



A study on adsorption of Copper (II) ions in aqueous solution by Chitosan reinforced by Banana stem fibre

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Abstract: The heavy metal contamination is an environmental threat as serious as global warming. Removal of Cu^{+2} ions in aqueous solution has been analysed by using Chitosan reinforced by Banana stem fibre. Batch adsorption experiments were carried as a function of adsorbent dosage, pH, contact time, initial metal ion concentration and temperature. The optimum pH was found to be 5. The experimental data were tested with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and the data have been fitted very well with the Langmuir isotherm. The energy of adsorption showed that the adsorption of Copper by Chitosan-Banana stem fibre beads was physical adsorption. Adsorption kinetics data were modeled with the application of Pseudo first order, Pseudo second order, Elovich and Intra-particle diffusion models. The results revealed that the Pseudo second order model was the best fitting model. . The adsorption mechanism 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 the adsorption process of Copper (II) ions by Chitosan-Banana stem fibre beads.

Keywords: Heavy metal removal, Chitosan-Banana stems fibre beads, Adsorption isotherms, Kinetics, Mechanism.

INTRODUCTION

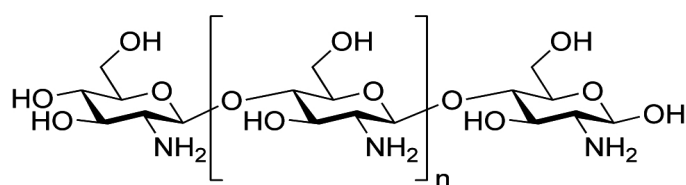
The effective removal of heavy metals from various aqueous wastes is a significant issue worldwide. Industries such as Chemical, Leather, Mechanical and Electrical are the significant sources of heavy metal pollution. Contamination by Copper ion is chiefly from the industries such as paints, pesticides,

metal plating and mining as well as agricultural sources where fertilisers and fungicidal spray intensively used. 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 shellfish for the synthesis of haemoglobin, 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 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.

Heavy metal ions are non-biodegradable and they have to be removed from water sources by various physical and chemical methods like chemical precipitation, evaporation, electrolysis, ion exchange, membrane separation and adsorption¹. In particular, adsorption is an effective and economic method for removal of pollutants from wastewater². 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 recognised as adsorbents of heavy metal ions.

Chitosan has been recognised 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. Chitosan is a linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Adsorption experiments with Copper³⁻⁶, Mercury⁷, Chromium^{8,9} and Lead¹⁰ 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 the second most abundant bio polymer in earth after cellulose. Consequently, 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 capacity¹¹. 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 adsorption¹².



However, unlike Chitin, Chitosan is soluble in acids. Hence attempts were made to increase the chemical stability of Chitosan and cross linking is one of the methods to enhance the chemical stability of Chitosan¹³. In this study, the mechanical strength of Chitosan has been improved by the reinforcement of Banana stem fibre and thus it could be applied to acidic and alkaline solutions. The adsorption of Copper (II) ions by Chitosan reinforced by Banana stem fibre has been analysed. Banana stem fibre is a Lignocellulosic material; it consists of Cellulose (32 %), Hemicellulose (16 %) and Lignin (16 %). Materials that contain cellulose (like bagasse, banana peel, banana stem) can be used to treat heavy metal waste. Cellulose can be used as an adsorbent for the carboxyl and hydroxyl functional group which becomes the active binding site of the metal¹⁴. Also Lignin has been tried as an adsorbent of heavy metals in several researches. Hence the Banana stem fibres were used to reinforce the Chitosan and also to

increase the adsorption capacity. Various researches have proved the metal binding capacity of Banana stem fibres^{15,16}. The adsorbent has been made in the form of small beads of size around 1.5 mm diameter. Hence the mixing of Banana stem fibre with Chitosan is aimed to reinforce the Chitosan, to enhance the mechanical strength and also to boost up the adsorption capacity.

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, Sodium hydroxide pellets were in AR grade and manufactured by SD Fine Chem Limited, Mumbai, India. The AR grade of Cupric Sulphate penta hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was used for the preparation of Cu^{+2} ions. 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).

Method of Preparation Of Adsorbent (Chitosan Reinforced By Banana Stem Fibre): 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 ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 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 analysed 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_0 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 litres, W is the weight of adsorbent in each beaker in grams and q_e is in mg/g.

Typical blue colour got stuck on the Chitosan – Banana stem fibre beads after Cu^{+2} adsorption by simply showing that Copper ions were chelated.

RESULT AND DISCUSSIONS

Effect of Adsorbent Dosage: Adsorbent dosage 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 starting from 0.05 g to 0.2 g were carried out at room temperature (28°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. Among them, 0.2 g of Chitosan – Banana stem fibre beads were found effective and it derived 100 % adsorption of Copper in 100 ppm solution in 120 minutes.

