



## Biosorption of Cr (III) from aqueous solution by the leaf biomass of *Calotropis procera* – ‘Bom bom’

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**ABSTRACT:** The biosorption of Cr (III) onto the leaf biomass of *Calotropis procera* popularly known as ‘bom bom’ in western Nigeria, over a wide range of reaction conditions were studied. The batch experiments showed that the biosorption of Cr (III) onto *Calotropis procera* leaf biomass is a rapid process reaching equilibrium within 10 minutes at an optimum pH value of 5. Other reaction conditions such as biomass dosage, initial metal ion concentration and temperature were also found to influence the biosorption process. Both Langmuir and Freundlich isotherms were employed to describe the biosorption process and both proved to be applicable. However, Langmuir gave a better fit with an R-Squared value of 0.967 (closer to unity than that of Freundlich), Langmuir constant,  $K_L$  of 0.0188 and monolayer adsorption capacity,  $q_m$  of 32.26 whereas the R-squared value for the Freundlich plot was 0.948 with adsorption capacity  $K_F$  and adsorption intensity,  $n$  of 1.156 and 1.146 respectively. The biosorption process followed the pseudo-second order kinetic model evident by an R-squared value of 0.999 and the pseudo second order rate constant,  $K_2$  of  $0.3668 \text{ mg g}^{-1} \text{ min}^{-1}$ . Thermodynamic studies revealed negative value of change in free energy,  $\Delta G^0$  ( $-4.046 \text{ kJ mol}^{-1}$ ) as an indicator of feasibility and spontaneity of the Cr (III) biosorption process. A positive value of enthalpy,  $\Delta H^0$  ( $26.099 \text{ kJ mol}^{-1}$ ) was obtained which indicated the endothermic nature of the biosorption process. FT-IR studies of the biosorbent before and after the biosorption process indicated that carboxylate, amino and nitro functional groups were involved in the sorption of Cr (III) onto *Calotropis procera* leaf biomass. These findings indicate that the leaf of biomass of *Calotropis procera* could be employed in the removal of Cr (III) from aqueous solutions and industrial effluents. @ JASEM

Chromium is one of the most abundant elements on earth and is of considerable environmental concern as it is widely used in leather tanning, electroplating, metal finishing, chromate preparation, wood preservation and manufacture of dyes and pigments (Krishna *et al.*, 2004; Shali and Indu 2005). Chromium occurs in aqueous systems in trivalent and hexavalent forms. Chromium (III) is used in tanneries as chromium sulphate which may be converted to Chromium (VI) in the effluent. Cr (VI) may be converted to Cr (III) under reduced environment, which is much less toxic and less soluble by several microorganisms which possess chromate reductase and thus reduction by these enzymes affords a means of chromate bioremediation (Shaili and Indu, 2005). Airborne emissions from chemical plants and incineration facilities are common sources of chromium. They are also derived from effluents of chemical plants, contaminated landfill, topsoils and rocks. Cr (III) often accumulates in aquatic life adding to the danger of eating fish that may have been exposed to high levels of  $\text{Cr}^{3+}$  (Greaney, 2005). Chromium (III) proves to be biologically essential to mammals as it maintains effective glucose, lipid and protein metabolism (Krishna *et al.*, 2004). However, long time contact causes skin allergy and cancer (Yun *et al.*, 2001). Cr (III) can also be oxidized to the more carcinogenic and mutagenic Cr (VI) by  $\text{MnO}_2$  in the environment or by some bacteria in soil under proper conditions (Ahmet *et al.*, 2008). Cr (III) is also toxic to fish when its concentration in water exceeds 5.0 mg/L. It therefore becomes imperative that the level of Cr (III) in the environment be kept as

minimal as possible. The hexavalent chromium has higher toxicity and leads to liver damage, pulmonary congestion, skin irritation, resulting in ulcer formation and is carcinogenic (Parke *et al.*, 2000). The maximum permissible levels of Cr (VI) in potable and industrial waste water are 0.05 and 1.0 mg/L respectively (Goyal *et al.*, 2003), yet levels as high as 80 ppm have been observed in paper mill effluents (Sudhakar *et al.*, 1991). Chemical precipitation methods are commonly employed for the removal of chromium but this leads to formation of chrome-bearing solid wastes plus the fact that it is uneconomical when the concentration of the chromium in the effluent is low (Onyanha *et al.*, 2008). Therefore, various kinds of biomaterials have been investigated for chromium removal and have been found efficient under various conditions such as pH, biosorbent dose, agitation time and initial metal ion concentration.

