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Research Article

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Studies on the adsorption of copper ion from aqueous solution by using *Brassice oleracea* activated carbon

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ABSTRACT

The batch removal of copper(II) ions from aqueous solution under different experimental conditions using Brassice oleracea (Cabbage) has been studied. The copper(II) uptake was dependent on the initial pH and initial copper concentration, with the pH 4 being the optimum value. The equilibrium data were fitted using Langmuir and Freundlich isotherm model, with the maximum copper(II) uptake of 66.66% determined at pH 4. Further, Venkobachar and Bhattacharya and Lagergren kinetic stidies were also conducted to prove that the reaction followed first order kinetics. At various initial copper(II) concentrations 50 to 750 ppm sorption equilibrium was attained between 30 to 180 minutes. The copper(II) uptake by Brassice oleracea best described by first order and rate constant.

Key words: Copper(II), Kinetics, Adsorption isotherm, *Brassice oleracea*

INTRODUCTION

The increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high levels of heavy metals, creating serious environmental disposal problems[1]. Heavy metals released into the environment has been increasing continuously as a result of industrial activities, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in the nature[2]. Exposure of heavy metals contamination has been found to cause kidney damage, liver damage and anemia in low doses, and in high concentrations, heavy metals can be carcinogenic. Copper is one of the most toxic metals that find its way to water sources from various industries, such as, electroplating, mining, electrical and electronics, iron and steel production, non ferrous metal industry, printing and photographic industries. Environmental Protection Agency (EPA) standards, the permissible limit of copper discharge in industrial effluents into water bodies is limited to 0.25 mg/litre[3]. Copper cause many diseases and disorders such as liver damage[4,5], nausea, salivation, purgation, abdominal pain, convulsions, paralysis[6] and lung cancer[7]. Waste waters from industries are released into nearby land or rivers without any prior treatment, because the conventional methods of removal of metals from the aqueous system include solvent extraction[8], ion-exchange, reverse osmosis, coagulation, membrane separation etc. are expensive. Therefore, there is need for an alternative technique, which is efficient and cost effective. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat waste water containing different classes of metal ions recognizing the economic draw back of commercial activated carbon[9]. The present study aims at to evaluate the ability of *Brassice oleracea* to remove Cu(II) ions from aqueous solution. Also basic parameters of copper adsorption equilibrium were determined at various pH values.

EXPERIMENTAL SECTION

(A) Batch Experiments:

(1) Preparation of Adsorbent

Brassice oleracea (Figure1) was collected and sun dried. Dry biomass was cut into irregular shaped particles between 1mm to 3mm in size. The biomass was then washed with distilled water, filtered and finally dried over night at 60ºC and subsequently used for adsorption experiments .

Figure 1 *Brassice oleracea* (Cabbage)

(2) Preparation of synthetic copper solution

The stock copper solution was prepared by dissolving accurately analar grade of 3.928g of $CuSO_4.5H_2O$ in 1000ml of DM water to make it stock solution 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750 ppm solutions were prepared by diluting it suitably.

Batch equilibrium experiments were conducted by adding 300mg biomass to Erlenmeyer flask containing 50 ml of different test solutions at desired pH conditions. The initial solution pH was adjusted by using 0.1M HCl or 0.1M NaOH. The flasks were agitated at 150 rpm in rotary shaker. After 3hrs of contact time, the biomass separated from the test solution by filtration. The copper content in the supernatant liquid was determined using photoelectric calorimeter. Prior to analysis, the equipment was initially calibrated using standard copper solution. When necessary, the samples were diluted with distilled water before analysis. The amount of copper adsorbed by biomass was calculated from the difference between the concentration of copper in test solution and the concentration of copper in the supernatant liquid using the following equation

$$\text{Percent adsorption } (\%) = \frac{C_o - C}{C_o} \text{ X } 100$$

Where C_o is the initial concentration and C is the solution concentration at the end of adsorption.

