic model.

3.5.1 PSEUDO-FIRST ORDER MODEL

The pseudo first-order kinetic model has been widely used to predict the metal adsorption kinetics. The metal adsorption kinetics following the pseudo first-order model is given by (Ho and McKay, 1999a):

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (3)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (13) becomes.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (4)$$

By plotting $\log(q_e - q_t)$ versus t , the adsorption rate can be calculated.

3.5.2 PSEUDO-SECOND ORDER MODEL

The adsorption kinetic data can be further analyzed using Ho's pseudo second-order kinetics (McKay and Ho, 1999 b,c). This is represented by:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Integration of Eq. (15) and application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (6)$$

Where k_2 (g/(mg min)) is the rate constant, k_2 and q_e can be obtained from the intercept and slope.

3.6 ADSORPTION ISOTHERM

Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed (Allen et al., 2003). The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid

phase concentration (C_e) of solute Adsorption isotherm explains the interaction between adsorbate and adsorbent and is critical for design of adsorption process. The Langmuir, Freundlich and Temkin isotherms are the most frequently used models to describe the experimental data of adsorption. In the present work these three isotherms were applied to investigate the adsorption process of Cu (II) and Zn (II) on chitosan at different conditions of process parameters. The adsorption equilibrium study was carried out for metal concentrations varying from 10 to 120mgL⁻¹.

3.6.1 LANGMUIR ISOTHERM MODEL

The Langmuir adsorption is the best model among the entire isotherm model and it is successfully applied in many adsorption processes.

The Langmuir equation is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

The linearization of it gives the following form:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (8)$$

Where C_e , equilibrium metal concentration, q_m and K_L are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (1/mg), respectively.

3.6.2 FREUNDLICH ISOTHERM MODEL

Freundlich isotherm model is one of the most widely used mathematical models which fit the experimental data over a wide range of concentration. This isotherm model is based on heterogeneous surface, distribution of active sites and their energies and enthalpy changes logarithmically.

The Freundlich equation is given by (Singh et al., 2011):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (9)$$

The logarithmic form of equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

Where q_e is the amount of metal ion adsorbed after adsorption per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), K_F and n are Freundlich equilibrium constants.

3.6.3 TEMKIN ISOTHERM MODEL

Temkin isotherm contains a factor that clearly taking into the account of adsorbent–adsorbate interactions. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage on ignoring the extremely low and large value of concentration. Temkin isotherm is given by the following equation (Temkin and Pyzhev, 1940):

$$q_e = \frac{RT}{b} \ln(aC_e) \quad (11)$$

Linear form of this model is given by the following equation:

$$q_e = a + b \ln C_e \quad (12)$$

Where q_e is the amount of metal ion adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), a is equilibrium binding constant (g^{-1}) and b is related to heat of adsorption (J/ mol) which are Temkin constants.

3.7 THERMODYNAMIC PARAMETERS

K is equilibrium constant that's why its dependence with temperature can be used to predict thermodynamic parameters including change in the free energy (G^0), enthalpy (H^0) and entropy (S^0) associated to the adsorption process and were determined by using following equations (Ozcan et al., 2005):

$$\Delta G^0 = -RT \ln K \quad (13)$$

Where K = Langmuir constant

T = absolute temperature ($^{\circ}K$)

R = universal gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$)

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

The plot of $\ln K$ as a function of $1/T$ yields a straight line from which H° and S° can be calculated from the slope and intercept, respectively.

4.1 COPPER

4.1.1 EFFECT OF PARAMETERS

4.1.1.1 EFFECT OF pH

Figure 4.1 illustrated that pH obviously influenced the removal efficiency of the copper ions in the aqueous solution. The results indicated that Cu (II) removal was increased to maximum and then decreased with pH variation from 4 to 9 at temperature 25⁰C and agitation speed of 100 rpm. The maximum % removal of Cu (II) was about 89% at pH 5. The dominant species of copper was free Cu(II) and was mainly involved in the adsorption process when the pH was lower than 5. When the pH greater than 5, copper ions started to precipitate as Cu (OH)₂, this had been confirmed by Ramya et al., (2005). Increases in metal removal with increased pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (>pH 5) is due to formation of soluble hydroxy complexes (R. Ramya et al., 2003). The adsorption of Cu (II) ion was found mainly to be influenced by solution pH.

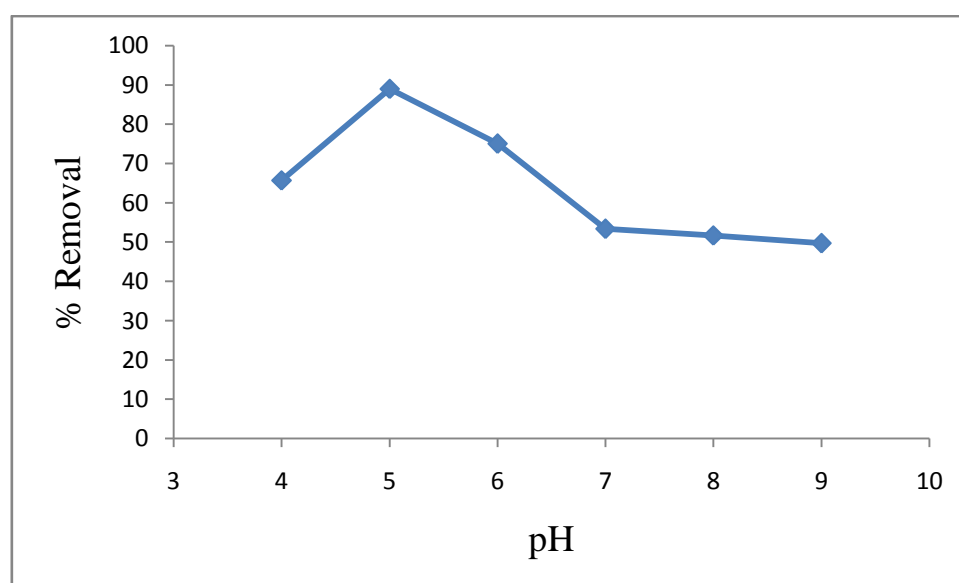


Figure 4.1: Effect of pH on adsorption of Cu

4.1.1.2 EFFECT OF CONTACT TIME

Figure 4.2 indicated that metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dose of adsorbent and pH of solution were kept constant. The results indicated that Cu (II) removal was increased from 15 to 89% with the contact time variation from 10 to 360 minutes. From 360 to 400 minutes, the percentage removal of Cu (II) remains constant (89%), which showed that equilibrium was reached at 360 minutes itself. Thus the results illustrated that the optimum contact time for maximum removal (89%) of Cu (II) was 360 minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment system.

