

***CHAPTER III:  
Optimization of Conditions for Removal of  
Copper(II) using Sugarcane Bagasse as an  
Adsorbent***

## **Abstract**

Sugarcane bagasse have been used as alternative substitution of activated carbon for the removal of Cu(II) from aqueous solution. Different variable conditions such as pH, initial metal ion concentration, adsorbent dose, contact time and temperature were included for find out the adsorption capacity of adsorbent. SEM, FT-IR and BET analysis were used to characterization and analysis for the adsorbent. All the data were obtained from experimental analysis by using the Langmuir and Freundlich adsorption Isotherms. The results showed that the sugarcane bagasse can be utilized as a low-cost adsorbent for the removal of Cu(II) ions from its aqueous solution. It's easy availability and plenty makes it a strong choice in the investigation of economic way of Metal removal.

## **III.1 Introduction**

The Sugar mill industry in India is one of the oldest and largest industries in the country. Sugar mills require large volume of water and generate equally large volume of waste water which is highly complex and contaminated with organic and inorganic toxic materials. Many of the past disasters due to the contamination of heavy metals including organic and inorganic toxic metals in aquatic streams are Minamata tragedy in Japan due to methyl mercury contamination and “Itai-Itai” due to contamination of cadmium in Jintsu river of japan [1]. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to the health hazards and environmental degradation. Conventional methods for removal of toxic metal ions from solutions include chemical precipitation,

ion exchange, chemical oxidation/reduction, electro dialysis, ultra filtration etc [2]. Conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair [3]. Nowadays many techniques are available but adsorption is one of the most powerful technology for detoxification of heavy metals by activated carbon for treating domestic and industrial waste water [4]. However the high cost of activated carbon and its loss during the regeneration restricts its application. Since 1990's the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum [5]. Among them Sugar cane bagasse, an agro industry waste, to remove the metal contaminants from industrial waste material, adsorption has become one of the most effective and economical method [6]. Thus this process has considerable interest during recent years. The use of cheap and ecofriendly adsorbent have been studied as an alternative substitution of activated carbon for the removal  $Cd^{2+}$  and  $Fe^{2+}$  from waste sugar cane bagasse [7]. Adsorbent prepared from sugarcane bagasse an agro industries waste were successfully used to remove the  $Cu^{2+}$  from an aqueous solution [8-10]. Currently our study has focused on modified or innovative approach that more adequately address the removal of pollutants containing metals from waste material. The heavy metals like Zn, Cr, Pb, Hg, Ni and As originate from metal plating, mining activities, smelting, battery manufacture, pesticides, pigment manufacture, printing and photographic industries etc. [11] produced rough activated carbons from sugarcane bagasse by the physical method using steam as the activating agent. [12]. The adsorption capacities of both formaldehyde treated and sulphuric acid treated baggase were examined at varying pH, initial  $Cu^{2+}$  concentration [13], adsorbent dosage, contact time and

temperature to compare the performance of treated sugarcane bagasse [14,15] with commercially available powdered activated carbon, similar experiment were produced with powdered activated carbon. This study demonstrated that treated sugarcane bagasse is an effective and cheap adsorbent for the removal of  $\text{Cu}^{2+}$  from the aqueous solution and the possibility of using it for a simple and expensive method [16] of  $\text{Cu}^{2+}$  removal form sugarcane bagasse in batch or stirred tank reactors. The data obtained may be designing an economical and optimise treatment process using batch or stirred tank reactors for the removal of  $\text{Cu}^{2+}$  from industrial effluents.

### **III.2 Preparation of copper Solutions**

Copper sulphate solutions of desired concentrations have been prepared by dissolving calculated quantity, supplied by Sigma Aldrich All other chemicals used in this study were AR Grade supplied by Sigma Aldrich.

