



## **Kinetic, Thermodynamic and Equilibrium Studies for the Removal of Chromium from an aqueous solution on to MI Leaves powder**

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**Abstract :** Enhanced current development after the mechanical change has incited the arrival of chemicals, which causes normal and general therapeutic issues. The proximity of overpowering metals in the earth is of noteworthy worry because of their uncommon noxious quality and slant for bioaccumulation in the common pecking request even in modestly low core interests. The present work investigates the developing of Madhuca indica leaves powder on biosorption of Chromium metal present in a watery fluid game-plan. The impacts of different parameters (Time, pH, Dosage, Size, Concentration and Temperature) on biosorption of Chromium are considered. Ejection of Chromium accomplished an adjust most outrageous of 40 minutes. Additionally, hardly decreases with extending Chromium obsession. The trial information gave solid match with Langmuir isotherm taken after by Freundlich and Temkin isotherms.

**Key Words :** Biosorption; Madhuca indica; Isotherms.

### **Introduction**

Overhauled present day development after the mechanical change has provoked the arrival of chemicals, which causes characteristic and general restorative issues. The closeness of overpowering metals in the earth is of genuine worry because of their silly noxious quality and slant for bioaccumulation in the developed lifestyle even in decently low concentrations [1, 2]. Water has the central part in intervening overall scale natural framework shapes, interfacing condition, lithosphere and biosphere by moving substances among them and enabling compound reactions to happen. Overpowering metals of concern fuse cobalt, lead, chromium, mercury, uranium, selenium, arsenic, cadmium, silver, gold, nickel et cetera. On account of their conveyability in consistent water natural groups and their toxic quality to higher living things, overpowering metal particles in surface and ground water supplies have been sorted out as major inorganic contaminants in nature. Overpowering metal sully in the land and water proficient structure has transformed into a bona fide chance today and of phenomenal biological stress as they are non-biodegradable and in like manner steady. To keep up a vital separation from prosperity threats, it is crucial to remove these toxic overpowering metals from squander water before its exchange. Thus, the lawmaking body has constrained a couple of stringent biological affirmation rules. This has obliged the legitimate and current gathering to work towards disinfection of the effluents. Among each one of the effluents treatment of risky metal bearing wastewater needs excellent thought owing to its non-biodegradable nature when appeared differently in relation to other common pollutions. The surveys made on examination of money related and convincing systems for the ejection of overpowering metals

have achieved the change of new division headways. Natural treatment, molecule exchange, coagulation, electrochemical operation and filtration are typically associated with the treatment of mechanical effluents [3, 4, 5].

### Preparation of Biosorbent:

In the present critique *Madhuca indica* leaves were used as biosorbent. At first the *Madhuca indica* leaves were assembled from close by angalakuduru town conduit, Tenali. Later the leaves were washed with refined water a couple of times to clear contaminating impacts present on it and after that they were kept under sunlight for around 2 to 3 weeks for complete the process of drying. At long last *Madhuca indica* leaves were ground and disconnected around 5 one of a kind sizes using BSS. A while later it was secured in air settled holder until required

### Preparation of stock solution

The standard stock arrangement of chromium (1000 mg/L) was set up by dissolving 2.828 g of 99.9 % logical review  $K_2Cr_2O_7$  in 1000 mL of refined water. The grouping of chromium was differed from 20 to 160 mg/L by weakening the stock arrangements with required amount of deionized water. The pH of the working arrangement was balanced utilizing either 0.1 N HCL or 0.1N NaOH

## Results and Discussion:

### Effect of agitation time:

The impacts of different parameters on chromium biosorption are talked about underneath. The rate biosorption is appeared against tumult time in fig.1. The % biosorption is found to increment up to 40 min. The most extreme rate of biosorption is achieved at 40 min of disturbance and winds up plainly steady after 40 min (73%). [7,8,9,10,11].