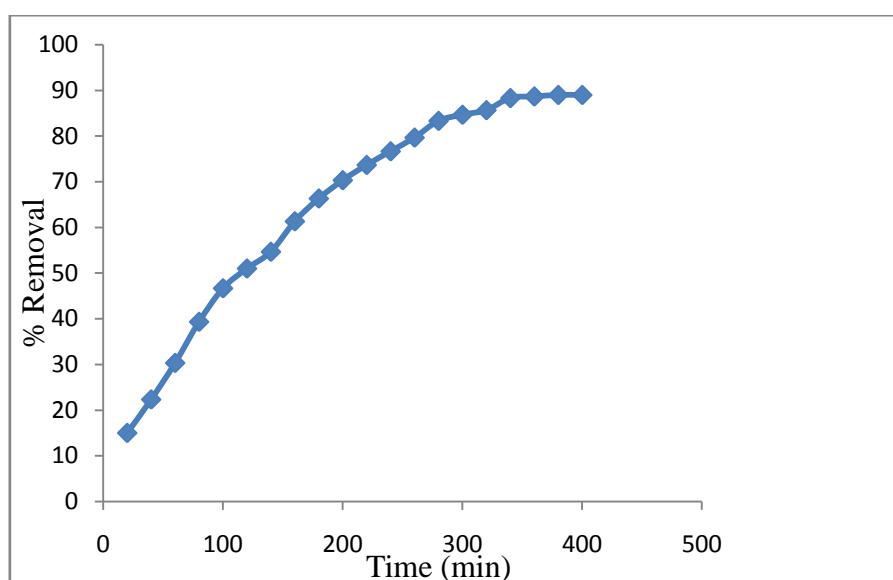


Figure 4.2: Effect of contact time on adsorption of Cu

4.1.1.3 EFFECT OF ADSORBENT DOSE

Adsorption efficiency of Cu (II) adsorption was studied by varying the amount of adsorbents from 50 to 200 mg keeping other parameters (pH, and contact time) constant. The figure 4.3 shows that removal efficiency of the copper usually improved on increasing adsorbent doses. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. From the figure it is clear that the no further increase in adsorption after a certain amount of adsorbent was added (200 mg). The maximum % removal of Cu (II) was about 88.17% at the dosage of 200 mg. This result also suggest that after a certain dose of adsorbent, the equilibrium conditions reached and hence

the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent.

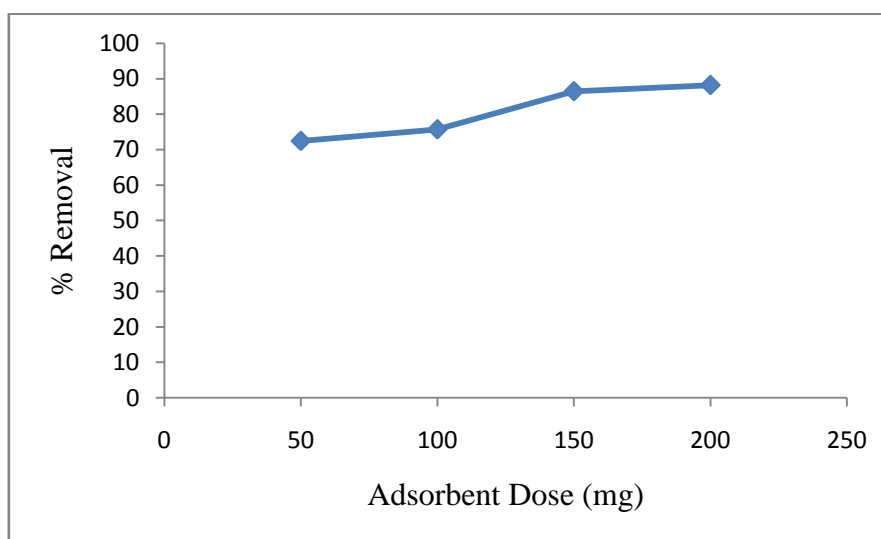


Figure 4.3 Effect of adsorbent dosage on adsorption of Cu

4.1.1.4 EFFECT OF TEMPERATURE

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the negative effect on adsorption of copper onto chitosan. The temperature effect on removal of copper ion using chitosan was studied within the range of 25-55⁰C. Other parameters such as dose of adsorbent and pH of solution were kept constant. With increase in temperature from 25-55⁰C the percent removal of copper ions was decreased from 83.3% to 75.37%. From the figure 4.4 it is clear that the low temperatures are in favour of copper ion removal. This may be due to a tendency for the Copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of Copper is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature.

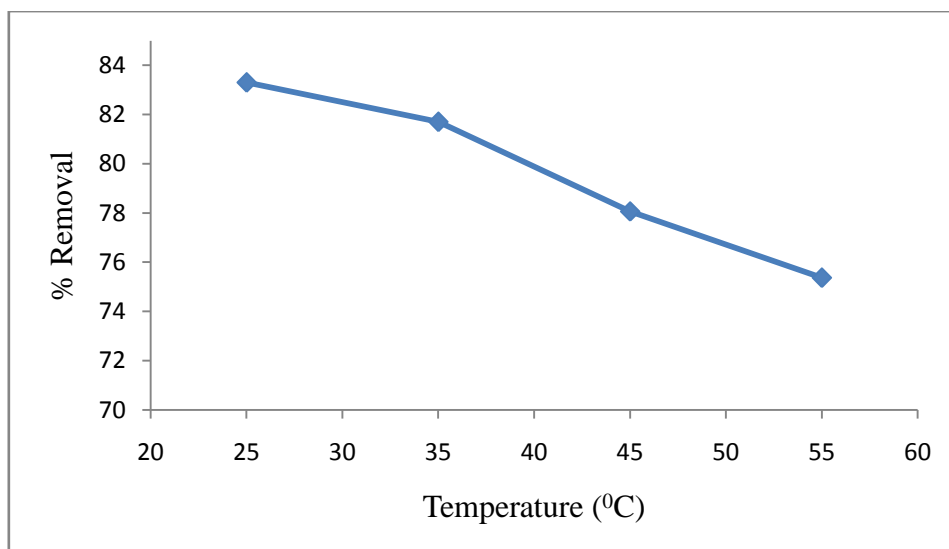


Figure 4.4: Effect of temperature on adsorption of Cu

4.1.1 5 EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial copper concentration on the copper adsorption rate was studied in the range (3-100mg/L) at pH 5, temperature 25°C, and 360 min contact time. The results presented in the Fig 4.5. From the figure it was observed that the percentage of removal decreased with increasing in initial copper concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial copper concentration. Therefore it was evident from the results that copper adsorption was dependent on the initial metal concentration.

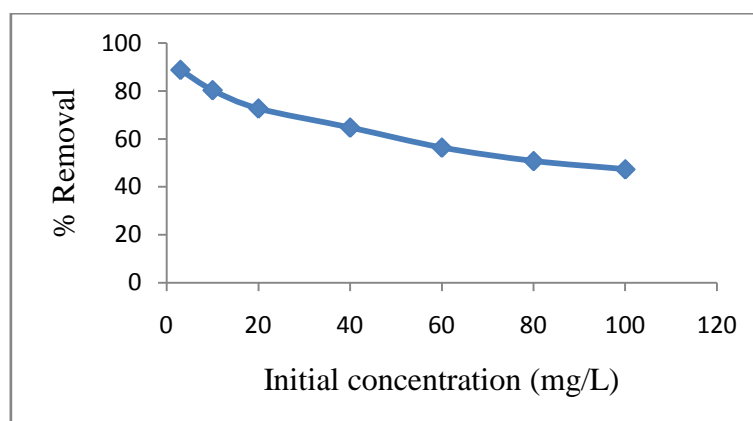


Figure 4.5: Effect of initial metal ion concentration on adsorption of Cu

4.1.2 ADSORPTION KINETICS

The kinetics of adsorption was studied for a contact time ranging 10-360 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (fig 4.5 & fig 4.6). The reported R^2 value indicates that the experimental results shows better fit to pseudo-second order model. Hence, the copper adsorption seems to be more pseudo-second order.

