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Decolourization of Methylene Blue by Using Eucalyptus Globulus Leaf Powder As A Adsorbent

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ABSTRACT
In the present study, the feasibility of using low-cost adsorbent Eucalyptus Globulus leaf powder for the cationic dyes adsorption from aqueous solutions have been investigated. Batch adsorption studies are conducted to study conducted to the different parameters are adsorbent dosage of 2-20 g/L, initial dye concentration of 50-250 mg /L, Temperature of 293^{o}K, 303 ^{o}K and 313 ^{o}K on adsorption of methylene blue dye at equilibrium time of 80 minutes respectively and optimal pH of 5.0. The equilibrium data is analysed with isotherm models are Langmuir and Freundlich and kinetic models are Pseudo-first order, Pseudo-second order model. The adsorption equilibrium and kinetic data fitted well to Freundlich isotherm model for methylene blue dye and Pseudo-second order model for methylene blue dyes. The adsorption is an Endothermic and it is energetically favourable adsorption. The result demonstrates that Eucalyptus Globulus leaf powder could be employed as effective and low-cost adsorbent for the removal of methylene blue and from aqueous solutions.

Keywords: Adsorption, Equilibrium isotherms, kinetics, Methylene blue and Thermodynamics.

Introduction

Water is undeniably the most valuable natural resource exciting on our planet, which has been most lavishly used by human beings. This unusual compound with unique physical properties is also known as the compound of life. Without water life on the earth would be non-exist. In split of knowing this fact, water pollution resources are common occurrence. There are many sources of water pollution; in them untreated industrial effluents are headstones.

Dyes, the most impending materials used in large quantities in many industries including textiles, leather, cosmetics, paper, printing, plastic, pharmaceuticals, food, etc., to colour their products[1]. Till date 1,00,000 dyes with an annual production over 7×105 tons worldwide were reported to be commercially available. It was also reported in the literature that up to 10% of the dyes used in industry were lost in the industrial effluents[2]. The textile industry ranks first in the consumption of the dyes and effluents released from textile dyeing, which is intensely coloured and poses serious problems to various segments of the environment. According to a survey indicates that on an average of 150-200 L water is consumed and about 125 L of effluent is generated per kg of finished textile produced in India. That is about one million liters of effluent is discharged per day by an average sized textile mill having a daily production of 8000 kg of finished products [3].

The presence of dyes in effluents is a major concern due to their adverse effects to many forms of life. The dye and dyeing effluents contain large amount of suspended solids and also they have high chromaticity and high COD content [4]. The colour is the first contaminant to be recognized in wastewater. The presence of even very small amount of dyes in water-less than 1 ppm for some dyes is highly visible and undesirable. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons, [5]. Many dyes or their metabolites have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and humans [1]. It causes a major environmental issue.

Untreated textile effluents are highly toxic as they contain a large number of complex dyes. Dyes even in low concentration are visual; affect aquatic life and the food web. These coloured compounds are not only aesthetically displeasing but also inhibit the passage of sunlight into the stream and thus affect the photosynthesis.

Methodology

Adsorption process can be performed via several modes; of which, batch and continuous. Continuous modes of operation are frequently employed to conduct laboratory scale adsorption processes. Although most of industrial applications prefer a continuous mode of operation, batch experiments have to be used to evaluate the adsorbent capacity, % removal of dye and optimal experimental conditions. The adsorption of Methylene blue from aqueous solutions by Eucalyptus Globulus leaf powder is carried out in a batch mode.

Preparation Of Methylene Blue Stock Solution

The stock solution of Methylene blue is prepared separately by dissolving equivalent weight of Methylene blue powder into a 1000 ml of distilled water, which is equal to 1000 ppm. The experimental solutions of desired concentrations are prepared by diluting stock solution with distilled water.

Preparation Of Eucalyptus Globulus Leaf Powder

Eucalyptus Globulus leaves are collected in Sri Venkateswara University Campus, Tirupati. The leaves are washed thoroughly with tap water followed by distilled water to remove surface impurities and sun dried. The dried leaves are ground in a domestic mixer and are analysed with sieve shaker using B.S.S standard sieves of mesh sizes 80, 100,120 and 200 (177, 149, 125 and 74µm). fractions, are collected in to separate bottles. The samples are stored in separate air tight bottles for experimental use.

