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Kinetic, Thermodynamic and Equilibrium Studies for the Biosorption of Chromium from an aqueous solution on to *Ipomeapalamata* Leaves powder.

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ABSTRACT

The present study investigates the budding of Ipomeapalmata leaves powder on biosorption of chromium metal present in an aqueous solution. The effects of various parameters (Time,pH,Dosage,Size,Concentration& Temperature) on biosorption of chromium are studied. The obtained results followed the both first order and second order kinetics. The experimental data gave good fit with Freundlich isotherm followed by Langmuir and Temkinisotherms.
Keywords: Biosorption;Ipomeapalmate;Isotherms.

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INTRODUCTION

Enhanced industrial activity after the industrial revolution has led to the discharge of chemicals, which causes environmental and public health problems. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations[1,2]. The studies made on investigation of economic and effective methods for the removal of heavy metals have resulted in the development of new separation technologies. Biological treatment, ion exchange, coagulation, electrochemical operation and filtration are commonly applied to the treatment of industrial effluents [3,4].Biosorption is a process that uses inexpensive biomaterials to sequester metals from aqueous solutions and the biomaterials used in this process are termed as biosorbents.This present study investigates the budding of Ipomeapalmata leaves powder on biosorption of chromium metal present in an aqueous solution. The effects of various parameters on biosorption of chromium are studied. The experiments are carried out by agitating known volume of aqueous solution with a pre-weighed amount of dry Ipomeapalmata leaves powder for a pre-determined time interval in a batch operation. The various parameters studied areAgitation time (t), Biosorbent size (d_p), pH of the aqueous solution,Initial concentration of chromium in the aqueous solution (C_o), Biosorbent dosage (w),Temperature (T),Isotherms, Kinetics and Thermodynamics.

Preparation of Biosorbent:

In the present study Ipomeapalmata leaves were used as biosorbent. At first the Ipomeapalmata leaves were collected from near by angalakuduru village canal, Tenali. Later the Ipomeapalmata leaves were washed with distilledwater several times to remove impurities present on it and then they were kept under sunlight for about 2 to 3 weeks for complete drying. At last Ipomeapalmata leaves were ground and segregated around 5 different sizes using BSS. Afterward it was stored in air tightened container until required.

Effect of agitation time:

The equilibrium agitation time for % biosorption of chromium is determined by agitating 50mL of aqueous solution, containing 20 mg/L of chromium in the agitation time intervals of 1 to 180 min (3 h). The pH of the aqueous solution is 7. The % removal of chromium is drawn against agitation time in fig 1.

It is found from the plot that the % removal is significantly increased in the first 50 min of agitation. Beyond the agitation time of 50 min, the % removal is more or less constant. So the equilibrium agitation time for Cr biosorption is 60 min.

Effect of biosorbent size:

The results obtained for removal of Cr with change in biosorbent size are shown in fig.2. The percentage removal of Cr is gradually decreased with increasing biosorbentsize.The % removal is increased from 47.5 to 65.5 % (0.95 to 1.31 mg/g) as the biosorbent size decreases from 152 µm to 53 µm.

Effect of pH of the aqueous solution:

pH is an important controlling parameter in all the biosorption studies. A plot is drawn in fig.3 between % removal of Cr and pH of the aqueous solution. A significant increase in percentage removal of Cr is observed as pH is increased from 2 to 5 and decrease in % removal is noted as pH is increased from 5 to 8. The metal uptake capacity is increased from 1.14 mg/g to 1.46 mg/g as pH is increased from 2 to 5. Lower pH values depresses biosorption of Cr , which is due to competition of Cr ions with H+ ions for appropriate sites on the biosorbent outer surface. However, with increasing pH, this competition weakens and Cr ions replace H+ bound to the biosorbent for forming part of the surface functional groups such as – OH, - COOH etc.

Effect of initial Cr concentration in aqueous solution:

The effect of initial concentration of Cr in the aqueous solution on the percentage removal of chromium at equilibrium agitation time is shown in fig.4. The percentage removal is gradually decreased from 73 to 61.25 % (1.46 to 9.8 mg/g) by increasing Cr concentration from 20 to 160 mg/L.

Effect of biosorbent dosage:

Fig.5.represents the variation in percentage removal of Cr from the aqueous solution (pH = 5) with biosorbent dosage at equilibrium agitation time for d_p = 53 µm. The % removal is increased from 73 % to 88.5 % (1.46 to 0.3933 mg/g) as the dosage is increased from 0.5 to 2.25 g (10 to 45 g/L).