1.Effect of Contact Time and Initial Concentration

To about 100ml solutions of each 50 to 750 ppm of Cu(II), 1g of *Brassice oleracea* powder was added and left for a period of 5 hours at room temperature (30ºC±1) with intermittent shaking. Appropriate control flasks without adsorbent were also maintained. The results of adsorption were recorded to calibrate the equilibrium time. The effect of initial concentration on the removal of Copper(II) was also observed.

2.Effect of pH

About 50ml of 50 ppm Cu(II) aqueous solutions were prepared and the pH adjusted to 1-6 by using 0.1M HCl or 0.1M NaOH. Each solution was treated with 500 mg of the adsorbent and kept for a contact time of 3 hours at room temperature with intermittent shaking. The residual Cu(II) concentrations were measured.

3.Effect of adsorbent dosage

About 50ml solution of 50-250 ppm Cu(II) concentrations with pH 4 was taken. 1 to 5 gms of the adsorbent was treated with each solutions with intermittent shaking at room temperature and the adsorption results were recorded.

(B) Adsorption Studies

In order to determine the adsorption potential of the biosorbent, the study of sorption isotherm is essential in selecting an adsorbent for the removal of copper. Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. An equilibrium study gives the capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium.

1. Freundlich Adsorption Isotherms

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as[10]:

$$q_e = K_f \, C_e^{1/n}$$

where,
q_e = x / m, the amount adsorbed (mg/g)
C_e = the equilibrium concentration of the adsorbate (mg/L)
K_f = the Freundlich constant related to the adsorption capacity
$1/n$ = the Freundlich constant related to the adsorption intensity

This above equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

2. Langmuir Isotherm

The most widely used isotherm equation for modeling equilibrium [11**]** is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules. The Langmuir isotherm expressed as:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_a q_{\max}} + \frac{1}{q_{\max}} C_{eq}$$

where q_{eq} is the adsorbate loading (mg/g) at equilibrium,

C_{eq} the equilibrium concentration in the fluid (mg/L), q_{max} the adsorption capacity (mg/g) and K_a sorption equilibrium constant (L/mg). q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with heavy metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. A plot of C_{eq} / q_{eq} versus C_{eq} should indicate a straight line

(C) Kinetic Studies

The kinetics of adsorption have been studied by applying two first order kinetic equations proposed by Lagergren as cited [12] and Bhattacharya and Venkobachar [13]

Lagergren's equation : $\log (q_e – q_t) = \log qe – [k/2.303] t$

Bhattacharya & Venkobachar equation : $\log[1-U (T)] = – [k/2.303] t$

Where q_e and q_t are the amount of Cu adsorbed per unit mass of the adsorbent (in mg/ g) and at time t respectively, U(T) = (Co – Ct) /(Co – Ce), Ce is equilibrium Cu concentration (in ppm) and k is the first order adsorption rate constants (in min-1). The values of Log (q_e / q_t) and Log (1-U (T)) were correlated with time which gives a straight line and it confirms the first order kinetics.

RESULTS AND DISCUSSION

The experimental data obtained from the different batch type experiments in the present investigation was analyzed and interpreted with the help of standard relations existing the adsorption ability of the adsorbent material *Brassice oleracea* powder.

Batch Type Experiments

In the present study, *Brassice oleracea* powder was used for the successful removal of Cu(II). Similarly, Kuppusamy et.al [14] has reported the removal of copper using marine green algae *Uluva reticulate*.

Equilibrium Time

A plot of time of contact versus % removal of copper was plotted (Fig.2) indicated that maximum adsorption has taken place at the 3rd hour, therefore a marked increase was not observed. Hence, the equilibrium time has been calibrated as 3 hours. Similarly 6 hours equilibrium time was observed by using *Ablesmoschus esculentus* plant material .

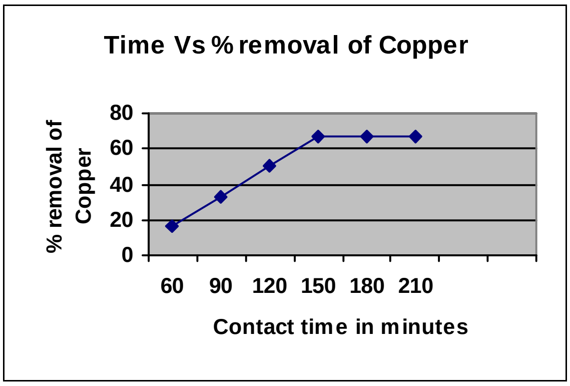

Figure 2. Effect of contact time on the adsorption of copper ion

The result showed that, time taken for the completion of adsorption was 150 minutes (within 2.5 hours).