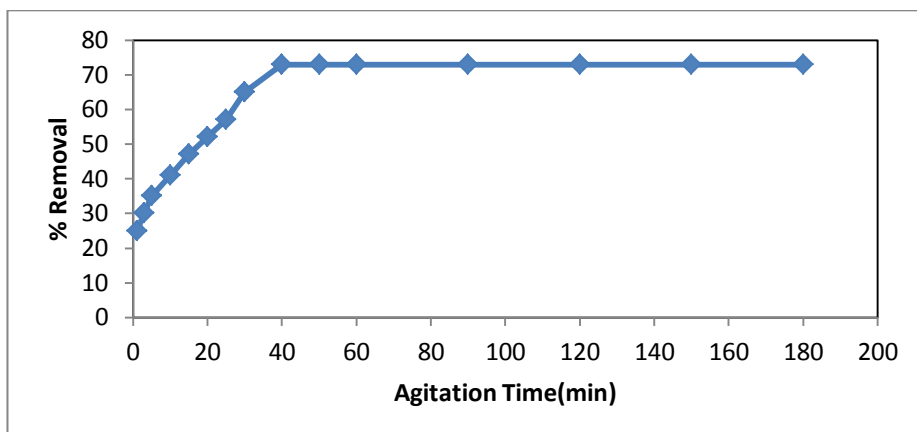


Fig.1. Effect of agitation time

### Effect of biosorbent size:

Fig.2. shows rate biosorption of chromium as a component of molecule estimate. The rate biosorption is expanded from 55 to 73 % as the biosorbent measure is diminished from 152 to 53  $\mu$ m. The higher evacuation with the littler molecule has been credited to more noteworthy access to the inward pores. i.e. shorter way lengths and to the expansive surface are per unit weight of biosorbent. [12].

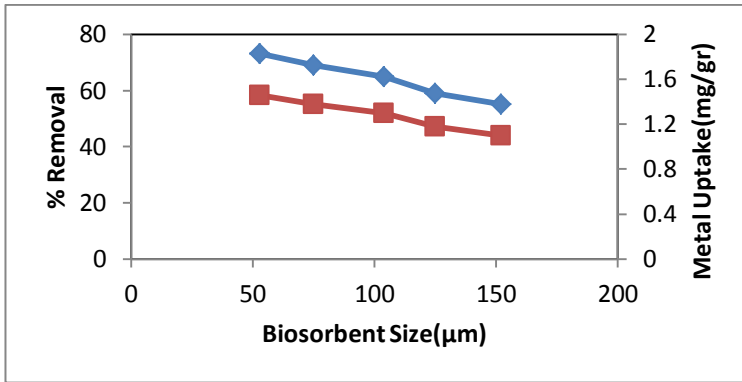


Fig.2.Measurement of % removal of chromium for biosorbent size

**Effect of pH:**

The effect of pH of aqueous solution on percentage biosorption of chromium is drawn in fig 3. The percentage biosorption is increased from 70 % to 80% as pH is increased from 2 to 4. The percentage biosorption is decreased from 80 % to 69 % as pH increases from 4 to 8. [13].

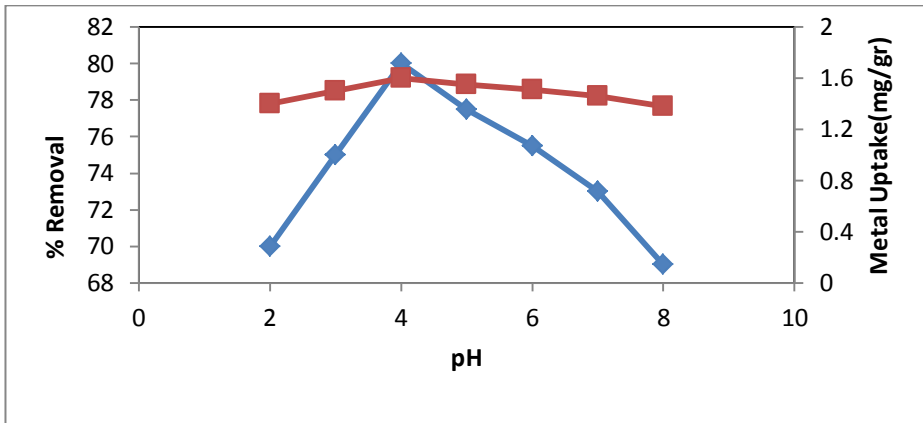


Fig. 3. Dependence of % biosorption on pH of aqueous solution using Madhuca indica

**Effect of initial concentration of chromium:**

A graph is drawn in fig.4.withpercentage biosorption of chromium as a function of initial concentration of chromium. The percentage biosorption is decreased from 80 to 64 % as the initial concentration of chromium in the aqueous solution increases from 20 mg/L to 160 mg/L. This can be explained that the biosorbent has a limited number of active sites.[14,15].