### **III.3 Batch mode adsorption equilibrium studies**

The adsorption experiments were conducted by mixing various amounts of sugarcane bagasse powder (0.25–5.0 g/L) in conical flasks containing 100 mg/L metal concentration. The effect of pH was studied in the range of 2.0–5.0 at a fixed metal concentration of 100 mg/L and a sorbent dosage of 3.0 g/L. The effect of metal ions concentration was studied in the range of 10-150mg/L at optimal conditions of pH and adsorbent dose. The effect of temperature on adsorption capacity was studied in the range of 30-80 °C by a thermostatic water bath shaker. The results obtained by equilibrium studies were verified with Langmuir and Freundlich isotherms.

#### **III.4 Kinetic studies**

The kinetic studies were conducted to estimate the contact time required for the attainment of equilibrium between the dissolved and solid bound adsorbate. For copper removal kinetic experiments, a metal solution containing 50 mg/L copper was agitated with 6.0 g of adsorbent in a 500 mL sealed flask at optimal pH placed in a shaker operating at 400 rpm and 30 °C. Similar experiments were carried out by agitating with 500 mL of metal solutions whose concentrations were 100, 150 and 200 mg/L at the optimum conditions as given above.

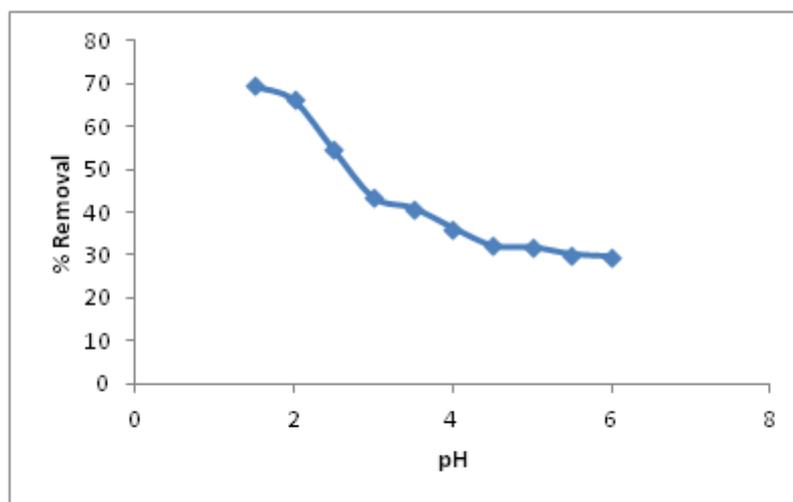
#### **III.5 Analysis of the metal**

Samples of solutions were filtered through filter paper and then the filtrates were collected and analyzed for metal concentration using UV-Visible spectrophotometer (systronic 2203). The amount of metal adsorbed during the contact time with activated sugar cane bagasse was estimated using the calibration curve (Abs vs Concentration).

#### **III.6 Effect of pH**

The pH of the aqueous metal solution have a specific importance in the adsorption process because it changes the solubility of metal ions, concentration of the metal ions on the functional groups of the adsorbent and the degree of ionization. The effect of pH on the adsorption of copper by sugarcane bagasse was studied by varying the initial pH in the range of 1.5–6.0 under constant process parameters at equilibrium conditions and was presented in Fig. 1 ( $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})_2$ ). At a higher pH, more Copper appears in a neutral or negatively charged form  $\text{Cu}(\text{OH})_2$ ,  $\text{CuSO}_4^-$  and these cannot be adsorbed on a negatively charged adsorbent surface resulting more interaction between the negative charge and positive

charge copper species but for activated carbon the adsorption was not affected much by pH variation there by percentage removal almost remaining same for all pH values.

