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## Removal of methylene blue from aqueous solution onto a new cheap adsorbent (*Araucaria cookii* bark powder)

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### ABSTRACT

In the present investigation, the biosorption is carried out to test the suitability of abundantly available plant based material *Araucaria cookii* bark powder as a biosorbent for removal of methylene blue dye from aqueous solution. The equilibrium studies were systematically carried out in a batch process, covering various process parameters that include contact time, adsorbent size and dosage, initial dye concentration and pH of the aqueous solution. It observed that there is a significant increase in percentage removal of methylene blue as pH increases from 2 to 4 and then decreases from 4 to 10. The optimum pH and contact time was found to be 4 and 15 minutes respectively. Equilibrium isotherm data were analyzed using the Langmuir, Freundlich and Temkin isotherms. The Freundlich model yields a much better fit than the other two models. In order to investigate the mechanism of sorption, kinetic data were modeled using the pseudo- first-order and pseudo-second-order models. Pseudo-second-order equation was the best applicable model to describe the sorption process. The maximum adsorption capacity of adsorbent was 91.46 mg/g

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### KEYWORDS

*Araucaria* cookie;  
Adsorption isotherms;  
Kinetic studies;  
Dye removal.

### INTRODUCTION

Colored materials and dyes constitute the focus of many environmental concerns because of their non-biodegradable and polluting nature<sup>[8,34]</sup>. Thus, prior to their discharge into receiving waters, there is a considerable need to treat colored effluents efficiently<sup>[19,26,27]</sup>.

The conventional methods for treating dye containing wastewaters are electrochemical treatment<sup>[9,13]</sup>, coagulation and flocculation<sup>[29]</sup>, chemical oxidation<sup>[24]</sup>, liquid-liquid extraction<sup>[21]</sup> and adsorption<sup>[20,32]</sup>. Adsorption has been shown to be an effective way for remov-

ing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.

Consequently recent research work has been focused towards alternative low cost adsorbents for the sorption of dyes on to media, namely agricultural solid waste<sup>[22]</sup>, sand<sup>[28]</sup>, cellulose based waste<sup>[14]</sup>, palm kernel fibre<sup>[4]</sup>, dead fungal biomass like *funalia trogii*<sup>[6]</sup>, fly ash<sup>[30]</sup>, cephalosporium aphidicola cells<sup>[16]</sup>, aspergillus niger<sup>[31]</sup> etc., have been studied.

In the present work, *Araucaria cookii* bark (ACB) was used as low cost adsorbent for removing methylene

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blue (MB) from aqueous solutions. Being cheap precursor, it has been used as biosorbent. Several process parameters such as contact time, pH, initial dye concentration, average particle size and biosorbent dosage were explored. The rate limiting step of the basic dye onto the biosorbent was determined from the adsorption kinetic results. The sorption equilibrium data were analyzed using Langmuir, Freundlich and Temkin isotherms.

## METHODS

### Adsorbent preparation

The *Araucaria cookii* bark used in the present study was collected from the GMR Institute of Technology, Rajam. The collected bark was washed with deionized water several times to remove dirt particles and sun dried for 30 days. The resulting product was directly used as biosorbent. The bark was then powdered using domestic mixer. Particles with 81-211.5 $\mu$ m size were used for the experiment.

### Reagents and equipments

All chemicals used in this work were of analytical reagent grade and were used without further purification. The concentrations of the dye before and after sorption were determined using UV-visible spectrophotometer by monitoring the absorbance for the dye used.

### Batch decolorization operation

The biosorption experiment of the ACB were carried out in 100ml conical flasks containing 0.1g of the biosorbent in 30ml of methylene blue solution (20–100 ppm) separately at room temperature on a rotary shaker at constant agitation speed. The effect of pH on biosorption rate was investigated in a pH range of 2.0-10 (which was adjusted with 0.1N HCl or 0.1N NaOH at the beginning of the experiment) the effect of biosorbent dosage was studied in the range of 0.02-0.1g. For optimization of contact time for biosorption of MB, 30 ml of dye solution with a desired dosage of the biosorbent were agitated at a desired rpm. Samples were collected at definite time intervals, filtered and residual dye concentration in the filtrates were analyzed by UV Spectrophotometer. Batch experiments investigating the effects of initial dye concentration varied from 20 to 100mg/l. The dye solutions were filtered after the

desired contact time and MB concentrations in the filtrate were determined. Each experiment was repeated three times and the results are given as averages. The percent biosorption of MB was calculated as follows:

$$\% \text{ Biosorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

## RESULTS AND DISCUSSIONS

### Effect of contact time

The experimental results reveal that the uptake of dye is faster at initial stages of contact and it becomes slower at equilibrium. This is due to the availability of a large number of vacant sites for adsorption during initial stages and remaining vacant sites are difficult to be occupied at later stages of adsorption, and also most likely due to repulsive forces between the solute molecules on the adsorbent and aqueous solution.