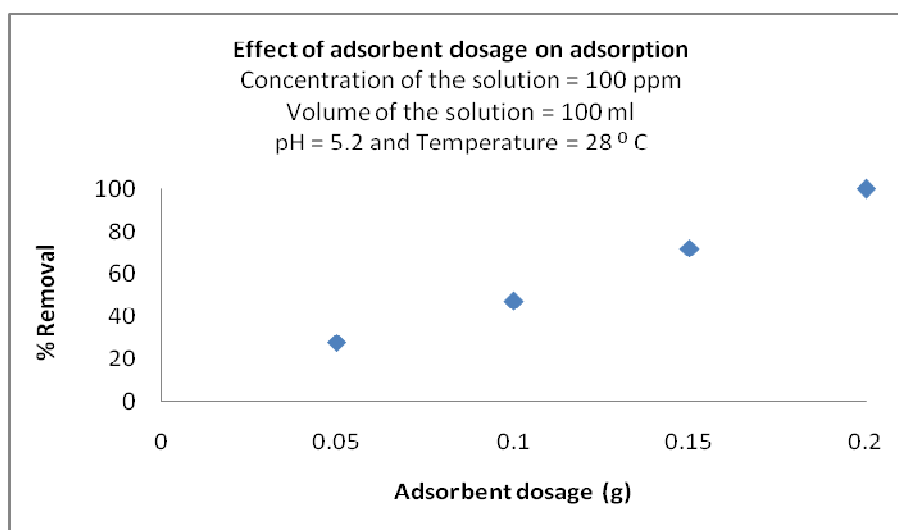


Fig.1: Effect of adsorbent dosage on the adsorption of Copper on to Chitosan-Banana stem fibre beads

Effect of pH on Adsorption: The pH of the solution had significant impact on the uptake of heavy metal ions. The batch experiments were carried out with a pH range of 2 to 10. A wide pH range was 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 and the Chitosan-Banana stem fibre beads very slightly dissolved in the solution. The adsorption of Copper reached maximum at pH of 6. The adsorption slowly decreased from pH of 7. 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 sites¹⁷. 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. The beads of Chitosan reinforced by Banana stem fibre proved a good chemical stability in the pH range of 3 to 10.

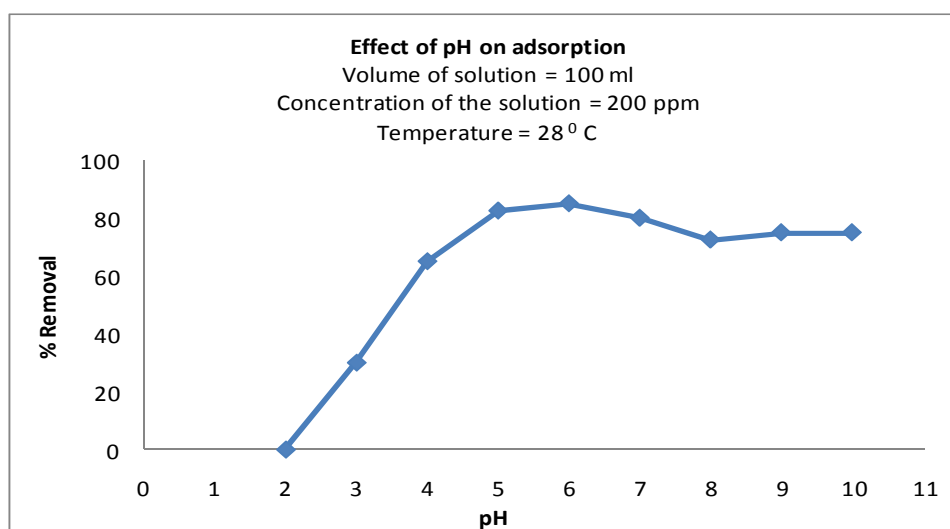


Fig.2: Effect of PH on the adsorption of Copper on to Chitosan-Banana stems fibre beads

Effect of Contact Time on Adsorption: The removal of Copper ions increased with time and attained saturation in about 210 minutes. The removal was very fast at the beginning and it gradually decreased with time till it attained equilibrium. The experimental data showed a rapid 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 the case of adsorption of Copper (II) ions by Chitosan-Banana stem fibre beads.

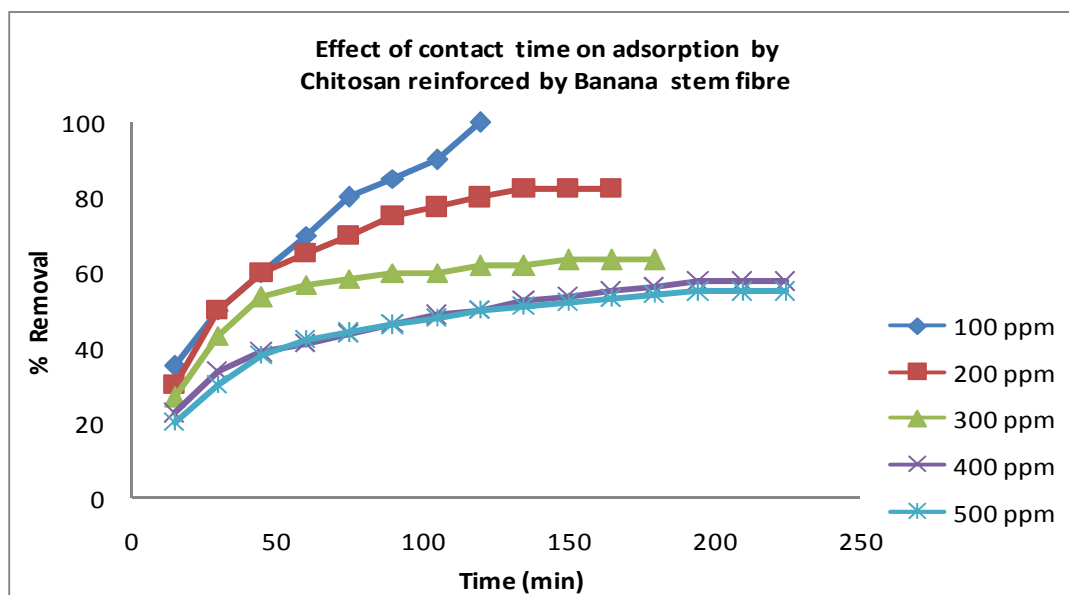


Fig.3: Effect of Contact time on the adsorption of Copper on to Chitosan-Banana stems fibre beads

Effect 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.