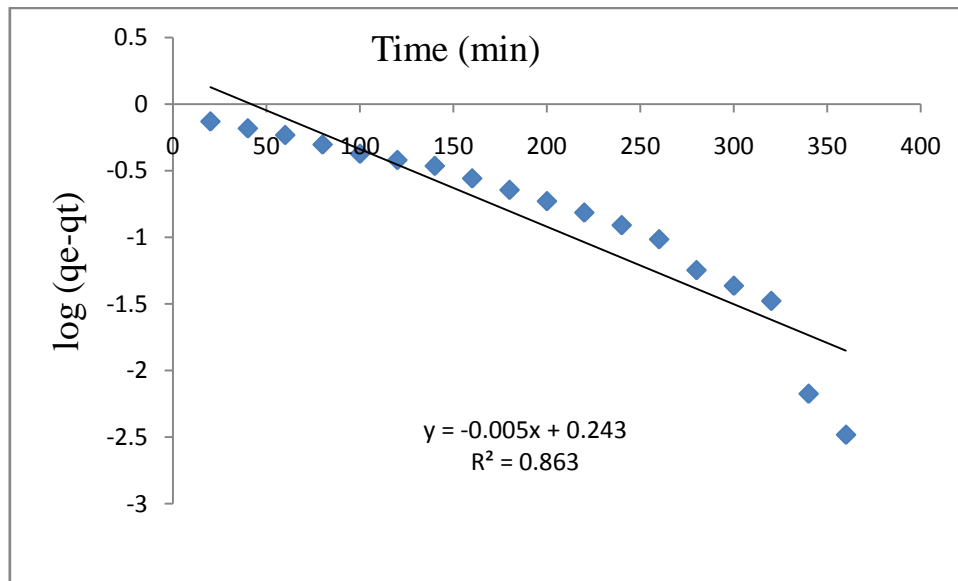


Figure 4.6: Pseudo first order kinetics plot for Cu adsorption

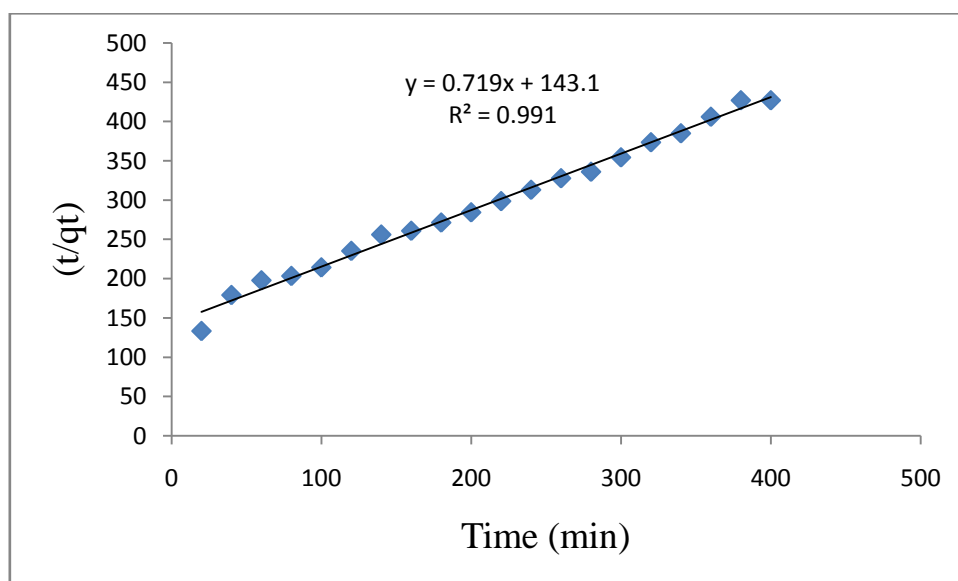


Figure 4.7: Pseudo second order kinetics plot for Cu adsorption

4.1.3 ADSORPTION ISOTHERM

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as to compare the effectiveness of different adsorbent materials under different operational conditions and also to design and optimize an adsorption system. Heavy metal adsorption is usually modelled by the classical adsorption isotherms. In this study, three isotherms models were used, Langmuir, Freundlich, Temkin isotherms using Eqs (8),(10),and(12) respectively. The values of various constants of the four models were calculated and were represented in the Table 4.1.

