*International Journal of Applied Engineering and Technology ISSN: 2277-212X (Online)*
*An Online International Journal Available at http://www.cibtech.org/jet.htm*
*2013 Vol. 3 (1) January-March, pp.35-60/Thilagan et al.*

***Research Article***

# A COMPARATIVE STUDY ON ADSORPTION OF COPPER (II) IONS IN AQUEOUS SOLUTION BY; (A) CHITOSAN BLENDED WITH CELLULOSE AND CROSS LINKED BY FORMALDEHYDE, (B) CHITOSAN IMMOBILISED ON RED SOIL, (C) CHITOSAN REINFORCED BY BANANA STEM FIBRE

***J Thilagan, S Gopalakrishnan and T Kannadasan**
*Department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore-641014,*
*Tamil nadu, India*
**Author for Correspondence*

## ABSTRACT

The effective and economic removal of heavy metals from industrial effluents is one of the significant issues globally. Removal of $Cu^{+2}$ ions in aqueous solution was analyzed by Chitosan blended with Cellulose and cross linked by Formaldehyde, Chitosan immobilized on Red Soil and Chitosan reinforced by Banana stem fibre. The adsorbents were made in the form of beads. Batch adsorption experiments were carried as a function of adsorbent dosage, pH, contact time, initial metal ion concentration and temperature. The adsorption process was found to be highly pH dependent. The experimental data were tested with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The energy of adsorption showed that the adsorption processes by the above mentioned adsorbents were Physical adsorption. Adsorption kinetics data were modeled with the application of Adsorption reaction models and Adsorption diffusion models. The results revealed that the Pseudo second order model was the best fitting model in all cases. The mechanism of adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads followed two stages in which the first one was fast and the other was slower. The Boyd plot exposed that the intra-particle diffusion was the rate controlling step of all adsorption processes. The adsorption thermodynamics revealed that the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads were spontaneous and the adsorption of Copper (II) ions by Chitosan-Red Soil beads was non-spontaneous.

***Key Words:*** *Heavy Metal Removal, Cross Linked Chitosan-Cellulose Beads, Chitosan-Red Soil Beads, Chitosan-Banana Stem Fibre Beads, Adsorption Isotherms, Kinetics, Mechanism, Thermodynamics*

## INTRODUCTION

Heavy metal contamination is an environmental threat as serious as global warming. Heavy metals are metals and metal compounds that may harm human health when absorbed or inhaled. In very small amounts, some heavy metals support life. But when taken in large amounts, they can become toxic. Examples of heavy metals include arsenic, cadmium, chromium, copper, lead, mercury and zinc. Generally, heavy metals have densities above 5 $g/cm^3$. As the heavy metals cannot be degraded or destroyed, they are persistent in all parts of the environment. Human activity affects the natural geological and biological redistribution of heavy metals through pollution of the air, water, and soil.

Copper is an essential trace nutrient that is required in small amounts (1-1.5 mg per day in food) by humans, other mammals, fish and shell fish for the synthesis of hemoglobin, carbohydrate metabolism and the functioning of more than 30 enzymes. Although Copper can be an essential trace element, it could be harmful when it exceeds the tolerance limit. Copper is extensively used in the manufacture of fungicides, anti-fouling paints and also in electrical industries. Copper fume causes irritation of the eyes, nose, and throat, headaches, stomach aches, dizziness, vomiting and diarrhoea and an illness called metal fume fever. High uptakes of copper may cause liver and kidney damage and even death. When copper ends up in soil, it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water, Copper can travel great distances, either suspended on sludge particles or as free ions. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On Copper-rich soils, only a limited number of plants have the chance of survival and hence there is not much plant diversity near copper disposing factories Write Work (No Date).

Many materials of biological origin (e.g., fungi, yeast, bacteria, Chitosan, seeds of papaya, moringa oleifera and tamarind, peels of orange, banana and pomegranate and agricultural wastes) have been recognized as adsorbents for heavy metal ions.

Chitosan is the second most abundant bio polymer in earth after cellulose. Chitosan has been recognized as a biopolymer with significant potential for use as biosorbent for removal of metal ions from wastewater. Chitosan is commercially produced by the deacetylation of Chitin which is found in the outer skeleton of shrimp, crab, lobster and crayfish shells. Chitin and Chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to cellulose (1.25%). Adsorption experiments with Copper - Wan *et al.*, (2004); Kaminiski *et al.*, (2008); Peter *et al.*, (2009); Majeti *et al.*, (2000), Mercury - Miretzky *et al.*, (2009), Chromium - Singh and Anjali (2012); Zofia *et al.*, (2006) and Lead - Shengling *et al.*, (2006) ions indicated that Chitosan can be effectively used to adsorb these metals by establishing their different interactions with its amino and hydroxyl groups. Chitosan is insoluble at neutral and alkaline pH, but formed water soluble salts with inorganic and organic acids including glutamic, hydrochloric, lactic and acetic acids. Chitosan offers a lot of promising benefits for wastewater treatment applications today. Cost of Chitosan is much lower than activated carbon and it has excellent binding capacity, Sandhya and Tonni (2003). Chitosan has the characteristic feature of having amine groups in which nitrogen is a donor of electron pair that is attractive to most heavy metals and OH groups also take part in the adsorption, Kaminiski *et al.*, (2008).

However, unlike Chitin, Chitosan is soluble in acids. Although cross linking reduces adsorption capacity, it improves the resistance of Chitosan in both acid and alkaline medium. Hence the cross-linking widens the application of Chitosan in a broad pH range, Wen-Li *et al.*, (2009).

Chitosan has found numerous applications in various fields such as treatment of water and industrial effluents, agriculture, fabric and textiles, cosmetics, nutritional enhancement, and food processing. Chitosan and its blends exist in various physical forms including resins, microspheres, hydrogels, membranes and fibers. The selection of one particular physical form depends mainly on the system configuration to be used for particular applications. The process of shaping chitosan blends into desired physical form starts from mixing the blend components in the liquid form and applying the appropriate shaping method, Esam *et al.*, (2011).

## MATERIALS AND METHODS

### *Materials*

Chitosan flakes with a deacetylation degree of 85 % were acquired from Pelican Biotech & Chemicals Labs Pvt. Ltd., Kuthiathode, Kerala, India. The chemicals used in this study such as Acetic acid, Cellulose powder, Formaldehyde solution, Hydrochloric acid, Sodium hydroxide pellets were in AR grade and manufactured by SD Fine Chem Limited, Mumbai, India. The AR grade of Cupric Sulphate penta hydrate ($CuSO_4.5H_2O$) was used for the preparation of $Cu^{+2}$ ions. Red Soil has been collected from our college campus itself. Banana stem fibres have been obtained by mechanically crushing the fresh Banana stems and the extracted fibres were dried for 48 hours. Then they were cut in to very small particles (less than 0.3 mm).

In this research work, adsorption of Copper (II) ions in aqueous solution has been analyzed by,

(i) Chitosan blended with Cellulose and cross linked by Formaldehyde;
(ii) Chitosan immobilized on Red Soil;
(iii) Chitosan reinforced by Banana stem fibre.

*Cellulose:*

Cellulose has a ribbon shape which allows it to twist and bend in the direction out of the plane, so that the molecule is moderately flexible. There is a relatively strong interaction between neighbouring cellulose molecules in dry fibres due to the presence of the hydroxyl (–OH) groups, which stick out from the chain and form intermolecular hydrogen bonds. Cellulose constitutes the most abundant and renewable polymer resource available worldwide. It is estimated that by photosynthesis, $10^{11}$–$10^{12}$ tons of cellulose are synthesized annually in a relatively pure form, David *et al*., (2008).

*There are Three Mechanisms for Metal Ions to Bind to Cellulose:*

a. Hydrated alkali ions present in aqueous systems swell the cellulose by penetration into it and also an exchange of hydrated shell with OH groups of cellulose can occur.

b. Electrostatic interaction between metal ions and cellulose occurs in the absence of ligand in the solution. Carboxylic groups of cellulose exchange cations, i.e. hydrogen leaves carboxylic group and metal ions attaches instead.

c. Metal ion and co-ligand (e.g., ethylene-diamine, ammonia, tartaric acid, etc) form complexes in solution. In the presence of cellulose which acts as ligand, competition for the metal ion occurs between ligand and co-ligand. When the stability of metal ion and co-ligand complex is sufficient weak, cellulose complexes with the metal ion are formed and the co-ligand is released, Hale *et al.*, (2007).

*Red Soil:*

Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing mineral particles (sand, silt and clay), soil organic matter (SOM) and fluid phases (the soil water and the soil air), which interact with each other and ions entering the soil system, Heike (2004). Sand is a naturally occurring granular material composed of finely divided rock and mineral particles. Silt is granular material of size somewhere between sand and clay whose mineral origin is quartz and feldspar. Silt may occur as a soil or as suspended sediment in a surface water body. Clay is a general term including many combinations of one or more clay minerals with traces of metal oxides and organic matter. Clay minerals are hydrous aluminum phyllosilicates, sometimes with variable amounts of iron, magnesium, alkaline earth metals (Be, Mg, Ca, Sr, Ba and Ra) and other cations, Soil (2012).

Soil organic matter (SOM) represents the organic constituents in soils including undecayed plant and animal tissues, their partial decomposition products, and soil biomass. Thus the term includes identifiable, high-molecular weight organic materials such as polysaccharides and proteins, simpler substances such as sugars, amino acids, and other small molecules and humic substances. On the other hand SOM is frequently said to consist of humic substances and non humic substances. Non humic substances are all those materials that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fats and so on. Humic substances are the other, unidentifiable components. This apparently simple distinction, however, is not as clear-cut as it might appear. From the point of view of sorption properties of Soils, humic substances have a major importance. Soil Organic Matter may range in soils from 0.1% in desert soils to 90% in organic soils. Humic substances make up approximately 85-90% of the total organic carbon, Dube *et al.*, (2001).

*Generally, the interaction between heavy metal ions and soil can occur mainly in the following four ways:*

a. Ion exchange
b. Adsorption
c. Complications and
d. Precipitation.

The Exchange Capacity of soil is a measure of its ability to hold and release various elements and compounds. Cation-exchange capacity is defined as the degree to which a soil can absorb and exchange cations. It is based on the availability of negatively charged sites in soil. We are mostly concerned with the ability of soil to hold and release plant nutrients, obviously. Specifically here today, we are concerned with the ability of soil to hold and release positively charged nutrients. There are two types of cations, acidic or acid-forming cations, and basic or alkaline-forming cations. Both types of cations may be adsorbed onto either a clay particle or soil organic matter (SOM). All of the nutrients in the soil need to be held there somehow, or they will just wash away when you water the garden or get a good rainstorm. Clay particles almost always have a negative charge, so they attract and hold positively charged nutrients and non-nutrients. Soil organic matter (SOM) has both positive and negative charges, so it can hold on to both cations and anions, Soil Minerals (2012).

*Banana Stem Fibers:*

Lignocellulosic materials are mainly composed of Cellulose, Hemicellulose and Lignin. Banana stem fibre is one of the lignocellulosic materials. It consists of Cellulose (32 %), Hemicellulose (16 %) and Lignin (16 %). Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. One cubic inch of a lignocellulosic material, for example, with a specific gravity of 0.4, has a surface area of 15 square feet. Even when the lignocellulosic material is ground, the adsorptive surface increases only slightly. Thus, the sorption of heavy metal ions by lignocellulosic materials does not depend on particle size. Lignocellulosic materials are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicellulose and lignin. Thus, through absorption and adsorption, aqueous solutions come into contact with a very large surface area of different cell wall components. Lignocellulosic materials have ion exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations. *Lignocellulosic resources all contain, as a common property, poly phenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations,* Beom-Goo *et al.,* (2004).

### *Methods of Preparation of Adsorbents*

*Preparation of Cross Linked Chitosan-Cellulose Beads:*

2 g of Chitosan were dissolved in 200 ml of 1% Acetic acid and stirred for 3 hours to make a Chitosan gel. Then 2 g of Cellulose powder was added and stirred for 3 hours for uniform mixing. Formaldehyde solution (10% v/v) was added for the cross linking of polymer chain and stirring continued for another 3 hours. Then the cross linked Chitosan - Cellulose gel was injected through a syringe (without needle) over the surface of 1 M NaOH solution in a wide glass tray. The cross linked Chitosan - Cellulose beads were obtained on the surface of NaOH solution and they were allowed to stay in it for 12 hours. Then the beads were carefully separated from NaOH solution, cautiously washed many times with distilled water and allowed to be dried for 48 hours at room temperature. The ratio of Chitosan: Cellulose in the adsorbent beads was 50: 50.