Cr (III) ions are found to bind more strongly as the pH is increased from 3 to 5. The pH dependence occurs when metal ions and protons compete for the same active metal binding sites such as carboxylate or amino groups on the biomass surface (Loukidou *et al.*, 2004). Above pH 5, a decrease in  $\text{Cr}^{3+}$  adsorption capacity of *Spirogyra condensata* was observed. For *Rhizoclonium heiroglyphicum* adsorption capacity increased from pH 3-4 but decreased above pH 4. The highest adsorption capacity values were observed at pH 4 and 5 for *Rhizoclonium heiroglyphicum* and *Spirogyra condensata* respectively (Onyanha *et al.*, 2008). The effect of

pH on the biosorption of Cr (III) ions onto *Hyloconium splendens* biomass also showed that  $\text{Cr}^{3+}$  adsorption increases with increase in pH from 3 -5 with maximum adsorption occurring at pH 5. Above this pH, there is dramatic decrease in the amount of Cr (III) adsorbed (Sari *et al.*, 2008). This may be due to precipitation of the metal hydroxides at this pH (Onyanha *et al.*, 2008). Whereas, for the biosorption of Cr (VI) using the tusk of Bengal gram and *Dunaliella* species, the highest uptake values were found at pH 2 and further increase in pH brought about significant decrease in Cr (VI) adsorption (Ahalya *et al.*, 2005; Donmez & Aksu, 2002).

The biosorption efficiency for Cr (III) ions as a function of biomass dosage has been investigated by different researchers. Ahmet *et al.*, 2008, reported that the percentage of the metal biosorption, steeply increases with the biomass loading up to 4 g/L. Maximum adsorption of 99% of Cr (III) ions was attained at 4g/L and the increase was insignificant at higher dosages of 10 mg/L and 20 mg/L. An increase in biomass concentration or dose generally increases the amount of biosorbed Cr (VI) ions (Razmovski & Sciban 2008) and Cr (III) ions (Baig *et al.*, 1999), using waste tea fungal biomass and silverleaf nightshade biomass respectively. Several other researchers have reported similar trend for Cr (III) and Cr (VI) biosorption on various biosorbents (Han *et al.*, 2008).

Though maximum binding of most metals occur rapidly within the first 10 – 15 minutes and remain fairly uniform in the next 120 minutes, Baig *et al.*, 1999, reported a gradual increase in binding of Cr (III) over time on biomass of silverleaf nightshade (*Solanum Elaeagnifolium*). Oninla (2008), reported maximum adsorption of Cr (III) on *Basella alba* biomass within 6 minutes of agitation after which a decrease in metal uptake was noticed until equilibrium was reached after 10 minutes. However, Razmovski & Sciban (2008) reported maximum contact time for Cr (VI) biosorption by waste tea fungal biomass as 60 minutes.

This study is aimed at increasing the biomass data bank by checking the efficiency of biosorption of  $\text{Cr}^{3+}$  onto *Calotropis procera* which is known to be locally used in coagulation of milk to cheese. This implies that it might have some abilities to coagulate or adsorb metallic macromolecules and therefore expected to sorb heavy metals from aqueous solutions containing them. A deeper knowledge by which this takes place will be necessary; hence this work has looked at the kinetics of the sorption process, equilibrium modeling and thermodynamics

of the system as well as the means by which the process takes place.

## MATERIALS AND METHODS

All chemicals employed in this work, were of analytical grade and were used without further purification. Jenway 3510 model pH meter was used to measure pH values in the aqueous phase and a Buck scientific Flame Atomic Absorption spectrometer (FAAS) model 2004 (Germany) was used for residual metal ion analysis. Spectroscopy grade standards were used to calibrate the instrument which was periodically checked for instrument response. All measurements were done in air/acetylene flame. The batch experiments were carried out in triplicates and the mean computed for each set of values to maintain accuracy. For functional group analysis, Fourier – Transform Infra-Red (FT-IR) spectra of unloaded biomass at pH 5 and metal loaded biomass were recorded at 400 – 4000  $\text{cm}^{-1}$  wave number range using a Nicolet Avater 3300 Thermo Electron Corporation IR spectrometer.

Leaves of the naturally abundant *Calotropis procera* popularly known as ‘*bombom*’ in western Nigeria were plucked from Moniya in Ibadan, Oyo State of Nigeria. They were washed thoroughly from sand and then washed twice with deionized water. They were then air-dried for six days. The air-dried leaves were pulverized and sieved through a 150  $\mu\text{m}$  size mesh screen and stored in air-tight polyethene bags, ready for use

Chromium (III) stock solution (8mM) was prepared by dissolving a known mass of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in deionized water, in a standard volumetric flask and made up to the mark. The stock solution was then diluted to 0.1mM, 0.3 mM, 0.5 mM, 0.7 mM, 1.0 mM, 1.5 mM, 2.0 mM and 3.0 mM solutions. All dilutions were carried out with deionized water.