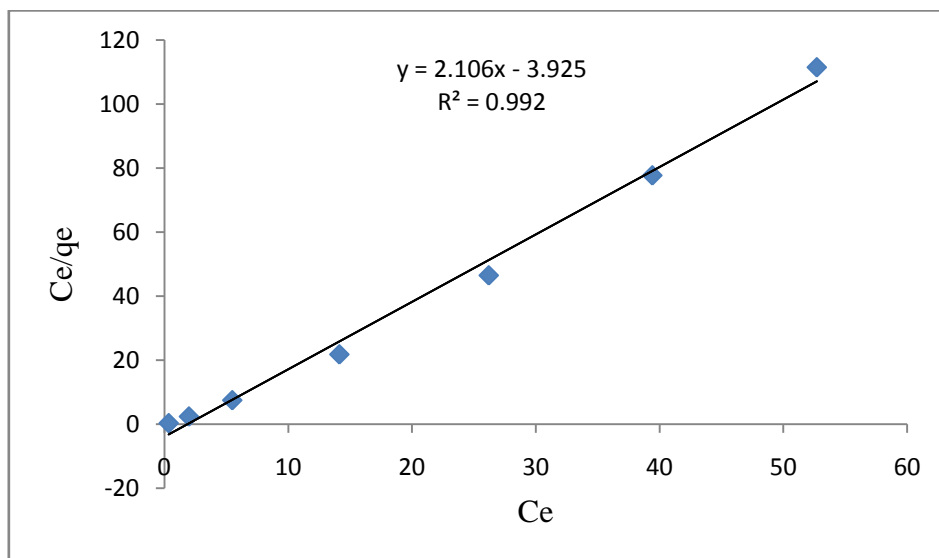


Figure 4.8: Langmuir adsorption isotherm for Cu adsorption

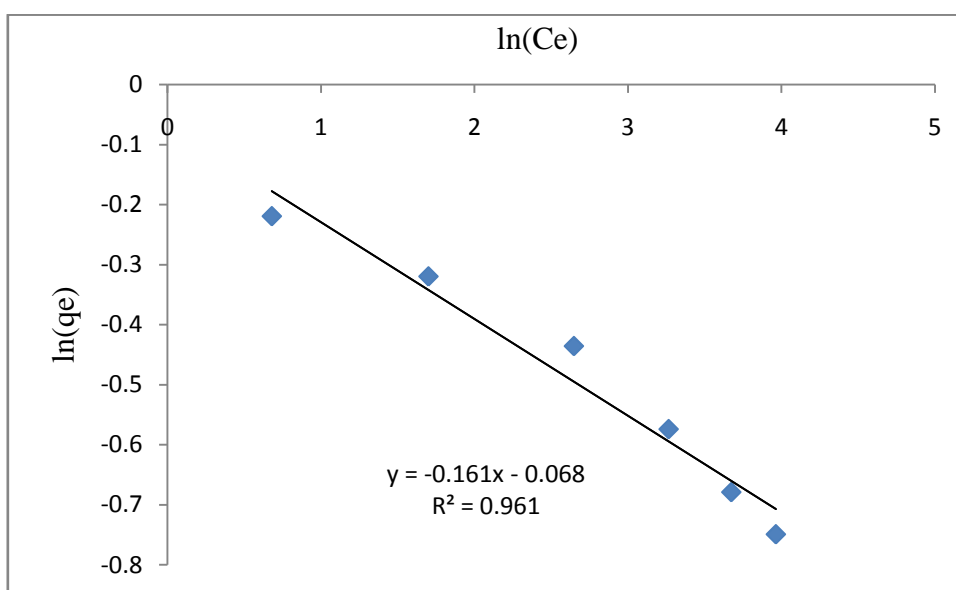


Figure 4.9: Freundlich adsorption isotherm for Cu adsorption

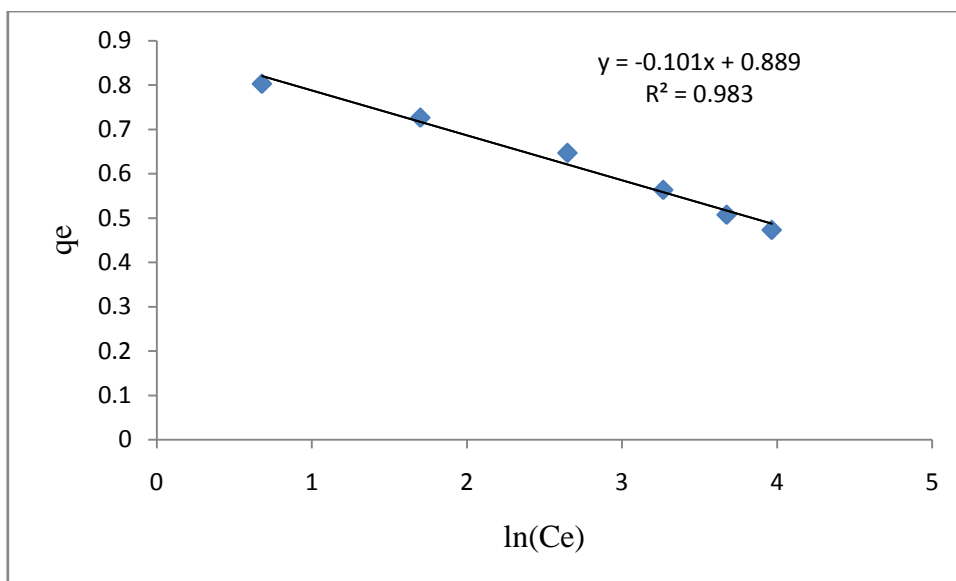


Figure 4.10: Temkin adsorption isotherm for Cu adsorption

TABLE 4.1: Isotherm constants for Cu adsorption

Isotherms	Values
Langmuir	
q_m (mg/g)	0.4748
K_L (L/mg)	0.5366
R^2	0.992
Freundlich	
K_F (mg/Kg)	6.211
N	1.07
R^2	0.961
Temkin	
A	0.883
B	0.101
R^2	0.983

Langmuir, Freundlich and Temkin adsorption isotherms for copper from aqueous solution is presented in Figs 4.7-4.19 respectively. It indicates that the experimental data

fitted well to all the isotherm models. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites.

4.1.4 THERMODYNAMIC PARAMETER

The values of ΔH^0 and, ΔS^0 were determined from the slopes and intercept of the plot of $\ln K$ vs. $(1/T)$ Figure 4.11 and listed in Table 4.2. The negative value of ΔG^0 at all temperatures indicates that the copper adsorption reaction was spontaneous in nature and it was also observed that as the temperature increases. So, it can be inferred that the reaction is spontaneous in nature.

As the ΔG^0 ranges from -1.259 to -0.0537 kJ/mol, the adsorption process is predominantly a physical adsorption process. The negative value of ΔH^0 for the removal of copper confirms that the adsorption process was exothermic in nature.

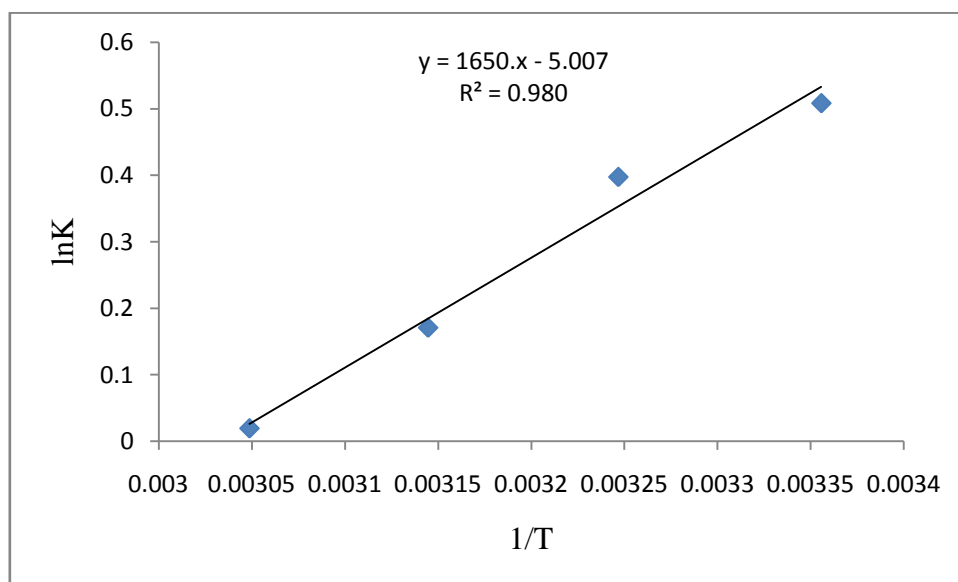


Figure 4.11: The Vant Hoff's plot of $\ln K$ vs. $1/T$

TABLE 4.2: Thermodynamic parameters of copper adsorption

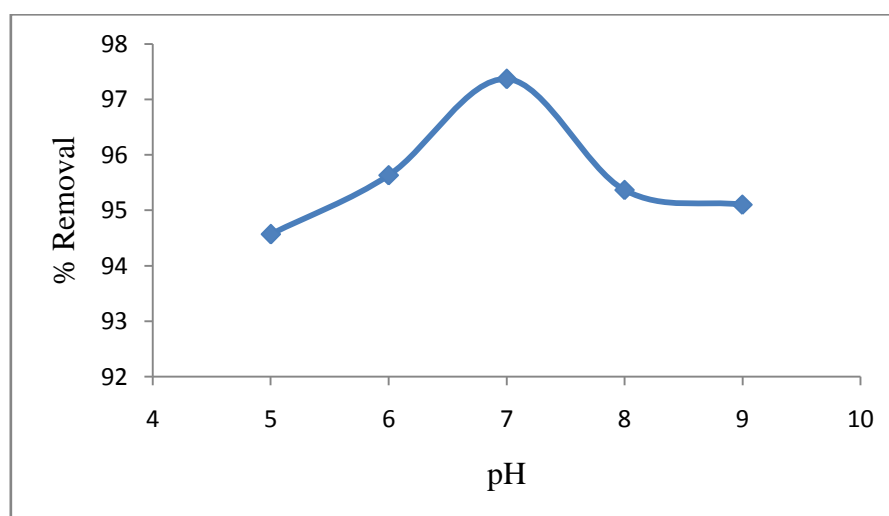
T(K)	ln K	$\Delta G(\text{KJ mol}^{-1})$	$\Delta H(\text{KJ mol}^{-1})$	$\Delta S(\text{J mol}^{-1} \text{K}^{-1})$
298	0.508	-1.259		
308	0.397	-1.017	-13.72	-41.63
318	0.1709	-0.452		
328	0.0196	-0.0537		

4.2 ZINC

4.2.1 EFFECT OF PARAMETERS

4.2.1.1 EFFECT OF pH

Figure 4.12 illustrated that pH obviously influenced the removal efficiency of the zinc ions in the aqueous solution. The results indicated that Zn (II) removal was increased to maximum and then decreased with pH variation from 5 to 9 at temperature 25⁰C and agitation speed of 100 rpm. The maximum % removal of Zn (II) was about 94% at pH 7. The dominant species of zinc was free Zn(II) and was mainly involved in the adsorption process when the pH was lower than 7. When the pH greater than 7, zinc ions started to precipitate as Zn (OH)₂, this had been confirmed by Karthikeyan et al.,(2004). Increases in metal removal with increased pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (>pH 7) is due to formation of soluble hydroxy complexes (R. Ramya et al., 2003). The adsorption of Zn (II) ion was found mainly to be influenced by solution pH.