Batch Study

In adsorption process, many parameters will affect the adsorption capacity of adsorbent. Those are particle size, contact time, adsorbent dosage, pH, initial dye concentration and temperature. A set of labelled flasks, containing 50 ml solution each of 50 ppm of dye are taken and the solution pH is adjusted. A measured quantity of adsorbent is added and the flasks are agitated at constant speed in a rotary incubator shaker at room temperature. Flasks are with- drawn at suitable intervals, the content filtered and filtrate is analyzed in UV-visible double beam spectrophotometer for equilibrium dye concentration. Similarly, the procedure is repeated with varied levels of contributing parameters to make a complete study. Percentage removal of dye is calculated using the formula[6].

$$\text{Removal } \% = \frac{C_o - C_t}{Co} \times 100 \qquad 1$$

The equilibrium dye uptake capacity is calculated as per equation

$$q_e = (C_0 - C_e)x\, V/m \qquad 2$$

Results and Discussion

Operating parameters

1. Effect of contact time:

In adsorption studies, size of the adsorbent particles used is a key parameter. Usually practically suitable smallest particle size is chosen for adsorption, as such particles provide

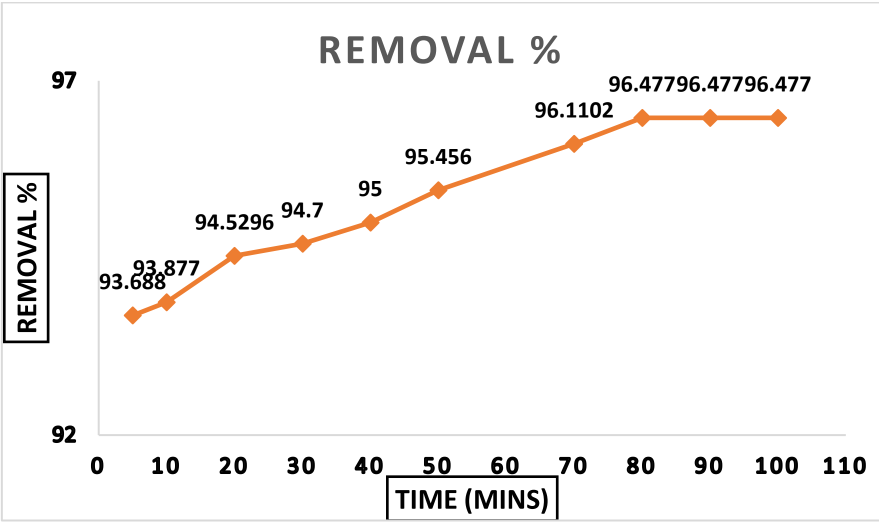

Fig 1. Plot of Time vs Removal %

greater area for transfer and binding of the adsorbate. Smallness is a problem as far as reclaiming of adsorbent after adsorption is concerned. It becomes difficult if the solids to be separated from the solid-liquid mixture are small. In the present experimentation, particles of size 125 μm (passing through 120 and retained by 200 mesh) are used in all the studies.

The time course of the binding is studied, with an objective of identifying the transfer necessary to attain equilibrium and the results obtained.

As can be seen from the plot 1, the operation slows down as the driving force deceases and the sites on the adsorbent surface are occupied. % Removal after 80 minutes remained steady indicating that there is no further binding and the adsorbent is saturated. So, a contact time of 80 minutes is chosen as the optimum contact time for Methylene blue.

2. Effect of pH:

pH is another factor, that would influence the removal. This effect on methylene blue and malachite green adsorption is studied in the range of 2 to 12, and the results are plotted and shown as figure 2.