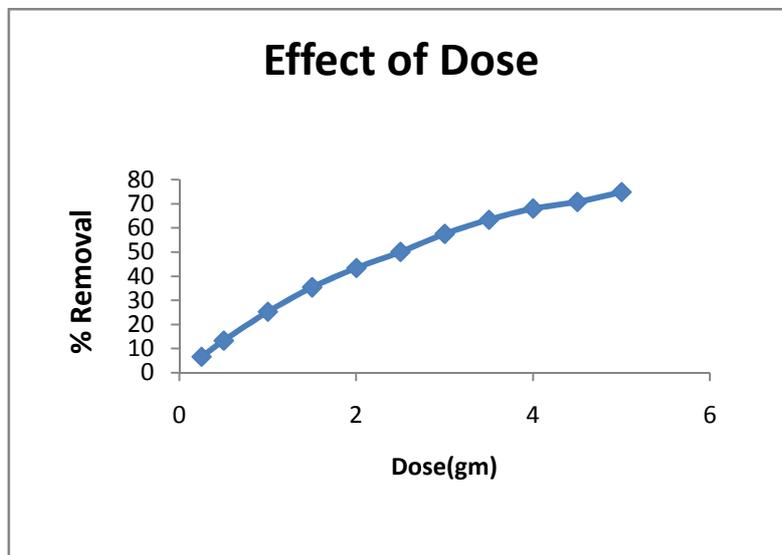


**Figure III.1** Effect of pH on % removal of copper ion by sugar cane bagasse adsorbent.

### **III.7 Effect of sorbent dosage**

Effect of the adsorbent dose of sugarcane bagasse powder on copper removal was studied in the range of 1.0–6.0 g/L at an optimal pH of 5.0 and initial metal concentration 100 mg/L. As illustrated in Figure III.2, the percentage metal removal increased with increasing adsorbent dose and almost stabilised after 4gm/L. The increase in adsorption removal percentages with increasing activated sugarcane bagasse dosage is related to the increase in surface area and by extension the increased number of ion exchangeable sites available for interaction with copper ions. A superficial adsorption onto the adsorbent surface that produces a lower metal concentration in the solution is reported to occur at high ratios of adsorbent to adsorbate concentrations. The decrease in metal uptake with increase in dosage is due to the split in flux between the copper

concentrations in the solution and the adsorbent surface. Thus, the optimal adsorbent dosage was identified as 5.0 g/L.