Table 1. Effect of Adsorbent dosage on removal of Cu(II)

Temp:30ºC±1, Solution pH:4, Particle size:0-63µ

Contact time (t) minutes	% of Copper removal				
	50ppm	100ppm	150ppm	200ppm	250ppm
1.0	66.66	45.00	22.00	1.0	0
1.5	75.00	56.00	34.00	12.0	2.00
2.0	84.00	66.66	45.00	22.00	12.00
2.5	92.00	78.00	56.00	34.00	21.00
3.0	100.00	89.00	66.66	45.00	30.00
3.5	-	100.00	78.00	56.00	39.00
4.0	-	-	89.00	66.66	48.00
4.5	-	-	100.00	78.00	58.00
5.0	-	-	-	100.00	66.66

Effect of Initial Concentrations on Metal Removal

Percentage of Cu(II) uptake was found to increase with initial sorbate concentrations(Fig 3).This may be probably due to the fact that for affixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. Hence the percentage removal of copper has shown a reduction with increase in the initial sorbate concentrations. Table 1 gives the effect of dosage of adsorbent on copper removal. Various amounts of adsorbent *Brassice oleracea* ranging from (15g) were taken. The percentage removal of copper ions varied linearly with the amount of the adsorbent *Brassice oleracea* and amount of adsorbate (copper solution).

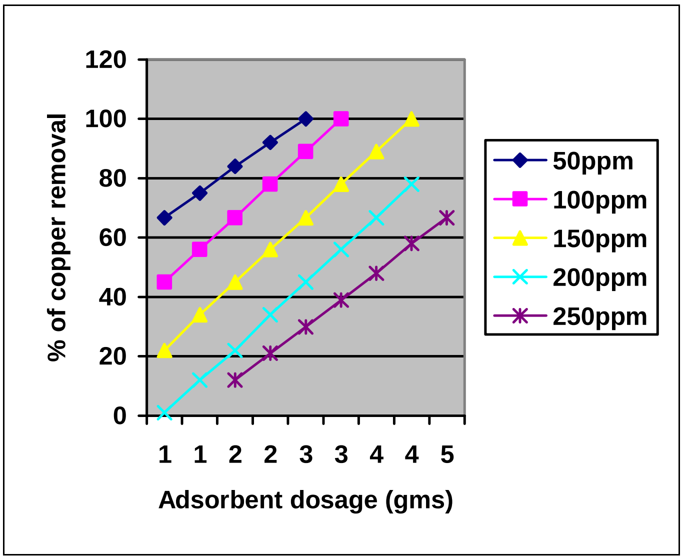

Figure 3. Effect of adsorbent dosage on removal of Cu(II)

It is observed that percentage of Cu(II) uptake was found to be constant (66.66%) for initial sorbate concentrations of 150 ppm, 300 ppm, 450 ppm, 600 ppm and 750 ppm with adsorbent dosages of 1g, 2g, 3g, 4g and 5g respectively are shown in Figure 4.