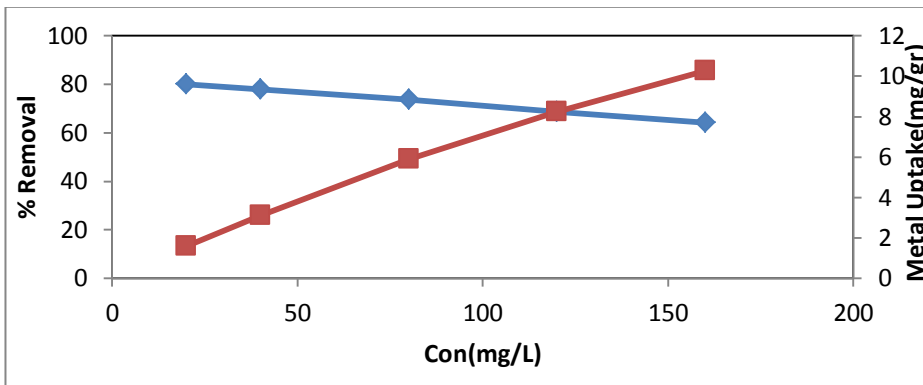


Fig. 4. % biosorption as a function of initial concentration of chromium

### Effect of biosorbent dosage:

For abiosorbent size of 53 $\mu$ m, percentage biosorption increases from 80 % to 90 %, as dosage is increased from 10 to 30 g/L, this is due to the lack of specific surface area of the sorbent.[16,17].

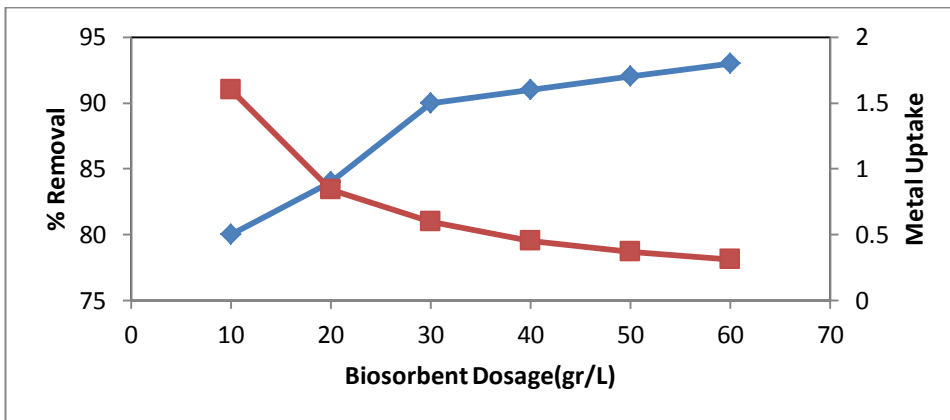


Fig. 5. Dependence of % biosorption of chromium on biosorbent dosage

### Effect of temperature

Temperature dependence of the biosorption process is associated with several thermodynamic parameters. The effect of temperature on biosorption of chromium using biomass is investigated at different temperatures (283, 293, 303, 313 and 323K) as given in Fig. 6. For lower temperatures, equilibrium sorption occurs rapidly at lower metal ion concentrations in the first phase and becomes relatively constant at higher concentrations and higher temperatures[18,19].