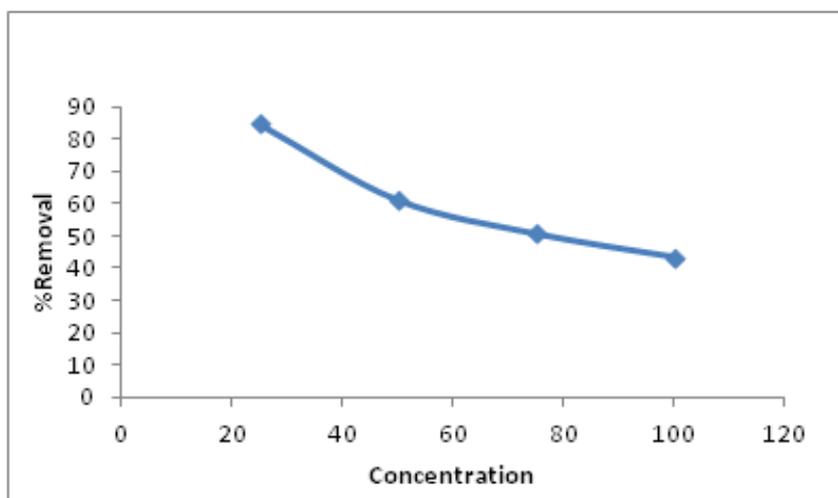


**Figure III.2:** Effect of dose on % removal of copper ion by sugar cane bagasse adsorbent.

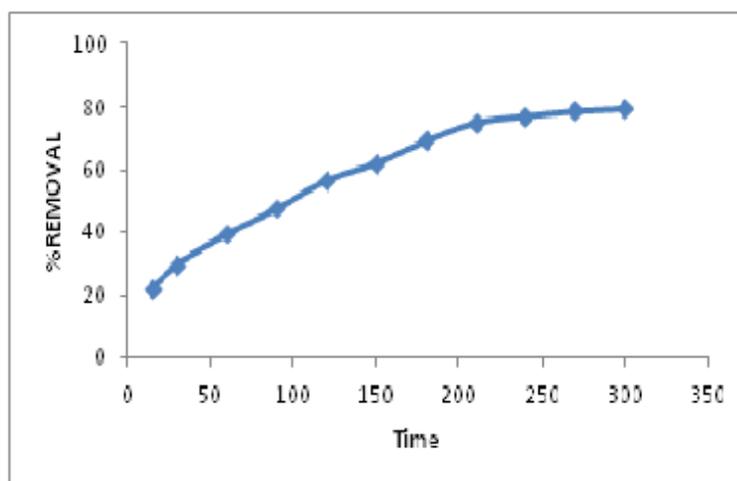
### **III.8 Effect of contact time and initial metal concentration**

In order to establish time dependence of adsorption systems under various conditions, it is required to study the influence of contact time. The experimental runs measuring the effect of contact time and initial metal concentration on the batch adsorption of metal solution containing 100 mg/L of copper at 30 °C and initial pH 5.0 is shown in Figure III.3. It was observed that the general uptake rate was fast during the initial phase of 30 min after which a steady state adsorption was achieved. The initial rapid uptake rate within the first 30 min may be due to physical adsorption or ion exchange at the adsorbent surface and due to complexation and micro-precipitation of the binding sites during the later phase resulted in reduced uptake. Moreover, the concentration gradient is more during the initial stages of the adsorption process. The equilibrium

time increased with increase in metal concentrations. At low metal concentrations, the adsorbent sites took the metal ions quickly whereas at high concentrations, the metal ions need to diffuse to the inner sites of the sorbent. Saturation of sites was reported to occur at high metal/adsorbent ratios leading to reduced metal removal efficiency.



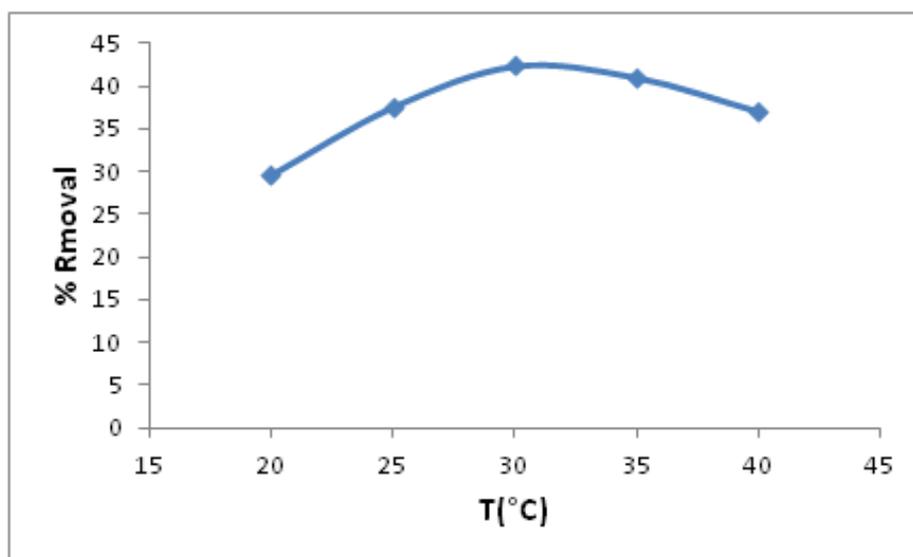
**Figure III.3** Effect of concentration on % removal of copper ion by sugarcane baggase adsorbent.