Using 0.05g of the biosorbent for each batch equilibrium experiment, the effect of pH (ranging from 2 to 8) on sorption of Cr (III) ions by *Calotropis procera* was investigated. 0.1M  $\text{HNO}_3$  and 0.1M NaOH were used to adjust the pH of solution to the corresponding pH under investigation. The biomass was then contacted with 20 ml, 0.3 mM solution of the salt and agitated on a shaker at 150 rpm for 2 hours. After agitation, the mixtures were then filtered and the concentrations of the residual metal ions were determined by FAAS. Each experiment was carried out in triplicate.

The rate of Cr (III) biosorption by *Calotropis procera* was studied as follows: 0.05 of biosorbent was mixed

with 20 ml of 0.3 mM Cr (III) solution at the optimum pH value of 5. The mixtures were equilibrated on a shaker at 150 rpm. The resulting mixture was then filtered with 90 mm whatman no 1 filter paper and filtrate analyzed for residual metal ions by FAAS. Experiments were carried out in triplicates.

The results were fitted into the pseudo-first order and pseudo-second order kinetic models and appropriate plots made from which the correlation co-efficient  $R^2$  values were obtained to determine the most fitting model and the corresponding kinetic parameters deduced accordingly from the slope and intercept of such plots.

The effect of biosorbent dose on biosorption of Cr (III) by *Calotropis procera* was investigated as follows; samples of *Calotropis procera* of varied masses of 10, 30, 50, 80, 110 and 150 mg were added to 20 ml of 0.3 mM of the metal solution at the optimum pH value. The mixtures were agitated on a shaker at 150 rpm for 30 minutes and then filtered. Filtrates were then analyzed for residual metal ions. The amount of metal ions taken up ( $q_e$ ) as a function of initial metal ion concentration was determined by contacting 0.11g of biosorbent with 20ml of metal ion solution in the concentration range of 0.1Mm to 0.3mM at the optimum pH. The mixtures were agitated for the respective optimum contact time obtained for Cr (III) biosorption and then filtered. The filtrates were then analyzed for residual metal ion concentration by FAAS.

The effect of temperature on the biosorption of Cr (III) onto *Calotropis procera* and the thermodynamics of the process were investigated as a function of concentration of metal ion solution by contacting 20 ml of 0.3 mM, 0.5 mM, 0.7 mM and 1.0 mM of the metal ion solution at the optimum pH, with 0.15 g of biosorbent. The mixture was agitated in a constant temperature shaker bath for the optimum time predetermined for the metal. The temperature of the shaker bath was adjusted to 10, 20, 27, 40 and 50 °C for each set of concentration under study. Agitated mixtures were filtered thereafter. The filtrates were analyzed by FAAS for residual metal ion concentration. The amount of Cr (III) adsorbed by biomass was calculated using a mass balance equation expressed as:

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

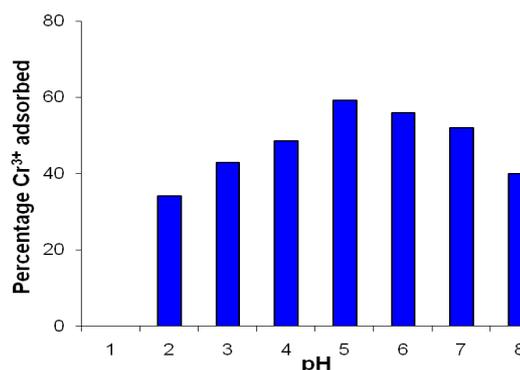
where  $q_e$  = metal ion uptake at equilibrium (mg/g),  $C_e$  is the metal ion concentration remaining in solution at equilibrium,  $C_0$  is the initial metal ion concentration in solution (mg/L),  $v$  is the volume of

metal solution used (L) and  $m$  is the mass of biomass used.

FT-IR analysis of unloaded and metal-loaded *Calotropis procera* at pH 5 was carried out to ascertain the functional groups on the walls of the biosorbent which are responsible for the biosorption process. This was done by mixing approximately 1 mg each of dried sample of metal unloaded and metal loaded *Calotropis procera* with 5 mg KBr (1:5). The mixture was ground to fine powder and pressed under vacuum into pellets. The pellets were then analyzed in the range 4000 – 400  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

**Effect of pH:** pH is an important parameter that affects the biosorption of heavy metals from aqueous solutions. The variation of the percentage of Cr (III) sorbed by *Calotropis procera* at various pH values (2 to 8) at 27°C and an initial metal ion concentration of 0.3 mM is shown in fig. 1.