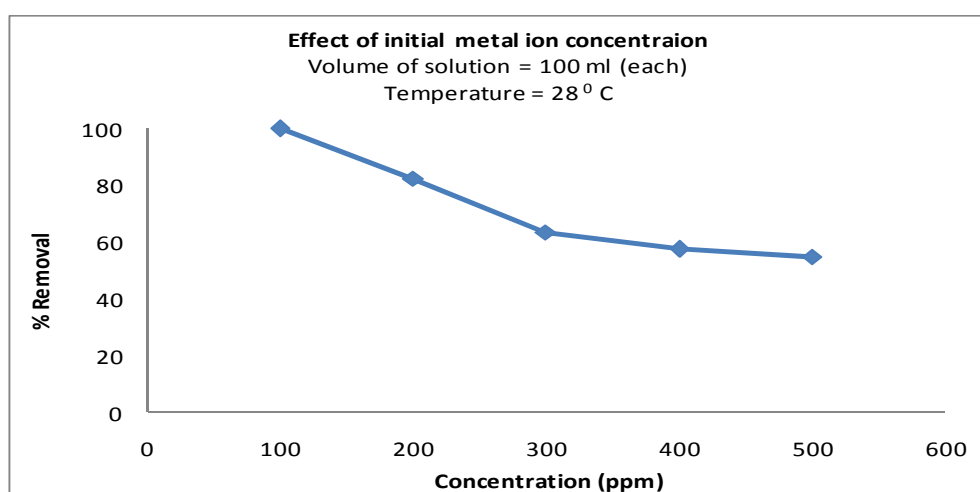


Fig.4: Effect of initial metal ion concentration on the adsorption of Copper on to Chitosan-Banana stem fibre beads

Effect of Temperature: A temperature range started from 30⁰ C in the multiples of 5⁰ C were analysed up to 55⁰ C. The adsorption increased 2.5 % between 30⁰ C and 40⁰ C and then decreased up to 10 % when the temperature was further raised.

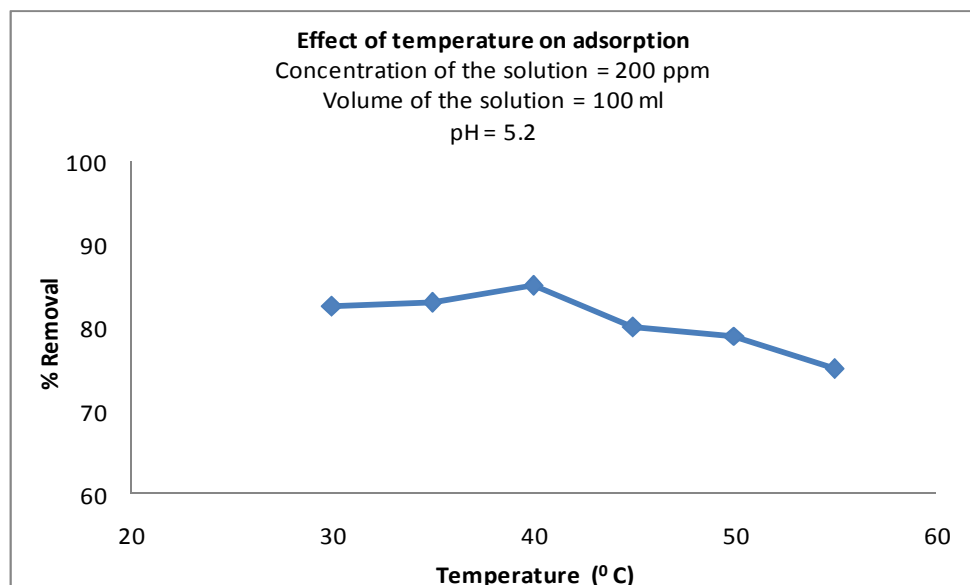


Fig.5: Effects of temperature on the adsorption of Copper on to Chitosan-Banana stem fibre beads

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

The experimental data showed that the adsorption of Copper (II) ions by the Chitosan-Banana stem fibre beads increased with an increase in initial metal ion concentration significantly. At lower initial Copper 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 analysed 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). The plot of C_e/q_e versus C_e is shown in figure below.