**Figure III.4** Effect of contact time on % removal of copper ion by sugarcane baggase adsorbent.

### III.9 Effect of operating temperature

The uptake of copper by activated sugarcane bagasse at different temperatures (20, 25, 30, 35 and 40 °C) is shown in Figure III.5. The result demonstrated that the uptake capacity increases with increase in temperature and thus confirms the endothermic nature of adsorption process. The enhancement in uptake is attributed to better interaction between metal ions and adsorbent, creation of new adsorption sites and increased intraparticle diffusion at higher temperatures.



**Figure III.5** Effect of Temperature on % removal of copper ion by sugarcane bagasse adsorbent.

### III.10 Adsorption isotherm models

Adsorption isotherms are used to represent the equilibrium relationship between the mass of the solute adsorbed per unit mass of the adsorbent and the equilibrium concentration of the solute. In this study, Langmuir and Freundlich models [Equations 1 and 2 respectively] were employed to fit the experimental data. Langmuir considered adsorption of an ideal gas on ideal surface. Langmuir isotherm is based on the assumption that

the adsorption takes place at specific homogeneous sites on the adsorbent. Freundlich isotherm is based on the assumption of heterogeneous adsorption surface and the active sites with different energy (Equations 1 and 2)

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L} \quad \dots (1)$$

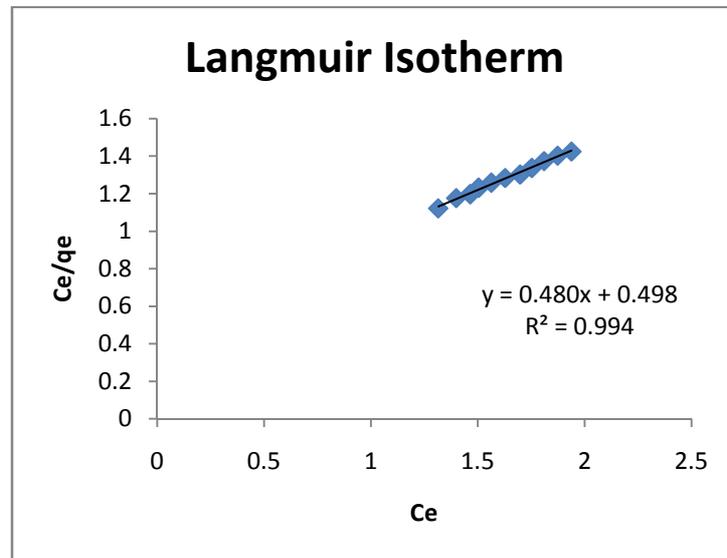
or

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \dots (2)$$

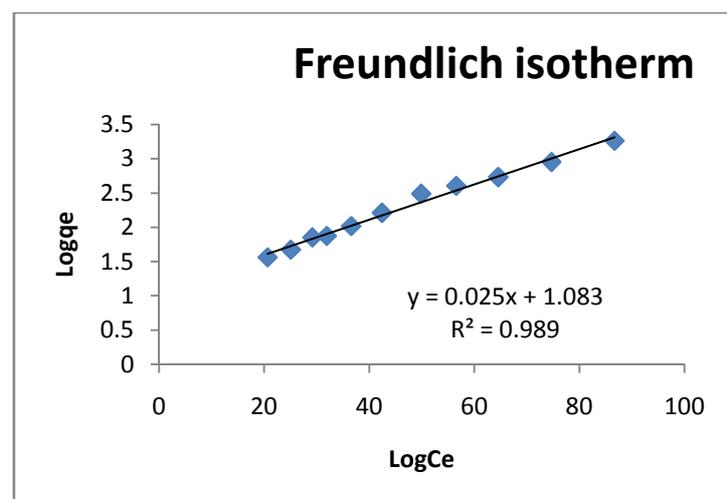
Where  $q_{\max}$  (mg/g) is the maximum adsorption capacity and  $K_L$  (L/mg) is the Langmuir constant related to the free energy of adsorption,  $K_f$  (mg/g) is the Freundlich constant which is an estimate of relative adsorption capacity of adsorbent and  $\frac{1}{n}$  is the adsorption intensity. The experimental data were applied to the equation above and a plot of  $\frac{C_e}{q_e}$  vs  $C_e$  was drawn to verify the applicability of Langmuir isotherm and was shown in Figure 6. A linear plot of  $q_e$  vs  $C_e$  was tried to verify the suitability of Freundlich isotherm, as shown in Figure III.7. The constants in the isotherm equations were evaluated and reported in Table 1. From the table, it was observed that Langmuir isotherm represented the equilibrium adsorption of copper and the value of regression coefficient ( $R^2$ ) was comparatively higher for Langmuir isotherm than Freundlich isotherm. This result suggests monolayer coverage of the surface of activated sugarcane bagasse by copper ions since the Langmuir isotherm assumes that the surface is homogeneous. Similar isotherm fit for adsorption of copper has been reported. As expected for an endothermic process, the values of  $q_{\max}$  and  $K_L$  increased with increase in temperature