*Preparation of Chitosan-Red Soil Beads:*

95 g of Red Soil (size less than 0.296 mm) was thoroughly mixed with 300 ml of 5% Hydrochloric acid and 5 g of Chitosan was added to the semi-solid mixture (Chitosan : Red Soil ratio = 5 : 95) and then stirred for 7 hours to make a Chitosan-Red Soil gel. Then the Chitosan – Red Soil gel was injected through a syringe (without needle) over the surface of 1 M NaOH solution in a wide glass tray. The Chitosan – Red Soil beads were obtained on the surface of NaOH solution and they were allowed to stay in it for 12 hours. Then the beads were carefully separated from NaOH solution, cautiously washed many times with distilled water and allowed to be dried for 48 hours at room temperature.

*Preparation of Chitosan-Banana Stem Fibre Beads:*

3 g of Chitosan were dissolved in 200 ml of 1% Acetic acid and stirred for 5 hours to make a Chitosan gel. Then 3 g of Banana stem fibre was added and stirred for 1 hour for uniform mixing. Then the Chitosan – Banana stem fibre gel was injected through a syringe (without needle) over the surface of 1 M NaOH solution in a wide glass tray. The Chitosan – Banana stem fibre beads were obtained on the surface of NaOH solution and they were allowed to stay in it for 12 hours. Then the beads were carefully separated from NaOH solution, cautiously washed many times with distilled water and allowed to be

dried for 48 hours at room temperature. The ratio of Chitosan: Banana stem fibre in the adsorbent beads was 50: 50

*Adsorption Experiments:*

Adsorption of $Cu^{+2}$ ions was carried out in batch process with initial concentration ranged from 100 ppm to 500 ppm. $Cu^{+2}$ solutions of necessary concentrations were prepared by dissolving Cupric Sulphate penta hydrate ($CuSO_4.5H_2O$) in distilled water. Batch adsorption experiments were carried out in 250 ml glass beakers filled with 100 ml of solution. Beads of adsorbent were added in the beaker and stirred by mechanical stirrer at 250 rpm. The concentration of $Cu^{+2}$ ions after various adsorption processes were analyzed by UV-Vis Spectrophotometer under visible lamp range with a wave length of 820 nm.

Equilibrium adsorption capacity ($q_e$) = $[(C_0 – C_e) / W] * V$

Where, $C_o$ and $C_e$ are the initial and final $Cu^{+2}$ concentrations (mg/L) of the solution in each adsorption experiment. V is the volume of the Copper solution in liters, W is the weight of adsorbent in each beaker in grams and $q_e$ is in mg/g. In the adsorption experiments, cross linked Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads turned into blue colour after $Cu^{+2}$ adsorption. In the case of Chitosan-Red Soil beads, typical blue colour got stuck on the beads after $Cu^{+2}$ adsorption. In all cases it had been visually shown that Copper ions were cheated.

## Results

### *Effect of Adsorbent Dosage:*

Adsorbent dosage had strongly affected the sorption capacity. With the fixed metal ions concentration, the percentage removal of metal ions increased with increasing weight of the adsorbents. This was due to more availability of active sites or surface area at higher concentration of adsorbent. Adsorption experiments of various dosages of each adsorbent starting from 0.05 g to 0.5 g were distinctly carried out at room temperature ($28^0$ C) in separate 250 ml beakers and each beaker contained 100 ml of 100 ppm concentration. The pH of the solution was 5.2 The samples were tested in every 15 minutes time interval. From the experiments, 0.2 g of cross linked Chitosan-Cellulose beads, 0.5 g of Chitosan-Red Soil beads and 0.2 g of Chitosan-Banana stem fibre beads were found effective and they derived 100 % adsorption of Copper in 100 ppm solution in 120, 90 and 120 minutes respectively.

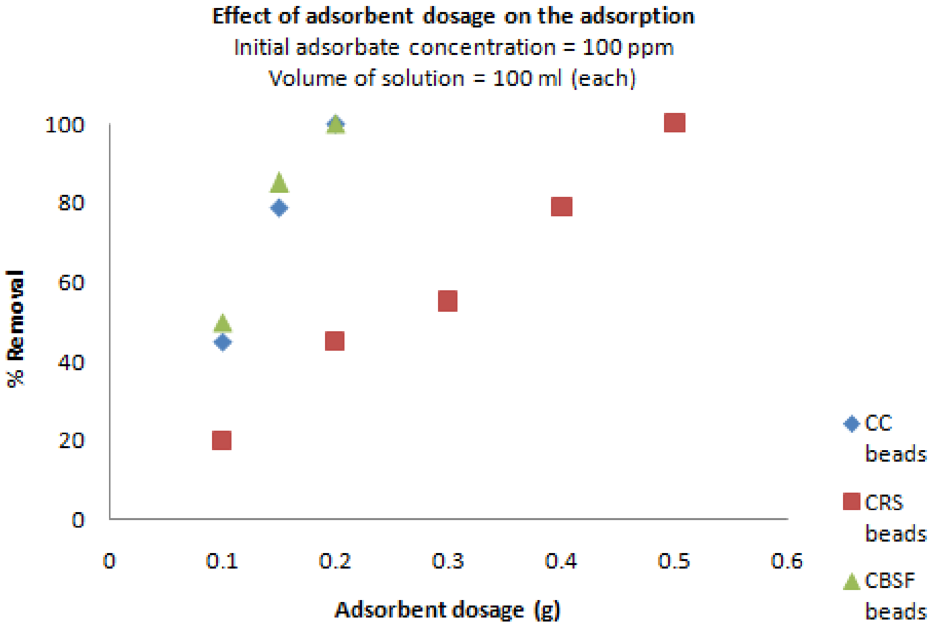

**Figure 1: Effect of adsorbent dosage on the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads**

*Effects of pH on Adsorption:*

The batch experiments were carried out with a pH range of 2 to 10. A wide pH range has been used also to test the insolubility of the adsorbent in strong acidic and alkaline media. 1 M HCl and 1 M NaOH solutions were used to alter pH of the solution. The result showed that there was no adsorption at pH of 2. The adsorption of Copper (II) ions reached maximum at pH of 5 and slowly decreased from pH 6 in the case of cross linked Chitosan-Cellulose and Chitosan-Red Soil beads. For the Chitosan-Banana stem fibre beads, the maximum adsorption was at pH 6 and the adsorption slowly decreased from pH of 7. The cross-linked Chitosan-Cellulose beads proved a good chemical stability in the pH range of 2 to 10. But the Chitosan-Red Soil and Chitosan-Banana stem fibre beads very slightly dissolved at pH of 2 and they showed chemical stability in the pH range of 3 to 10. The pH of the solution had significant impact on the uptake of heavy metal ions. Hence it was clear that the adsorption of the adsorbent was pH dependent. According to Low et al., little sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites, Low *et al*., (1993). At higher pH range, the Copper ions precipitated as their hydroxides which decreased the adsorption rate and as a result of reduction in the percentage removal of Copper ions.

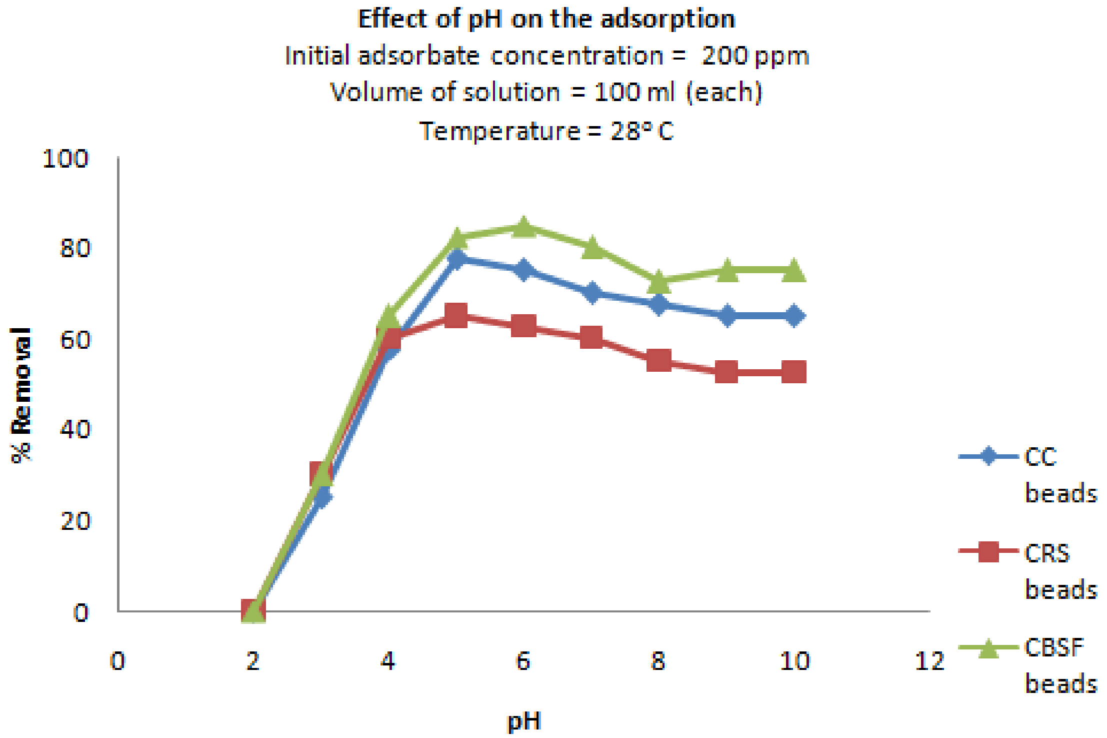

**Figure 2: Effect of pH on the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads**

*Effects of Contact Time on Adsorption:*

The removal of Copper ions increased with time and attained saturation in about 180, 150 and 210 minutes in the case of cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads respectively. The removal was very fast at the beginning and it gradually decreased with time till it reached equilibrium. The experimental data showed considerably fast adsorption during the first 15 minutes of adsorbent - adsorbate contact and it slowly decreased with time due to the saturation of the adsorption sites. Hence a two stage adsorption mechanism with the first rapid and the second slower had been seen in all cases.