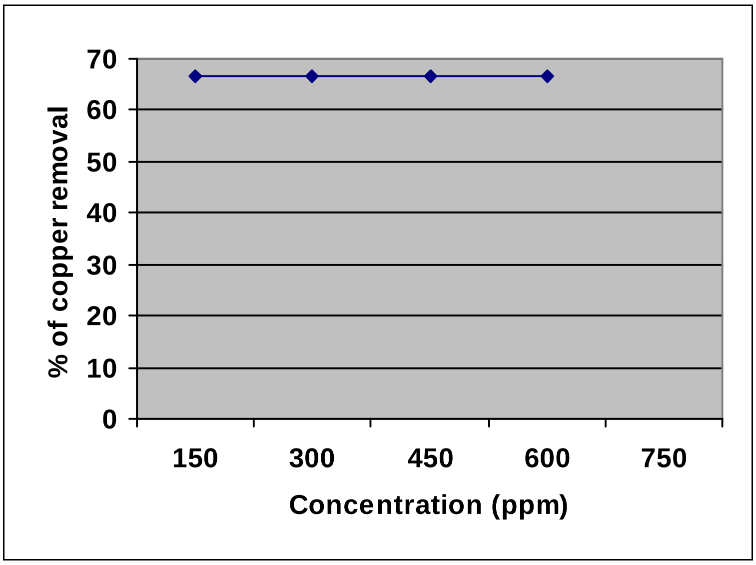

Figure 4. Effect of initial concentration and adsorbent dosage on removal of Cu(II)

Effect of pH

pH is an important parameter for the adsorption of metal ions from the aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [15]. To examine the effect of pH on the Cu removal efficiency, the pH was varied from 1.0 to 6.0. As shown in Figure5 the uptake of free ions Cu depends on pH, were optional metal removal efficiency occurs at pH 4 and then declining at higher pH.

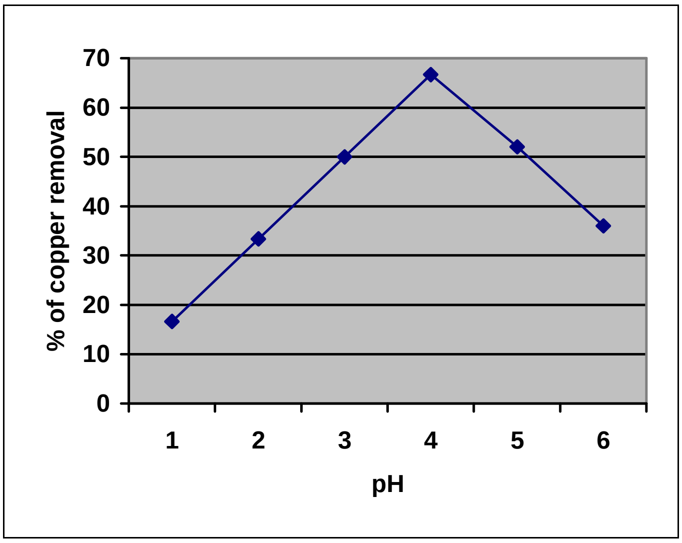

Figure 5. Effect of pH on removal of Cu(II)

Kinetic studies

A linear trace for the plot (lagegren plot) of log(qe-qt) Vs time shows that adsorption kinetics follows first order kinetics. This is shown in Figure6.

First order kinetics was further confirmed by Bhattacharya and Venkobachar plots(Figure7). The plot of log[1-U(T)] Vs time gave a straight line and it confirmed the first order kinetics.

