

# Kinetic and thermodynamic study on the removal of methyl orange from aqueous solution by adsorption into pine cone

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## ABSTRACT

In this study, cone pine a forest solid waste, was used as an adsorbent for the removal of methyl orange from an aqueous solution. The influence of the initial dye concentration, pH, dosage of biosorbent and temperature were investigated in batch experiments. The kinetic study was modeled using the pseudo-first order, pseudo-second order and intra particle diffusion model. Among these models, the pseudo-second-order equation was the best applicable model to describe the sorption process. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the two models. Thermodynamic parameters such as  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were calculated. These parameters indicate that the sorption of the MO by cone pine is a spontaneous process and exothermic. The adsorbent was characterized using Fourier transform infrared spectroscopy and DRX. These results demonstrate that cone pine is effective in the removal of MO from aqueous solution.

**KEY WORDS:** Sorption, Methyl orange, Cone pine, Kinetic, Equilibrium, Thermodynamics.

## 1. INTRODUCTION

Accumulation of dyes in waste water from industries such as, paper, printing, pharmaceutical, textile cosmetic, and rubber has been regarded as a significant source of water pollution. Synthetic dyes and pigments have been considered as carcinogens and dangerous micropollutants even when they exist in trace amounts. Most of them have high water solubility and aromatic structure which make them non-biodegradable, non oxidisable and their removal from effluent by the use of conventional physic-chemical and biological processes is difficult. Reducing the organic micropollutants by adsorption on activated carbon remained for a long time and so far the most method used and effective (Santos, 2007; Joshi, 2004; O'Neill, 1999; Forgacs, 2004; Laasri, 2007). While activated carbon has many advantages (high adsorbing due to its large surface area), the chemical pre-oxidation with chlorine and the high cost of the periodic regeneration of materials led, since 1980, many laboratories to research new adsorbents based on natural materials (Padmesh, 2006; Bayramoglu, 2006; Mou, 1991; Allen, 2004; Bulut, 2006; Aksu, 2005; Senturk, 2010; Dogdu, 2009; Banat, 2007; Boubberka, 2005; Choy, 1999).

Natural materials, that are available in large quantities, may have an inexpensive potential sorbents. The abundance and availability of agricultural products is good sources of raw materials for activated carbons such as rice bran, sugar cane bagasse, coconut, sugar industry waste, nutshells, apple residues (Elbariji, 2006; Peterlene, 1999; Gupta, 2003).

In this study, the biosorbent was prepared from low cost adsorbent (pine cones) as a new adsorbent for the removal of methyl orange from aqueous solutions. The effect of different parameters such as temperature, contact time, the dose of adsorbent and the initial dyes concentration were studied. Kinetic data and equilibrium adsorption studies were carried out batch to understand the adsorption process.

## 2. MATERIALS AND METHODS

**2.1. Preparation of the adsorbate solution:** Reactive methyl orange ( $C_{14}H_{14}N_3NaO_3S$ ) is an anionic dye (Figure 1). It was used as received without further purification. In order to prepare a dye stock solution of (1000mg/l), 1.0g of M.O was weighed and dissolved in 1000ml of distilled water and suitably diluted to required initial concentration. The concentration of the dye was determined at 466nm using a double beam UV-Vis spectrophotometer (1605 shimadzu).

**2.2. Adsorbent preparation:** The cone pine were washed several times with distilled water and dried in air and soaked for 24h in a solution of  $H_2SO_4$  (10%). After decantation, the sample was washed with distilled water then was dried in an oven at 110°C overnight. The dried material was stored in desiccators.

**2.3. Equilibrium studies:** Batch adsorption experiments were carried out at room temperature (20°C) in 500ml glass-stoppered flask. 100ml of dye solution of different initial concentrations (5-100 ppm) was shaken at the constant agitation speed (200rpm) with a required dose of adsorbents (0.1g) in a mechanical shaker. After shaking the flasks for the corresponding equilibrium times, the residual concentration of dye was determined by using a double beam UV-Vis spectrophotometer (1605 Shimadzu) at 466nm.

The amount of dyes adsorbed at equilibrium onto the samples,  $Q_e$  (mg/g), was calculated by the following mass balance relationship:

$$Q_e = (C_o - C_e)V/m \dots\dots\dots(1)$$

Where  $C_o$  and  $C_e$  are the initial and equilibrium concentration of dye (mg/g) respectively.