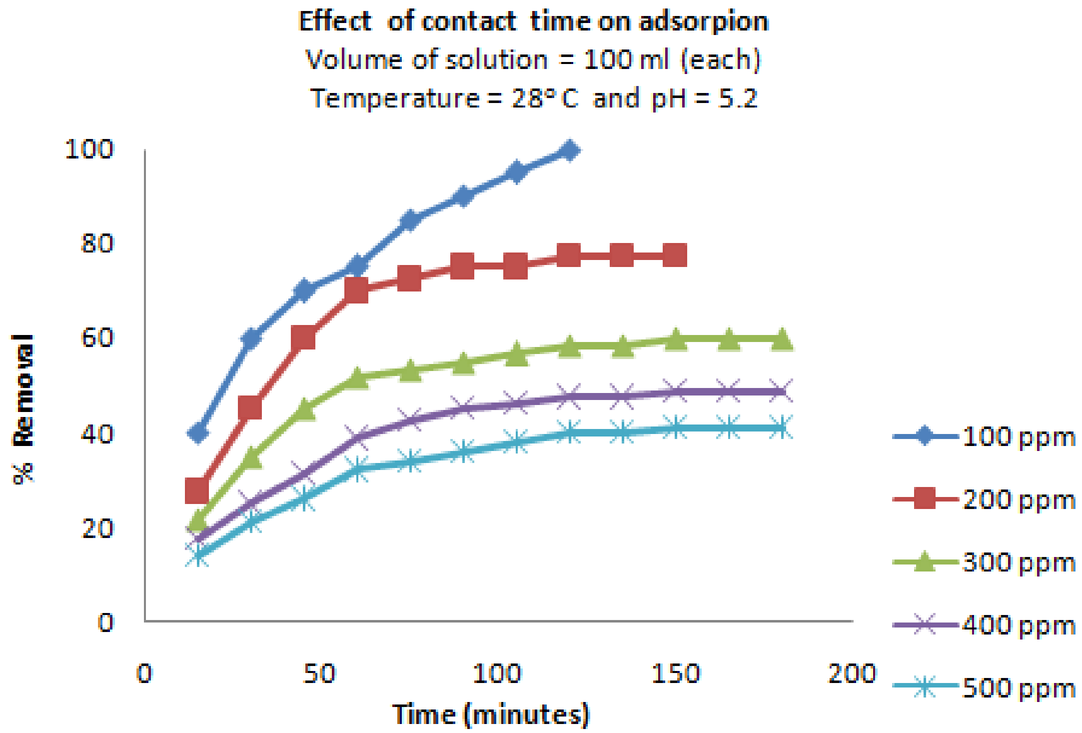

**Figure 3: Effect of Contact time on the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads**

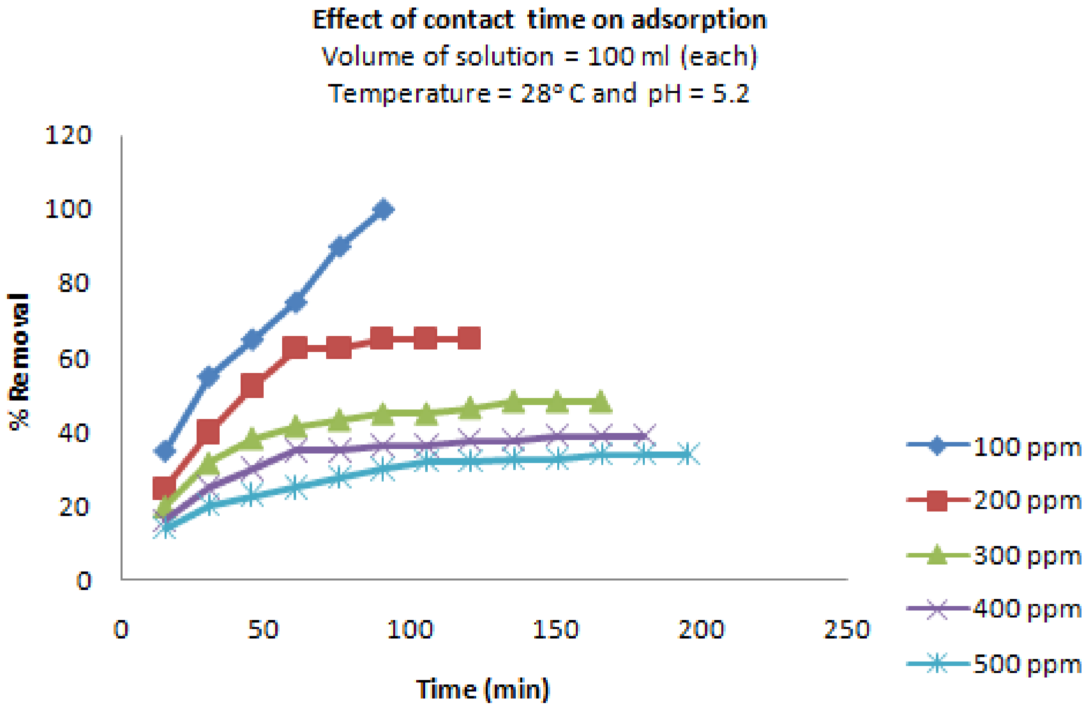

**Figure 4: Effect of Contact time on the adsorption of Copper (II) ions on to Chitosan-Red Soil beads**

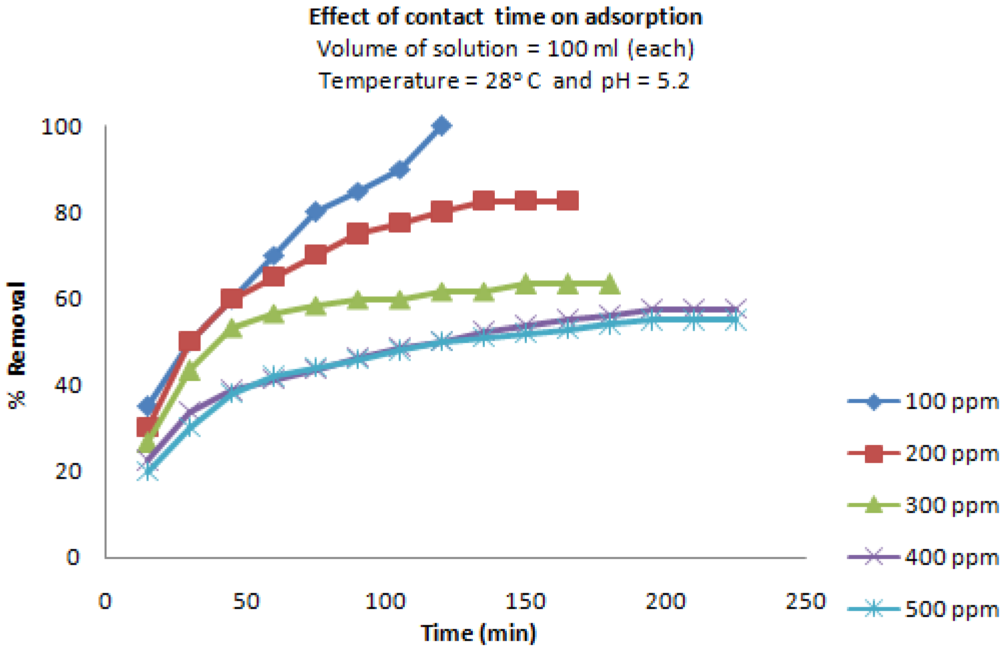

**Figure 5: Effect of Contact time on the adsorption of Copper (II) ions on to Chitosan-Banana stem fibre beads**

*Effects of Initial Metal Ion Concentration on Adsorption:*

The metal uptake mechanism depended on the initial metal ion concentration. Metals were absorbed by specific sites at low concentrations. But the adsorption amount did not increase proportionally for higher metal ion concentrations since the active sites were filled and saturated. Hence it was very clear that the percentage removal of metal ion decreased with increase in metal ion concentration.

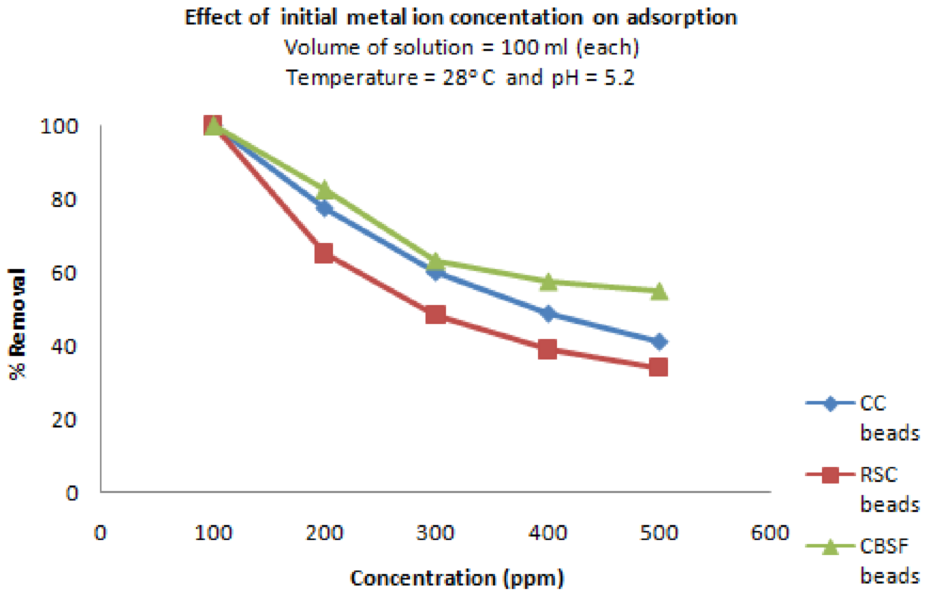

**Figure 6: Effect of initial metal ion concentration on the adsorption by the cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads**

*Effect of Temperature on Adsorption:*

A temperature range started from 30$^0$ C in the multiples of 5$^0$ C was analyzed up to 55$^0$ C. In the case of adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, the adsorption increased slightly (2 %) between 35$^0$ C and 45$^0$ C and then decreased up to 10 % when the temperature was raised up to 55$^o$ C. For adsorption by Chitosan-Red Soil beads, the adsorption increased 4 % between 35$^0$ C and 45$^0$ C and then decreased up to 9 % when the temperature was raised up to 55$^o$ C. In the case of Chitosan-Banana stem fibre beads, the adsorption increased 2.5 % between 30$^0$ C and 40$^0$ C and then decreased up to 10 % when the temperature was raised up to 55$^o$ C.

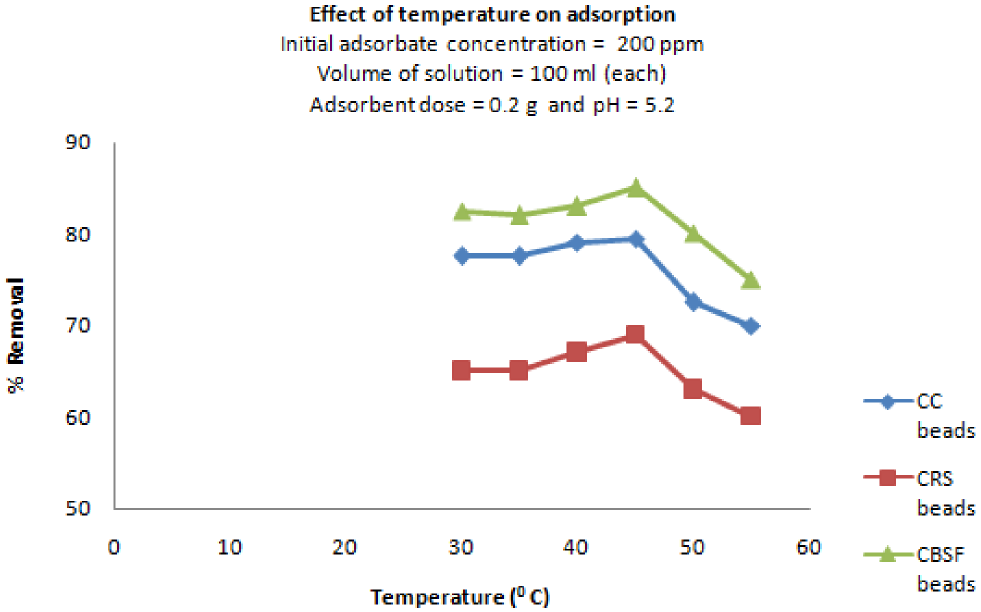

**Figure 7: Effect of temperature on the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads**

*Adsorption Isotherms:*

Adsorption isotherms describe the interaction of adsorbates with adsorbents. The experimental adsorption data of Copper (II) ions on the cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

The experimental data showed that the adsorption of Copper (II) ions by the Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads increased with an increase in initial metal ion concentration significantly. At lower initial Copper (II) ion concentrations, the adsorption increased linearly. At higher initial Copper ion concentrations, the adsorption capacity did not increase proportionally due to the limitation of number of active sites on the surface of adsorbent beads.

*Langmuir Isotherm:* The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes. The adsorption isotherm data were analyzed by the Langmuir isotherm model in the linearised form,

$$C_e/q_e = C_e/q_{max} + 1/(b\ q_{max})$$

Where $q_e$ is the equilibrium adsorption capacity of the adsorbent (mg/g), $C_e$ is the equilibrium Cu concentration in solution (mg/l), $q_{max}$ is the maximum amount of Cu that could be adsorbed on the adsorbent (mg/g) and b is the Langmuir adsorption equilibrium constant (L/mg).

*Freundlich Isotherm:* The Freundlich model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The experimental data were analyzed by Freundlich isotherm model in the linearised form,

$$\log q_e = 1/n \log C_e + \log K_F$$

where $K_F$ is the Freundlich adsorption constant and it is the maximum adsorption capacity of metal ions (mg/g) and n is the constant illustrates the adsorption intensity (dimensionless).

*Temkin Isotherm:* The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied in the Freundlich equation. The adsorption experiment data were analyzed by Temkin isotherm model in the linearised form,

$$q_e = B \ln C_e + B \ln A$$

where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), A is the equilibrium binding constant corresponding to the maximum binding energy (L/g), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The estimated values of the constants of the Langmuir, Freundlich and Temkin Isotherm models for the adsorption of Copper (II) ions by the Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads have been given in the tables below.