Figure 1 shows the time for adsorption of MB from aqueous solutions containing various concentrations of MB. It is evident from these figures that the adsorption equilibrium is established within 15min. This shows that the adsorption is quite fast. Such rapid adsorption process has been correlated with the characteristics of the biomass and its physico-chemical interactions with the dye ions. The rapid dye uptake is also desirable for the success of biosorbent for practical applications. There

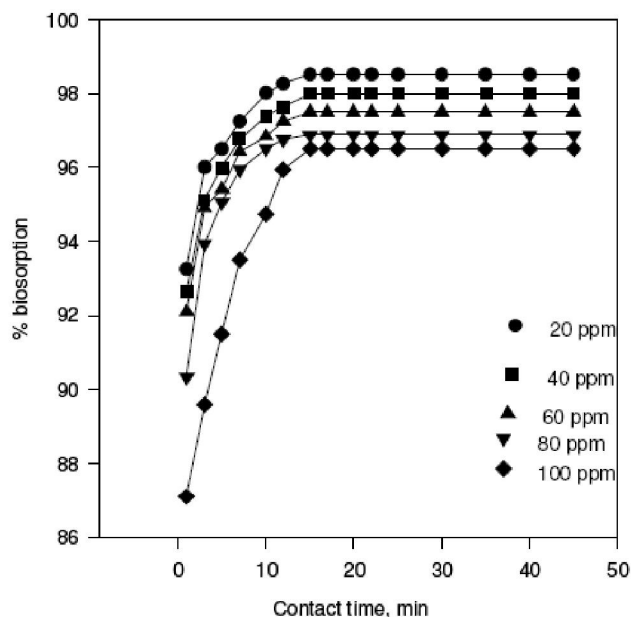


Figure 1 : Effect of contact time on % adsorption of MB for 0.1g of adsorbent/30ml solution

is no significant change in the amount of adsorbed dye ion with further increase in contact time after attaining equilibrium and the contact time corresponding to equilibrium is fixed as optimum contact time. The percentage adsorption increased from 93.25 to 98.5% for MB for 1 min to optimum contact time 15min with 20mg/l of aqueous solution.

### Effect of pH

The pH of an aqueous medium is an important factor that may affect the uptake of the adsorbate. The chemical characteristic of both adsorbate and adsorbent vary with pH. Studies were carried out to see the effect of pH in the range of 2-10. The effect of pH on the % removal of dye at 20 to 100mg/l using ACB was shown in figure 2.

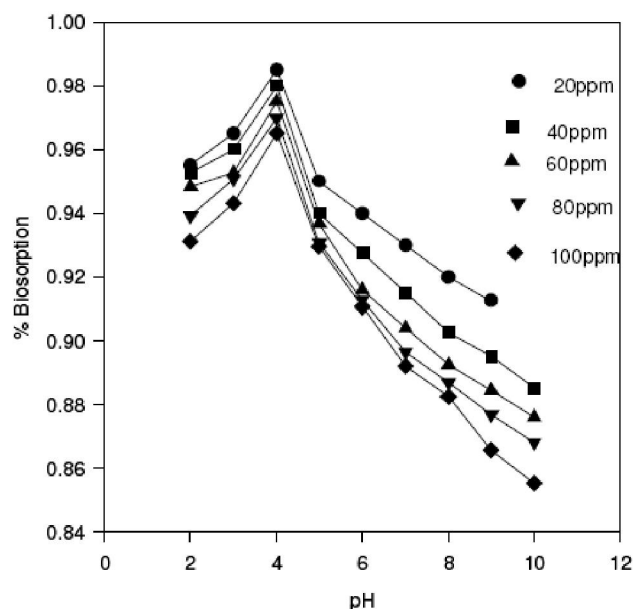


Figure 2 : Effect of pH on % adsorption of MB for 0.1g of adsorbent

The high adsorption yield was obtained at pH 4. The maximum adsorption efficiency was 98.5% at pH 4 and this pH value was selected as optimum pH for further studies. Lower adsorption of methylene blue at low pH is probably due to the presence of H<sup>+</sup> ions competing with the cations groups on the dye for adsorption sites. As surface charge density decrease with an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of the activated carbon is lowered, this may result in an increase in the rate of adsorption.