**2.4. Kinetic studies:** The aqueous sample was taken at different time intervals and the concentration of dye was similarly measured. The amount of adsorption at time  $t$   $Q_t$  (mg/g) was calculated by:

$$Q_t = (C_o - C_t) V/m \dots\dots\dots (2)$$

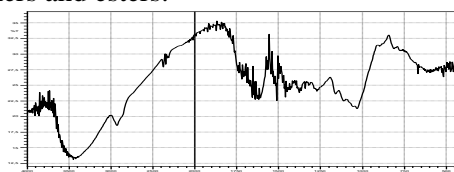
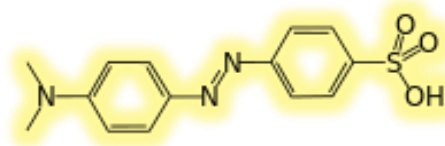
Where  $C_o$  and  $C_t$  (mg/l) are the liquid phase concentration of dye at initial and any time  $t$ , respectively,  $V$  is the volume of the solution (l) and  $m$  is the mass of adsorbent used (g).

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of the biosorbant:

**3.1.1. FTIR analysis:** To identify the functions of the biomass surface, the structure was observed by infrared spectroscopy. The spectrum obtained was showed in figure 2.

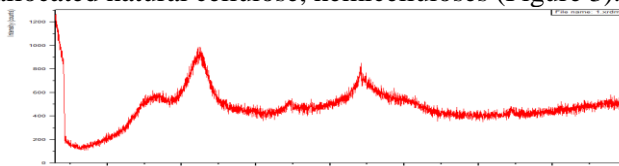
A strong absorption band was observed at round  $3400\text{cm}^{-1}$  and this is assigned to O-H stretching of carbonyl, phenols or alcohol or linked to amine groups N-H. Band at  $2800\text{cm}^{-1}$ ,  $2900\text{cm}^{-1}$  generally characterize the aliphatic CH stretching vibrations. The peak at  $1728\text{cm}^{-1}$  was attributed to C=O groups of carboxylic acids, acetate groups, ketone, aldehyde. The peak at  $1565\text{cm}^{-1}$  corresponds to an aromatic C-C stretching vibration. The band at  $1068\text{cm}^{-1}$  has been assigned to C-O stretching modes in alcohols, phenols, ethers and esters.



**Figure.1. Chemical structure of methyl orange (MO)**

**Figure.2. FTIR spectra of cone pine**

**3.1.2. X-Ray diffraction analysis:** The spectrum of the X-ray diffraction shows that this material is amorphous. The peak at  $2\theta=54^\circ, 53^\circ, 51^\circ, 32^\circ$  allocated natural cellulose, hemicelluloses (Figure 3).

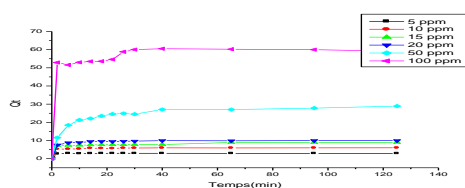


**Figure.3. X-ray diffraction of cone pine**

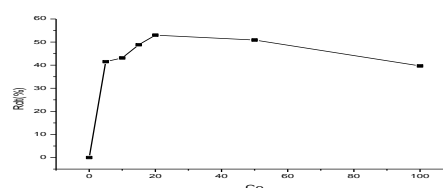
**3.2. Effect of operating conditions:** The efficiency of removal dye from aqueous solutions by the cone pine was experimentally studied by recording the adsorption isotherms, kinetic experiments, effects of temperature, effects of sorbent dosage and solution dosage.

**3.3. Effect of initial dye concentration on adsorption and contact time:** The influence of the initial concentration of MO on the dye removal capacity of cone pine was carried out at a fixed biosorbent dosage (0.1g), a pH 6 various dye concentration (5-100ppm) at different time intervals. From figure 4, it was observed that equilibrium uptake increased with the increase of initial metal concentration at the range of experimental concentration. This could be attributed to high mass transfer driving force generated by the initial dye concentration. The removal of MO sorbed after equilibrium was 2.814, 5.962, 7.320, 10.570, 27.05, 47.789 mg/g, respectively, at an initial concentration of 5, 10, 15, 20, 50, 100 ppm.

Also it is noticed that an increase in the initial MO concentration leads to a decrease in the metal removal (Figure 5). This is explained by the fact that at low concentrations the ratio of the active sites surface and the total dye in the solution is high, and therefore all the molecules may be retained by the adsorbent and eliminated from the solution. However, at high concentrations, the drive force due to the concentration gradient is higher, and the amount of MO adsorbed per unit mass of adsorbent  $Q_e$  is greater, which causes saturation of the support and thus an amount of dye remain free in solution giving a low yield. According, it can be concluded that the adsorbent is most effective for the wastewater in low dye concentrations and the purification efficiency can be increased by diluting the wastewater containing high concentrations.