**Table 1: Table of estimated values of constants of Isotherms for cross linked Chitosan-Cellulose beads**

| **Langmuir Isotherm** | | | **Freundlich Isotherm** | | | **Temkin Isotherm** | | |
|---|---|---|---|---|---|---|---|---|
| **$R^2$** | **$q_{max}$ (mg/g)** | **b (L/mg)** | **$R^2$** | **$K_F$ (mg/g)** | **1/n** | **$R^2$** | **b (J/mol)** | **A (L/g)** |
| 0.995 | 111.11 | 0.0918 | 0.999 | 43.95 | 0.149 | 0.998 | 18.96 | 7.47 |

*Based on the linear regression values ($R^2$ > 0.99) which are considered as a measure of the goodness-of-fit of data, the experimental data followed the order:*
*Freundlich > Temkin > Langmuir*

**Table 2: Table of estimated values of constants of Isotherms for Chitosan-Red Soil beads**

| **Langmuir Isotherm** | | | **Freundlich Isotherm** | | | **Temkin Isotherm** | | |
|---|---|---|---|---|---|---|---|---|
| **$R^2$** | **$q_{max}$ (mg/g)** | **b (L/mg)** | **$R^2$** | **$K_F$ (mg/g)** | **1/n** | **$R^2$** | **b (J/mol)** | **A (L/g)** |
| 0.990 | 34.48 | 0.0659 | 0.977 | 12.94 | 0.161 | 0.998 | 18.95 | 7.47 |

*Based on the linear regression values ($R^2$ > 0.99) which are considered as a measure of the goodness-of-fit of data, the experimental data followed the order,*
*Temkin > Langmuir > Freundlich*

**Table 3: Table of estimated values of constants of Isotherms for Chitosan-Banana stems fibre beads**

| **Langmuir Isotherm** | | | **Freundlich Isotherm** | | | **Temkin Isotherm** | | |
|---|---|---|---|---|---|---|---|---|
| **$R^2$** | **$q_{max}$ (mg/g)** | **b (L/mg)** | **$R^2$** | **$K_F$ (mg/g)** | **1/n** | **$R^2$** | **b (J/mol)** | **A (L/g)** |
| 0.951 | 142.86 | 0.0489 | 0.862 | 32.14 | 0.252 | 0.814 | 94.43 | 0.5297 |

*Based on the linear regression values ($R^2$ > 0.99) which are considered as a measure of the goodness-of-fit of data, the experimental data followed the order,*
*Langmuir > Freundlich > Temkin*

*Dubinin-Radushkevich Isotherm:* The Dubinin-Radushkevich isotherm equation is generally used to distinguish between physical and chemical adsorption. It is given in the linearised form as,

$$\ln q_e = K_{DR}\,\epsilon^2 + \ln q_{max}$$

where $q_e$ is the equilibrium adsorption capacity of the adsorbent (mg/g), $q_{max}$ is the maximum adsorption capacity (mg/g), $K_{DR}$ is the Dubinin-Radushkevich constant ($mol^2/kJ^2$) and $\epsilon$ is Polanyi potential given by,

$$\epsilon = RT \ln (1 + 1/C_e)$$

where R is the gas constant ($8.314 * 10^{-3}$ kJ/molK), T is the temperature in Kelvin and $C_e$ is the equilibrium concentration of metal ions (ppm). Thus the plot of $\ln q_e$ against $\epsilon^2$ gives a straight line with a slope of $K_{DR}$ and an intercept of $q_{max}$. The Dubinin-Radushkevich isotherm also gives the mean energy of adsorption by the equation,

$$E = (-2\,K_{DR})^{-1/2}$$

If the E value is less than 8 kJ/mol, the process follows physical adsorption, and if the E value lies between 8 and 16 kJ/mol, the process follows chemical adsorption.

The Dubinin-Radushkevich isotherm plots for the experimental data shown below.

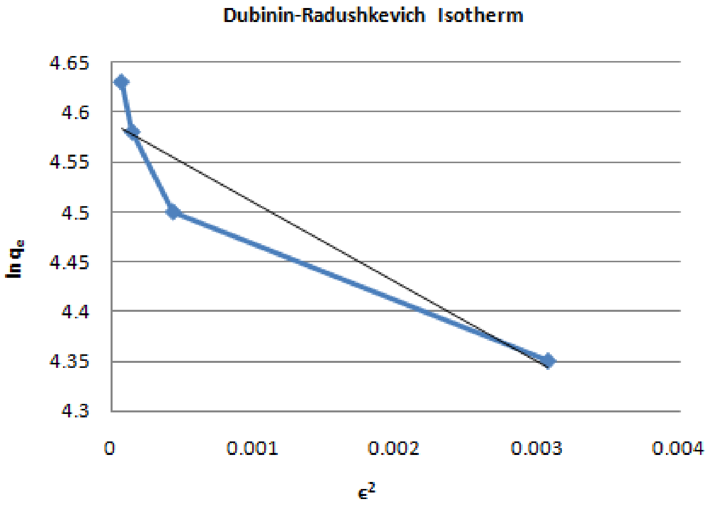

**Figure 7: Dubinin-Radushkevich isotherm for the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads**

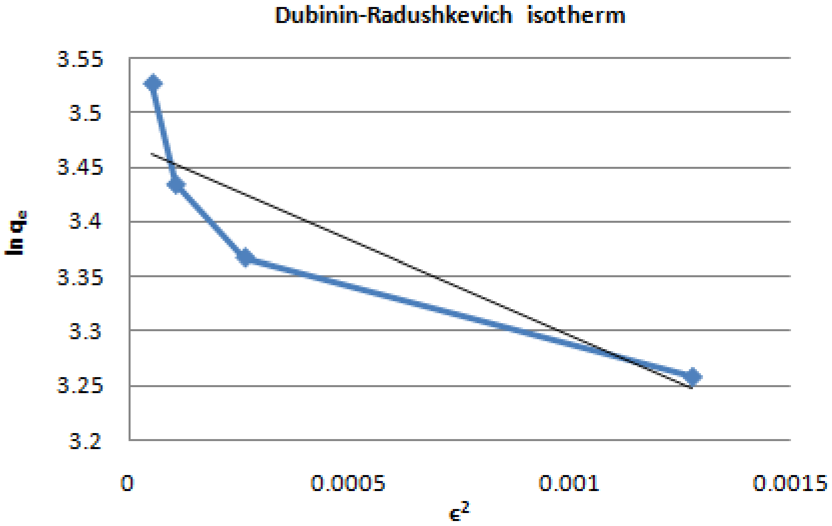

**Figure 8: Dubinin-Radushkevich isotherm for the adsorption of Copper (II) ions on to Chitosan-Red Soil beads**

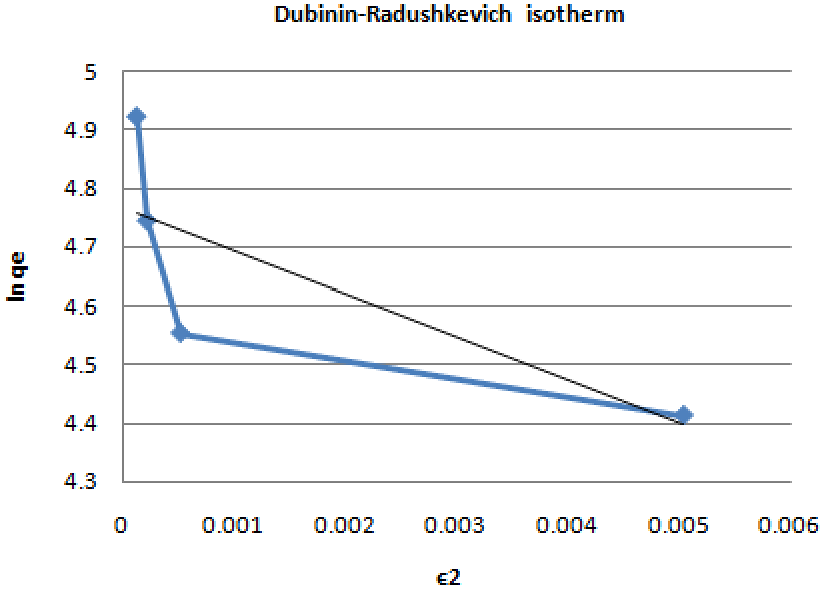

**Figure 9: Dubinin-Radushkevich isotherm for the adsorption of Copper (II) ions on to Chitosan-Banana stem fibre beads**

From the Dubinin-Radushkevich isotherm plot for the adsorption of copper (II) ions by cross linked Chitosan-Cellulose beads, the linear regression value $R^2$ was 0.884. The mean energy of adsorption was found to be 0.079 kJ/mol which is less than 8 kJ/mol, and hence it is clear that the adsorption of Copper ions by Chitosan-Cellulose beads was physical adsorption.

From the Dubinin-Radushkevich isotherm plot for the adsorption of copper (II) ions by Chitosan-Red Soil beads, the linear regression value $R^2$ was 0.791. The mean energy of adsorption was found to be 0.0535 kJ/mol which is less than 8 kJ/mol, and hence it is clear that the adsorption of Copper ions by Chitosan-Red Soil beads was physical adsorption.

From the Dubinin-Radushkevich isotherm plot for the adsorption of copper (II) ions by Chitosan-Banana stem fibre beads, the linear regression value $R^2$ was 0.608. The mean energy of adsorption was found to be 0.0827 kJ/mol which is less than 8 kJ/mol, and hence it is clear that the adsorption of Copper ions by Chitosan-Banana stem fibre beads was physical adsorption.

*Adsorption Kinetics:*

In order to investigate the mechanism of adsorption and its potential rate controlling steps, kinetic models have been used. The adsorption kinetic models are grouped into two classes and they are, ***Adsorption reaction models:*** Pseudo First order model (Lagergren model), Pseudo Second order model (Ho and McKay model) and Elovich model and ***Adsorption diffusion models:*** Intra-particle diffusion model (Weber and Morris model) and Boyd model.

*Pseudo First Order Model:* Lagergren's first order rate equation has been most widely used for the adsorption of an adsorbate from an aqueous solution. It is represented as,

$\ln (q_e - q_t) = \ln q_e - K\,t$

where $q_e$ is the equilibrium adsorption capacity (mg/g), $q_t$ is the mass of metal ions adsorbed at time t (mg/g), K is the first order rate constant ($min^{-1}$). The pseudo first order considers the rate of occupation of adsorption sites is directly proportional to the number of unoccupied sites. A plot of $ln\ (q_e - q_t)$ against $t$ should give a linear relationship for the applicability of the first order kinetic.

The following figure represents the Pseudo First order sorption kinetics of Copper (II) ions on to cross linked Chitosan-Cellulose beads for various initial concentrations (100, 200, 300, 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.2 g, temperature $28^o$ C and pH 5.2

***Research Article***

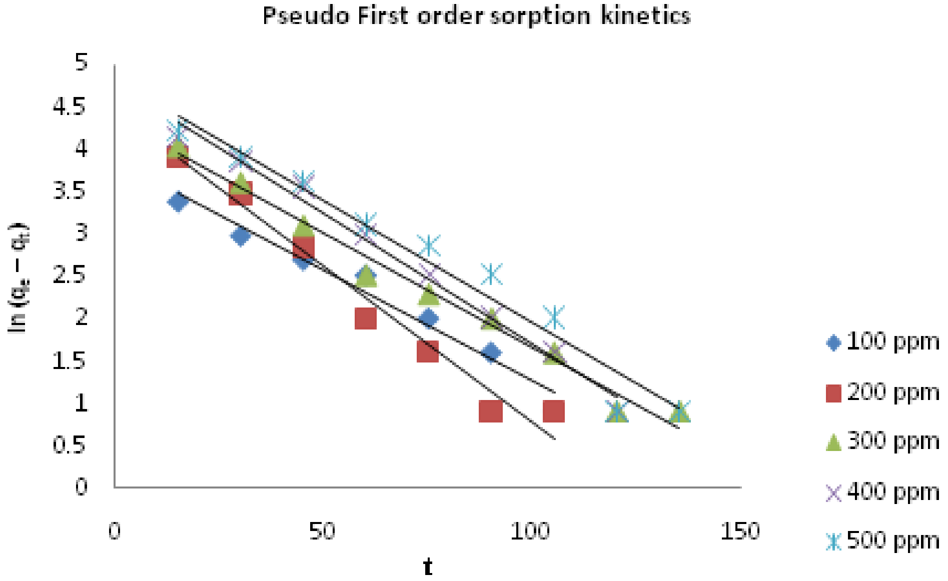

**Figure 10: Pseudo First order kinetic plot for the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads**

The following figure represents the Pseudo First order sorption kinetics of Copper (II) ions on to Chitosan-Red Soil beads for various initial concentrations (100, 200, 300, 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.5 g, temperature 28° C and pH 5.2