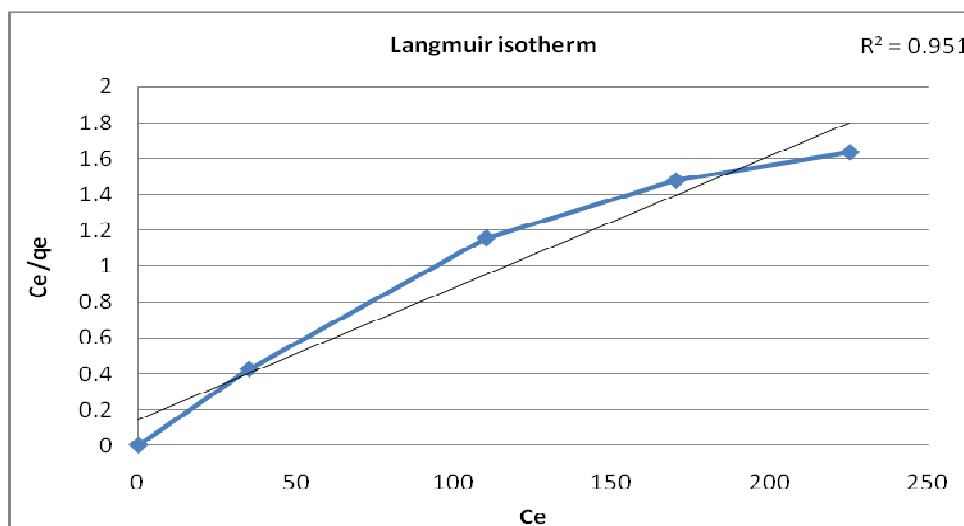


Fig.6: Langmuir isotherm plot for the adsorption of Copper by Chitosan-Banana stem fibre beads

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 analysed 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). The plot of $\log q_e$ versus $\log C_e$ is shown below.

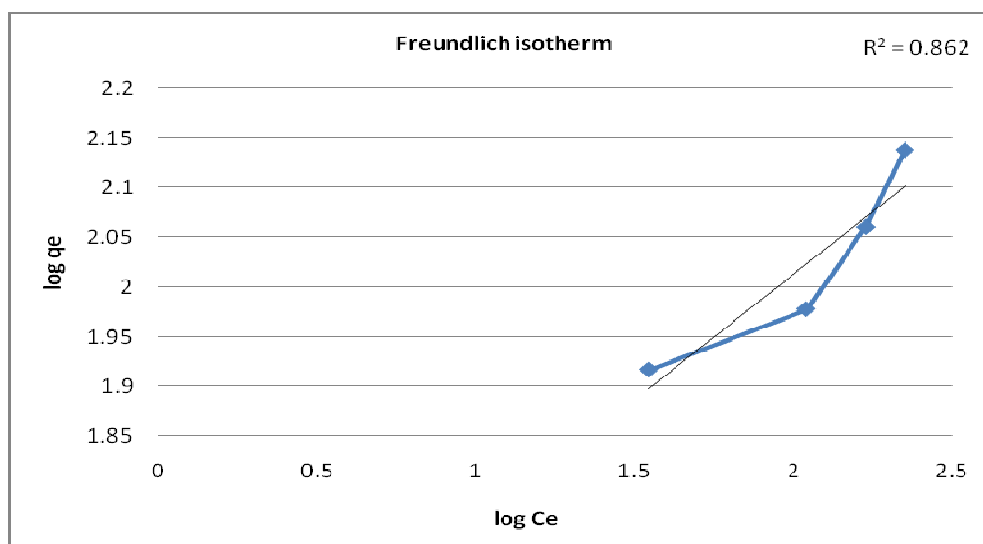


Fig.7: Freundlich Isotherm plot for the adsorption of Copper by Chitosan-Banana stem fibre beads

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 analysed 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 plot of q_e against $\ln C_e$ is given below.

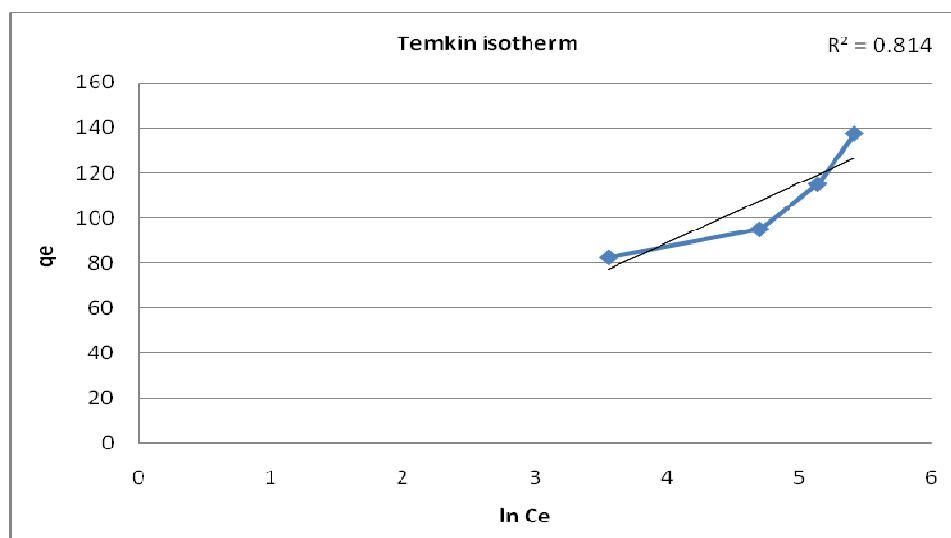


Fig.8: Temkin Isotherm plot for the adsorption of Copper by Chitosan-Banana stem fibre beads

The estimated values of the constants of the Isotherm models for the adsorption of Copper by the Chitosan – Banana stem fibre beads are given in the table below.

Table-1: Table of estimated values of constants of Isotherms

Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
R^2	q_{\max} (mg/g)	b	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 follow 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,

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

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 \square is Polanyi potential given by,

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

where R is the gas constant ($8.314 \times 10^{-3} \text{ kJ/mol K}$), 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 \square^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 plot for the experimental data as follows.