**Table III.1 Langmuir and Freundlich adsorption isotherms for the adsorption of the Cu(II) on the sugarcane biosorbent**

Langmuir Isotherm			Freundlich Isotherm		
$q_{\max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	n	$K_F$ (mg/g)	$R^2$
52.0204	0.2394	0.98	1.8328	1.9943	0.86



**Figure III.6 Langmuir adsorption isotherm for the adsorption of Cu(II) on the sugarcane biosorbent**



**Figure III.7 Freundlich adsorption isotherm for the adsorption of Cu(II) on the sugarcane biosorbent**

### **Kinetic studies**

The studies on the rate of removal are essential for the proper design of waste water treatment facilities. In this study, the pseudo-second-order equation (Equation 4) and intraparticle diffusion model (Equation 5) have been applied to the experimental data to analyze the adsorption kinetics of copper ions:

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_1} t \quad \dots (4)$$

Where  $q_1$  (mg g/l) is the maximum adsorption capacity and  $q_t$  (mg g/l) is the amount of copper adsorbed at time,  $t$ , and  $k_2$  (g (mg min)/l) is the equilibrium rate constant for pseudo-second order adsorption. The intraparticle diffusion model is represented as

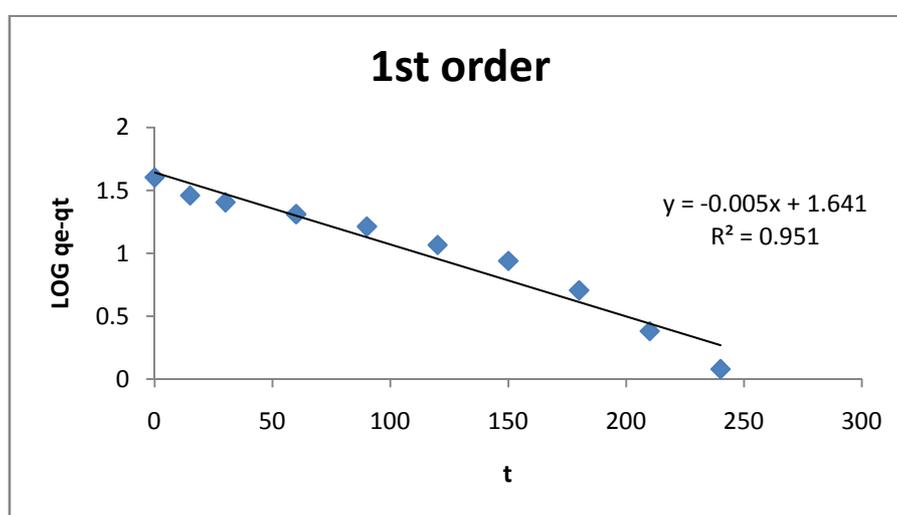
$$q_t = k_t t^{1/2} + I \quad \dots (5)$$