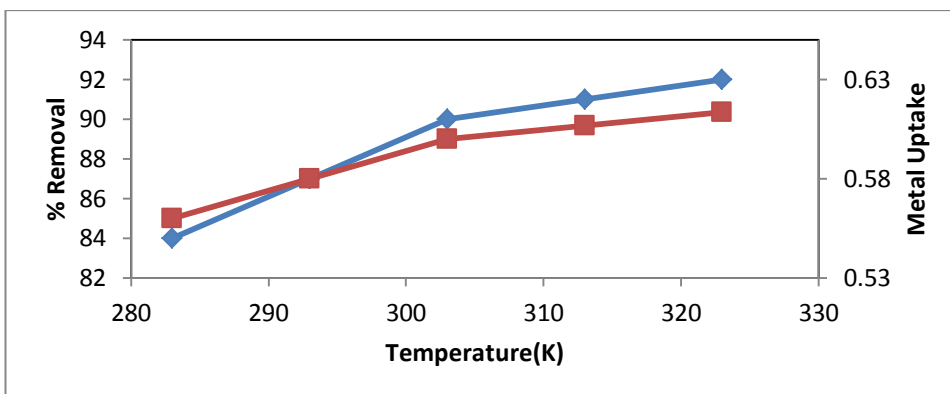
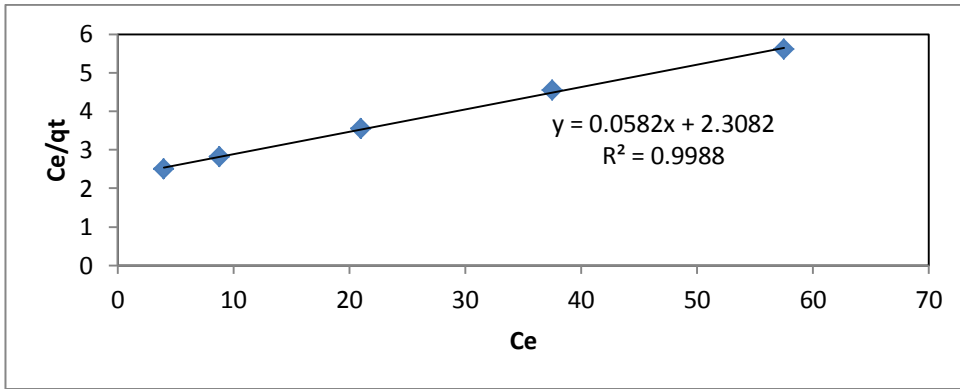


Fig. 6. Variations of % biosorption of chromium on temperature

### Isotherms

(i) Langmuir Isotherm: Langmuir isotherm, drawn in fig. 7., for the present data has yielded the equation:  $(C_e/q_e) = 0.058 C_e + 2.308$   $R^2 = 0.998$

The correlation coefficient value of 0.998 indicates strong binding of chromium ions to the biosorbent .

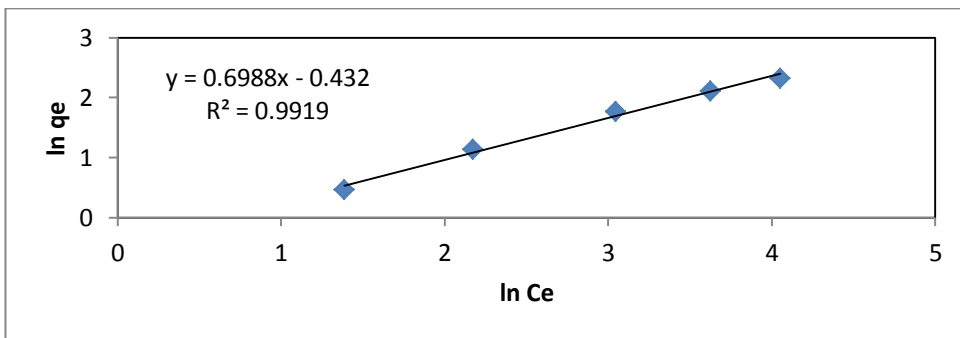


**Fig.7.Langmuir isotherm**

**(ii) Freundlich Isotherm:**

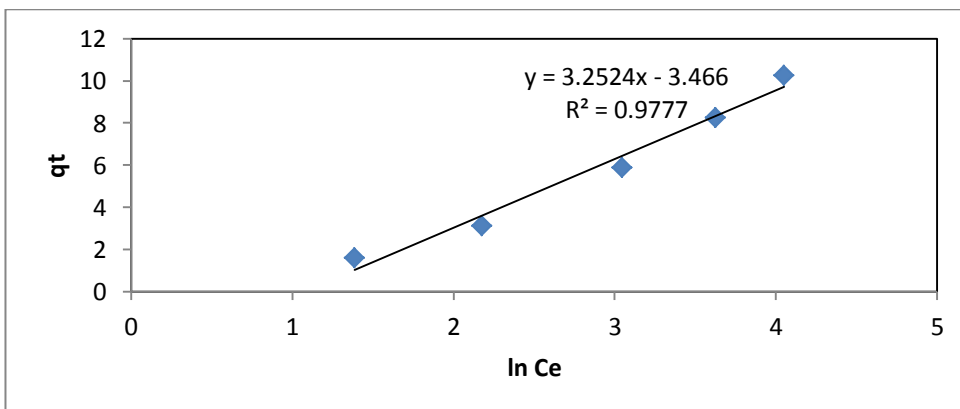
Fig.8, drawn between  $\ln C_e$  and  $\ln q_e$ , has resulted the equation:

$$\ln q_e = 0.698 \ln C_e - 0.432$$



**Fig. 8.Freundlich isotherm**

**(iii) Temkin Isotherm:**



**Fig. 9.Temkin isotherm**

The isotherm constants of the three isotherms are compiled in table-1. The equilibrium data are well explained by Langmuir isotherm (0.998), Freundlich isotherm (0.991) and Temkin (0.977) [20].