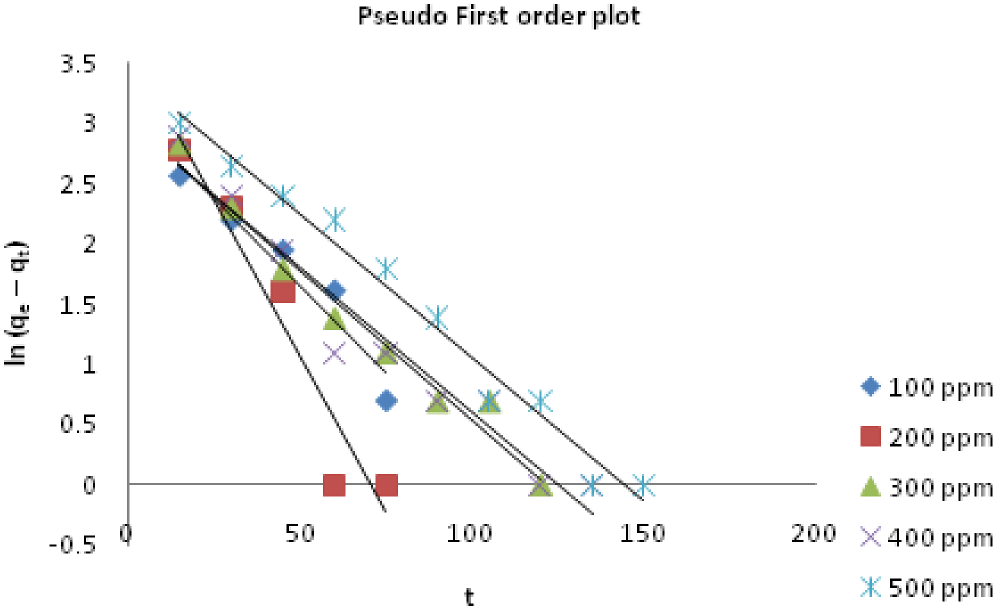

**Figure 11: Pseudo First order kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Red Soil beads**

The following figure represents the Pseudo First order sorption kinetics of Copper (II) ions on to Chitosan-Banana stem fibre beads for various initial concentrations (100, 200, 300, 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.2 g, temperature 28° C and pH 5.2

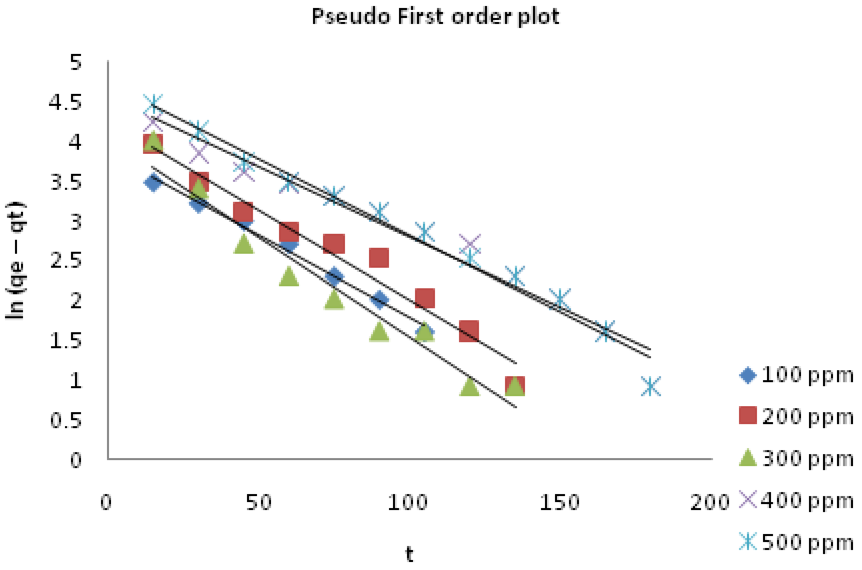

**Figure 12: Pseudo First order kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Banana stem fibre beads**

*Pseudo Second Order Model:* The Pseudo Second order model considers that the rate of adsorption metal ions is based on the square of number of vacant sites on the adsorbent. The pseudo second order rate equation is represented as,

$$t/q_t = 1/(K\ q_e^2) + t/q_e$$

A plot of $t/q_t$ versus $t$ should give a linear relationship for the applicability of the second order kinetic.
The following figure represents the Pseudo Second order sorption kinetics of Copper (II) ions on to cross linked Chitosan-Cellulose beads for various initial concentrations (100, 200, 300, 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.2 g, temperature 28° C and pH 5.2

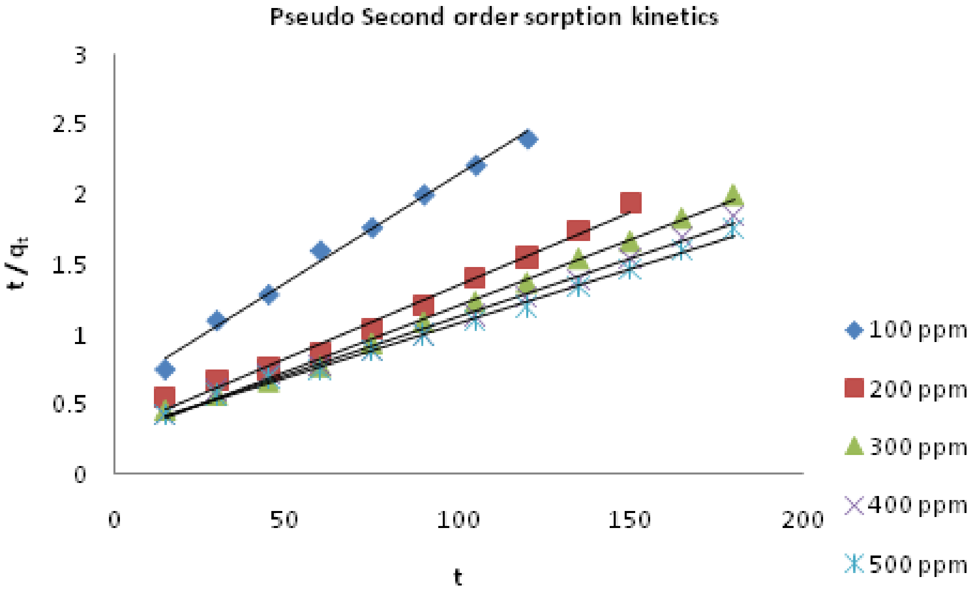

**Figure 13: Pseudo Second order kinetic plot for the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads**

The following figure represents the Pseudo Second order sorption kinetics of Copper (II) ions on to Chitosan-Red Soil beads for various initial concentrations (100, 200, 300, 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.5 g, temperature 28$^o$ C and pH 5.2

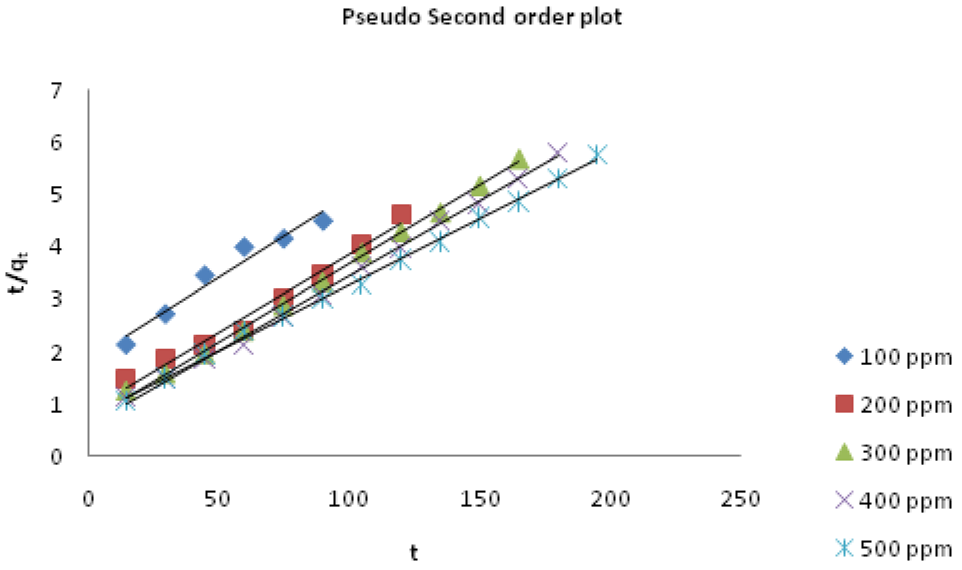

**Figure 14: Pseudo Second order kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Red Soil beads**

The following figure represents the Pseudo Second order sorption kinetics of Copper (II) ions on to Chitosan-Banana stem fibre beads for various initial concentrations (100, 200, 300, 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.2 g, temperature 28$^o$ C and pH 5.2

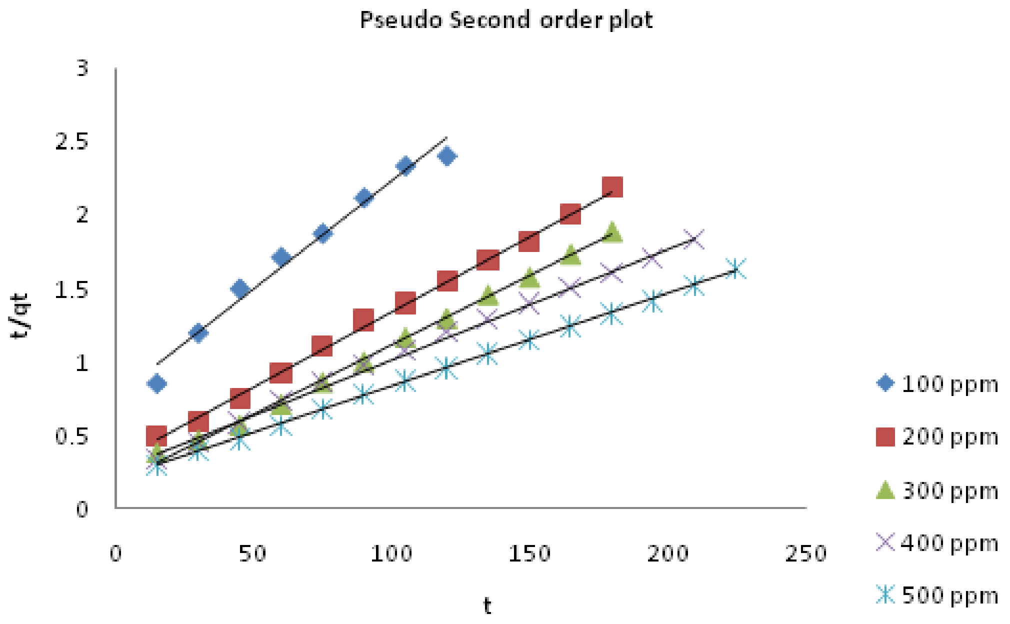

**Figure 14: Pseudo Second order kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Banana stem fibre beads**

*Simple Elovich Model:* Elovich equation has been used to describe the adsorption of gas on to solid systems. It has also been applied to describe the adsorption of pollutants from aqueous solutions such as Cadmium removal from effluents using bone char and Cr (VI) and Cu (II) adsorption by Chitin and Chitosan, Hui *et al.*, (2009).

The simple Elovich model is expressed in the form,

$$q_t = \alpha + \beta \ln t$$

where $q_t$ is the amount adsorbed at time t, α and β are the constants obtained from the experiment. A plot of $q_t$ against *ln t* should give a linear relationship for the applicability of the simple Elovich kinetic.