**Figure 4.12:** Effect of pH on adsorption of Zn

4.2.1.2 EFFECT OF CONTACT TIME

The effect of contact time on zinc adsorption process was determined by conducting adsorption experiments at different contact time between the adsorbate and adsorbent in the range of 10–180 minutes. The concentration of metal ions was 3mg/L, pH was kept as 7.0, and temperature 25°C, while the amount of adsorbent added was 50 mg. From Fig 4.13, the plot depicts that the rate of percent removal of zinc was higher at the beginning. This may be due to the larger surface area of the adsorbent being available at beginning for the adsorption of zinc ions. Equilibrium adsorption was reached after 180 minutes indicating that the adsorption sites are well exposed (Orumwense , 1996). It is clear for the results that the adsorption of zinc was dependent on contact time. Based on these results, all the batch experiments were conducted with a contact time of 10-180 minutes.

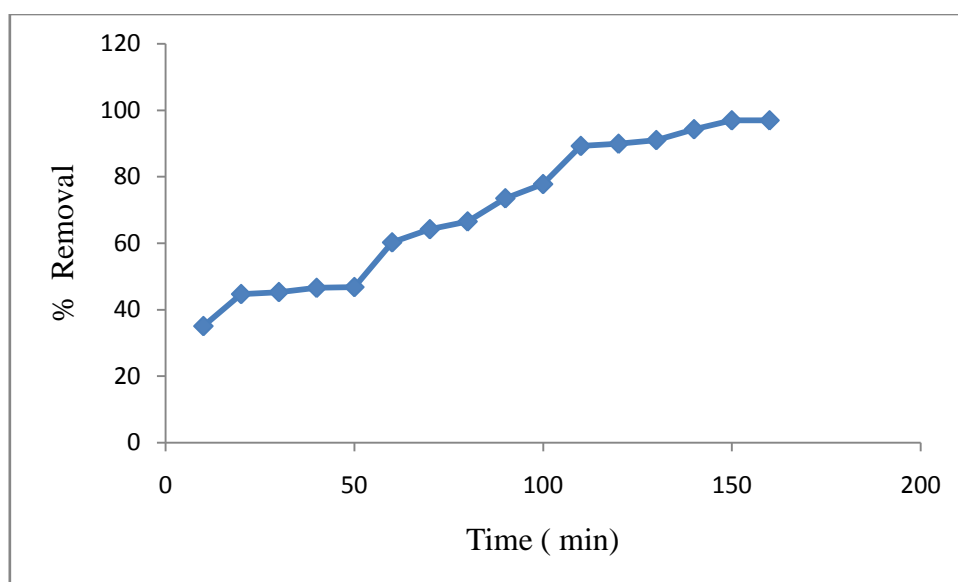


Figure 4.13: Effect of contact time on adsorption of Zn

4.2.1.3 EFFECT OF ADSORBENT DOSE

Adsorption efficiency of Zn (II) adsorption was studied by varying the amount of adsorbents from 50 to 250 mg keeping other parameters (pH, and contact time) constant. The figure 4.14 shows that removal efficiency of the zinc usually improved on increasing adsorbent doses. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. From the figure it is clear that the no further increase in adsorption after a certain amount of adsorbent was added (200 mg). The maximum % removal of Zn (II) was about 95.5% at the dosage of 200 mg. This result also suggest that after a certain dose of adsorbent, the equilibrium conditions reached and hence

the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent.

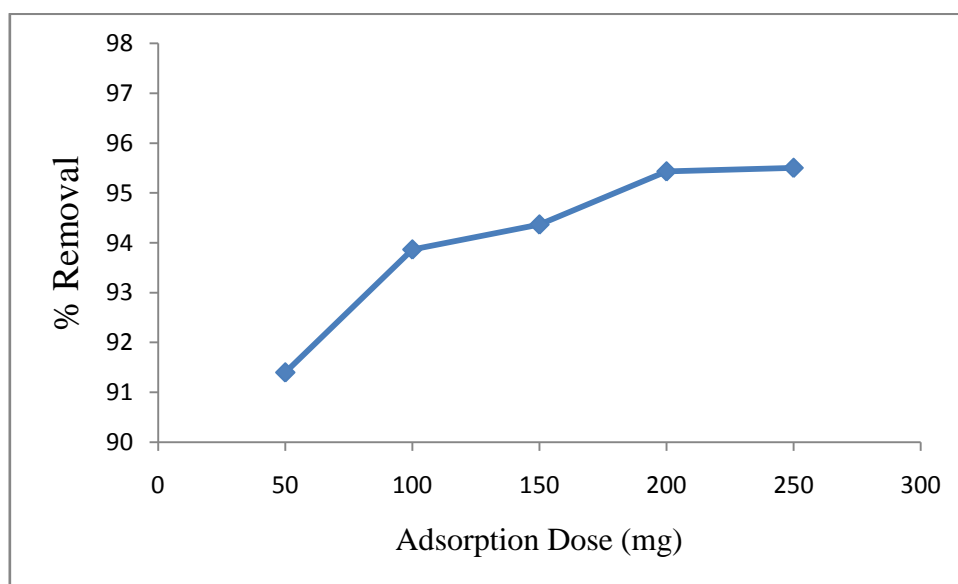


Figure 4.14: Effect of adsorbent dose on adsorption of Zn

4.2.1.4 EFFECT OF TEMPERATURE

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the negative effect on adsorption of zinc onto chitosan. The temperature effect on removal of zinc ion using chitosan was studied within the range of 25-40⁰C. Other parameters such as dose of adsorbent and pH of solution were kept constant. With increase in temperature from 25-40⁰C the percent removal of zinc ions was decreased from 93.7% to 72.4%. From the figure 4.15 it is clear that the low temperatures are in favour of zinc ion removal. This may be due to a tendency for the zinc ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of zinc is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature.

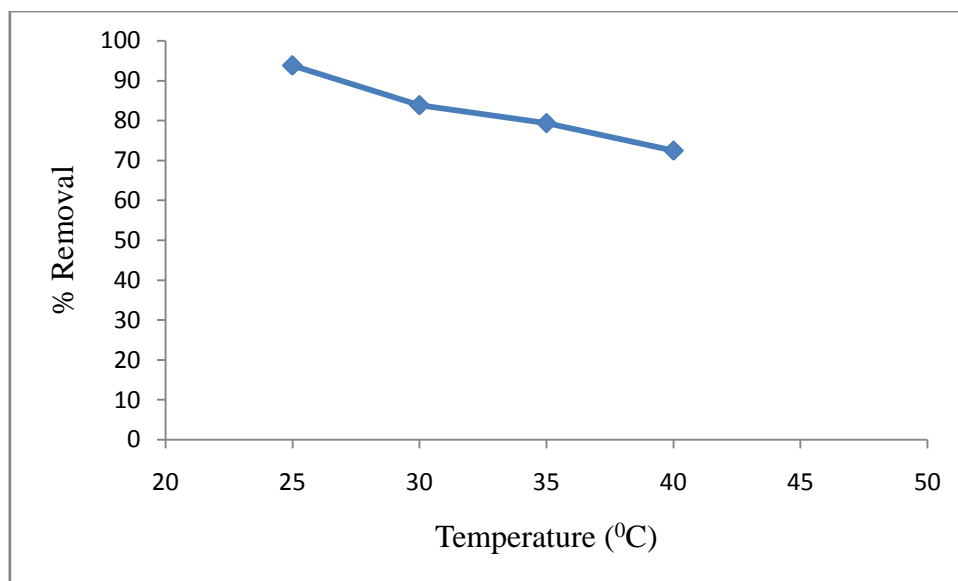


Figure 4.15: Effect of temperature on adsorption of Zn

4.2.1.5 EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial copper concentration on the copper adsorption rate was studied in the range (10-100mg/L) at pH 7, temperature 25°C, and 180 min contact time. The results presented in the Fig 4.16. From the figure it was observed that the percentage of removal decreased with increasing in initial zinc concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of zinc to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial zinc concentration. Therefore it was evident from the results that zinc adsorption was dependent on the initial metal concentration.