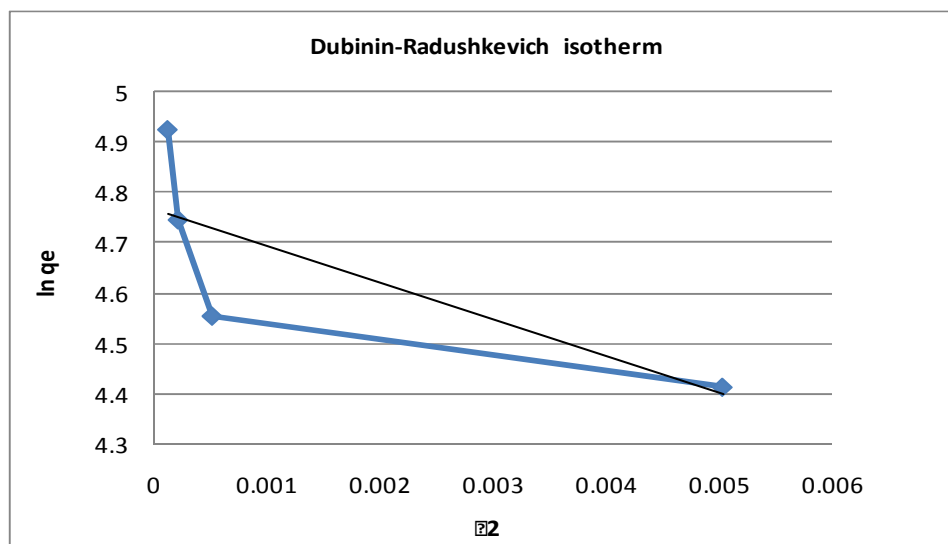


Fig.9: Dubinin-Radushkevich isotherm plot for the adsorption of Copper by Chitosan-Banana stem fibre beads

From the Dubinin-Radushkevich isotherm plot, 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 kinetics of heavy metal ions are analysed by the pseudo first order, pseudo second order and simple Elovich kinetic models.

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 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

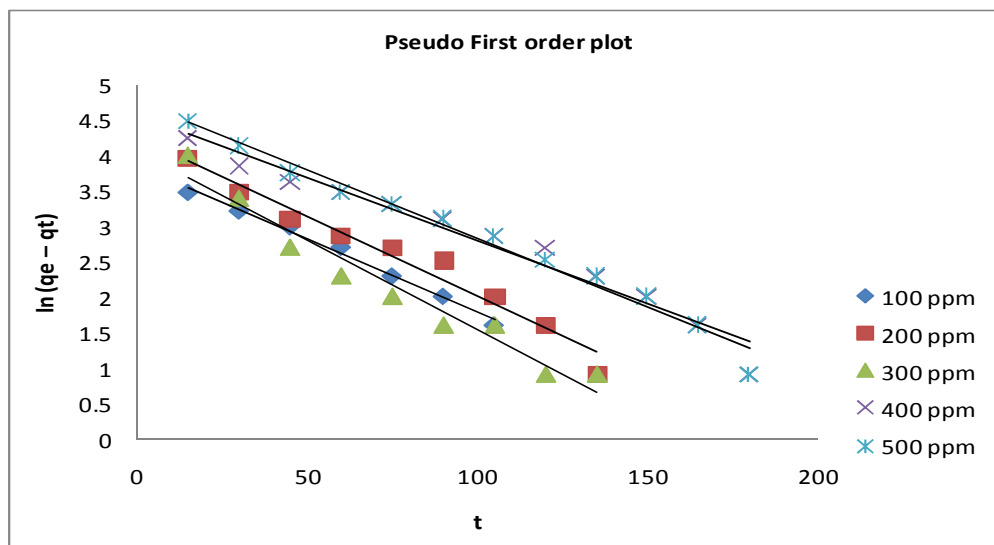


Fig.10: The Pseudo First order kinetic sorption kinetics for various initial concentrations

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 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

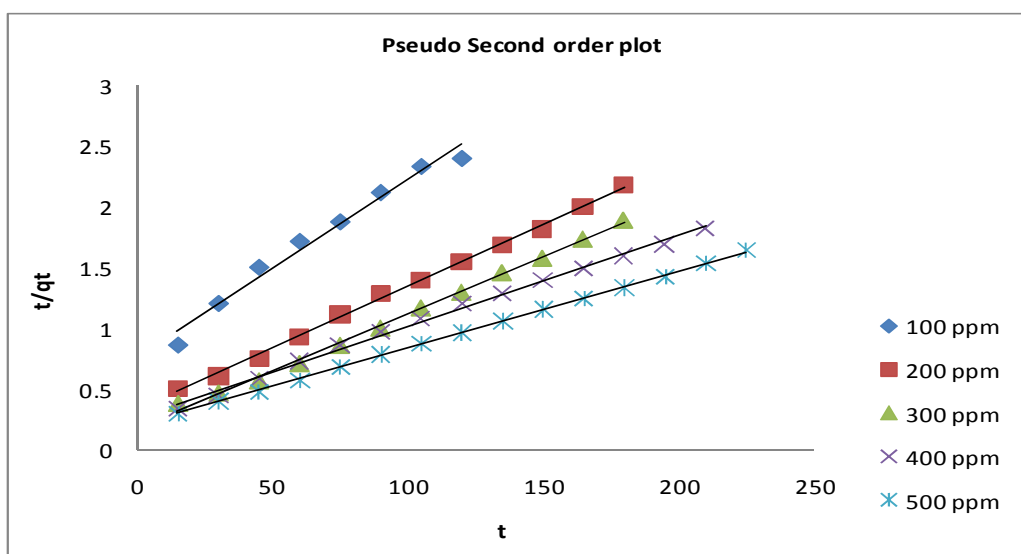


Fig.11: The Pseudo Second order sorption kinetics for various initial concentrations