Effect of temperature:

The effect of temperature on the equilibrium metal uptake was significant. The effect of changes in the temperature on the chromium uptake is shown in Fig.6. When temperature was lower than 303 K, Chromium uptake increased with increasing temperature (81.0 to 88.5 %), but when temperature was over 303 K, the results slowed down and the increase is marginal (88.5 to 91 %).

Freundlich Isotherm

The Linearized Freundlich Isotherm equation is given as

$$\ln q_e = \ln K_f + n \ln C_e \quad \text{(i)} \qquad [5\text{-}9]$$

Langmuir Isotherm

The Linearized Langmuir Isotherm equation is given as

$$(C_e / q_e) = 1/bq_m + C_e/q_m \quad \text{(ii)} \qquad [5\text{-}9]$$

Temkin Isotherm:

Temkin and Pyzhev considered the effects of indirect biosorbate/ biosorbate interactions on biosorption isotherms. The heat of biosorption of all the molecules in the layer would decrease linearly with coverage due to biosorbate/ biosobate interactions.

$$q_e = (RT/ b_T) \ln(A_T) + (RT/b_T) \ln(C_e) \quad \text{(iii)} \qquad [5\text{-}9]$$

Kinetics of chromium biosorption using ipomea palmate leaves powder:

Pseudo first order

$$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303)\, t \quad \text{(iv)} \qquad [5\text{-}9]$$

Pseudo second order

$$(t/q_t) = (1/ Kq_e^2) + (1/q_e)\, t \quad \text{(v)} \qquad [5\text{-}9]$$

Thermodynamics of Cr biosorption:

Net enthalpy change (ΔH) of biosorption is related to (ΔG) and (ΔS) as

$$\Delta G = \Delta H - T (\Delta S) \quad \text{(vi)} \qquad [10]$$

The Van't Hoff's equation is

$$\log (q_e/C_e) = - \Delta H/(2.303RT) + \Delta S/ (2.303R) \quad \text{(vii)}$$

where (q_e/C_e) is called the biosorption affinity and is the ratio of the amount per unit mass at equilibrium concentration of the biosorbate (q_e) to the equilibrium concentration C_e.

These parameters are obtained by carrying out biosorption experiments at different temperatures.The data are plotted in fig.12 with log (q_e/C_e) as a function of (1/T).

The slopes and the intercepts of the plots are determined. ΔH and ΔS values are calculated from the slopes and intercepts. Slope is -ΔH/2.303R and Intercept is ΔS/2.303. Thermodynamic parameters obtained for biosorption of Cr ontoipomea palmate leaves powder are also compiled (ΔS=42.4109 , ΔH = 16.44739, ΔG=–12834.1).