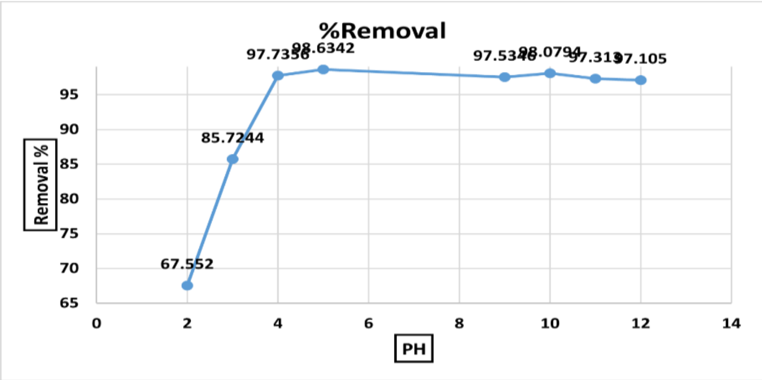

Fig 2 :- Plot of pH vs Removal%

Figure 2 clearly indicates that the maximum adsorption for Methylene blue dye is at a pH of 5.0 and the % removal on either side of this level. This behaviour can be interpreted in terms of the availability of suitable functional group binding sites. A pH of 5.0 is providing active functional groups with proper configuration to cause higher removal, while a deviation of pH from 5.0 is altering the structure to a less suitable form, thus lowering the dye binding.

3. Effect of Concentration:

The variations in % removal of MB from the aqueous solution with concentration variations are obtained. The percentage biosorption is increased from concentration 86% to 96.1% for MB and to as the concentration increases from 50 ppm to 250ppm. This phenomenon is depicted, as the concentration of the solution increases, removal of the solution for bioadsorption of Eucalyptus globulus leaf powder increases; thereby the number of active sites on the biosorbent also increases. Concentration of 250 ppm was selected for MB dye for further experimentation.

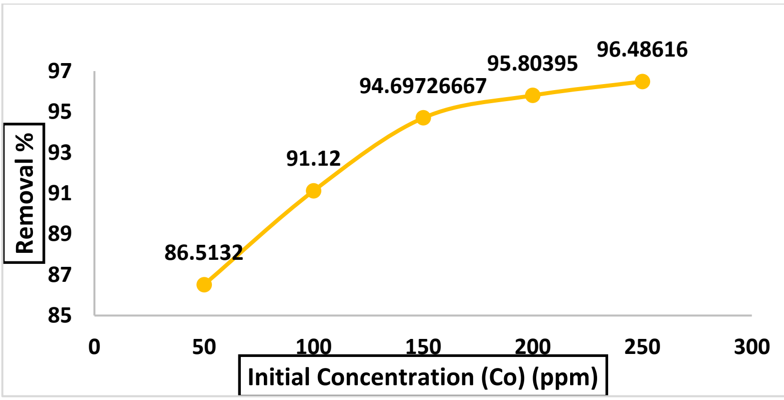

Fig 3 :- Plot of Initial concentration vs Removal %

4. Effect of adsorbent dosage:

The variations in % removal of MB from the aqueous solution with biosorbent dosage are obtained. The percentage biosorption is decreased from 96.4% to 92.1% for MB and to as the biosorbent size increases from 0.5 g to 2.5g. This phenomenon is depicted, as the size of the particle increases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases. Adsorbent amount of 0.5g was selected for MB dye for further experimentation due to high removal of MB at this point.

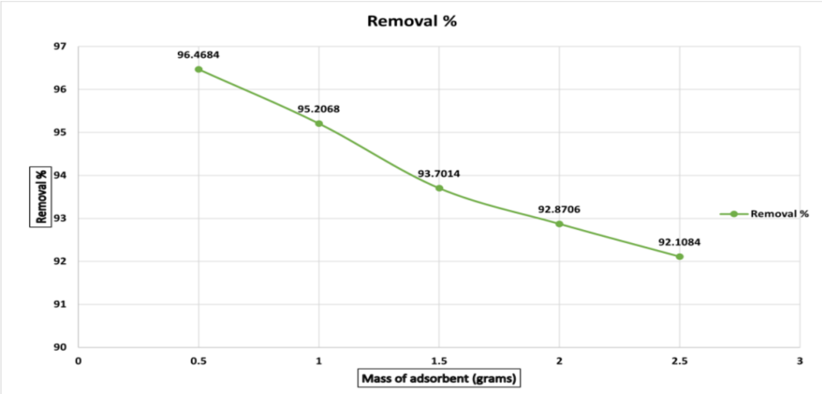

Fig 4 :- Plot of mass of adsorbent vs Removal %

5. Adsorption isotherms:

Equilibrium isotherms are used to know the interactions between Methylene blue ions and Eucallyptus leaf powder. And also, to know the adsorption capacity and equilibrium coefficient in adsorption process for Methylene blue removal. Two-parameter isotherm models are tried their suitability to represent equilibrium of MB removal.