Simple Elovich Model: 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 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

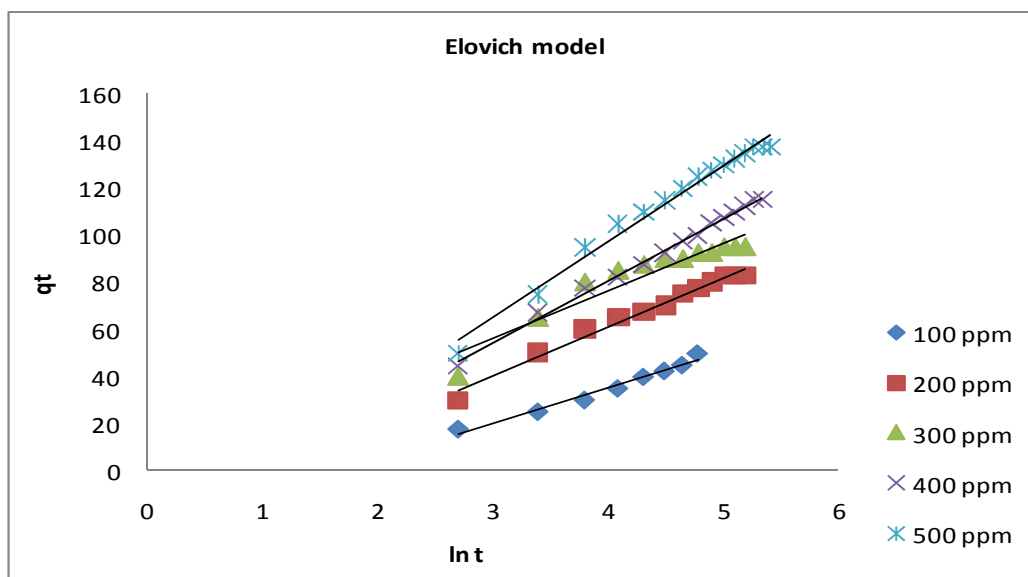


Fig.12: The simple Elovich sorption kinetics for various initial concentrations

Table of Estimated Parameters of Kinetic Models

The parameters of First order, Second order and Elovich kinetic models are estimated and given below.

Table- 2: Table of estimated parameters of Kinetic models

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	21.6
300	0.955	57.80	0.025	0.997	111.11	4.79×10^{-4}	0.898	-5.2	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

The values of equilibrium adsorption capacity (q_e) obtained from the experiments were 50, 82.5, 95, 115 and 137.5 (in mg/g) for the concentrations of aqueous solutions 100, 200, 300, 400 and 500 (in ppm)

respectively. Three kinetic models were applied on the experimental data to investigate the suitability. The linear regression values obtained from the Elovich kinetic model were much lower than the other two models 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 are much higher ($R^2 > 0.99$), and also the calculated q_e values agreed well with the experimental data. Hence it is very clear that the adsorption of Copper by Chitosan – Banana stem fibre beads has followed the Pseudo Second order kinetic model.

Intra-Particle Diffusion Model: The adsorption process on a porous adsorbent is generally a multi-step process. In order to analyse the mechanism of the adsorption of Copper by 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 the 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 analyse the possibility of intra-particle diffusion as the rate determining step. A two stage adsorption mechanism with first was rapid and second was slow has been observed from the experimental data.

The plot of q_t against $t^{1/2}$ is multi-linear and deviating from the origin, indicating more than one process has affected the adsorption¹⁸. Hence, the first portion of the plot indicates the external mass transfer and the second portion is due to intra-particle or pore diffusion.

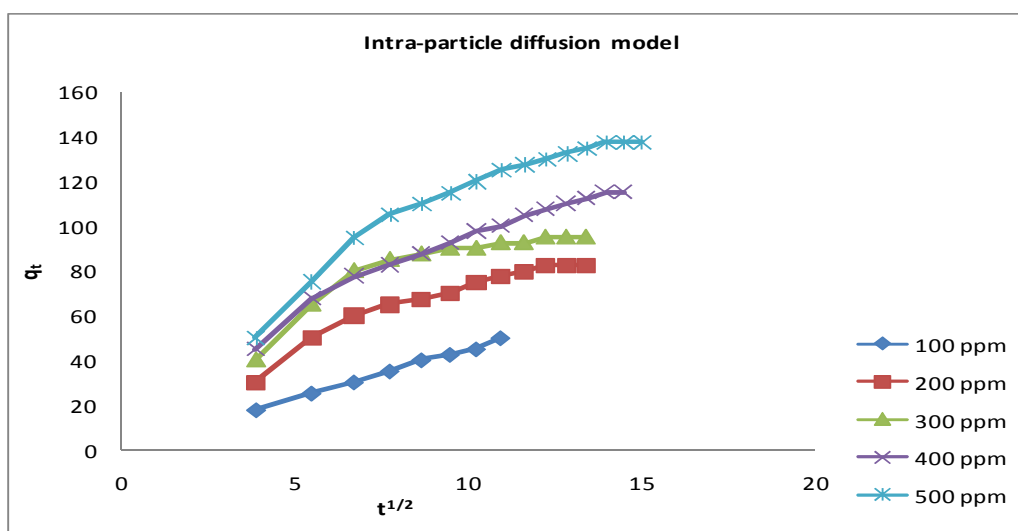


Fig.13: The intra-particle diffusion kinetics plot for various initial concentrations

The Estimated Parameters of Intra-Particle diffusion model: The parameters of intra-particle diffusion model are estimated and given in the following table.