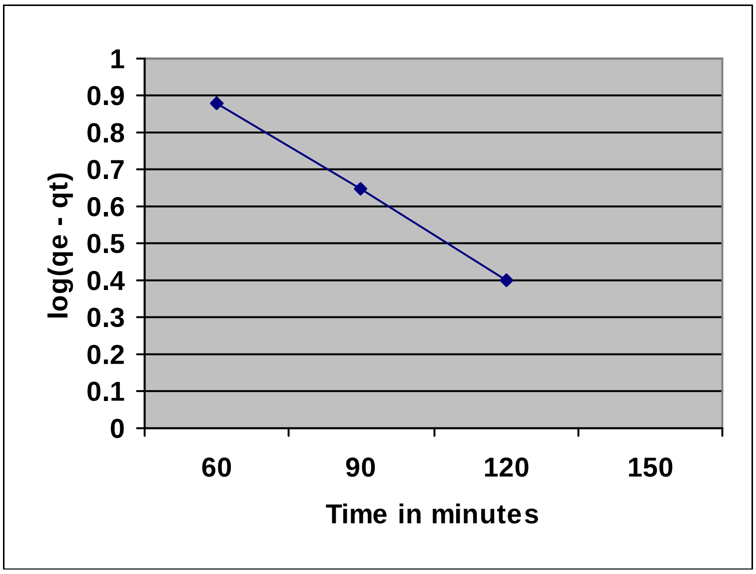

Figure 6. Data for Lagergren plot

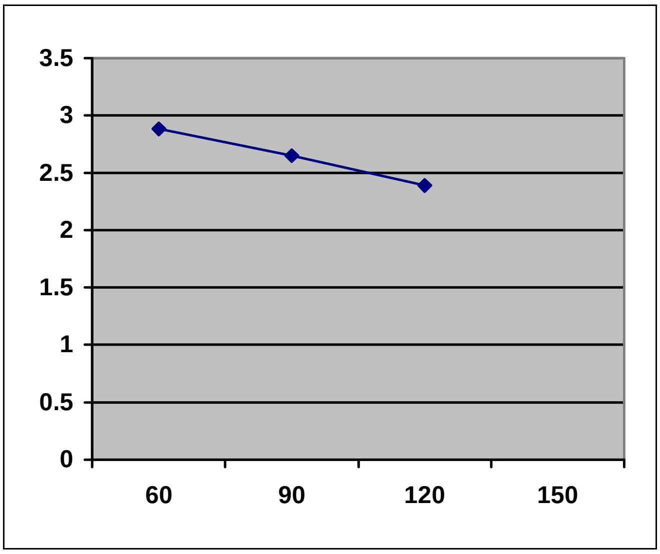

Figure 7. Data for Bhattacharya & Venkobachar plot

Isotherm studies

From the Langmuir adsorption adsorption isotherm, formation of unimolecular layer of adsorbate on the adsorbent can be verified. Linearity confirms unimolecular adsorption. This is shown in Figure8. Freundlich plot confirmed that the process of adsorption has taken place. This is shown in Figure9.