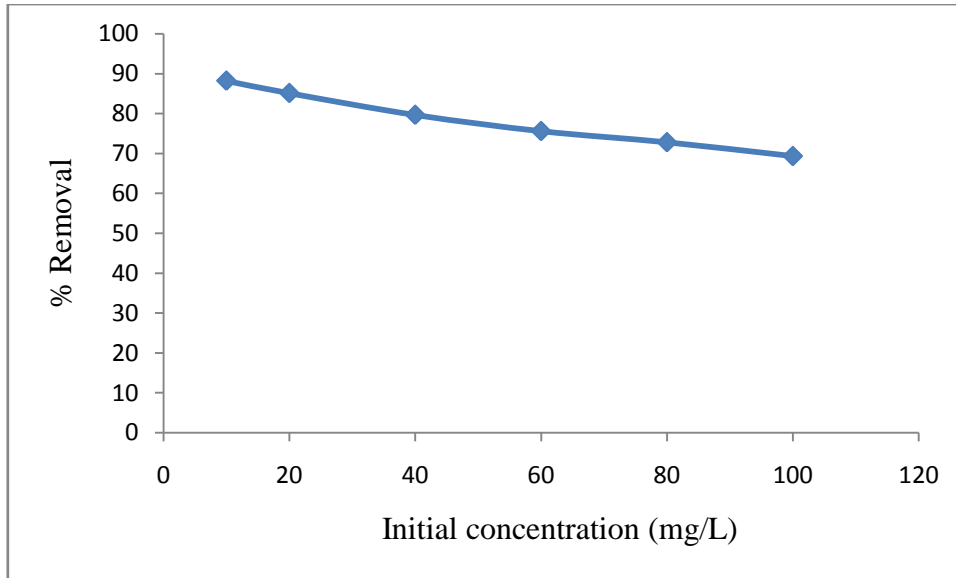


Figure 4.16: Effect of initial metal ion concentration on adsorption of Zn

4.2.2 ADSORPTION KINETICS

The kinetics of adsorption was studied for a contact time ranging 10-180 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (fig 4.17 & fig 4.18). The reported R^2 value indicates that the experimental results shows better fit to pseudo-second order model. Hence, the zinc adsorption seems to be more pseudo-second order.

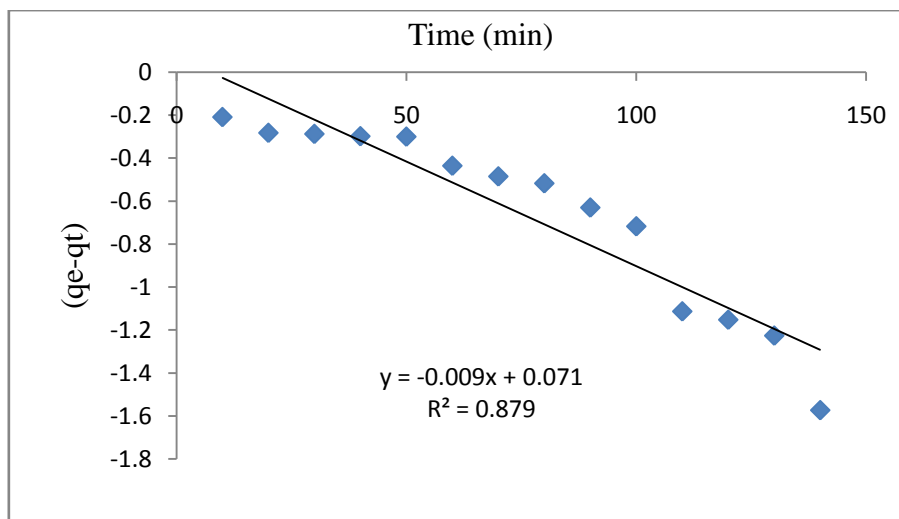


Figure 4.17: Pseudo first order plot for adsorption of Zn

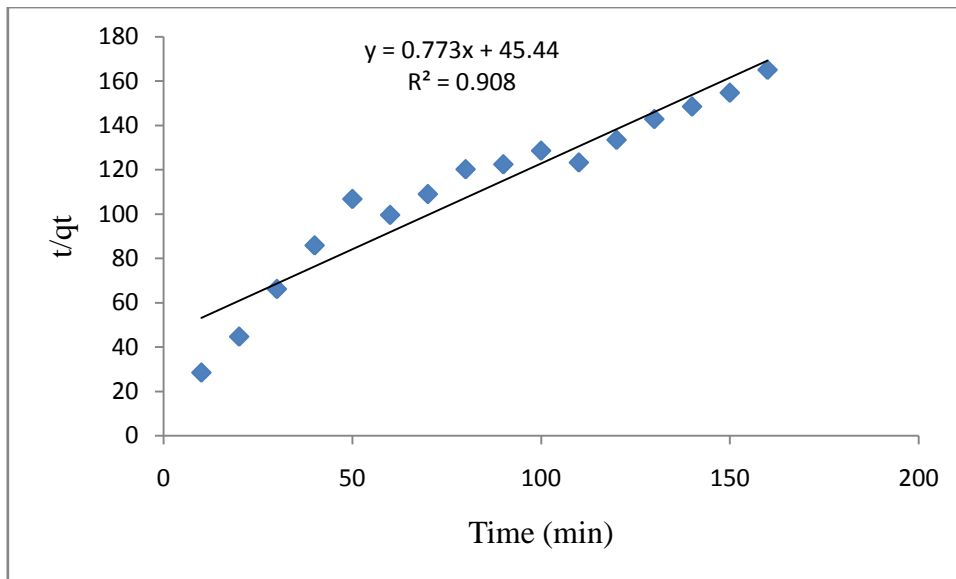


Figure 4.18: Pseudo second order plot for adsorption of Zn

4.2.3 ADSORPTION ISOTHERM

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as to compare the effectiveness of different adsorbent materials under different operational conditions and also to design and optimize an adsorption system. Heavy metal adsorption is usually modelled by the classical adsorption isotherms. In this study, three isotherms models were used, Langmuir, Freundlich, Temkin isotherms using Eqs (8),(10),and(12) respectively. The values of various constants of the four models were calculated and were represented in the Table 4.3.