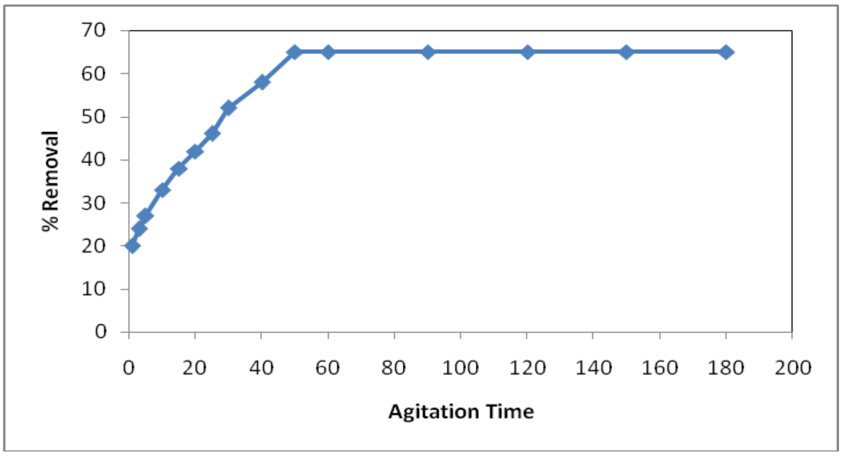

Fig.1. Effect of agitation time on % biosorption of chromium

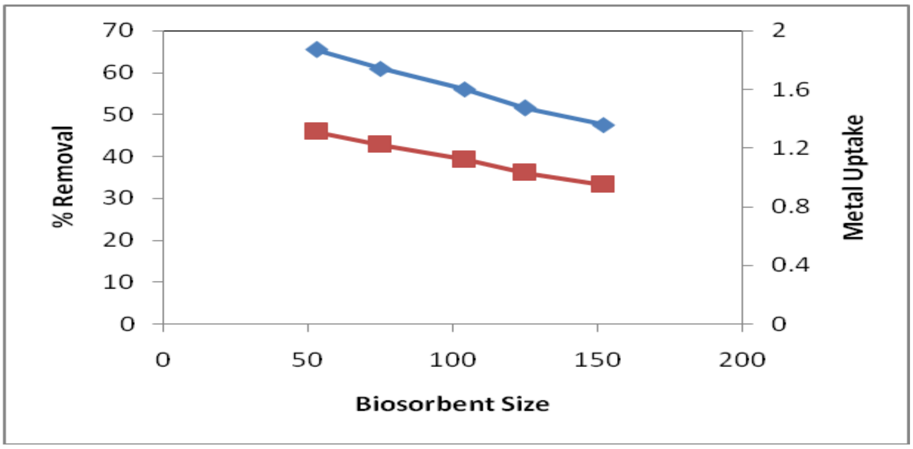

Fig 2. Effect of biosorbent size on % biosorption of chromium

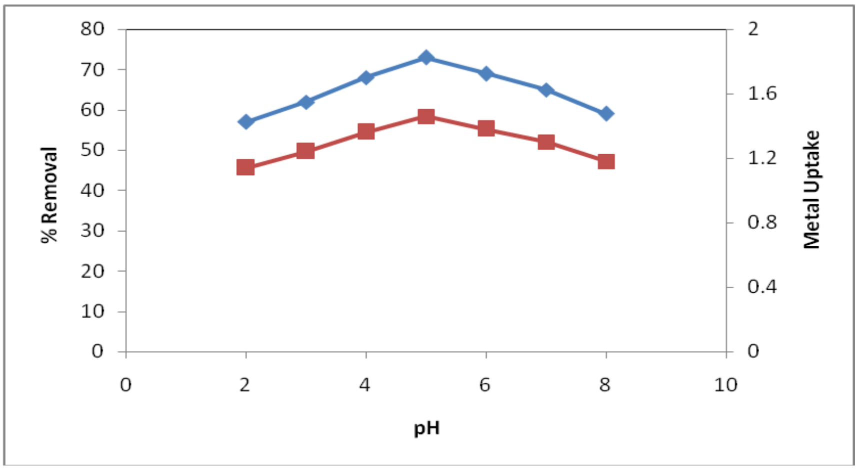

Fig. 3.Effect of pH on % biosorption of chromium

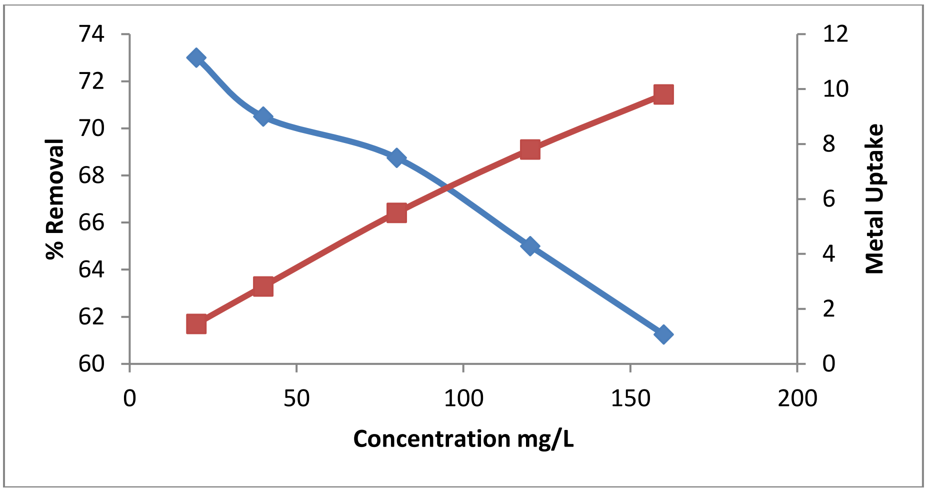