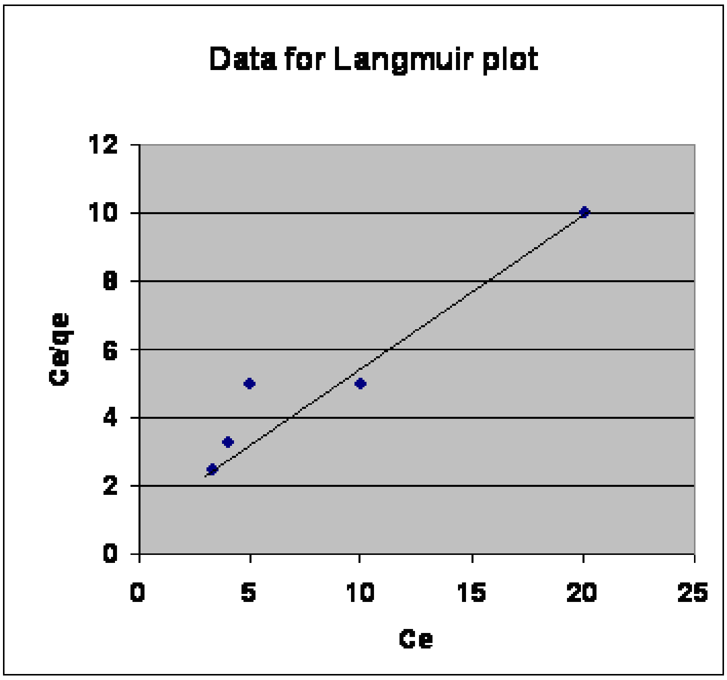

Figure 8.Langmuir isotherm for Cu(II) ion adsorption

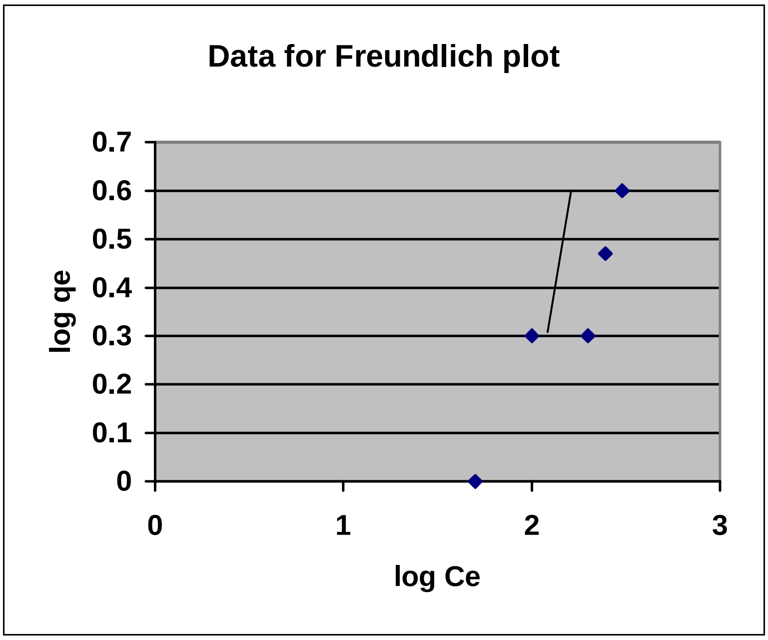

Figure 9. Frenudlich isotherm for Cu(II) ion adsorption

CONCLUSION

The present investigation shows that activated carbon made from *Brassice oleracea* is an effective adsorbent for the removal of heavy metal ion Cu(II) from aqueous solution. The removal of copper ion by *Brassice oleracea* activated carbon is strongly affected by parameters like initial concentration, pH and adsorbent dosage. Adsorption data obeyed Freundlich and Langmuir isotherms and first order kinetic equations. From the Lagegran and Bhattacharya and Venkobachar plot, a straight are found, which concludes that the kinetic is of first order. The results of this investigation are useful for developing an appropriate technology for designing waste water treatment plants for the removal of heavy metals, i.e. copper.

REFERENCES

[1] MW Sarwar; MA Hanif; U Rashid; K Rehman, *Indian J.Biol.Sci.*, **2004**,1(2),68-70.
[2] MH Nasir; R Nadeem; K Akhtar; MA Hanif; AM Khalid, *J Hazard Mater*, **2007,** 147(3), 1006-1014.
[3] S Arivoli; R Prabakaran; M Hema; C Kamatchi, *J.Chem.Pharm.Res*., **2011**, 3(5), 532-543.
[4] B. Zhu, T. Fan, D. Zhang, *J Hazard Mater* , **2008**, 153, 300-308.
[5] Amdur, M.O., Doull, J. and Klaasen, C., in Casarett and Doull's "Toxicology, the Basic Science of Poisons''. Pergamon Press New York, **1991**.
[6] GR Chatwal; MC Mehra; M Satake; T Katyal; ACAM Katya; T Nagahiro, *Encyclopedia of Environmental Pollution and its Control*, **1989**, 2, 51-53.
[7] RS Dave; GB Dave; VP Mishra; MK Pandya, *J.Chem.Pharm.Res*., **2011**, 3(3),271-276.
[8] AVALNSH Hariharan; D Murali Krishna; Ch Sudhakar, *J.Chem.Pharm.Res*., **2010**, 2(6), 381.
[9] J Samusolomon; P Martin Deva Prasath, *J.Chem.Pharm.Res.*, **2011**, 3(5), 478-490.
[10] Surya Narayan Dash; Ch V Ramachandra Murthy, *International Journal of Environmental Sciences*, **2010**, 1(3),296-313.
[11] SO Yong, *J Hazard Mater*, **2007**, 147, 91-96.
[12] AK Singh; DP Singh; KK Pandy; VN Singh, *J.Chem.Technol*., **1988**, 42, 39.
[13] AK Bhattacharya; C Venkobachar, *J Am Civ Engg.*, **1984**, 110, 110-116.
[14] Kuppusamy Vijayaraghavan, *Electronic J of Bio Technology*, **2004**, 7910, 62-71.
[15] Saifuddin M Nomanbhay; Kumaran Palanisamy, *Electronic J of Bio Technology*, **2005**, 8(1), 43-53.