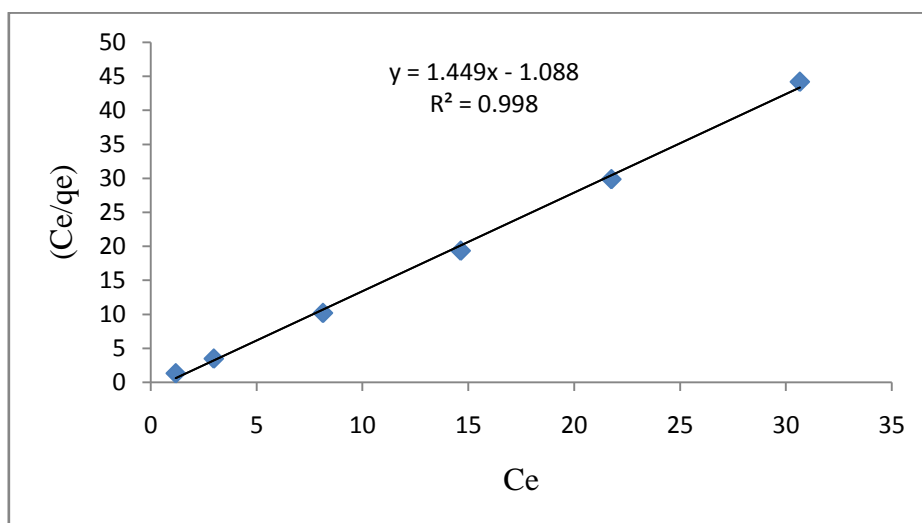


Figure 4.19: Langmuir adsorption isotherm for Zn adsorption

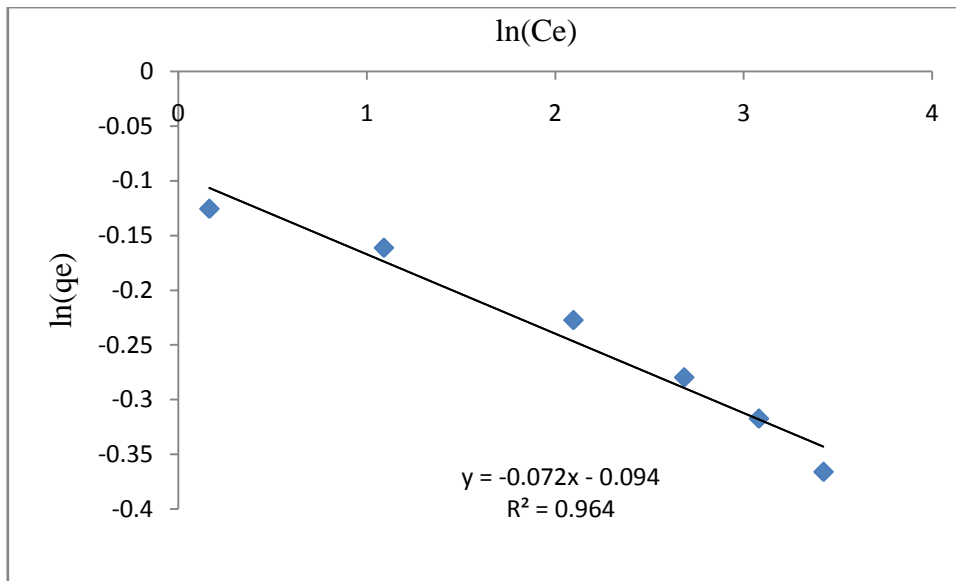


Figure 4.20: Freundlich adsorption isotherm for Zn adsorption

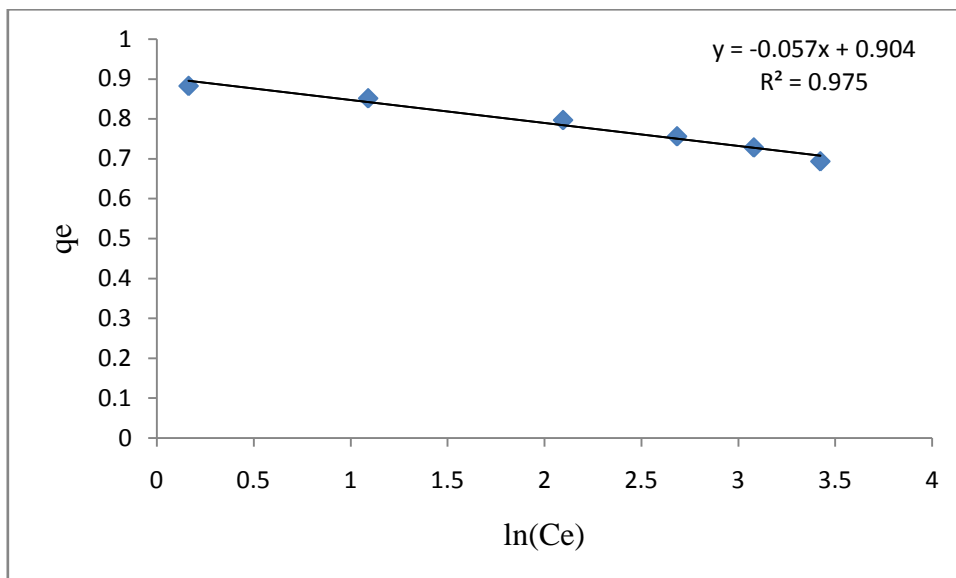


Figure 4.21: Temkin adsorption isotherm for Zn adsorption

TABLE 4.3: Isotherm constants for Zn adsorption

Isotherms	Values
Langmuir	
q_m (mg/g)	0.6901
K_L (L/mg)	1.332
R^2	0.998

Freundlich	
K_F (mg/Kg)	1.099
N	13.389
R^2	0.964
Temkin	
A	0.904
B	0.057
R^2	0.975

Langmuir, Freundlich and Temkin adsorption isotherms for copper from aqueous solution is presented in Figs 4.19-4.21 respectively. It indicates that the experimental data fitted well to all the isotherm models. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites.

4.2.4 THERMODYNAMIC PARAMETER

The values of ΔH^0 and, ΔS^0 were determined from the slopes and intercept of the plot of $\ln K$ vs. $(1/T)$ Figure 4.22 and listed in Table 4.4. The negative value of ΔG^0 at all temperatures indicates that the zinc adsorption reaction was spontaneous in nature and it was also observed that as the temperature increases. . So, it can be inferred that the reaction is spontaneous in nature.

As the ΔG^0 ranges from -3.995 to -0.357 KJ/mol, the adsorption process is predominantly a physical adsorption process. The negative value of ΔH^0 for the removal of zinc confirms that the adsorption process was exothermic in nature.

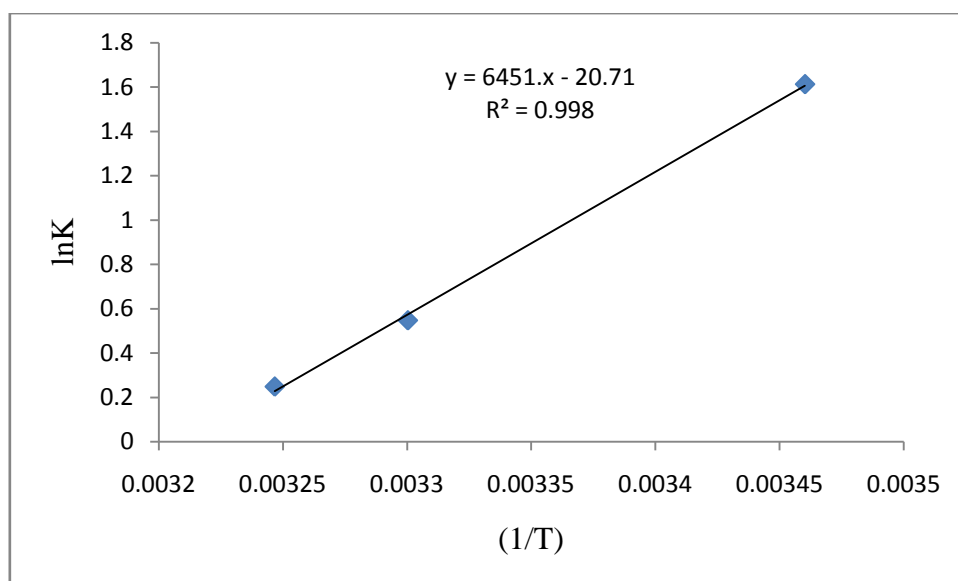


Figure 4.22: The Vant Hoff's plot of $\ln K$ vs. $1/T$

TABLE 4.4: Thermodynamic parameters of zinc adsorption

T(K)	ln K	$\Delta G(\text{KJ mol}^{-1})$	$\Delta H(\text{KJ mol}^{-1})$	$\Delta S(\text{J mol}^{-1} \text{K}^{-1})$
298	1.612	-3.995		
303	0.547	-1.401	-53.63	-172.18
308	0.240	-0.657		
313	-0.131	-0.357		

TABLE 4.5: Comparison of adsorption capacities of copper and zinc with other adsorbents at standard conditions.