**Figure.4. Dynamics of MO uptake by cone pine for various initial metal concentrations**



**Figure.5. MO concentration Vs metal removal**

**3.4. Effect of adsorbent dosage:** The study of removal of MO by cone pine from aqueous solutions was performed using the biosorbent in the range 0.1-2g using a dye solution concentration of 15 ppm, stirring speed (200 rpm), temperature (20°C) and pH 6 constant. The results are shown in figure 6. The amount of dye sorbet decreases from 7.822 to 0.361 mg/g with the increase in dose of adsorbent between 0.1g and 2g. The decrease in the amount of dye sorbed with increasing sorbent dosage is due to the split in the flux on the concentration gradient between dye concentration in the solution and on the sorbent surface.

**3.5. Effect of pH:** The effect of solution pH on the amount of MO sorbed was studied by varying the initial pH under constant process parameters at equilibrium conditions. From figure 7, it was observed that the sorption was strongly pH-dependent and reaches a maximum yield value of 88.22% at pH 2. This is can be explained by the fact that at low pH values (2-4), the number of negatively charged surface sites decreased and number of positively charged sites increased which increase the interaction of MO with sites of adsorbent. Whereas at high pH values (6-10) cone pine becomes negatively charged which decrease the retention of methyl orange then we can conclude that the molecule form has better retention then the anionic form.

**3.6. Effect of temperature:** The MO biosorption experiments were performed at different temperatures (20°C-40°C) for 15ppm of dye concentration. Figure.8 shows that the sorption capacity decreases with the increase in temperature. To confirm the adsorption nature and the inherent energetic changes involved during sorption, thermodynamic parameters were evaluated.

The thermodynamic constants, free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Therefore, the thermodynamic parameters were calculated from the variation of the distribution coefficient  $K_d$  with the change in temperature. The constant  $K_d$  for the adsorption reaction can be defined as:

$$K_d = Q_e/C_e \dots\dots\dots (3)$$

Where  $Q_e$  is the amount of MO sorbed at equilibrium (mg g<sup>-1</sup>),  $C_e$  is the concentration of dye at equilibrium solution (mg L<sup>-1</sup>). Values of  $K_d$  were therefore obtained by plotting  $\ln(Q_e/C_e)$  versus  $Q_e$  and extrapolating  $Q_e$  to zero. Its intercept give the values of  $\ln K_d$ . Therefore, the thermodynamic constants can be obtained from the following equations:

$$\Delta G = -RT \ln K_d \dots\dots\dots (4)$$

$$\ln K_d = -\Delta H/RT + \Delta S/R \dots\dots (5)$$

$\Delta H$  and  $\Delta G$  can be obtained from the slope and intercept of Van't Hoff plot of  $\ln K_d$  versus  $1/T$  (Seki, 2006). The data are presented in figure 9 and Table 1.

The negative  $\Delta G$  values confirm the spontaneous nature and feasibility of the adsorption process. The negative values of  $\Delta H$  further confirm the exothermic nature of the adsorption process, while the positive  $\Delta S$  values reflect the good affinity of MO to pine cone.

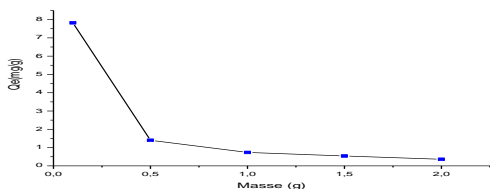


Figure.6.Effect of sorbent dosage on the sorption of MO by cone pine

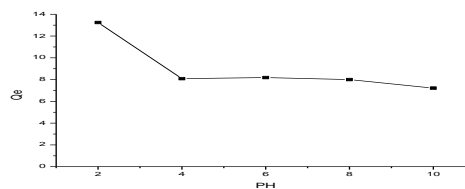


Figure.7.Effect of pH on the sorption of methyl orange by cone pine

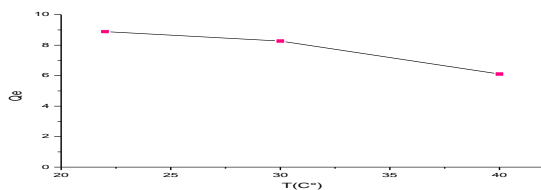


Figure.8.Effect of temperature on the sorption of methyl orange by cone pine

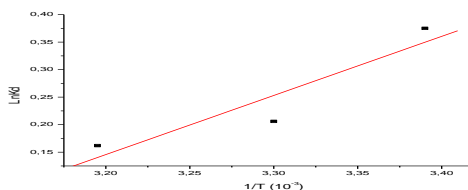


Figure.9.Plot of  $\ln K_d$  versus  $1/T$  for the determination of thermodynamic parameters