Fig.4.Effect of initial concentration of Cr for the biosorption of chromium

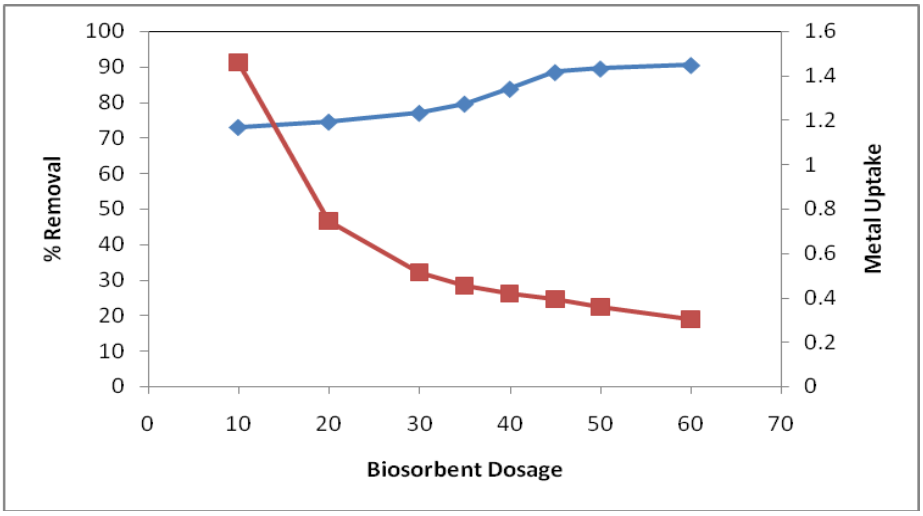

Fig. 5. Effect of biosorbent dosage on % biosorption of chromium

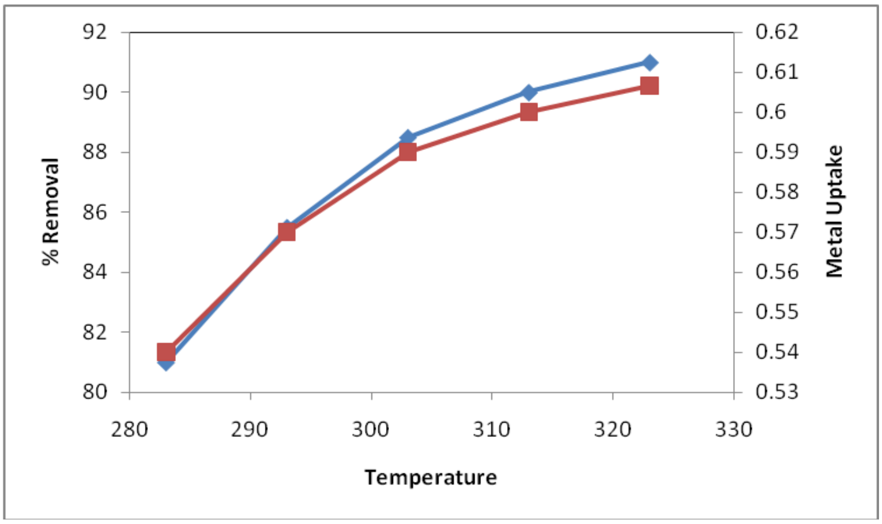

Fig.6. Effect of temperature for the biosorption of chromium

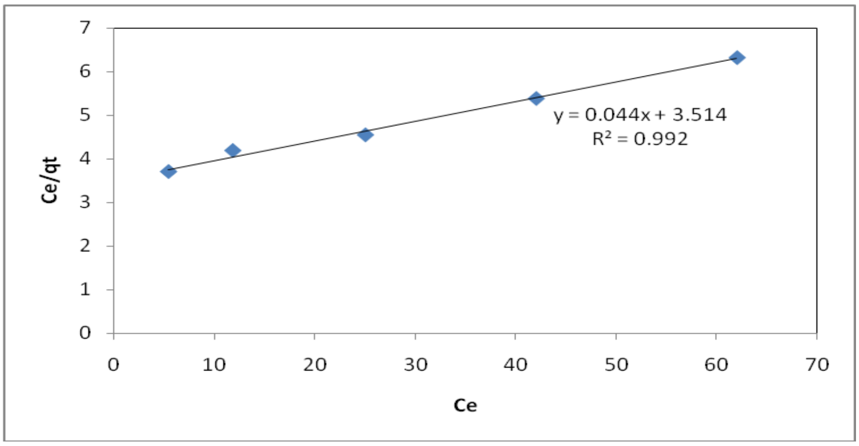