Table- 3: Table of estimated parameters of Intra-Particle diffusion model

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

The Boyd Model: Due to the double nature of intra-particle diffusion (both film and pore diffusion) and in order to determine the actual rate controlling step involved in the sorption process, the kinetic data have been analysed using the model given by Boyd et al¹⁹.

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

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 (cm²/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 plots¹⁹. A straight line passing through origin is indicative of sorption processes governed by particle diffusion mechanism; otherwise they are governed by film diffusion¹⁹.

The plots of Bt against t for the experimental data of various concentrations have been shown below.

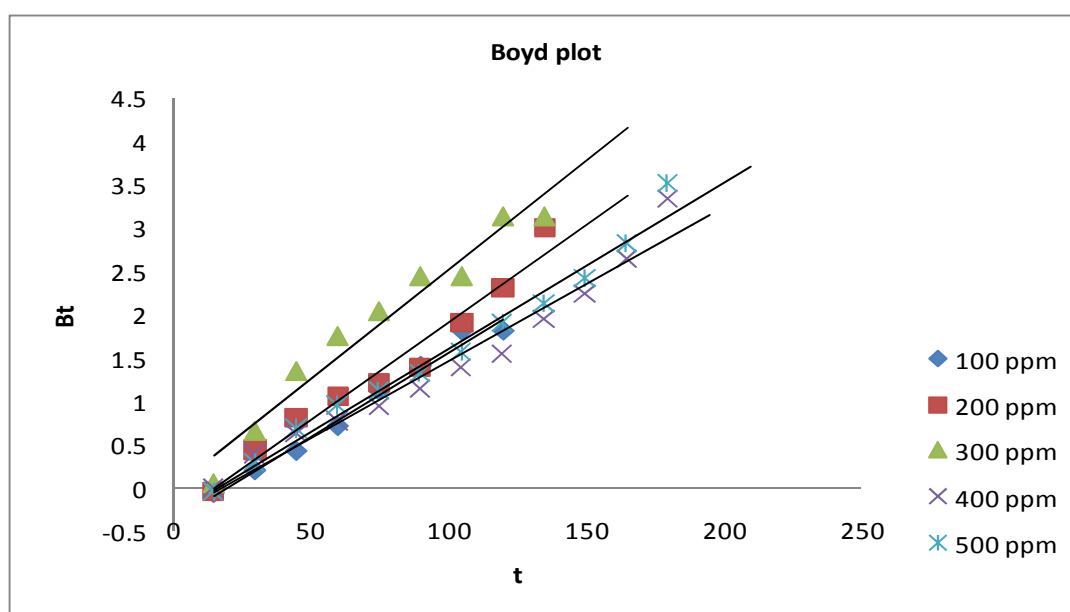


Fig.14: The Boyd plot (showing markers and trend lines) for the sorption kinetics

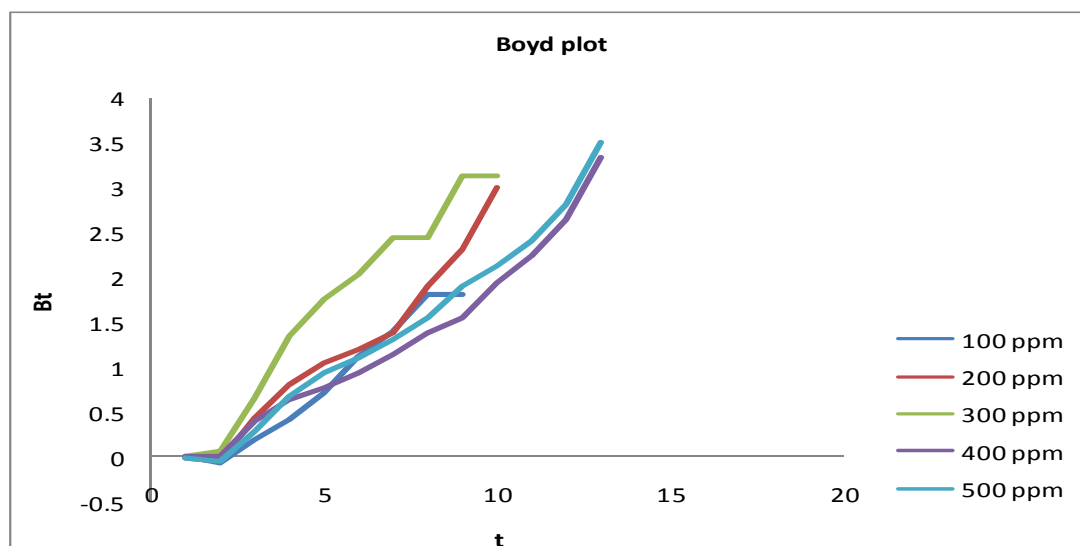


Fig.15: The Boyd plot (lines graph to show linearity) for the sorption kinetics

The plots very slightly deviated from the origin but they were greatly linear which revealed that the intra-particle diffusion was the actual rate controlling step of the adsorption process of Copper (II) ions by Chitosan-Banana stem fibre beads.