Table.1.Thermodynamic parameters for the sorption of methyl orange by cone pine

Parameter	Temperature °C		
	20	30	40
$\Delta G^\circ$ (KJ/mol)	-2.098	-1.448	-0.635
$\Delta H^\circ$ (KJ/mol)	-2.608	-2.608	-2.608
$\Delta S^\circ$ (J/mol)	-81.303	-81.303	-81.303

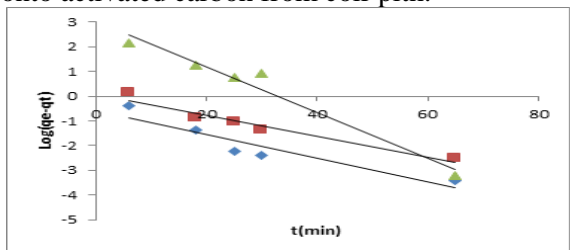
**3.7. Kinetics sorption:** Kinetic studies of adsorption are related to the adsorption mechanism and are necessary for optimizing the adsorption process [25]. Subsequently, three of the most common kinetic models, pseudo-first-order, pseudo-second-order and the intra-particle diffusion model were employed for evaluating the kinetic data. The linear form of the pseudo-first (Equation 6) and pseudo-second-order (Equation 7) models are as follows

$$\text{Log}(Q_e - Q_t) = \log Q_e - k_1 t/2.303 \dots \dots \dots (6)$$

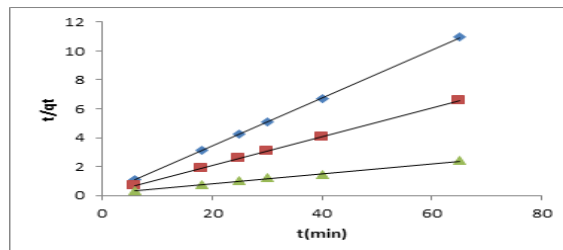
$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \dots \dots \dots (7)$$

Where  $Q_e$  and  $Q_t$  are the biosorption capacity at equilibrium and at time  $t$ , while  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the rate constants of the biosorption process of the pseudo-first-order and the second-order respectively. For the pseudo-first-order model, the values of  $Q_e$  and  $k_1$  were obtained from the intercept and slope of the plot of  $\log(Q_e - Q_t)$  versus  $t$  (Figure 10). However, in the case of the pseudo-first order model, we note that the  $R^2$  values are relatively low and between 0.875 and 0.963 and did not fit the experimental data well and thus eliminated from further discussion. For the pseudo-second-order model,  $Q_e$  was calculated from the intercept and slope of the plot of  $t/Q_t$  versus  $t$ , which is shown in Figure 11. The fitted experimental results for the pseudo-first order and the pseudo-second models are presented in Table 2. The correlation coefficients ( $R^2$ ) for the pseudo-second order model were higher than the  $R^2$  of the pseudo-first-order model and the calculated  $Q_e$  values were in good agreement with the data from the experiments. These results indicated that the rate of MO adsorption on pine cone is of the pseudo-second-order and that the overall rate of the dye adsorption process appears to be controlled by the chemisorption process (Hoy, 1998).

Furthermore, according to the table 2, the values of  $K_2$  decrease significantly by increasing the dye concentration. This trend suggesting that the mass transfer was the rate limiting step of the adsorption and the rate of dye mass transfer to pine cone is enhanced by increasing the dye concentration. Similar phenomena have been observed in the adsorption of direct dyes onto activated carbon prepared from sawdust and adsorption of congo red dye onto activated carbon from coir pith.