### Effect of initial concentration of dye

Experiments were undertaken to study the effect of the initial concentration on kinetics of MB removal from the solution. The results obtained are shown in Figure 3. The obtained curves show that the metal uptake increases with increase in initial concentration of dye while the percentage biosorption of MB decreases with an increase in initial dye concentration. At lower concentrations all MB present in the adsorption medium could interact with the binding sites on the surface of adsorbent so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites. Similar adsorption were obtained for adsorption of MB by Tripoli<sup>[3]</sup>.

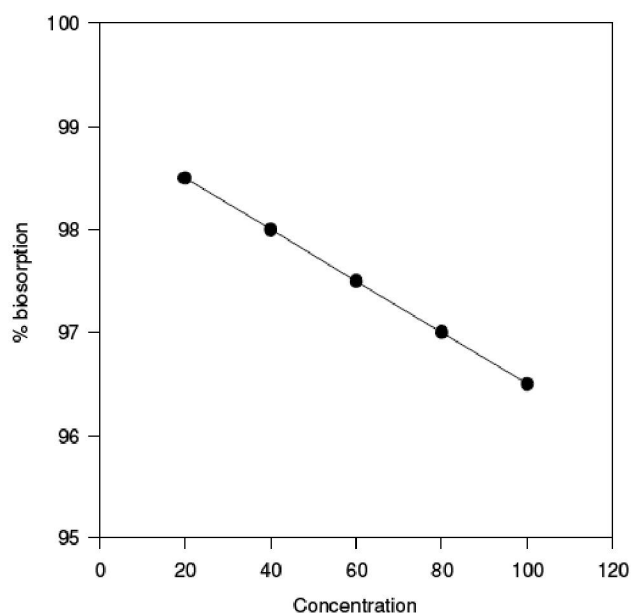


Figure 3 : Effect of initial concentration on % biosorption of MB for 0.1g of ACB

### Effect of adsorbent dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. Figure 4 shows that the increase in adsorbent dosage from 0.02 to 0.1g resulted in increase in % biosorption of MB from 83 to 98.5. It is readily understood that the number of available adsorption sites increases with the increase in the adsorbent dosage and it, therefore, results in the increase in the amount of adsorbed MB. The increase in the adsorbent dosage over 0.1g has not allowed any additional improvement in adsorp-

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tion. This seems to be due to the binding of almost molecules of MB to the sorbent and the establishment of equilibrium between the molecules bounded to the sorbent and unadsorbed molecules in the solution. Thus, all our subsequent experiments were performed at adsorbent dosage of 0.1 g.

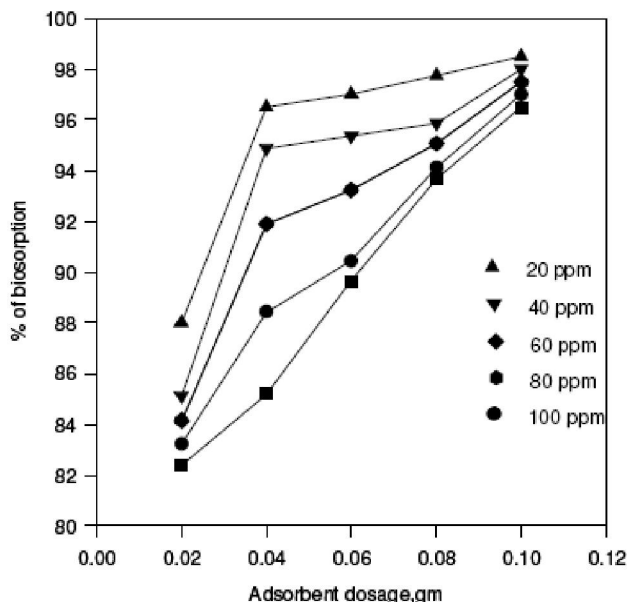


Figure 4 : Effect of biosorbent dosage on % biosorption of MB for various concentrations