**Fig.1.** Effect of initial solution pH on biosorption of Cr (III) onto the leaf biomass of *Calotropis procera*. (temp. 27°C, adsorbent concentration 50mg/L, initial metal ion concentration 0.3mM, contact time 10 mins.).

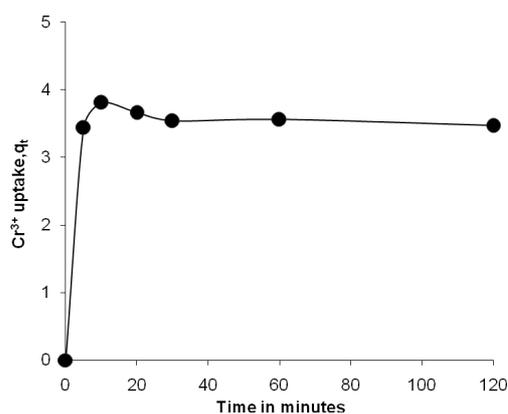
From the plot, the percentage adsorption of Cr (III) increased as pH is increased from 2 to 5 with the maximum adsorption efficiency (60%) occurring at pH 5. Further increase in the pH led to a decline in the amount of Cr (III) adsorbed.

This result therefore shows that weak acidic pH favours Cr (III) biosorption on *Calotropis procera*. At low pH value (i.e. in strongly acidic solution) there are many  $\text{H}^+$  ions in the solution competing with the metal ions and are more favorably bound to the negatively charged active sites on the adsorbent making these sites less available for the other cations. On the other hand, at high pH (alkaline solution), metal hydroxides are formed and both species are adsorbed at surface of adsorbent either by ion exchange mechanism or by

hydrogen bonding. Hence, decrease metal uptake is observed at high pH values (Razmovski & Sciban, 2008). In other words, the decrease in biosorption efficiency at higher pH values (7 & 8), may be attributed to the formation of hydroxide complexes and their competition with the active sites (Sari & Tuzen, 2008).

The corresponding increase in metal biosorption with increase in pH up to 5 may be suggestive of a chemisorption process (Dang et al., 2009). The effect of pH on biosorption efficiency may be attributed to the chemical form of heavy metals in the solution at a specific pH. That is, pure ionic metal form or hydroxyl-metal form. In addition, due to different functional groups on the biosorbent surface, which become active sites for metal binding at a specific pH, the effect of pH on biosorption can vary substantially. Therefore an increase in pH may cause an increase or decrease in the biosorbent capacity, resulting in different optimum pH values, depending on the type of biosorbent in use (Dang et al., 2009). It is worthy to note also that similar results for  $\text{Cr}^{3+}$  biosorption on *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* have been reported (Onyancha et al., 2008). Therefore pH 5 was taken as optimum pH for  $\text{Cr}^{3+}$  biosorption throughout the batch experiments.

**Effect of time and Adsorption Kinetics:** The rate at which Cr (III) was sorbed onto *Calotropis procera* was studied and results presented in fig.2 which represents a plot of uptake at time  $q_t$  against time, t.



**Fig.2.** Time profile for the adsorption of Cr (III) onto the leaf biomass of *Calotropis procera*. (temp. 27°C, adsorbent concentration 50mg/L, initial metal ion concentration 0.3mM, pH 5)

The initial rapid phase within the first ten minutes may be characteristic of a physical adsorption process or ion exchange at cell surface while the subsequent phase may be indicative of other mechanisms such as

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complexation, micro-precipitation or saturation of binding sites (Onyancha et al., 2008).

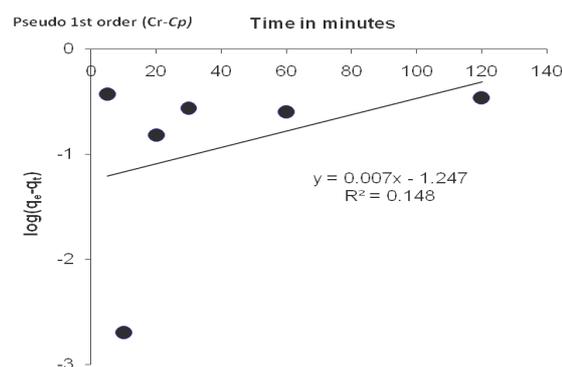
In an attempt to determine the rate of the adsorption process, the pseudo first order and the pseudo second order models were used to fit the kinetic data. The linear functions of these models (pseudo first order and pseudo second order) are given in equations (2) and (3) respectively.