**Figure.10.Pseudo-first-order kinetics of methyl orange sorption by cone pine at different initial dye concentration**



**Figure.11.Pseudo-second-order kinetics of methyl orange sorption by cone pine at different initial dye concentration**

**Table.2.Comparison of the pseudo-first-order ( $K_1$ ) and pseudo-second-order ( $K_2$ ) parameters for the sorption of methyl orange at various initial concentrations**

Co (mg/l)	Qe exp(mg/g)	Pseudo-premier- order			Pseudo-second-order		
		$K_1$ (min-1)	Qe calc (mg/g)	$R^2$	$K_2$ (min-1)	Qe calc (mg/g)	$R^2$
10	5.9622	0.1082	0.582	0.875	0.2169	6.024	0.999
20	9.93	0.0967	1.0768	0.942	0.11139	10.10	0.999
50	27.05	0.2279	1.1121	0.963	0.00889	29.41	0.998

**3.8. Sorption mechanism:** The biosorption process can also be expressed by the momentum of the dye molecules from the aqueous solution to the surface of the biosorbent, which takes place in several stages, commencing with diffusion of the dye onto the biosorbent surface, intra-particle diffusion and the sorption of solution into the interior part and the smaller pores of the biosorbent and finally sorption of molecules into the capillaries followed by the establishment of equilibrium. The intra-particle diffusion kinetic equation can be written as follows:

$$Q_t = k_i t^{1/2} + c \dots \dots \dots (8)$$

Where  $k_i$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the intra-particle diffusion rate constant and  $c$  is the intercept, related to the thickness of the boundary layer. The values of  $c$  and  $k_i$  are obtained from the intercept and slope of the plot of  $Q_t$  versus  $t^{1/2}$ .

The plots of intra-particle diffusion of MO onto pine cone at different initial dye concentrations are represented in Figure 12. The  $k_i$  values were obtained from the slope of the linear portions of the curve of different initial concentration and shown in table 3. The coefficient of regression values for this diffusion model was between 0.847 and 0.752. Whereas the plot did not pass through the origin, the plots have intercepts in the range 5.171-16.14 $\text{mgg}^{-1}$ , this is show that the intraparticle diffusion is not the only rate limiting step, but also other kinetic mechanisms may control the rate of sorption. The value of the intercept gives an idea about the boundary layer

thickness. As can be seen in table 3, the value of c increases with increasing concentration suggesting the abundance of solute in the boundary layer.

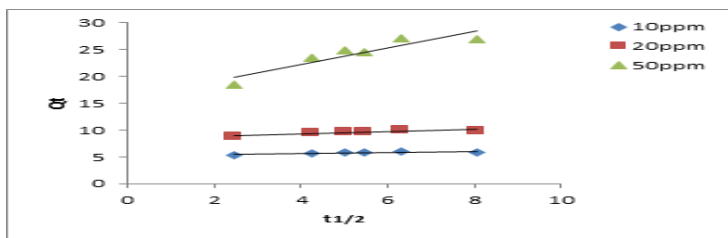


Figure.12. Intraparticle diffusion plot for the sorption at different initial dye concentrations

Table 3: Intraparticle diffusion parameters for the sorption of methyl orange at various initial concentrations

C <sub>0</sub> (mg/l)	k <sub>id</sub> (mg/gmin)	c(mg/g)	R <sup>2</sup>
10	0.113	5.171	0.752
20	0.193	8.537	0.783
50	1.536	16.14	0.847

**3.9. Biosorption equilibrium:** Isotherms represent the interaction between the sorbate and biosorbent. Subsequently, two of the most common adsorption isotherms, Langmuir and Freundlich were employed in this study. The amount of MO adsorbed at a state of equilibrium (Q<sub>e</sub>) (mg/g) was calculated using the following equation (Sag, 2000).

$$Q_e = V (C_0 - C_e)/m \dots \dots \dots (9)$$

Where C<sub>0</sub> (mg/l) is the initial MO concentration, C<sub>e</sub> (mg/l) the equilibrium concentration of MO solution, V (l) the volume of MO solution, and m (g) is the mass of adsorbent. The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites (Hayward et al., 1964). If MO adsorption conforms to the Langmuir model, the adsorption process can be expressed as:

$$C_e/Q_e = 1/(K_L \cdot Q_m) + C_e/Q_m \dots (10)$$

Where Q<sub>m</sub> (mg/g) is the maximum adsorption capacity and K<sub>L</sub> (l/g) is the Langmuir constant related to the adsorption equilibrium. The essential characteristics of the Langmuir isotherm can be expressed by means of ‘R<sub>L</sub>’ a dimensionless constant referred to as the separation factor or equilibrium parameter. The R<sub>L</sub> is defined as:

$$R_L = 1/(1+K_L \cdot C_0) \dots \dots \dots (11)$$

This parameter suggests the type of isotherm to be irreversible (R<sub>L</sub>=0), favorable (0<R<sub>L</sub><1), linear (R<sub>L</sub>=1), or unfavorable (R<sub>L</sub>>1). The calculated R<sub>L</sub> values versus initial MO concentration were represented in figure 13. As can be seen from Table 4, at all concentrations the R<sub>L</sub> values are between 0 and 1, indicating that the adsorption of MO onto pine cone is favorable.