### Effect of biosorbent particle size

The effect of particle size on adsorption of the dye on ACB was investigated by evaluating the per-

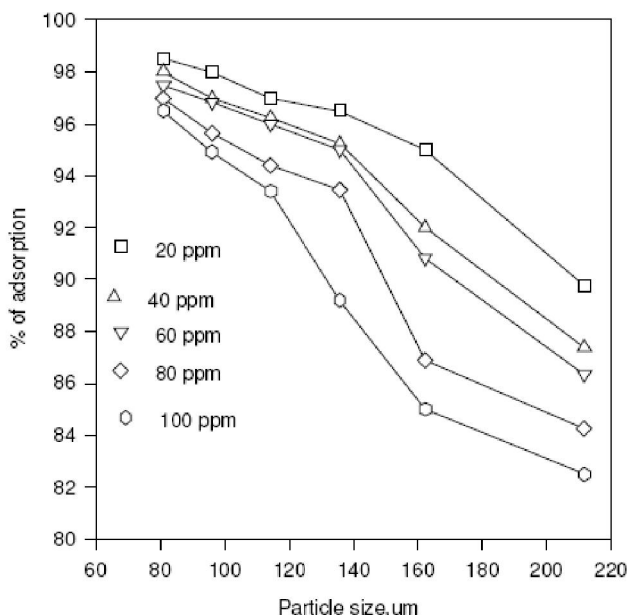


Figure 5 : Effect of particle size on % biosorption of MB for 0.1g of adsorbent/30ml solution

cent removal of the dye. Figure 5 reveals that with increase in particle size the % biosorption decrease. This can be attributed to the fact that the smaller particles have shortened diffusion paths and increases total surface area, and therefore, the ability to penetrate all internal pore structures of adsorbent is very high. For further studies, 81  $\mu\text{m}$  for ACB was chosen, based on their adsorption capacity.

### Adsorption isotherm constants

Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption systems. These data provide information on the capacity of the biosorbent or the amount of required for removing a unit mass of pollutant under the system conditions. Therefore, to optimize the design of sorption system to remove dyes from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Three isotherm equations have been tested in the present study, namely, Langmuir, Freundlich and Temkin.

The Langmuir adsorption isotherm is based on the assumption that all adsorption sites are equivalent and adsorption in an active sites is independent of whether the adjacent sites is occupied or not<sup>[2,18,25]</sup>:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bq_{max}} + \frac{1}{q_{max}} C_{eq} \quad (2)$$

where  $q_{eq}$  (mg/g) and  $C_{eq}$  (mg/L) are the amount of adsorbed dye ion per unit weight of biosorbent and unadsorbed dye ion concentration in solution at equilibrium, respectively. The constant  $b$  is the Langmuir equilibrium constant and the  $q_{max}$  gives the theoretical monolayer saturation capacity. Therefore, a plot of  $C_e/q_e$  versus  $C_e$  gives a straight line of slope  $1/q_{max}$  and intercepts  $1/b$ .

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor ( $R_L$ , also called equilibrium parameter) which is given by the following equation:

$$R_L = \frac{1}{1 + b C_0}$$

If  $R_L = 0$ , then irreversible,  $0 < R_L < 1$ , then favorable,  $R_L = 1$ , then linear,  $R_L > 1$ , then unfavorable. Our results show that the adsorption for MB on the ACB is favorable and has an  $R_L$  value between 0 and 1.

Other isotherms are as follows:

### Freundlich isotherm equation<sup>[11]</sup>

Freundlich isotherm theory describes the ratio of the amount of solute adsorbed onto given mass of sorbent to the concentration of the solute in the solution. It is applicable to adsorption on heterogeneous surfaces and can be represented by equation in linear form as

$$\ln q_{eq} = \ln K_f + \frac{1}{n_f} \ln C_{eq} \quad (3)$$

$K_f$  is the Freundlich constant and  $n_f$  the Freundlich exponent. Where  $K_f$  and  $n_f$  are constants representing the adsorption capacity and intensity of adsorption respectively. The slope  $1/n_f$  and intercept  $K_f((\text{mg/g})/(\text{L/g})^n)$  is obtained from the plot of  $\ln q_e$  versus  $\ln C_e$ .