Langmuir isotherm:

Adsorption model is used for the estimation of maximum dye adsorption[7]. This sorption model is based on two hypotheses: (a) adsorption on a homogeneous surface containing site will occur with equal energy that is equally available for adsorption and (b) as Langmuir isotherm is monolayer isotherm, there is no transmigration of adsorbate on the surface plane. The model is quite versatile and the mechanism involved for all the adsorbate-adsorbent systems is treated similarly. The Langmuir equation can be described by the equation (3) and the linearized form in equation (4).

$$\frac{q_e}{q_{max}} = \frac{bC_e}{1+bC_e} \qquad 3$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad 4$$

The slope and intercept of the plot between Ce/qe vs Ce will give q_m and b respectively. The applicability of the Langmuir isotherm depends on the separation factor, R_L can be determined from Langmuir plot as per the following relation

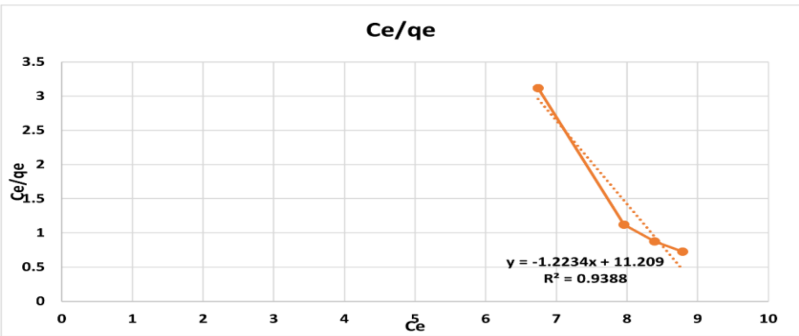

Fig 5 : Plot of Ce Vs Ce/qe

Where R_L values indicate the type of adsorption to be irreversible (= 0), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$).

$$R_L = \frac{1}{1 + (bc)}$$

Where q_{max} dye maximum uptake capacity, (mg/g).

Freundlich isotherm :

The Freundlich, (1909) adsorption isotherm is an empirical equation widely employed to describe solid-liquid adsorption, encompassing the surface heterogeneity. The mathematical expression for the Freundlich isotherm is written as

$$q_e = K_f C_e^{1/n} \quad 5$$

$$lnq_e = \frac{1}{n} lnC_e + lnK_f \quad 6$$

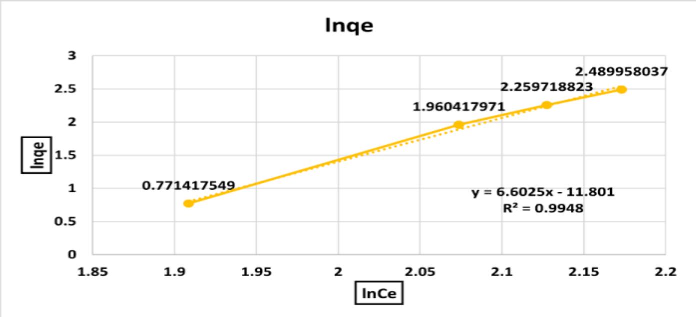

Fig 6 : Plot of lnCe vs lnqe

A plot of lnq_evs lnCe should be a straight line of slope $1/n$ and intercept lnK_f. According to Freundlich isotherm, the n value lie in between 1 to 10, this indicates favourable dye adsorption onto Ficus benghalensis at low concentrations and strong bond between dye and Eucalyptus Globulus surface[1].

Table -1 :-Equilibrium isotherms and parameters for adsorption of MB onto Eucalyptus Globulus at optimum conditions

ISOTHERM	PARAMETERS	MB (VALUES)
Langmuir	q_m(mg/g)	0.82
	b (L/ mg)	0.11
	R_L	0.45
	R^2	0.94
Freundlich	K_f	0.01
	n	0.15
	R^2	0.99

6. Adsorption Kinetics:

Kinetics studies are carried out by conducting batch adsorption experiments. The prediction of rate gives important information for designing batch adsorption systems and also, kinetics of solute uptake are required for selecting optimum operating conditions for full-scale batch process. The kinetics of the adsorption data are analysed using four kinetic models and are able to interpret the rate and mechanism of each adsorption process. These models are explained as follows.