$$\text{Log}(q_e - q_t) = \text{Log} q_e - k_1 t / 2.303 \quad (2)$$

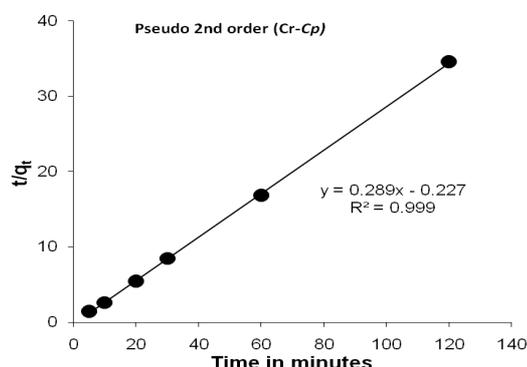
$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (3)$$

where  $q_e$  and  $q_t$  are the amount of metal ions adsorbed at equilibrium and at time t respectively,  $k_1$  and  $k_2$  are the Pseudo first order and Pseudo second order rate constants respectively.

A plot of  $\log(q_e - q_t)$  against t and  $t/q_t$  against t for pseudo-first and pseudo-second order kinetics respectively are shown in fig.3



**Fig.3a.** Pseudo first – order plot for the biosorption of Cr (III) onto the leaf biomass of *Calotropis procera*. (temp. 27°C, adsorbent concentration 50mg/L, initial metal ion concentration 0.3mM, pH 5, agitation time 10 minutes).



**Fig.3b.** Pseudo -second order plot for the biosorption of Cr (III) onto the leaf biomass of *Calotropis procera*. (temp. 27°C, adsorbent concentration 50mg/L, initial metal ion concentration 0.3mM, pH 5, agitation time 10 minutes).

From the  $R^2$  values (0.148 and 0.999 for pseudo first and pseudo second order plots respectively), it can be clearly seen that the pseudo first order equation did not provide a good description for the sorption of the Cr (III) onto *Calotropis procera*. No further consideration of this model was therefore attempted. However, a plot of  $t/qt$  against  $t$  provided a good fit ( $R^2 = 0.999$ ) as seen in fig.3. The pseudo 2<sup>nd</sup> order model suggests that the biosorption process follows a second-order mechanism. Therefore, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Zafar et al., 2006). The value of  $q_e$  and  $K_2$  were determined from the slope and intercept of the plot of  $t/qt$  vs  $t$  as 3.81mg and  $3.668 \text{ gm}^{-1}\text{min}^{-1}$ .

**Effect of Biosorbent Dose:** The effect of biomass dosage on biosorption was investigated in the range 10 mg – 150 mg and results represented in fig. 5.

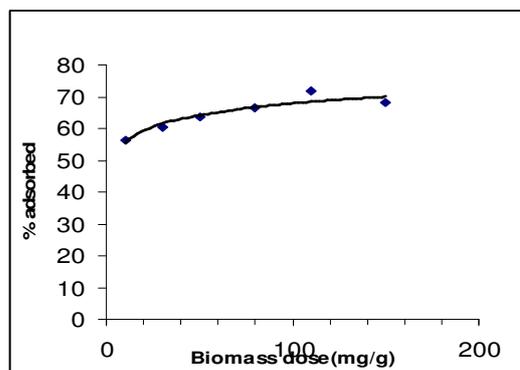


Fig.5: Effect of biosorbent dose on efficiency of Cr biosorption by *Calotropis procera*

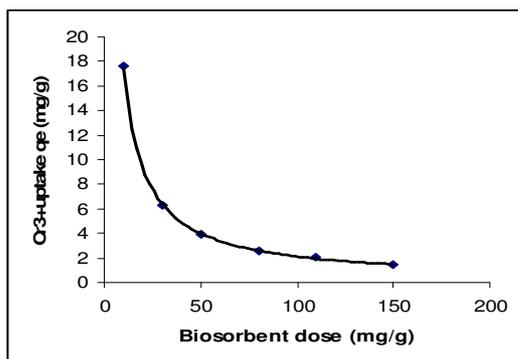


Fig.6: Effect of biosorbent dose on uptake of Cr (III) by *Calotropis procera*

Results show that biosorption efficiency is dependent on the increase in the dose of biomass. Cr (III) biosorption efficiency increased with increase in biosorbent dose up to 150 mg above which the efficiency of biosorption is reduced. Therefore the biosorbent dose of 150 mg was used as optimum dose

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for Cr (III) biosorption on *Calotropis procera*. An increase in biomass concentration generally increases the amount of biosorbed metal ions because of an increase in surface area of the biosorbent, which consequently increases the number of available binding sites (Esposito et al., 2001, Razmovski & Sciban, 2008). The decrease in biosorption efficiency with further increase in biomass dose above 110 mg could be explained as a consequence of a partial aggregation of biomass, which results in a decrease in effective surface area for the biosorption process (Sari & Tuzen, 2008; Karthikeyan et al., 2007).