### Temkin isotherm equation<sup>[15]</sup>

Temkin isotherm model contains a parameter that explicitly accounts for the interaction of adsorbate and adsorbing species. It is based on the assumption that the heat of adsorption of all the molecules in the layer diminishes linearly with coverage which is attributed to adsorbate-adsorbate repulsions. Contrary to Freundlich model, it assumes that fall in heat of adsorption is linear rather than Logarithmic. The equation can be expressed as

$$q_{eq} = B_T \ln A_T + B_T \ln C_{eq} \quad (4)$$

where  $B_T = RT/b$ ,  $q_{eq}$  (mg/g) and  $C_{eq}$  (mg/L) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively.  $A_T$  and  $B_T$  are the Temkin constants.

The isotherm constants were determined from linear isotherm graphs (Figure 6, 7 and 8) for each of the isotherm equations tested. The values of the isotherm constants with the correlation coefficients are given in TABLE 1 for the MB-ACB system. The Freundlich equation represents the better fit of experimental data than other isotherm equations. The maximum amount of dye adsorbed was 91.46mg/g for MB.

A comparison of the maximum capacity,  $q_{max}$ , of ACB powder with other adsorbents was given in TABLE 2. The biosorbent capacity of ACB powder was relatively high when compared with other adsorbents. Differences of dye uptake are due to the properties of each adsorbent such as structure, func-

tional groups and surface area.

### Kinetic studies

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Several kinetic models are available to understand the behavior of the adsorbents and to examine the controlling mechanism of the adsorption process. In the present investigation, the adsorption data