Fig. 7.Langmuir isotherm for biosorption of chromium

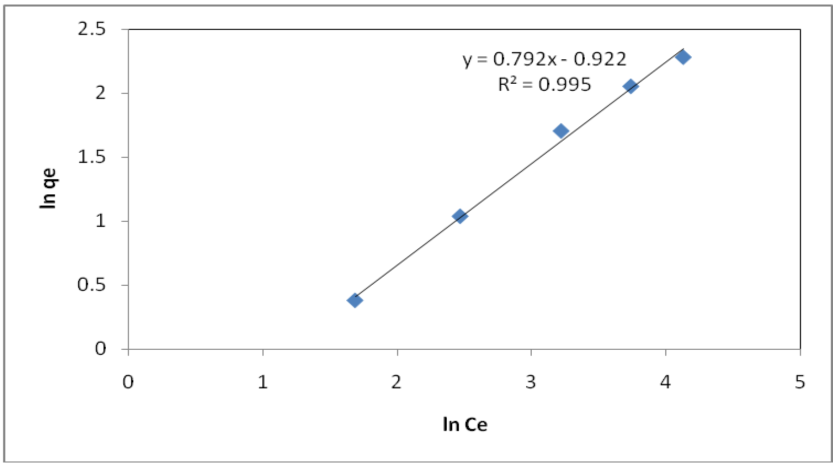

Fig.8.Freundlich isotherm for biosorption of chromium

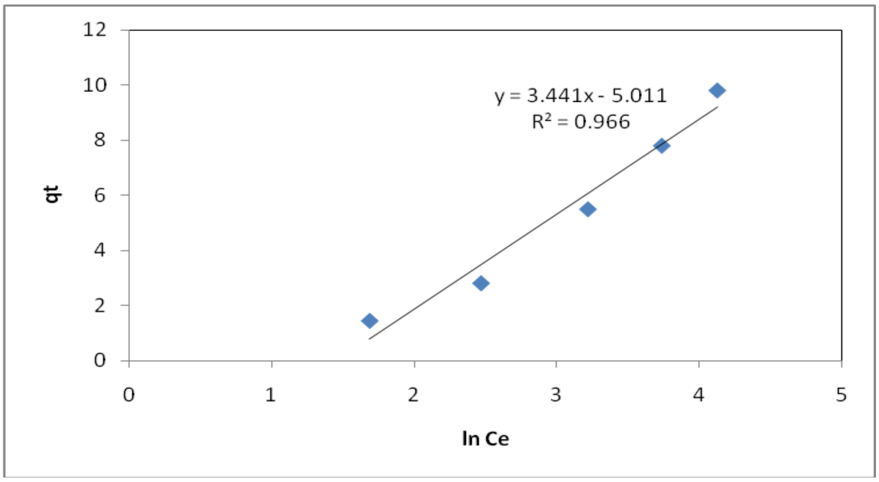

Fig. 9.Temkin isotherm for biosorption of chromium

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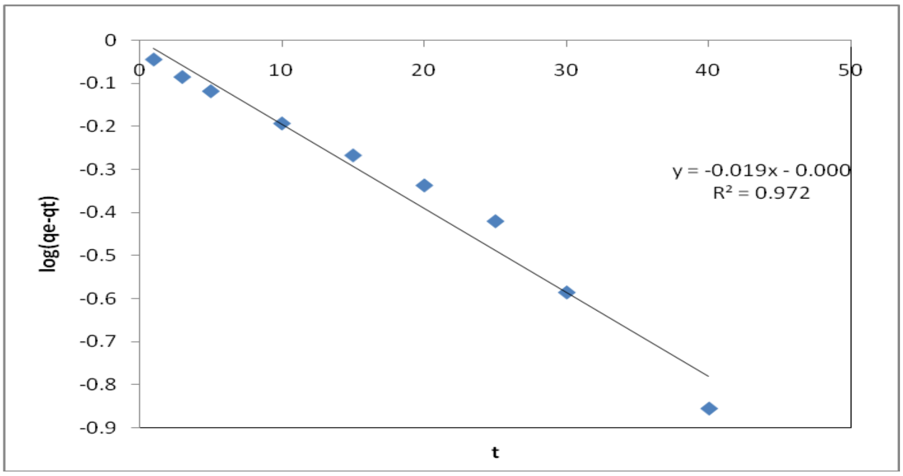