However, adsorption capacity or uptake  $q_e$  decreased as the biosorbent dose is increased from 10-150 mg (fig 6). This may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for sorption increases by increasing the sorbent dose. That is, reduction in metal uptake with increasing biomass dose can be attributed to an insufficiency of metal ions in solution with respect to available binding sites (Fourest & Roux, 1992).

**Effect of Metal ion concentration:** The experimental results of the uptake of Cr (III) onto the leaf biomass of

*Calotropis procera* at various initial metal ion concentrations was studied in the concentration range 0.1 to 3.0 mM. The sorption capacity or metal uptake,  $q_e$  increased from 0.725 mg/g to 19.35 mg/g, with increase in metal ion concentration (fig 7)

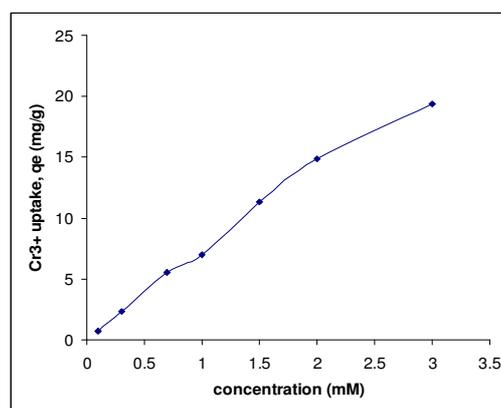


Fig.7: Effect of initial metal ion concentration on biosorption of Cr (III) by *Calotropis procera* (temp. 27°C, adsorbent concentration 150 mg, pH 5, Agitation time 10 minutes).

This increase can be attributed to competition for the available binding sites, that is, most binding sites are unoccupied. High initial concentration provides an important driving force to overcome mass transfer resistance of metal ion between the aqueous and solid phases (Ihan et al., 2004, Onyanha et al., 2008).

**Adsorption Isotherms:** To examine the relationship between metal uptake  $q_e$  and aqueous concentration at equilibrium  $C_e$ , sorption isotherm models are widely employed for fitting the experimental data. The Langmuir and Freundlich equations were used. The Langmuir equation (eg. 4) describes a monolayer adsorption onto a surface containing finite number of active sites.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

The linearized form of equation (4) gives

$$1/q_e = 1/q_m K_L + 1/q_m C_e \quad (5)$$

Where  $q_m$  is the Langmuir monolayer adsorption capacity  $K_L$  is Langmuir constant related to the affinity of binding sites for the metal ions and  $C_e$  is the aqueous concentration of metal ions at equilibrium. The experimental data were fitted into equation (5) by plotting  $1/q_e$  vs  $1/C_e$  from which  $K_L$  and  $q_m$  were obtained from the intercept and slope of the plot respectively. The empirical Freundlich

equation accounts for the sorption of metal ions on heterogeneous surfaces and is given in equation (6) as

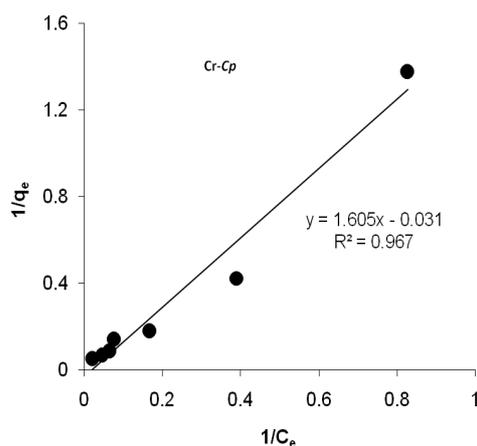
$$q_e = K_f (C_e)^{1/n} \quad (6)$$

Where  $K_f$  and  $n$  represent adsorption capacity and adsorption intensity respectively. Linearizing eq (6) gives

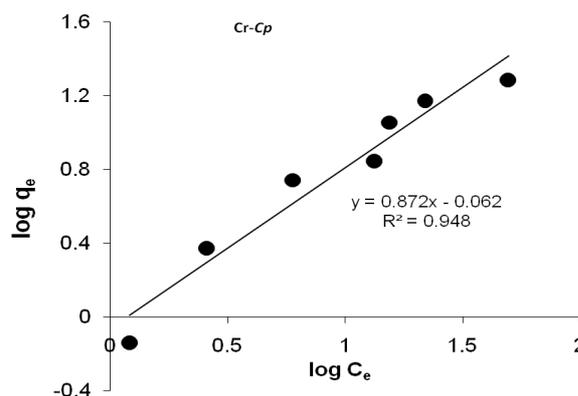
$$\log q_e = \log K_f + \log C_e \quad (7)$$

The adsorption constants  $K_f$  and  $1/n$  were obtained as intercept and slope of the plot of  $\log q_e$  against  $\log C_e$ .