**Table -1 Isotherm constants (linear method)**

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
$q_m = 17.27138 \text{ mg/g}$	$K_f = 0.649209 \text{ mg/g}$	$A_T = 0.3445 \text{ L/mg}$
$K_L = 0.02513$	$n = 0.600508$	$b_T = 774.6439$
$R^2 = 0.998$	$R^2 = 0.991$	$R^2 = 0.977$

### Kinetics

The experimental data are tested for Lagergren first order rate equation and pseudo second order rate equation. Lagergren plot of  $\log(q_e - q_t)$  vs agitation time (t) is shown in fig.10. and pseudo second order kinetics plot between  $t$  vs  $t/q_t$  for biosorption of chromium is drawn in fig.11.

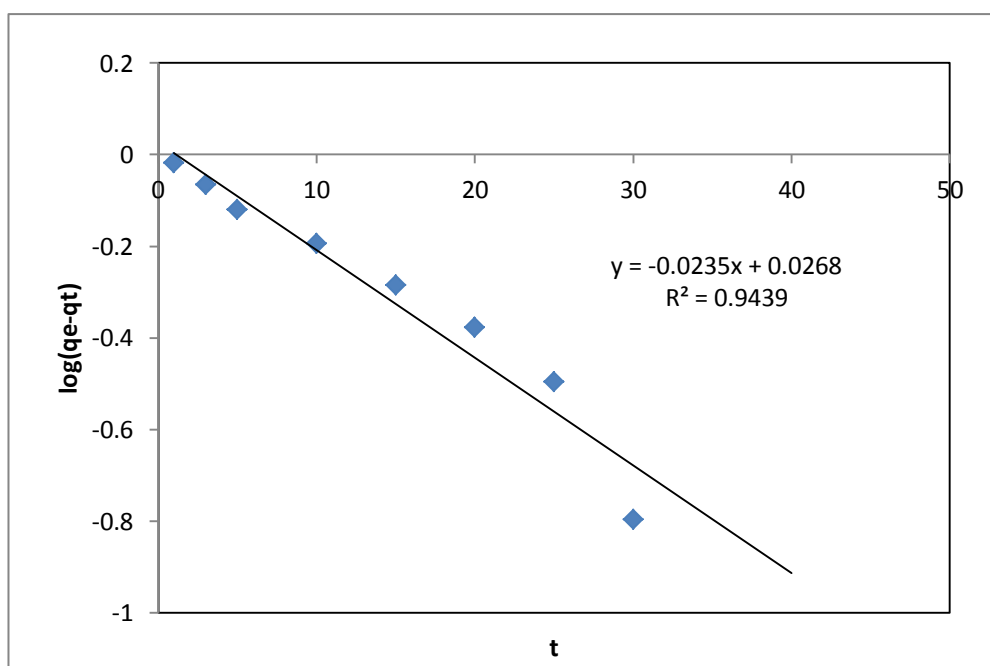
The equation obtained for Lagergren first order is  $\log(q_e - q_t) = -0.023 t + 0.026$