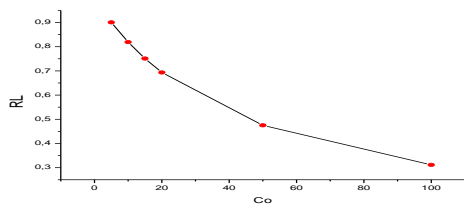
The Freundlich model is usually adopted for heterogeneous adsorption. One of its limitations is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. This isotherm can be described as:

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \dots \dots \dots (12)$$

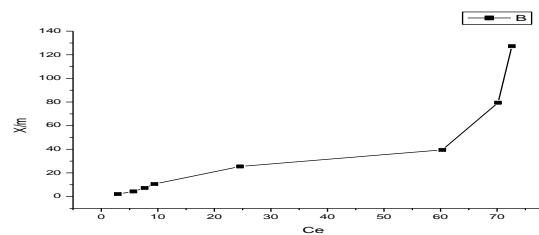
Where K<sub>F</sub> (mg<sup>1-1/n</sup>·l<sup>1/n</sup>/g) and n are the physical constants of the Freundlich isotherm, K<sub>F</sub> and n are indicators of an adsorption capacity and an adsorption intensity respectively, and n being a constant representing the mutual interaction of adsorbed species. Experimental values of n are usually greater than unity and this means that the forces between the adsorbed molecules are repulsive. The value of Freundlich exponent n in the range 1-10 indicates the favorable sorption. Figure 14 shows adsorption isotherms of MO adsorbed onto cone pine. This is of type II according to the classification of Brunauer and al. The equilibrium data were fitted to the Langmuir and Freundlich models (Figures 15, 16). The isotherm parameters for the adsorption of MO onto pine cone obtained are listed in Table 4. The results show that the retention of MO by the biosorption follows the two studied models.

Table.4. Parameters of the Langmuir and Freundlich isotherm models

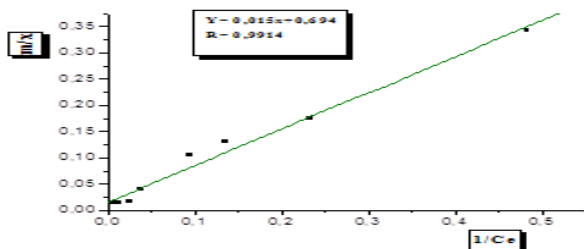
Langmuir			Freundlich		
Q <sub>m</sub> (mg/)	K <sub>L</sub>	R <sup>2</sup>	n	K <sub>F</sub>	R <sup>2</sup>
64,935	0,0221	0,0221	2,2967	2,2967	0,9809



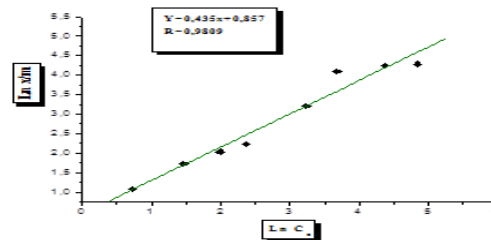
**Figure.13. Separation factor for the uptake of methyl orange by cone pine**



**Figure.14. Adsorption isotherm**



**Figure.15. Langmuir adsorption isotherm of methyl orange onto cone pine**



**Figure.16. Freundlich adsorption isotherm of methyl orange onto cone pine**

#### 4. CONCLUSION

In this study, cone pine was evaluated as a biosorbent for the removal of an anionic dye from aqueous solution. Experimental data indicated that the sorption capacity was dependent on operating variables such as: initial metal concentration, contact time, sorbent dosage, solution pH and temperature. Removal efficiency increased with the initial dye concentration and decreased as the mass of biosorbent increased. The process was strongly pH dependent. Kinetic measurements showed that the sorption process was rapid and the adsorption mechanism can be described by a pseudo kinetic second-order. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium of methyl orange dye onto adsorbent. The data were in good agreement with both Langmuir and Freundlich isotherms. The  $R_L$  values showed that the pine cone was favorable for the sorption of MO. The negative values of free energy change and enthalpy change indicated that the MO sorption process is spontaneous and exothermic.

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