The following figure shows the simple Elovich kinetics of Copper (II) ions on to cross linked Chitosan-Cellulose beads for various initial concentrations (100, 200, 300 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.2 g, temperature 28° C and pH 5.2

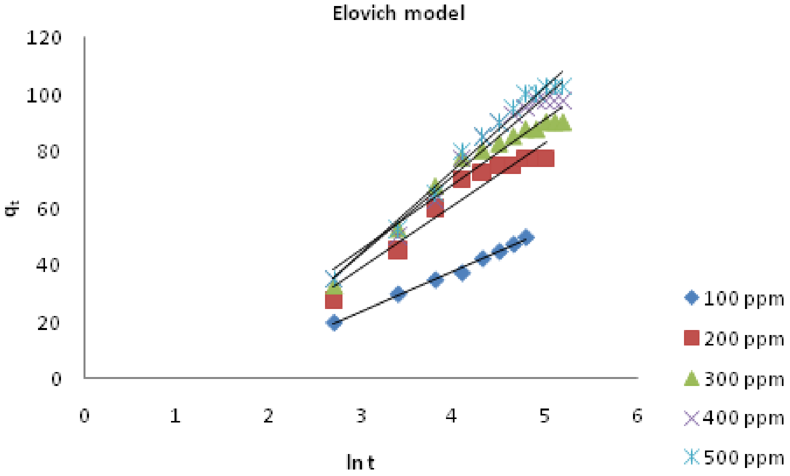

**Figure 15: The Simple Elovich kinetic plot for the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads**

The following figure shows the simple Elovich kinetics of Copper (II) ions on to Chitosan-Red Soil beads for various initial concentrations (100, 200, 300 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.5 g, temperature 28° C and pH 5.2

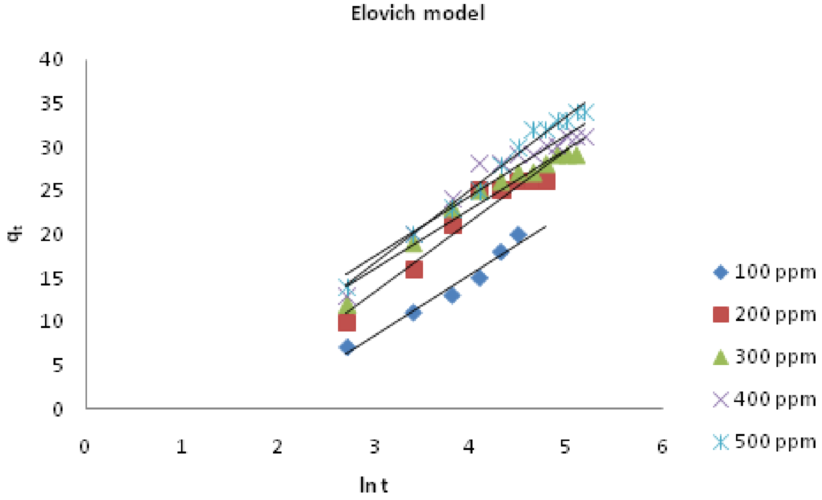

**Figure 16: The Simple Elovich kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Red Soil beads**

The following figure shows the simple Elovich kinetics of Copper (II) ions on to Chitosan-Banana stem fibre beads for various initial concentrations (100, 200, 300 400 and 500 ppm) of volume 100 mL (each), adsorbent dose 0.2 g, temperature 28° C and pH 5.2

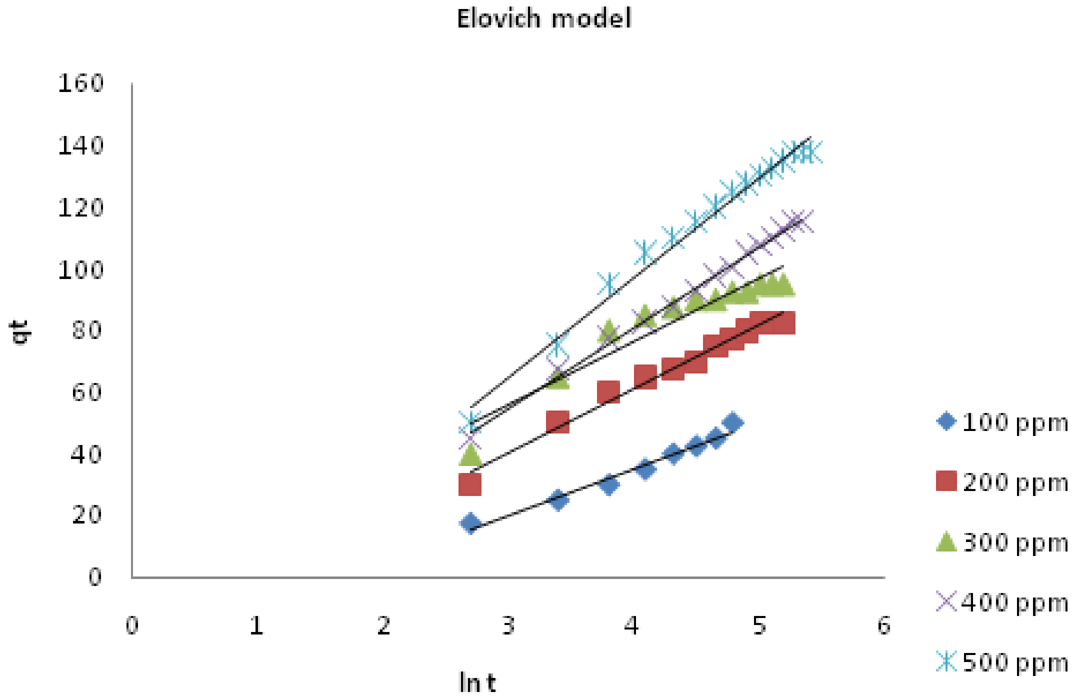

**Figure 17: The Simple Elovich kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Banana stem fibre beads**

The parameters of First order, Second order and Elovich kinetic models for the adsorption of Copper ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were estimated and given below.

**Table 1: Estimated parameters of Kinetic models for the adsorption by the cross linked Chitosan-Cellulose beads**

| Conc. of Aqueous Solution (ppm) | First Order Kinetic Model | | | Second Order Kinetic Model | | | Elovich Kinetic Model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $q_e$ (mg/g) | $K_{ad}$ ($min^{-1}$) | $R^2$ | $q_e$ (mg/g) | $K_{ad}$ (g/mg min) | $R^2$ | α | β |
| **100** | 0.970 | 47.94 | 0.026 | 0.993 | 62.50 | $4.27*10^{-4}$ | 0.993 | -18.69 | 14.16 |
| **200** | 0.972 | 84.47 | 0.036 | 0.987 | 90.91 | $3.94*10^{-4}$ | 0.935 | -28.40 | 23.22 |
| **300** | 0.984 | 70.59 | 0.026 | 0.996 | 100.0 | $3.89*10^{-4}$ | 0.946 | -23.58 | 22.96 |
| **400** | 0.989 | 120.30 | 0.030 | 0.992 | 111.11 | $2.71*10^{-4}$ | 0.963 | -38.97 | 27.53 |
| **500** | 0.964 | 140.05 | 0.028 | 0.996 | 125.0 | $2.08*10^{-4}$ | 0.970 | -43.57 | 29.20 |

***Research Article***

**Table 2: Estimated parameters of Kinetic models for the adsorption by the Chitosan-Red Soil beads**

| Conc. of Aqueous Solution (ppm) | First Order Kinetic Model | | | Second Order Kinetic Model | | | Elovich Kinetic Model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $q_e$ (mg/g) | $K_{ad}$ ($min^{-1}$) | $R^2$ | $q_e$ (mg/g) | $K_{ad}$ (g/mg min) | $R^2$ | α | β |
| **100** | 0.926 | 22.22 | 0.028 | 0.956 | 32.26 | $5.23 * 10^{-4}$ | 0.964 | - 12.68 | 7.012 |
| **200** | 0.927 | 40.08 | 0.052 | 0.980 | 34.48 | $9.48 * 10^{-4}$ | 0.938 | -11.11 | 8.18 |
| **300** | 0.973 | 20.80 | 0.025 | 0.998 | 33.33 | $13.33 * 10^{-4}$ | 0.953 | -4.632 | 6.871 |
| **400** | 0.946 | 20.23 | 0.024 | 0.997 | 35.71 | $13.27 * 10^{-4}$ | 0.929 | -3.55 | 6.985 |
| **500** | 0.979 | 31.25 | 0.023 | 0.997 | 40.00 | $8.22 * 10^{-4}$ | 0.983 | -7.906 | 8.22 |

**Table 3: Estimated parameters of Kinetic models for the adsorption by the Chitosan-Banana stem fibre beads**

| Conc. of Aqueous Solution (ppm) | First Order Kinetic Model | | | Second Order Kinetic Model | | | Elovich Kinetic Model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $q_e$ (mg/g) | $K_{ad}$ ($min^{-1}$) | $R^2$ | $q_e$ (mg/g) | $K_{ad}$ (g/mg min) | $R^2$ | α | β |
| 100 | 0.991 | 47.61 | 0.020 | 0.979 | 71.43 | $2.58 * 10^{-4}$ | 0.975 | -26.2 | 15.32 |
| 200 | 0.968 | 61.37 | 0.019 | 0.996 | 100.0 | $3.07 * 10^{-4}$ | 0.986 | -25.38 | 21.60 |
| 300 | 0.955 | 57.80 | 0.025 | 0.997 | 111.11 | $4.79 * 10^{-4}$ | 0.898 | -05.20 | 20.38 |
| 400 | 0.960 | 96.35 | 0.017 | 0.996 | 142.86 | $1.91 * 10^{-4}$ | 0.995 | -24.32 | 26.23 |
| 500 | 0.979 | 115.47 | 0.019 | 0.999 | 166.67 | $1.77 * 10^{-4}$ | 0.984 | -32.31 | 32.31 |

Three adsorption reaction models were applied on the data obtained from the adsorption experiments of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads to investigate the suitability. The linear regression values obtained from the Elovich kinetic model were lower than the other two models for each adsorbent and it showed the inapplicability of the model. The linear regression values of Pseudo First order sorption kinetics were also low and the $q_e$ values acquired from the Pseudo First order sorption kinetics were contrasted with the experimental values. But in the case of Pseudo Second order model, the linear regression values were considerably higher ($R^2 > 0.99$), and also the calculated $q_e$ values agreed better with the experimental data. Hence it was very clear that the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads have followed the Pseudo Second order kinetic model.

*Intra-Particle Diffusion Model by Weber-Morris:* The adsorption process on a porous adsorbent is generally a multi-step process. In order to analyze the mechanism of the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and the Chitosan-Banana stem fibre beads, the experimental data were tested against the intra-particle diffusion model. The adsorption mechanism of the adsorbate on to the adsorbent follows three consecutive steps: *mass transfer across the* *external film of liquid surrounding the particle, adsorption at the surface of pores and intra-particle diffusion.* The slowest of these steps determines the overall rate of the process. The possibility of intra-particle diffusion resistance which could affect the adsorption is explored by using the intra-particle diffusion model given in the equation,

$$q_t = K\, t^{1/2} + I$$

where K is the intra-particle diffusion rate constant and I is the intercept. A plot of $q_t$ against $t^{1/2}$ is drawn to analyze the possibility of intra-particle diffusion as the rate determining step. A two stage adsorption mechanism with first rapid and second slower has been observed from the experimental data for each adsorbent. The plot of $q_t$ against $t^{1/2}$ is multi-linear and deviating from the origin, indicating more than one process affected the adsorption, Ashtoukhy *et al.*, (2008). The first segment of the curves represented film diffusion and surface diffusion and the second segment represented intra-particle diffusion.

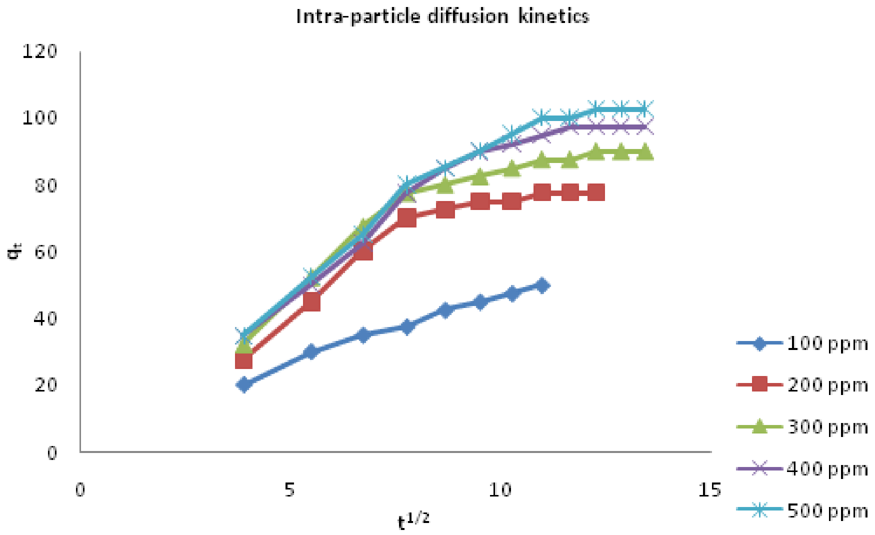

**Figure 18: The Intra-particle diffusion kinetic plot for the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads for various initial concentrations**

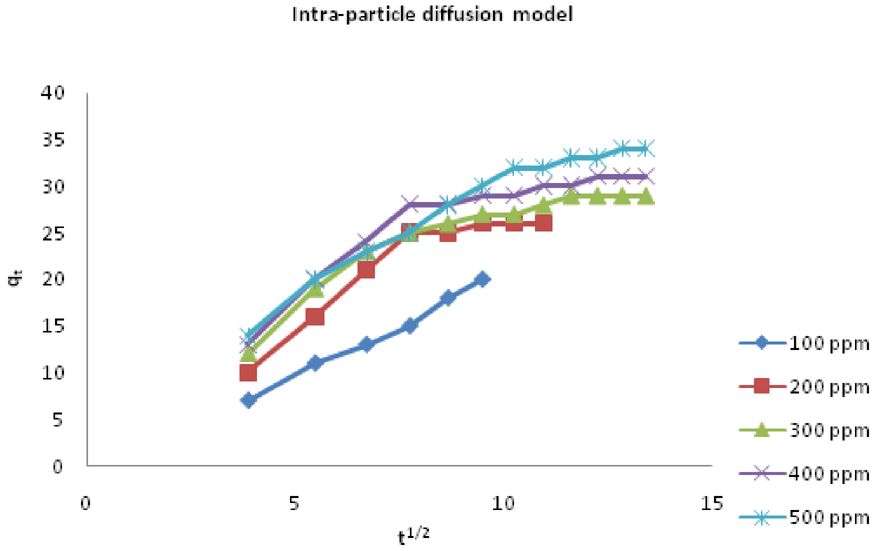

**Figure 19: The Intra-particle diffusion kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Red Soil beads for various initial concentrations**