Metal	Adsorbent	% Adsorption	Work reported by
Cu	Rice husk	51.4%	Nhapi et al., 2011
	Saw dust	98%	Lucaci et al., 2011
	Activated carbon	20.8 mg/g	Madhava et al., 2005
	Chitosan	89%	Present study
Zn	Rice husk	56.7%	Nhapi et al., 2011
	Activated carbon	40.87%	Khan et al., (2010)
	Oil palm fibre	75.6%	Akaninwor et al., 2007
	Chitosan	96.97%	Present study

CONCLUSIONS

Based on the results of this study following conclusions could be drawn:

1. The present investigation is carried out to study the suitability of a novel indigenous adsorbent, chitosan for the removal of heavy metal such as copper and zinc from the wastewater.
2. Influence of process parameters such as pH, adsorbent dosage, temperature, contact time, initial metal ion concentration were at moderate levels such that they can affect the removal efficiencies of the heavy metals were concerned.
3. The optimum pH of solution for Cu and Zn removal were found to be 5 and 7 respectively.
4. Within the scope of the experimental investigation the optimum temperature was found to be 25⁰C.
5. The optimum time for adsorption of zinc and copper was found to be 180 min and 360 min respectively.
6. Initial metal ion concentration showed the negative effect on adsorption efficiency i.e. at lower levels the adsorption was higher.
7. Kinetic studies of adsorption revealed that the adsorption process followed a pseudo second order kinetic model for both metal.
8. The adsorption data were fitted to different isotherm model equation and the Langmuir model was found to be the best model for both metals i.e. Cu and Zn with R² values 0.992, 0.998 respectively.
9. Thermodynamic parameter of adsorption studies revealed that the adsorption of heavy metals using chitosan is exothermic in nature; hence it can be concluded to be physical adsorption phenomenon.

FUTURE RECOMMENDATIONS

Following recommendations are suggested for future research:

- Studies of adsorption capacity of regenerated as well as modified chitosan might be carried out.
- Some other characteristics of chitosan useful in wastewater purification, should be investigated, such as for removal of suspended solids, dissolved solids, BOD, COD and free chlorine to establish its suitability.
- Like zinc and copper chitosan could be used for removal of some other heavy metals like cobalt, mercury, bismuth, lead and arsenic.

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APENDIX 1

TABLE OF OBSERVATIONS FOR COPPER

Table A.1 Effect of pH on Cu adsorption at 25⁰C, 100 rpm (initial conc. = 3 mg/L)

pH	Final conc. (mg/L)	Cu adsorbed (mg/L)	% Removal
4	1.03	1.97E4W	65.67
5	0.33	2.67	89
6	0.75	2.25	75
7	1.39	1.61	53.33
8	1.45	1.55	51.67
9	1.51	1.49	49.67

Table A.2 Effect of Adsorbent Dosage on Cu adsorption at 25⁰C, 100 rpm (initial conc. = 3mg/L), at pH=5

Adsorbent dosage (mg)	Final conc. (mg/L)	Cu adsorbed (mg/ L)	% Removal
50	0.827	2.173	72.43
100	0.729	2.271	75.7
150	0.407	2.593	86.43
200	0.355	2.645	88.17

Table A.3 Effect of temperature on Cu adsorption at 100 rpm, 5 pH, 50 mg adsorption dosage (initial conc. = 3 mg/L)

Temperature (⁰ C)	Final conc. (mg/L)	Cu adsorbed (mg/L)	% Removal
25	0.501	2.499	83.33
35	0.549	2.451	81.7
45	0.658	2.342	78.07
55	0.739	2.261	75.37

Table A.4 Kinetic Study for Cu at 25⁰C, 100 rpm, 50 mg adsorbent dosage, 5 pH (initial conc. = 3mg/L)

Time (min)	Final conc. (mg/L)	Cu adsorbed (mg/L)	% Removal
20	2.55	0.45	15
40	2.30	0.7	22.33
60	2.09	0.91	30.33
80	1.82	1.18	39.33
100	1.54	1.46	46.67
120	1.47	1.53	51
140	1.36	1.64	54.67
160	1.16	1.84	61.33
180	1.01	1.99	66.33
200	0.89	2.11	70.33
220	0.79	2.21	73.67
240	0.70	2.30	76.67
260	0.62	2.38	79.33
280	0.50	2.50	83.33
300	0.46	2.54	84.67
320	0.43	2.57	85.67
340	0.35	2.65	88.33
360	0.34	2.66	88.67
380	0.33	2.67	89
400	0.33	2.67	89

Table A.5 Isotherm study for Cu at 25⁰C, 100 rpm, 50 mg adsorbent dosage, 5 pH (initial conc. = 3mg/L)

Conc. (mg/L)	Final conc. (mg/L)	Cu adsorbed (mg/L)	% Removal
3	0.338	2.662	88.73
10	1.972	8.028	80.28
20	5.575	14.525	72.625
40	14.129	25.871	64.678
60	26.20	33.8	56.33
80	39.421	40.579	50.724
100	52.71	47.29	47.29

TABLE OF OBSERVATIONS FOR ZINC

Table A.6 Effect of pH on Zn adsorption at 25⁰C, 100 rpm (initial conc. = 3 mg/L)

pH	Final conc. (mg/L)	Zn adsorbed (mg/L)	% Removal
5	0.163	2.832	94.567
6	0.131	2.869	95.633
7	0.079	2.921	97.367
8	0.139	2.861	95.367
9	0.147	2.853	95.1

Table A.7 Effect of Adsorbent Dosage on Zn adsorption at 25⁰C, 100 rpm (initial conc. = 3mg/L), at pH=7

Adsorbent dosage (mg)	Final conc. (mg/L)	Zn adsorbed (mg/ L)	% Removal
50	0.258	2.742	91.4
100	0.184	2.816	93.867
150	0.169	2.831	94.367
200	0.137	2.863	95.433
250	0.135	2.865	95.5

Table A.8 Effect of temperature on Zn adsorption at 100 rpm, 7 pH, 50 mg adsorption dosage (initial conc. = 3 mg/L)

Temperature (⁰ C)	Final conc. (mg/L)	Zn adsorbed (mg/L)	% Removal
25	0.187	2.8233	93.767
30	0.485	2.515	83.833
35	0.619	2.381	79.367
40	0.826	2.174	72.467

Table A.9 Kinetic Study for Zn at 25⁰C, 100 rpm, 50 mg adsorbent dosage, 7 pH (initial conc. = 3mg/L)

Time (min)	Final conc. (mg/L)	Zn adsorbed (mg/L)	% Removal
10	1.947	1.053	35.1
20	1.658	1.342	44.733
30	1.640	1.36	45.33
40	1.602	1.398	46.6
50	1.595	1.405	46.83
60	1.192	1.808	60.267
70	1.073	1.927	64.23
80	1.003	1.997	66.567
90	0.794	2.206	73.53
100	0.666	2.334	77.8
110	0.322	2.678	89.267
120	0.302	2.698	89.93
130	0.339	2.661	88.7
140	0.171	2.829	94.3
150	0.091	2.909	96.97
160	0.091	2.909	96.97

Table A.10 Isotherm study for Zn at 25⁰C, 100 rpm, 50 mg adsorbent dosage, 7 pH (initial conc. = 3mg/L)

Conc. (mg/L)	Final conc. (mg/L)	Zn adsorbed (mg/L)	% Removal
10	1.179	8.821	88.21
20	2.976	17.024	85.12
40	8.132	31.868	79.67
60	14.638	45.362	75.603
80	21.6754	54.323	72.8075
100	30.654	69.346	69.346