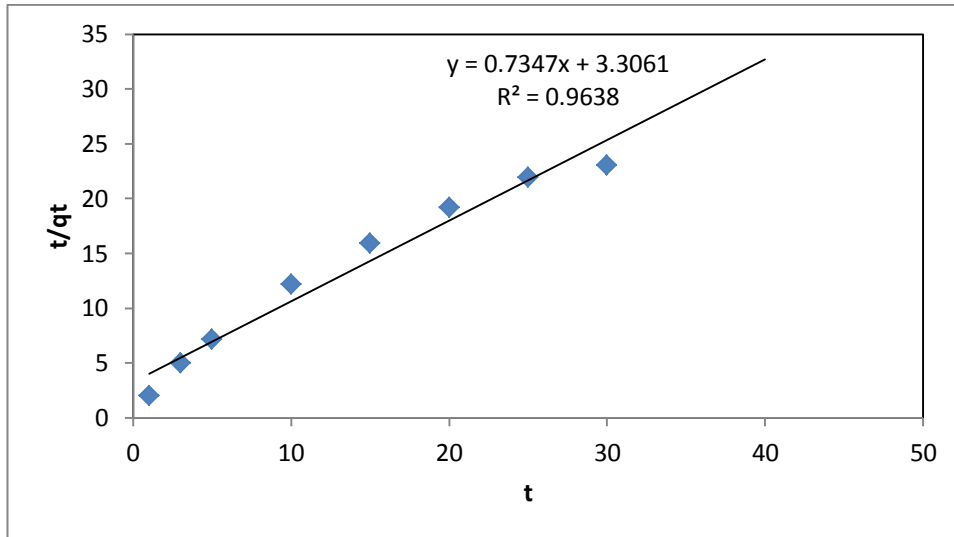
The equation obtained for pseudo second order is  $t/q_t = 0.734 t + 3.306$

Table-2 summarizes rate constant values for first and second order rate equations. It is noted that both first and second order rate equations explain the biosorption interactions [21].

**Table-2 Equations and rate constants**

Order	Equation	Rate constant	$R^2$
Lagergren first order	$\log(q_e - q_t) = -0.023 t + 0.026$	$0.052969 \text{ min}^{-1}$	0.943
Pseudo Second order	$t/q_t = 0.734 t + 3.306$	$0.1629 \text{ g}/(\text{mg}\cdot\text{min})$	0.963

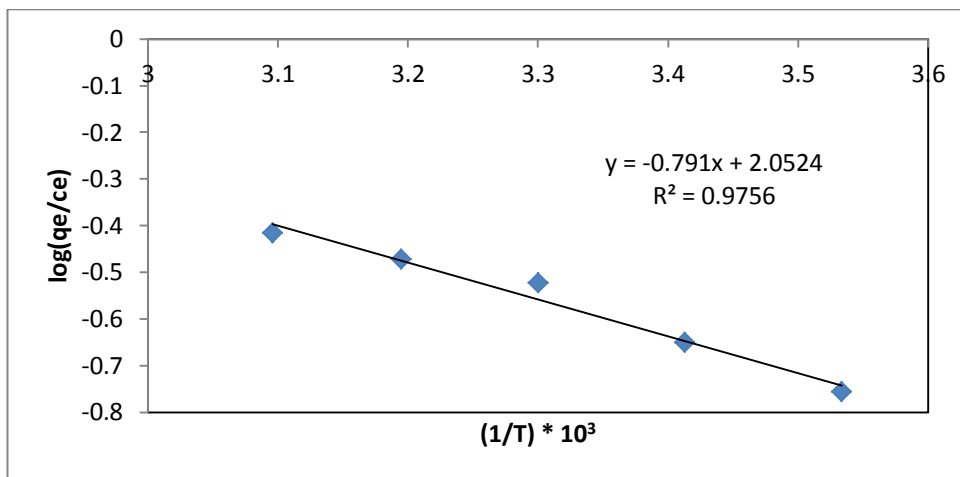
**Fig. 10. First order kinetics for biosorption of chromium**



**Fig.11.Second order kinetics for biosorption of chromium**

### Thermodynamics:

A progression of thermodynamic parameters - change in Gibbs free vitality ( $\Delta G$ ) change in enthalpy ( $\Delta H$ ) and change in entropy ( $\Delta S$ ) are resolved.  $\Delta G$  estimation of  $-11889.7$  J/mole shows that biosorption of chromium by *Madhuca indica* leaves powder could happen suddenly. Higher temperatures have profited biosorption and expanded the harmony biosorption limit. Positive  $\Delta H$  of  $15.14539$  J/mole shows demonstrates endothermic nature of biosorption while positive  $\Delta S = 39.28994$  J/mole-K demonstrates the liking of *Madhuca indica* leaves powder to chromium[21].



**Fig. 12.Vant Hoff's plot for biosorption**

### Conclusion:

In this paper the expulsion of chromium on *Madhuca indica* leaves powder has been explored. The chromium discharge handle is in a general sense influenced by different process parameters, especially, pH, adsorbent estimation, metal particle fixation and contact time. Most conspicuous clearing of chromium on *Madhuca indica* leaves powder was at pH 4.0. chromium sorption concurs Langmuir appear and took after the Freundlich ,Temkin models. Pseudo second request show has lit up the chromium sorption more successfully than first request.