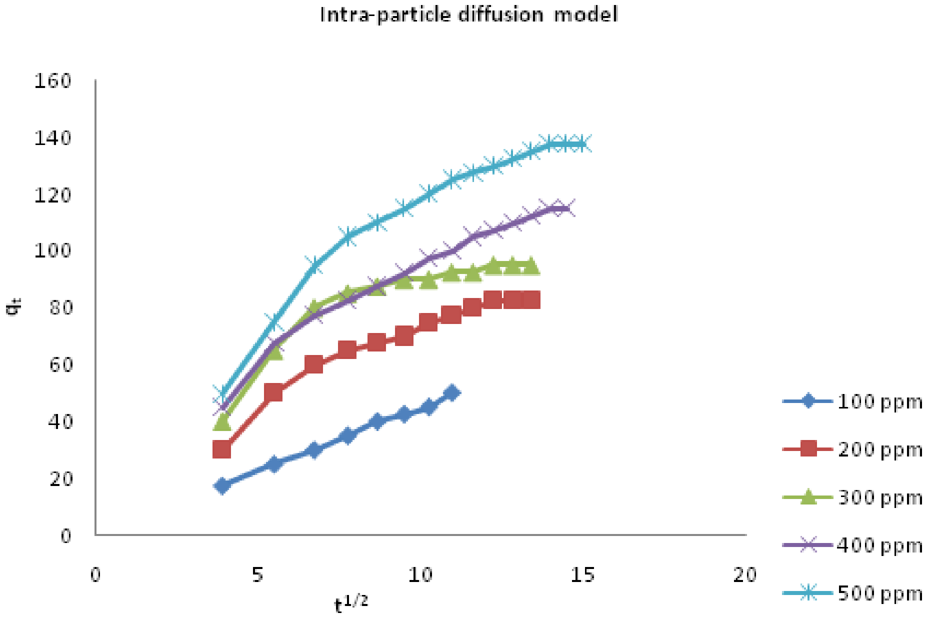

**Figure 20: The Intra-particle diffusion kinetic plot for the adsorption of Copper (II) ions on to Chitosan-Banana stems fibre beads for various initial concentrations**

The parameters of intra-particle diffusion model for the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil and Chitosan-Banana stem fibre beads were estimated and given in the following tables.

**Table 4: Estimated parameters of Intra-Particle diffusion model for the adsorption by cross linked Chitosan-Cellulose beads**

| Concentration of Aqueous Solution (ppm) | $R^2$ | $K_{ad}$ (g/mg $min^{0.5}$) | Intercept (I) |
|---|---|---|---|
| **100** | 0.985 | 4.076 | 6.26 |
| **200** | 0.839 | 5.647 | 16.60 |
| **300** | 0.844 | 5.421 | 25.69 |
| **400** | 0.895 | 6.631 | 18.85 |
| **500** | 0.922 | 7.079 | 17.34 |

**Table 5: Estimated parameters of Intra-Particle diffusion model for the adsorption by Chitosan-Red Soil beads**

| Concentration of Aqueous Solution (ppm) | $R^2$ | $K_{ad}$ (g/mg $min^{0.5}$) | Intercept (I) |
|---|---|---|---|
| **100** | 0.991 | 2.262 | -1.821 |
| **200** | 0.859 | 2.262 | 4.013 |
| **300** | 0.839 | 1.555 | 10.56 |
| **400** | 0.819 | 1.639 | 11.52 |
| **500** | 0.927 | 1.935 | 9.668 |

**Table 6: Estimated parameters of Intra-Particle diffusion model for the adsorption by Chitosan-Banana stem fibre beads**

| Concentration of Aqueous Solution (ppm) | $R^2$ | $K_{ad}$ (g/mg $min^{0.5}$) | Intercept (I) |
|---|---|---|---|
| **100** | 0.996 | 4.479 | 0.275 |
| **200** | 0.934 | 5.616 | 5.616 |
| **300** | 0.772 | 4.724 | 39.36 |
| **400** | 0.960 | 6.075 | 32.41 |
| **500** | 0.908 | 7.128 | 41.01 |

*Boyd Model:* Multi-linear plots were obtained from the intra-particle diffusion model for the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads and in order to determine the actual rate controlling step involved in the sorption process, the kinetic data have been analyzed using the model given by Boyd, Xin-Jian *et al*., (2011).

$$F = 1 - (6/\pi^2) \sum_{m=1}^{\infty} [(1/m^2) \exp(-m^2 Bt)]$$

Where $F$ is the fractional attainment of equilibrium at time $t$ and is obtained from the expression:

$$F = q_t / q_e$$

where $q_t$ (mg/g) is the amount of adsorbate taken up at time $t$ and $q_e$ (mg/g) is the maximum equilibrium uptake and

$$B = D_i \pi^2 / r^2$$

where $B$ is the time constant ($min^{-1}$), $D_i$ is the effective diffusion coefficient of the metal ions in the sorbate phase ($cm^2$/min), $r$ is the radius of the adsorbent particle (cm), assumed to be spherical, and $m$ is an integer that defines the infinite series solution. $Bt$ is given by the equation:

$$Bt = - 0.4977 - \ln(1 - F)$$

Thus the value of $Bt$ can be computed for each value of $F$, and then plotted against time to configure the so-called Boyd plots, Xin-Jian *et al*., (2011). A straight line passing through origin is indicative of sorption processes governed by particle diffusion mechanism; otherwise they are governed by film diffusion, Xin-Jian *et al*., (2011).The plots of $Bt$ against $t$ for the experimental data of various concentrations have been shown below.

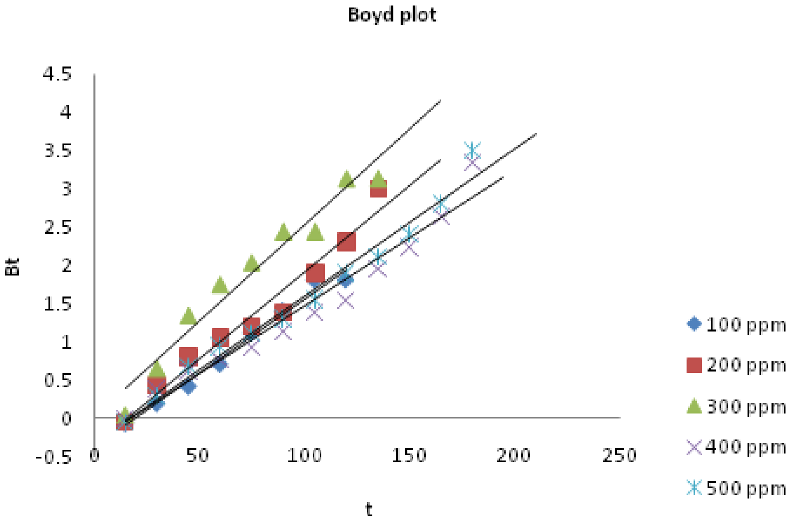

**Figure 21: The Boyd plot for the adsorption of Copper (II) ions on to cross linked Chitosan-Cellulose beads for various initial concentrations**

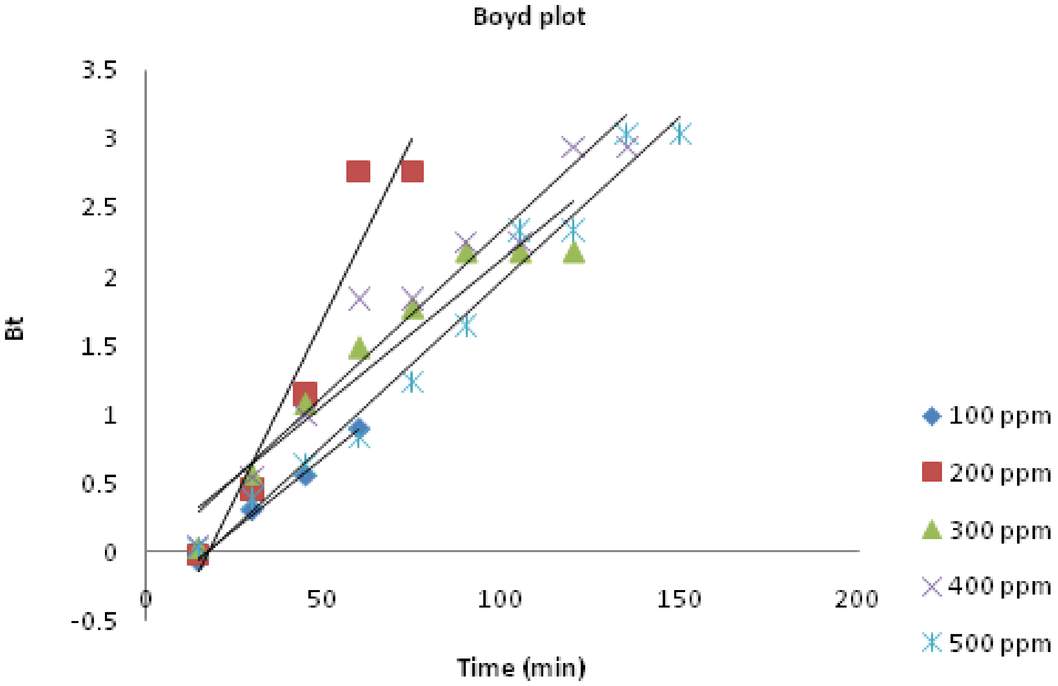

**Figure 22: The Boyd plot for the adsorption of Copper (II) ions on to Chitosan-Red Soil beads for various initial concentrations**

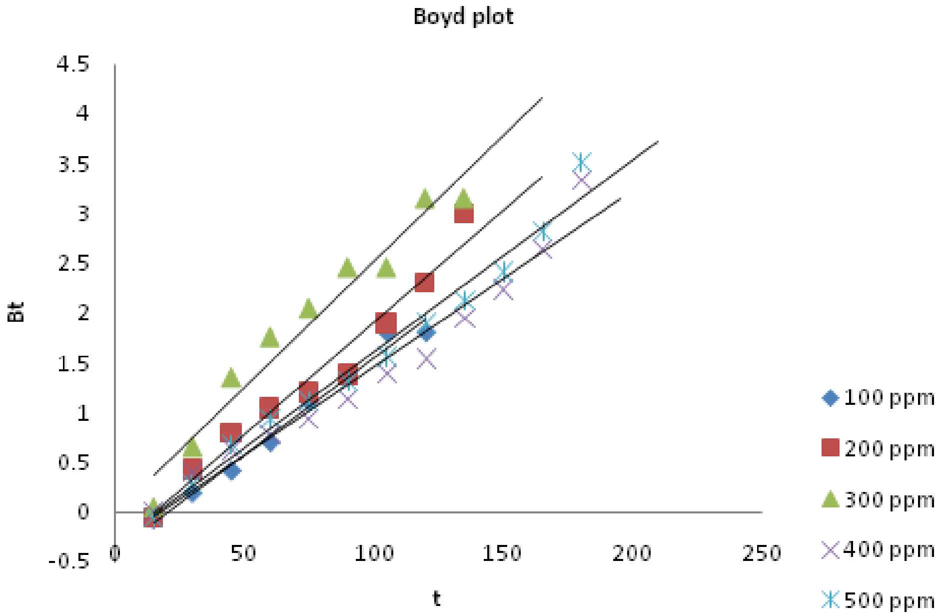

**Figure 23: The Boyd plot for the adsorption of Copper (II) ions on to Chitosan-Banana stem fibre beads for various initial concentrations**

The Boyd plots for the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads very slightly deviated from the origin but they were much linear which revealed that the intra-particle diffusion was the actual rate controlling step of all adsorption processes.

*Adsorption Thermodynamics:*

In order to find whether the adsorption process is spontaneous or non-spontaneous, the value of Gibbs free energy of adsorption ($\Delta G^o$) is calculated by the equation,

$$\Delta G^o = - RT \ln K_D$$

$$K_D = q_e/C_e$$

where $K_D$ is the distribution coefficient for the adsorption in g/L, $\Delta G^o$ is the Gibbs free energy in J/mol, R is the universal gas constant in J/mol K, T is the absolute temperature in K, Sugashini *et al.*, (2012). The values of Gibbs free energy ($\Delta G^o$) for various temperatures were calculated from the experimental data. The estimated values of $\Delta G^o$ were tabulated below.