Where  $q_t$  (mg/g) is the amount of metal adsorbed at time,  $t$ , and  $k_t$  (mg/ (g min<sup>1/2</sup>)) is the intraparticle diffusion rate constant and  $I$  (mg/g) is a constant that is related to boundary layer thickness. Results of the kinetic data modeling indicated that the pseudo-second order model (Fig. 8) describes the adsorption of copper better than the other model. The pseudo second order model assumes that two surface sites will be occupied by one adsorbate ion. The pseudo-second order model could not identify the diffusion mechanism. Due to this, intra-particle diffusion model was employed and was presented in Fig. 9 as  $q$  vs  $t^{1/2}$ . If the plot passes through the origin, then intraparticle diffusion is the rate controlling step. But, a larger intercept was observed in this experiment which confirmed that the boundary layer effect is greater. The correlation coefficients of pseudo-second order model is greater than that of intra

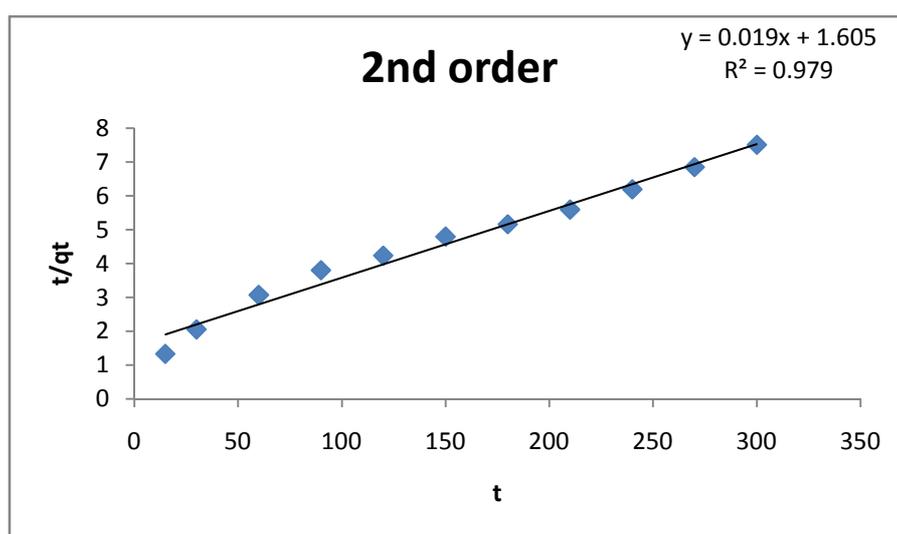
particle diffusion model. The constants in the kinetic models were presented in Table 2.

**Table III.2 Kinetics studies of the biosorption of Cu(II) on sugarcane biosorbent.**

Pseudo First Order		Pseudo Second Order	
$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\text{g/mg}\cdot\text{min}$ )	$R^2$
0.0131	0.95	$2.42 \times 10^{-6}$	0.98



**Figure III.7 pseudo-first order kinetics model for the biosorption of Cu(II) on the sugarcane biosorbent**



**Figure III.8 pseudo-second order kinetics model for the biosorption of Cu(II) on the sugarcane biosorbent**

### **III.11 Thermodynamic studies – Activation energy determination**

Thermodynamic analysis of the adsorption process is essential to conclude whether the process is spontaneous or not. The feasibility and spontaneous nature of the adsorption process is reflected by the thermodynamic parameters. The relationship between rate constant and temperature is represented by Arrhenius equation (Equation 6) and is given as:

$$\ln k = \ln A - \frac{E_a}{RT} \quad \dots(6)$$

where  $k$  is the rate constant obtained at different temperatures with the best fit kinetic model,  $E_a$ , (kJ/mol) is the activation energy,  $A$  (g/(mg min)), is the Arrhenius factor,  $R$ , is the gas constant and  $T$  (K) is the solution temperature. In this study, the rate constant,  $k_2$ , of the pseudo second order model (the best fit model) was used. The activation energy estimated for this process is 43.2kJ/mol.