Fig.10. First order kinetics for biosorption of chromium

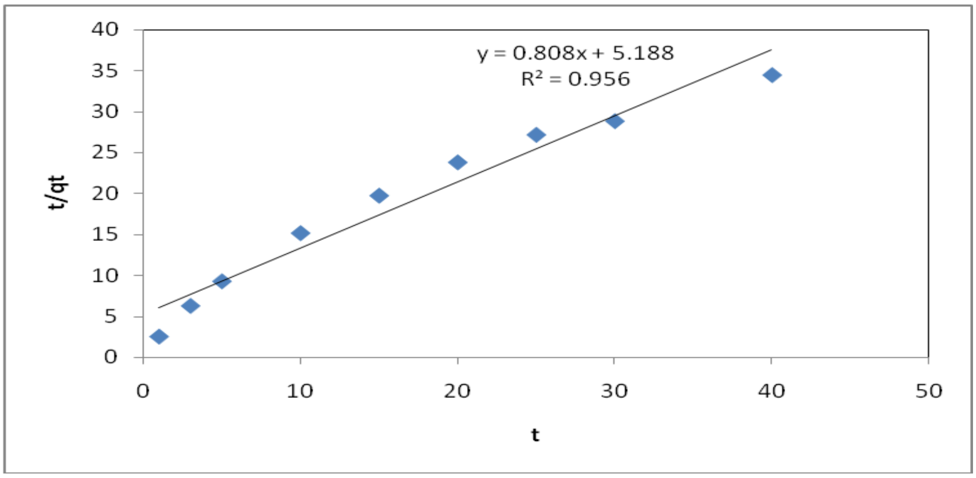

Fig.11. Second order Kinetics for biosorption of chromium

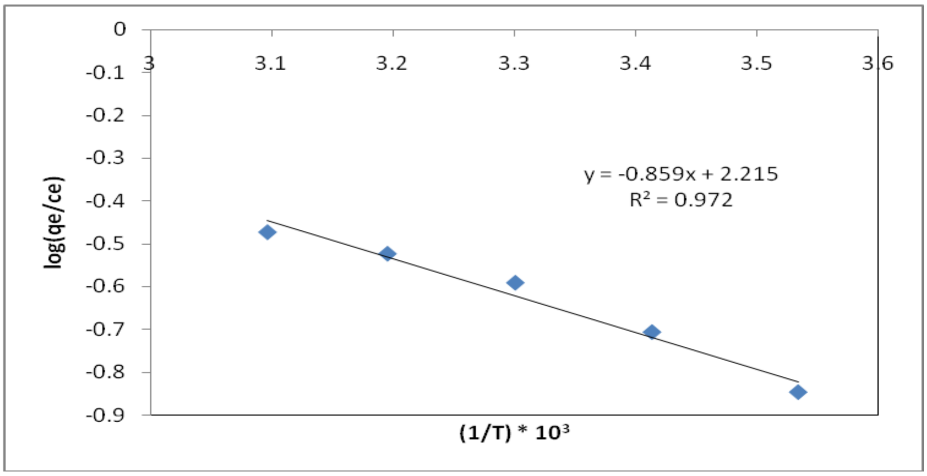

Fig.12. Vant Hoff's plot for biosorption

Freundlich isotherm	Langmuir isotherm	Tempkin
K_f = 0.3977 L/g	q_m = 22.727, mg/g	A_T = 0.233, L/mg
n = 0.6005, g/L	b = 0.01252, L/mg	b_T = 732.0959
R = 0.995	R = 0.992	R = 0.966

Table.1. Isotherm constants for ipomeapalmata leaves powder for chromium sorption

Order	Equation	K_{ad}, min^{-1}	R
LagergrenIst Order	$\log (q_e\text{-}q_t) = -0.019\ t + 0.518$	0.0437	0.972
Pseudo IInd order	$t/q_t = 0.808\ t + 5.188$	0.1258	0.956

Table.2. Kinetics and Equations

CONCLUSIONS

The practical results were systematically discussed on the study of removal of chromium from the aqueous solution of $K_2Cr_2O_7$ using Ipomea palmate leaves.

- Biosorption of chromium on to Ipomea palmate leaves showed that a contact time of 60 minutes was sufficient to achieve equilibrium.
- Biosorption of chromium decreases with increase in the initial concentration of chromium.
- Biosorption of chromium decreases with increasing particle size of egg shell powder.
- The amount of adsorbate adsorbed increases with the increasing the adsorbent dose.
- The experimental data gave good fit with Freundlich isotherm & the adsorption coefficient agreed well with condition of favorable adsorption.
- The 1^{st} order rate equation is best fitted with the adsorption process compared to 2^{nd} order rate equation.

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