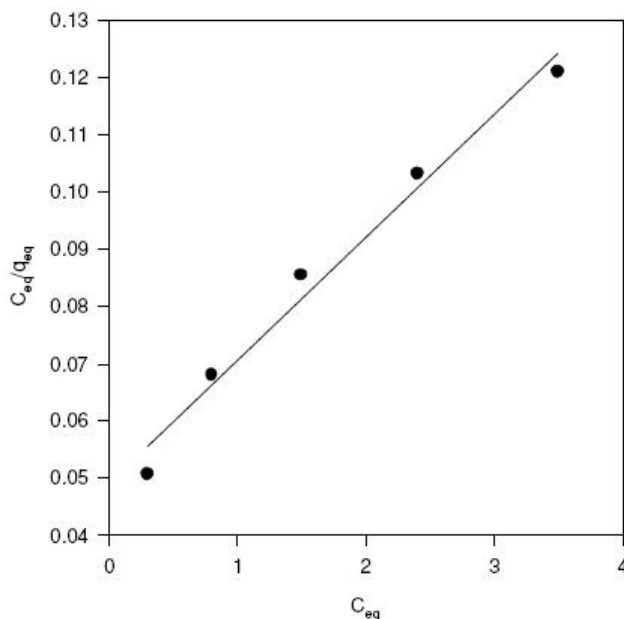


Figure 6 : Langmuir adsorption isotherm

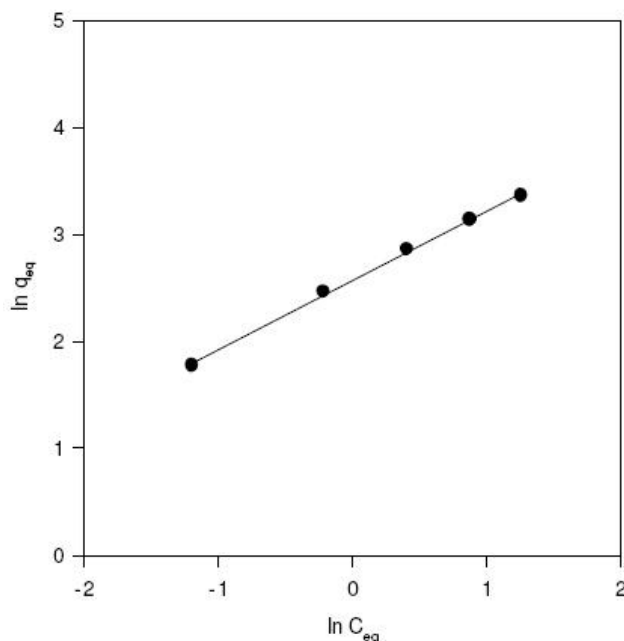


Figure 7 : Freundlich isotherm

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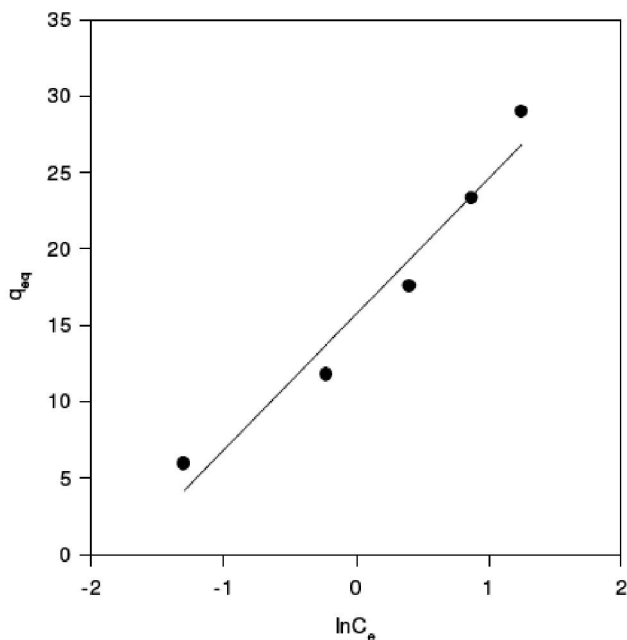


Figure 8 : Temkin isotherm

TABLE 1 : Parameter values of the isotherms for the methylene blue adsorption on to *Araucaria cookii* bark powder

Langmuir	Frendulich	Temkin
$q_{max} = 46.59$	$K_f = 13.19$	$B_T = 284.58$
$b = 0.54$ $R_L = 0.102$	$n_f = 1.547$	$A_T = 5.897$
$R^2 = 0.9803$	$R^2 = 0.9983$	$R^2 = 0.9558$

TABLE 2 : Comparison of the biosorption capacity of present work for methylene blue metal with those reported in the literature

Biosorbent	pH	Biosorption Capacity (mg/g)	References
Saw Dust	7	67.5	[25]
Natural Tripoli	8	16.6	[3]
Iron Oxide Coated porous Ceramic Filter	11	0.85	[10]
Fly Ash & clay & sand	7	3.88	[23]
Activated carbon prepared from Delomix Regia pods	7	24	[7]
Treated activated carbon	4.5	45.9	[33]
Carbon prepared from Guava Seeds	8.27	46.3	[17]
<i>Araucaria cookii</i> bark powder	4	91.46	Present study

TABLE 3 : Comparison of kinetic parameters for methylene blue on *Araucaria cookii*:

Initial conc (mg/L)	20		40		60		80		100	
Rate	$k_1$	0.264	$k_1$	0.235	$k_1$	0.224	$k_1$	0.235	$k_1$	0.242
Constant	$k_2$	1.694	$k_2$	0.1924	$k_2$	0.546	$k_2$	0.189	$k_2$	0.1299
q (calc)	0.40	5.91	0.746	11.757	1.029	17.54	1.427	23.07	3.865	29.10
q (expt)	5.94	5.94	11.84	11.84	17.66	17.66	23.41	23.41	29.6	29.6
$R^2$	0.9846	0.9999	0.9971	0.9999	0.9842	0.9999	0.9623	0.9999	0.9444	0.9999

were analyzed using four different kinetic models, namely the pseudo-first-order and pseudo-second-order.

The pseudo-first-order equation<sup>[5,12]</sup>, is

$$\ln(q_{eq} - q) = \ln q_{eq} - k_1 t \tag{5}$$

where  $q_e$  and  $q$  refer to the amount of MB adsorbed (mg/g) at equilibrium and at any time,  $t$  (min), respectively,  $k_1$  ( $\text{min}^{-1}$ ) is the equilibrium rate constant of pseudo-first-order sorption. Values of  $k_1$  were calculated from the plots of  $\ln(q_{eq} - q)$  versus  $t$  for different concentrations of the MB. The experimental  $q_e$  values do not agree with the calculated ones, obtained from the linear plots (TABLE 3). This shows that the adsorption of the MB onto ACB is not the first-order kinetics.