Modelling the experimental data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions. In this study, the experimental data fitted into both Langmuir and Freundlich isotherm equations at room temperature ( $27^\circ\text{C}$ ). However, the Langmuir isotherm gave a better fit than the Freundlich isotherm. (fig. 8 & 9)



**Fig. 8 :** Langmuir isotherm for the biosorption of  $\text{Cr}^{3+}$  (dose, 150 mg, agitation time, 10 mins, temperature,  $27^\circ\text{C}$ )



**Fig. 9 :** Freundlich isotherm for the biosorption of  $\text{Cr}^{3+}$  (pH 5 ; biomass dose, 150 mg, agitation time, 10 mins temperature,  $27^\circ\text{C}$ );

Table 1 Langmuir and Freundlich isotherm parameters

LANGMUIR ISOTHERM				FREUNDLICH ISOTHERM		
Metal ion	$R^2$	$q_{\max}$	$K_L$	$R^2$	$K_f$	$N$
$\text{Cr}^{3+}$	0.97	32.26	0.019	0.95	1.16	1.15

**Effect of Temperature:** The effect of temperature on  $\text{Cr}^{3+}$  biosorption onto *Calotropis procera* leaf is shown in Fig. 10

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Adsorption of chromium onto *Calotropis procera* increased from 1.934 mg/g to 2.432 mg/g as the temperature increased from  $10^\circ\text{C}$  to  $40^\circ\text{C}$ . Above this temperature, a decrease in biosorption efficiency occurred. The increase in adsorption efficiency with increase in temperature may be indicative of a chemisorption process while the reverse is true for physisorption. (Kara *et al.*, 2003). It may also be indicative of an endothermic process.

The eventual decrease in biosorption efficiency above 40°C may be attributed to many parameters; the relative increase in escape tendency of the Cr (III) ions from the solid phase to the bulk phase, deactivation of the biosorbent or destroying some active sites on the biosorbent surface due to bond ruptures (Meena et al., 2005; Sari & Tuzen, 2008) or due to the weakness of biosorptive forces between the active sites on the biosorbent and the sorbate species and also between the adjacent molecules of sorbed phase (Yadar & Tyagi, 1987). It has been noted however, that there are other conflicting observations of the effect of temperature on biosorption among various studies. This may be due to different types of biosorbent and/or different geographical locations where the same type of biosorbent was obtained (Dang *et al.*, 2009).

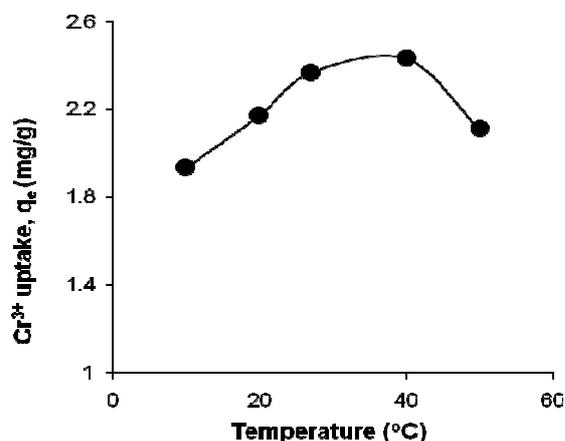


Fig.10. Effect of temperature on biosorption of Cr<sup>3+</sup> on *Calotropis procera* (adsorbent concentration 110 mg, pH 5, agitation time 10 minutes)

**Biosorption Thermodynamics:** The thermodynamic behaviour of the biosorption of Cr (III) onto *Calotropis procera* was described using thermodynamics parameters such as change in Gibb's free energy,  $\Delta G^{\circ}$ , enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ). These parameters were obtained from the equation below.

$$\Delta G^{\circ} = -RT \ln K_c \quad (8)$$

Where R is the universal gas constant (8.314 J/Mol/K), T is temperature in Kelvin and  $K_c$  is the thermodynamic equilibrium constant and is obtained from the below equation.

$$K_c = C_a / C_e \quad (9)$$

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Where  $C_a$  is mass of adsorbate per liter and  $C_e$  is equilibrium concentration of solution (Sarin and Pant, 2006). According to thermodynamics, the Gibb's free energy is also related to enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) at constant temperature by the Van't Hoff equation:

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (10)$$

The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were evaluated from the slope and intercept of Van't Hoff's plot of  $\ln K_c$  against  $1/T$  (fig. 11). The positive value of  $\Delta H^{\circ}$  (26.099 kJmol<sup>-1</sup>) for Cr (III) biosorption indicates that the process is endothermic while positive value of  $\Delta S^{\circ}$  (0.099 kJK<sup>-1</sup>mo<sup>-1</sup>) shows increased randomness at solid solution interphase (Dang et al., 2009). Also, the negative value of the change in Gibb's free energy is an indication of feasibility and spontaneous nature of the biosorption process.

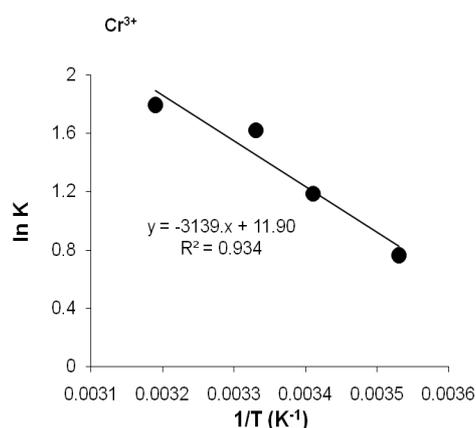


Fig.11. Van't Hoff's plot of Cr<sup>3+</sup> biosorption by *Calotropis procera* leaf.

**FT-IR analysis of unloaded and metal loaded Calotropis procera:** The FT-IR spectra of unloaded biomass at pH 5 (fig.12) showed a number of distinct absorption bands indicating the complex nature of the biomass. For example, several distinct and sharp absorptions around 3448 cm<sup>-1</sup> are indicative of -OH and -NH<sub>2</sub> groups. The weak band around 2910 cm<sup>-1</sup> indicates presence of C-H stretch of alkane. The absorption band around 1637 cm<sup>-1</sup> depicts mainly C=O stretch and bands around 1560 cm<sup>-1</sup> suggest -NH, -CN and NO stretch. Pandey et al., 007, have reported similar bands in leached and unleached root biomass of *Calotropis procera*.

Bands around 1100 cm<sup>-1</sup> in unloaded biomass at pH 5 could be attributed to COH stretch of sugar.

To confirm the involvement of functional groups in relation to biosorption of the metals and possibly to explain the mechanism of biosorption, FT-IR study was also carried out on the metal loaded biomass at the same pH of 5. Comparing the spectra of Cr (III) – loaded biomass with that of the unloaded, it is seen that the band at  $3448\text{ cm}^{-1}$  broadens and its intensity is reduced and the band shifts to a lower wave number after Cr (III) biosorption. Also the band around  $2910\text{ cm}^{-1}$  is now more intense. It is also seen that several new bands in the finger print region appear after biosorption indicating that a new compound is formed (Kalsi, 2004). Based on the FT-IR findings, it can be concluded that the metal binding on biomass of *Calotropis procera* takes place essentially by substitution of amine, nitro and carboxylic groups by the Cr (III) ions. It is interesting to note also that *Calotropis procera* root bark has been reported to adsorb heavy metals by ion exchange mechanism involving substitution in carboxylic, amine and nitro groups which were confirmed by the FT – IR spectra of the biomass root bark and an increase in the pH of the system after biosorption had taken place (Pandey *et al.*, 2007).

**Conclusion:** Biosorption of Cr (III) by *Calotropis procera* leaf biomass is found to be influenced by the solution pH, biosorbent dose, contact time, temperature and initial metal ion concentration. The Cr (III) biosorption process is rapid occurring within 10 minutes and described by a Pseudo-second order model based on the assumption that the rate limiting step may be a chemical sorption process. Langmuir and Freundlich adsorption isotherms were found to be good fits for the adsorption process though Langmuir model gave a better fit. Considering the thermodynamic parameters, the negative value of  $\Delta G^0$  shows that the process is feasible and spontaneous and therefore industrially applicable while the positive value of enthalpy change ( $\Delta H^0$ ) indicates an endothermic process.

The FT-IR studies of the biosorbent before and after being loaded by the metals revealed that carboxylate, amine and the nitro functional groups may be involved in the sorption process as the intensities and wave numbers of these bands changed after the biosorption. Hence the use of the leaf biomass of *Calotropis procera* can be employed as good biosorbent for the removal of Cr (III) from aqueous solutions and as an alternative method of their removal from industrial effluent.

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