### **Conclusion**

The study successfully demonstrated the application of sugarcane baggase powder as an adsorbent for the removal of Cu (II) ions. An increase in pH was favorable up to 5.0 whereas increase in adsorbent dose resulted in increased removal efficiencies and decreased uptake capacities. Higher temperature was favoured confirming the endothermic nature of adsorption process. The Langmuir isotherm was demonstrated to provide the best fit for the equilibrium sorption data confirming a monolayer adsorption pattern. The pseudo-second order model fitted well (with  $R^2 > 0.99$ ) for the kinetic data. Activation energy for this adsorption process was evaluated using the Arrhenius theory model. From this study,

we conclude that activated sugar cane bagasse powder merits further exploration in large-scale continuous systems to evaluate the practical applicability of its use in effluent treatment plants.

### References

- 1 Friberg, L. and Elinder, C. G. Encyclopedia of Occupational Health, third ed. International Labor Organization, Geneva. (1985).
- 2 Gardea-Torresdey, J. L.; Gonzalez, J. H.; Tiemann, K. J.; Rodriguez, O. Phytofiltration of hazardous cadmium, chromium, lead, and zinc ions by biomass of *Medicago sativa*(alfalfa). *J. Hazard. Mater.* 57, 29–39
- 3 Ahluwalia, S. S.; Goyal, D. Removal of heavy metals from waste tea leaves from aqueous solution. *Eng. Life Sci.* (2005) 5, 158.
- 4 Hosea, M.; Greene, B.; McPherson, R.; Henzl, M.; Alexander, M. D. and Darnall, D.W. 1986. Accumulation of elemental gold on alga *Chlorella vulgaris*. *Inorg. Chim. Acta* . (1986) 123, 161.
- 5 Bailey, S. E.; Olin, T. J.; Bricka, R. M. and Adrian, D. D. A review of potentially low-cost sorbents for heavy metals. *Water Res.* (1999) 33, 2469.
- 6 Taylor, A. K, From raw sugar to raw materials. *Chemical Innovation* (2000) ,30, 45.
- 7 Anil, K. and Omprakash, S. *world J., Chem., Edu.* (2013) 1, 17.
- 8 Ferro-Garcia, A. M.; Rivera-Utrilla, J.; Rodriguez-Gordill, J.; Bautista-Toledo, I. Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by products, *Carbon*, (1988) 26, 363.
- 9 Gupta, S. S.; Krishna, G. and Bhattacharyya, *J. Environmental* (2008) 87, 46.

- 10 Haluk Aydm, Yasemin Blut, Cigdem Yerlikaya, *J. Environmental* (2008) 87, 37.
- 11 Mukesh, P. and Lokendra, S. T. *Int. J. Plant, Animal, environmental sci.* (2013) ,3 ,3.
- 12 International Journal of Innovative Technology and Exploring Engineering (IJITEE) ISSN: 2278-3075, Volume-2, Issue-4, March 2013 International Journal of Chemical Engineering and Applications, Vol. 1, No. 4, December 2010 ISSN: 2010-0221.
- 13 International Journal of Innovative Technology and Exploring Engineering (IJITEE) ISSN: 2278-3075, Volume-2, Issue-4, March 2013
- 14 *American journal of Applied science.* (2005) ,9 ,2 .
- 15 Inglezakis, V. J.; Loizidou, M. D. and Grigoropoulou, H. P. *J. Colloid Interface Sci.* (2003), 216 , 49.
- 16 Sonja Milicevic, Tamara Boljanac, Sanja Martinovic, Milica Vlahovic, Vladan Milosevic, Biljana Babic *Fuel Processing Tech.* (2012) 95, 1.