On the other hand, a pseudo-second-order equation<sup>[5,12]</sup>, based on the adsorption capacity is expressed in the form:

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{6}$$

where  $k_2$  is the rate constant for pseudo-second-order

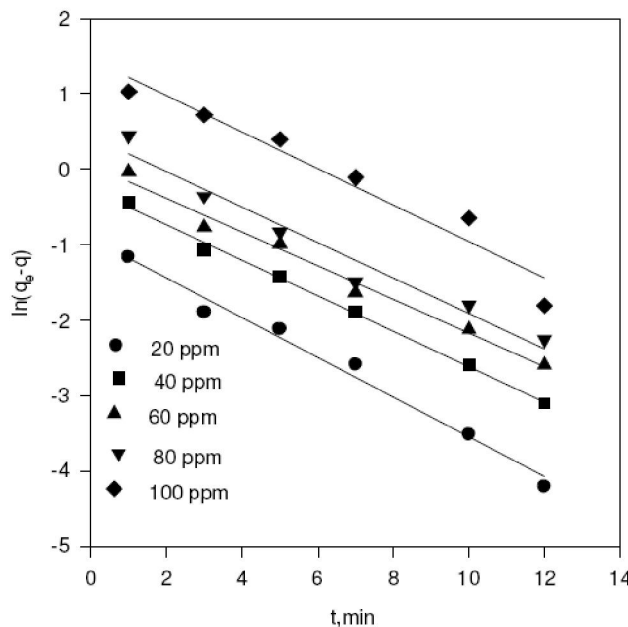


Figure 9 : Pseudo first order kinetic model

kinetics (g/g h). If the second order kinetics is applicable, the plot of  $t/q$  versus  $t$  should show a linear relationship. There is no need to know any parameter beforehand and  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot. The linear plot of  $t/q$  versus  $t$  (Figure 10) show a good agreement between experimental and calculated values (TABLE 3).

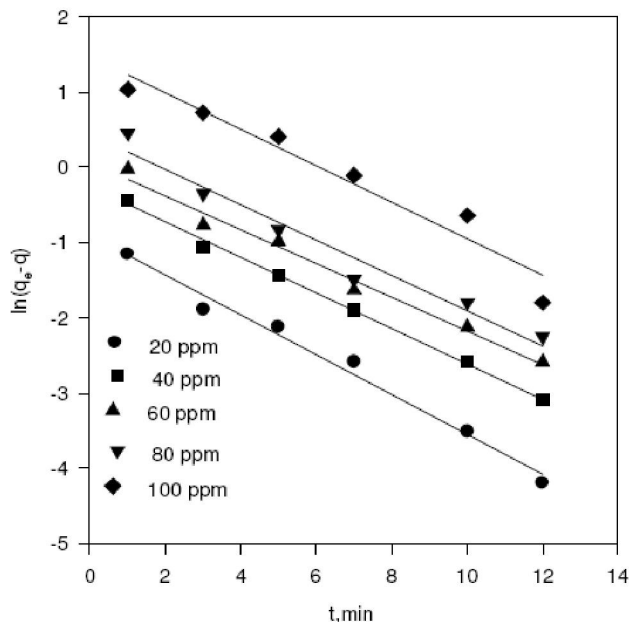


Figure 10 : Pseudo second order kinetic model

From TABLE 3 it can be concluded that the pseudo-second-order kinetic model fits for the adsorption of MB on the ACB. It indicates chemical sorption in the adsorption process, which may be partly due to the hydrogen-binding between the hydroxyl groups of MB and the active functional groups in the ACB, and it may be the rate-limiting step.

## CONCLUSIONS

From the Experimental data we conclude that the biosorption performances are strongly affected by parameters such as initial concentration, pH, biosorbent dosage and biosorbent particle size. The plot of pH versus percentage biosorption shows the significant biosorption takes place at 4. The present work helped in identifying a new source of biosorbent for removal of metals from effluent wastes containing low concentrations of metals. The Freundlich model for MB proved to be the best adjustment of the experimental data for ACB powder. However, comparing the representative

models of the biosorption between the biosorbents, a better adjustment of the equilibrium data was observed by the biosorbent ACB powder. The results obtained in these studies open perspectives with relation to the utilization of ACB powder, in the removal of MB, in treatment of wastewater provided from industrial effluents. The value of the separation factor,  $R_L$ , indicated that dye/ACBs system was a favorable adsorption. The kinetics of the biosorption of MB on ACB powder can be better described with second-order kinetics.

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