**References:**

1. P. Malakul, K. R. Srinivasan, H.Y.Wang, "Metal biosorption and desorption characteristics of surfactant modified clay complexes, *Ind. Eng. Chem. Res.* 37 (1998) 4296-4301.
2. D. Mohan, K.P. Singh, "Single and multi-component biosorption of cadmium and zinc using activated carbon derived from bagasse -an agricultural waste, *Water Res.*36(2002)2304-2318.
3. A.Sari, M. Tuzen, M. Soylak, "Biosorption Of Pb(II) and Cr(II) from aqueous solution on Celtek clay, *J. hazard. Mater. B* 141 (2007) 258-263.
4. P.Xiangliang, W. Jianlong, Z.Daoyong, " Biosorption of Pb(II) by pleurotus ostreatus immobilized in calcium alginate gel, *Process Biochem.* 40 (2005) 2799-2803.
5. K Kumaraswamy, BV Dhananjayulu , P Vijetha and Y Prasanna Kumar, "Kinetic and Equilibrium Studies For the Removal of Chromium Using Eggshell Powder", *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, January - February 2015 RJPBCS 6(1) Page No. 529–536.
6. Kim, Cha Young, Hyung-Min Choi, and Hyeon Tae Cho. "Effect of deacetylation on sorption of dyes and chromium on chitin." *Journal of applied polymer science* 63.6 (1997): 725-736.
7. Deepa, K. K., et al. "Sorption of Cr (VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillusflavus*." *Chemosphere* 62.5 (2006): 833-840.
8. Romero-Gonzalez, J., et al. "Determination of thermodynamic parameters of Cr (VI) adsorption from aqueous solution onto *Agave lechuguilla* biomass." *The Journal of chemical thermodynamics* 37.4 (2005): 343-347.
9. Isaacson, Peter J., and Charles R. Frink. "Nonreversible sorption of phenolic compounds by sediment fractions: the role of sediment organic matter." *Environmental science & technology* 18.1 (1984): 43-48.
10. Schmuhl, R., H. M. Krieg, and K. Keizer. "Adsorption of Cu (II) and Cr (VI) ions by chitosan: Kinetics and equilibrium studies." *Water Sa* 27.1 (2004): 1-8.
11. Lin, Su-Hsia, and Ruey-Shin Juang. "Heavy metal removal from water by sorption using surfactant-modified montmorillonite." *Journal of Hazardous Materials* 92.3 (2002): 315-326.
12. Fiol, Núria, Carlos Escudero, and Isabel Villaescusa. "Chromium sorption and Cr (VI) reduction to Cr (III) by grape stalks and yohimbe bark." *Bioresource Technology* 99.11 (2008): 5030-5036.
13. Gao, Hui, et al. "Characterization of Cr (VI) removal from aqueous solutions by a surplus agricultural waste—rice straw." *Journal of Hazardous Materials*150.2 (2008): 446-452.
14. Zheng, Hong, et al. "Sorption isotherm and kinetic modeling of aniline on Cr-bentonite." *Journal of hazardous materials* 167.1 (2009): 141-147.
15. Bai, Sudha, and T. Emilia Abraham. "Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*." *Bioresource Technology* 79.1 (2001): 73-81.
16. Manceau, A., et al. "Sorption and speciation of heavy metals on hydrous Fe and Mn oxides. From microscopic to macroscopic." *Applied Clay Science*7.1-3 (1992): 201-223.
17. Stewart, M. A., et al. "Influence of soil geochemical and physical properties on the sorption and bioaccessibility of chromium (III)." *Journal of Environmental Quality* 32.1 (2003): 129-137.
18. Qaiser, Suleman, Anwar R. Saleemi, and Muhammad Mahmood Ahmad. "Heavy metal uptake by agro based waste materials." *Electronic Journal of Biotechnology* 10.3 (2007): 409-416.
19. Gil, R. A., et al. "Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination." *Talanta* 68.4 (2006): 1065-1070.
20. Schroeder, David C., and G. Fred Lee. "Potential transformations of chromium in natural waters." *Water, Air, and Soil Pollution* 4.3-4 (1975): 355-365.
21. Chien, S. H., and W. R. Clayton. "Application of Elovich equation to the kinetics of phosphate release and sorption in soils." *Soil Science Society of America Journal* 44.2 (1980): 265-268.

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