**Table 7: Table of estimated values of Gibbs free energy ($\Delta G^o$) at various temperatures**

| S. No | T (K) | Cross linked Chitosan-Cellulose Beads | Chitosan-Red Soil Beads | Chitosan-Banana Stem Fibre Beads |
|---|---|---|---|---|
| | | $\Delta G^o$ (J/mol) | $\Delta G^o$ (J/mol) | $\Delta G^o$ (J/mol) |
| **1** | 303 | -1369.12 | 2495.15 | -2159.99 |
| **2** | 308 | -1392.01 | 2536.32 | -2285.41 |
| **3** | 313 | -1643.99 | 2345.06 | -2710.13 |
| **4** | 318 | -1750.69 | 2139.49 | -1832.58 |
| **5** | 323 | -741.89 | 2893.11 | -1696.52 |
| **6** | 328 | -291.70 | 3283.22 | -1105.70 |

The negative values of Gibbs free energy change $\Delta G^o$ obtained for the adsorption of Cu (II) ions by cross linked Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads at various temperatures showed the spontaneous nature of the adsorption process. But the positive values of Gibbs free energy change $\Delta G^o$ obtained for the adsorption of Cu (II) ions by Chitosan-Red Soil beads at various temperatures showed the non-spontaneous nature of the adsorption process.

## RESULTS AND DISCUSSION

A comparative study was made on the adsorption experiments carried out by the cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads and the following similarities and dissimilarities had been found out.

i. Adsorbent dosage had strongly affected the sorption capacity. With the fixed Copper (II) ions concentration, the percentage removal of Copper (II) ions increased with increasing weight of adsorbents of cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads.
ii. pH of the solution had significant impact on the adsorption of Copper (II) ions. Hence the adsorption processes of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were pH dependant.
iii. The optimum pH was found to be 5 for the adsorption by cross linked Chitosan-Cellulose beads and Chitosan-Red Soil beads, and it was 6 for Chitosan-Banana stem fibre beads.
iv. In case of cross linked Chitosan-Cellulose beads, the blending of Cellulose, has made the adsorbent beads mechanically stronger and the cross linking with Formaldehyde has extended the application in a wide pH range.

In case of Chitosan-Red Soil beads, the mixing of Red Soil has made the adsorbent beads considerably denser. Hence the beads have been used in acidic (up to pH of 3) and alkaline media without the need of cross linking.

In case of Chitosan-Banana stem fibre beads, the mixing of Banana stem fibre has reinforced the Chitosan polymer and improves the application in both strong acidic (up to pH of 3) and alkaline media without the need of cross linking.

v. The removal of Copper (II) ions from aqueous solution by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads increased with time.

vi. Adsorption experiments by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were very fast during the first 15 minutes of adsorbate-adsorbent contact and it slowly decreased with time. Hence a two stage adsorption mechanism with the first being rapid and the other being slow had been observed in all cases.

vii. The percentage removal of Copper (II) ions decreased with increase in Copper (II) ion concentration for the adsorption by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads.

viii. The adsorption increased 2 % when the temperature was raised from $35^o$ C to $45^o$ C and then the adsorption decreased up to 10 % when the temperature was raised up to $55^o$ C for the adsorption in 100 ml of 200 ppm solution by 0.5 g cross linked Chitosan-Cellulose beads.

The adsorption increased 4 % when the temperature was raised from $35^o$ C to $45^o$ C and then the adsorption decreased up to 7 % when the temperature was raised up to $55^o$ C for the adsorption in 100 ml of 200 ppm solution by 0.5 g Chitosan-Red Soil beads.

The adsorption increased 2.5 % when the temperature was raised from $30^o$ C to $45^o$ C and then the adsorption decreased up to 10 % when the temperature was raised up to $55^o$ C for the adsorption in 100 ml of 200 ppm solution by 0.2 g Chitosan-Banana stem fibre beads.

**Table 8: Removal of $Cu^{+2}$ ions by the three adsorbents with respect to various temperatures**

| S. No | Temperature ($^o$C) | Cross Linked Chitosan-Cellulose Beads | Chitosan-Red Soil Beads | Chitosan-Banana Stem Fibre Beads |
|---|---|---|---|---|
| | | % Removal | % Removal | % Removal |
| **1** | 30 | 77.5 | 65 | 82.5 |
| **2** | 35 | 77.5 | 65 | 83 |
| **3** | 40 | 79 | 67 | 85 |
| **4** | 45 | 79.5 | 69 | 80 |
| **5** | 50 | 72.5 | 63 | 79 |
| **6** | 55 | 69 | 60 | 75 |

ix. The experimental data of adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads followed isotherms in the order:

Freundlich > Temkin > Langmuir

The experimental data of adsorption of Copper (II) ions by Chitosan-Red Soil beads followed isotherms in the order:

Temkin > Langmuir > Freundlich

The experimental data of adsorption of Copper (II) ions by Chitosan-Banana stem fibre beads followed isotherms in the order:

Langmuir > Freundlich > Temkin

x. The Dubinin-Radushkevich isotherm showed that the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were Physical adsorption.
xi. The analysis of adsorption reaction models revealed that the Pseudo Second order model was the best fitting model for the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads.
xii. The adsorption diffusion models showed that the intra-particle diffusion was the rate controlling step in the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads.
xiii. The adsorption thermodynamics showed that the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads were spontaneous and the adsorption of Copper (II) ions by Chitosan-Red Soil beads was non-spontaneous.
xiv. The heavy metal binding capacity of Cellulose, Red Soil and Banana stem fibre were discovered by numerous researches. Hence the combination of Chitosan with Cellulose, Red Soil and Banana stem fibre not only strengthened the polymer matrix and also enhanced the sorption capacity.
xv. The equilibrium adsorption capacity ($q_e$) for the adsorption of Copper (II) ions of concentration 100, 200, 300, 400 and 500 (in mg/L) by cross linked Chitosan-Cellulose beads were 50, 77.5, 90, 97.5 and 102.5 (in mg/g), by Chitosan-Red Soil beads were found to be 20, 26, 29, 31 and 34 (in mg/g) and by Chitosan-Banana stem fibre beads were 50, 82.5, 95, 115 and 137.5 (mg/g).

The equilibrium adsorption capacities (qe) of adsorbent beads have followed the order: *Chitosan-Banana stem fibre > Cross linked Chitosan-Cellulose > Chitosan-Red Soil*

## CONCLUSION

The cross-linking with Formaldehyde extended the application of the adsorbent to a wide pH range by enhanced its chemical stability. If the application of adsorbent extends up to pH of 2, then the cross linked Chitosan-Cellulose beads will be the right choice. Chitosan-Red Soil beads found to be more economic than others since the ratio of Chitosan-Red soil was just 5:95 and if cost of Chitosan is a main consideration, then the Chitosan-Red Soil beads may be the good choice (but adsorption capacity will be lower). In the case of Chitosan-Banana stem fibre beads, the Banana stems are very easily available and can be obtained free of cost. The mechanical pressing of the stems, separation and drying of the fibres also can be made very easily either with less machine power or manually. Hence the cost of making the Chitosan-Banana stem fibre beads would be lower than the making of cross linked Chitosan-Cellulose beads. Since the Banana stem fibre is a lignocelluloses material, the necessity of purchasing Cellulose is not needed. Furthermore, the equilibrium adsorption capacity of Chitosan-Banana stem fibre beads is much higher than the other two adsorbents.

Hence the choice of adsorbent beads will be based on the specific application and economic considerations. The experimental results and the comparative studies made would be useful for the effective application of cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads as adsorbents to treat industrial effluents.

## REFERENCES

**Write Work (No Date):** *Environmental Effects of Copper and How Copper is Processed.* Available at: http://writework.com. [Accessed on: October 28, 2012]

**Wan Ngah WS, Kamari A and Koay YJ (2004).** Equilibrium and kinetics studies of adsorption of copper (II) on Chitosan and Chitosan/PVA beads. *International Journal of Biological Macromolecules* **34** 155-161.

**Kaminiski W, Tomczak E and Jaros K (2008).** Interactions of metal ions sorbed on Chitosan beads. *Desalination* **218** 281-286.

**Peter O Osifo, Hein WJP Neomagus, Raymond C Everson, Athena Webster and Marius A VD Gun (2009).** The adsorption of Copper in a packed bed of Chitosan beads: Modeling, multiple adsorption and regeneration. *Journal of Hazardous Materials* **167** 1242-1245.

**Majeti NV, Kumar R and A Review of Chitin and Chitosan Applications (2000).** *Reactive and Functional Polymers* **46** 1-27.

**Miretzky P and Cirelli AF (2009).** Hg (II) removal from water by Chitosan and Chitosan derivatives: a review. *Journal of Hazardous Materials* **167**(1-3) 10-23.

**Singh Dhanesh and Singh Anjali (2012).** Chitosan for the Removal of Chromium from Waste Water. *International Research Journal of Environment Sciences* **1**(3) 55-57.

**Zofia Modrzejewska, Witold Sujka, Malgorzata Dorabialska and Roman Zarzycki (2006).** Adsorption of Cr (VI) on crosses linked Chitosan beads. *Separation Science and Technology* **41**(1) 111-122.

**Shengling Sun, Li Wang and Aiqin Wang (2006).** Adsorption properties of cross linked carboxymethyl-chitosan resin with Pb (II) as template ions. *Journal of Hazardous Materials* **136**(3) 930-937.

**Sandhya Babel and Tonni Agustiono Kurniawan (2003).** Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* **97**(1-3) 219-243.

**Kaminiski W, Tomczak E and Jaros K (2008).** Interactions of metal ions sorbed on Chitosan beads. *Desalination* **218** 281-286.

**Wen-Li Du, Shan-Shan Niu, Zi-Rong Xu and Ying-Lei Xu (2009).** Preparation, Characterizations and Adsorption properties of Chitosan microspheres cross linked by Formaldehyde for Copper (II) from aqueous solution. *Journal of Applied Polymer Science* **111** 2881-2885.

**Esam A, El-Hefian, Mohamed Mahmoud Nasef and Abdul Hamid Yahaya (2011).** Chitosan Physical Forms: A Short Review. *Australian Journal of Basic and Applied Sciences* **5**(5) 670-677.

**David William O'Connell, Colin Birkinshaw and Thomas Francis O'Dwyer (2008).** Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology* **99** 6709-6724.

**Hale Bahar Ozturk, Hai Vu-Manh and Thomas Bechtold (2007).** Interaction of Cellulose with Alkali metal ions and complexes heavy metals. *Lenzinger Berichte* **87** 142-150.

**Heike B Bradl (2004).** Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science* **277** 1-18.

**Soil (2012)**. *Soil.* Available at: http://en.wikipedia.org. [Accessed on: November 14, 2012]

**Dube A, Zbytniewski R, Kowalkowski T, Cukrowska E and Buszewski B (2001).** Adsorption and Migration of Heavy Metals in Soil. *Polish Journal of Environmental Studies* **10**(1) 1-10.

**Soil Minerals (2012).** *Cation Exchange Capacity in Soils and Simplified.* Available at: http://www.soilminerals.com. [Accessed on: September 05, 2012]

**Beom-Goo Lee, Roger M and Rowell (2004).** Removal of Heavy Metal Ions from aqueous solutions Using Lignocellulosic Fibres. *Journal of Natural Fibers* **1**(1) 97-108.

**Low KS, Lee CK and Lee KP (1993).** Sorption of Copper by dye-treated oil-palm fibres. *Bio-Resources Technology* **44** 109-112.

**Hui QIU, Lu LV, Bing-Cai PAN and Qing-Jian Zhang (2009).** Critical review in adsorption models. *Journal of Zhejiang University Science* **10**(5) 716-724.

**Ashtoukhy SZ, Amin NK and Abdelwahab O (2008).** Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination* **223** 162-173.

**Xin-Jian Hu, Jing-Song Wang, Yun-Guo Liu, Xin Li, An-Wei Chen, Zheng-Lei Bao and Fei Long (2011).** Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic Chitosan resin: Isotherms, kinetics and thermodynamics. *Journal of Hazardous Materials* **185** 306-314.

**Sugashini S, Gopalakrishnan S and Studies on the Performance of Protonated Cross Linked Chitosan Beads (PCCB) for Chromium Removal (2012).** *Research Journal of Chemical Sciences* **2**(6) 55-59.