CONCLUSION

Chitosan-Banana stem fibre beads can be successfully used as an adsorbent for Cu^{+2} ions from aqueous solutions. Banana stem fibre has been recognised as an adsorbent for heavy metals by various researches. The addition of Banana stem fibre with Chitosan enhanced the adsorption capacity and also made the adsorbent beads mechanically stronger. Hence the adsorbent beads were applicable in a wide pH range (3 to 6) without the necessity of cross linking. The maximum adsorption was at a pH of 6. The removal of copper ions increased with agitating time and saturated in about 210 minutes. There was a two stage adsorption mechanism in which the first was rapid and the second was slower has been observed. The adsorption data were best fitted with Langmuir isotherm. The value of mean energy of adsorption (E) from the Dubinin – Radushkevich isotherm has showed that the adsorption of Copper by Chitosan-Banana stem fibre beads followed the physical adsorption. Adsorption kinetics followed the Pseudo Second order kinetic model. The intra-particle diffusion model was used to analyse the sorption mechanism. Boyd plot explored that the intra-particle diffusion was the rate controlling step. The results obtained would be useful for the effective application of Chitosan-Banana stem fibre beads as an adsorbent to treat industrial effluents.

REFERENCES

1. Nan Li, Renbi Bai, "Copper adsorption on Chitosan - Cellulose beads: Behaviours and mechanisms", *Separation and Purification Technology*, 2005, **42**, 237 – 247.
2. Arh-Hwang Chen, Sheng-Chang Liu, Chia-Yun Chen, "Comparative adsorption of Cu (II), Zn (II) and Pb (II) ions in aqueous solution on the cross linked Chitosan with epichlorohydrin", *Journal of Hazardous materials*, 2008, **154**, 184 – 191.
3. W.S. Wan Ngah, A. Kamari, Y.J. Koay, "Equilibrium and kinetics studies of adsorption of copper (II) on chitosan and chitosan/PVA beads", *International Journal of Biological Macromolecules*, 2004, **34**, 155 – 161.

4. K.H. Chu, "Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics", *Journal of Hazardous Materials*, 2002, **90**, 77–95.
5. Peter O. Osifo, Hein W.J.P. Neomagus, Raymond C. Everson, Athena Webster, Marius A. Vd Gun, "The adsorption of Copper in a packed bed of Chitosan beads: Modeling, multiple adsorption and regeneration", *Journal of hazardous materials*, 2009, **167**, 1242–1245.
6. N.V. Majeti, R. Kumar, "A review of Chitin and Chitosan applications", *Reactive and Functional Polymers*, 2000, **46**, 1 – 27.
7. P. Miretzky, A.F. Cirelli, "Hg (II) removal from water by Chitosan and Chitosan derivatives: a review", *Journal of hazardous materials*, 2009, **167(1-3)**, 10-23.
8. Singh Dhanesh, Singh Anjali, "Chitosan for the Removal of Chromium from Waste Water", *International Research Journal of Environment Sciences*, 2012, **1(3)**, 55–57.
9. S. Sugashini, S. Gopalakrishnan, "Studies on the Performance of Protonated cross linked Chitosan Beads (PCCB) for Chromium Removal", *Research journal of Chemical Sciences*, 2012, **2(6)**, 55-59.
10. Shengling Sun, Li Wang, Aiqin Wang, "Adsorption properties of cross linked carboxymethyl-chitosan resin with Pb(II) as template ions", *Journal of hazardous materials*, 2006, **136(3)**, 930–937.
11. Sandhya Babel, Tonni Agustiono Kurniawan, "Low-cost adsorbents for heavy metals uptake from contaminated water: a review", *Journal of hazardous materials*, 2003, **97(1-3)**, 219–243.
12. W. Kaminiski, E.Tomczak, K. Jaros, "Interactions of metal ions sorbed on Chitosan beads", *Desalination*, 2008, **218**, 281 – 286.
13. Wen-Li Du, Shan-Shan Niu, Zi-Rong Xu, Ying-Lei Xu, "Preparation, Characterisation and Adsorption properties of Chitosan microspheres cross linked by Fomaldehyde for Copper (II) from aqueous solution", *Journal of applied polymer science*, 2009, **111**, 2881 – 2885.
14. Aliya Nur Hasanah, Fani Rizkiana, Driyanti Rahayu, "Banana Peels and Stem (*Musa x paradisiaca* Linn.) as Biosorbent of Copper in Textile Industry Wastewater", *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2012, **3(3)**, 1171.
15. W.S. Wan Ngah, M.A.K.M. Hanafiah, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review", *Bioresource Technology*, 2008, **99**, 3935–3948.
16. Kathiresan Sathasivam, Mas Rosemal Hakim mas Haris, "Banana trunk fibres as an efficient biosorbent for the removal of Cd(II), Cu(II), Fe(II) and Zn(II) from aqueous solutions", *Journal of the Chilean Chemical Society*, 2010, **55(2)**, 278-282.
17. K.S. Low, C.K. Lee and K.P. Lee, "Sorption of Copper by dye-treated oil-palm fibres", *Bio-resources technology*, 1993, **44**, 109 – 112.
18. S.Z. Ashtoukhy, N.K. Amin, O. Abdelwahab, "Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent", *Desalination*, 2008, **223**, 162 – 173.
19. Xin-jian Hu, Jing-song wang, Yun-guo Liu, Xin Li, An-wei Chen, Zheng-lei Bao, Fei Long, "Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic Chitosan resin: Isotherms, kinetics and thermodynamics", *Journal of hazardous materials*, 2011, **185**, 306 – 314.

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