Pseudo-first order kinetic model

Pseudo-first order model was described empirically by Lagergren and theoretically and Lagergren pseudo-first order kinetic model, and is described by the given equation[8&9].

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad 7$$

$$\log(q_e - q_t) = \log(q_{e(the)}) - \frac{K_1}{2.303}t \quad 8$$

A plot of log(qe-qt) against time t, it gives an intercept and slope. K1 can be calculated from the slope and qe(the) from intercept. If qe(the) is largely deviates from the qe(exp) then Adsorption process does not follow the pseudo-first order.

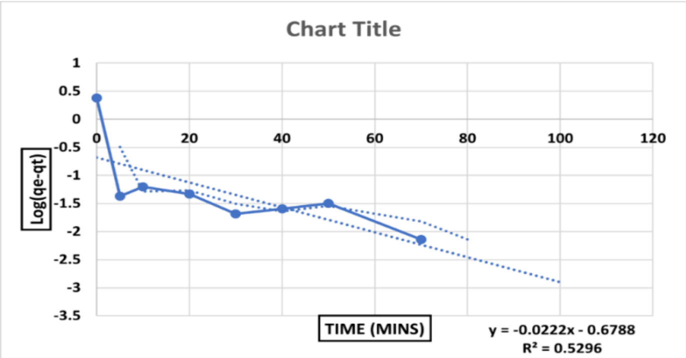

Fig 7: A plot of log(q_e-q_t) vs time t

Pseudo-second order kinetic model:

Pseudo-second order model proposed by researchers [10], this model is based on the assumption that the adsorption mechanism follows second order chemisorption. The pseudo- second order model can be expressed as

$$\frac{dq}{dt} = K_2\,(q_{e(the)} - q)^2 \quad 9$$

linear pseudo-second order model is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e(the)^2}} + \frac{1}{q_{e(the)}}t \quad 10$$

Correlation constants $q_{e(the)}$ and K_2 can be determined by plotting t /qt versus t which gives a linear relationship. If $q_{e(the)}$ agreement with the $q_{e(exp)}$ then adsorption process does follow the pseudo-second order and this is as shown in figure 8. The values are tabulated in table 2.

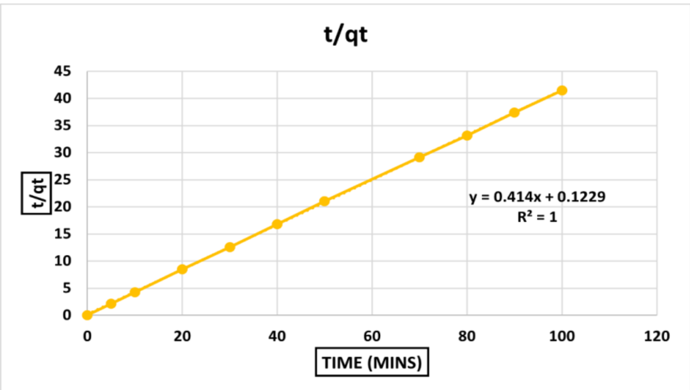

Fig 8 : Plot of t/q_t vs Time(t)

Table 2 : Adsorption Kinetic models and parameters for adsorption of MB onto Eucalyptus Globulus leaf powder.

Kinetic order	PARAMETERS	MB (VALUES)
Pseudo first order	qe(the)(mg/g)	0.05
	qe(exp)(mg/g)	2.41
	K1	0.0154
	R2	0.5296
Pseudo second order	qe(the)(mg/g)	2.41
	qe(exp)(mg/g)	2.41
	K2	1.4
	R2	1.0

THERMODYNAMICS STUDIES:

Thermodynamic data is obtained at the following set of conditions time of 80 minutes for MB dye concentration of 250ppm, pH value of 5.0, Eucalyptus Globulus leaf powder , 0.5g particle size of 125 µm and temperature from 293 to 313°K. The corresponding Van't Hoff plot is as shown in figure 9.

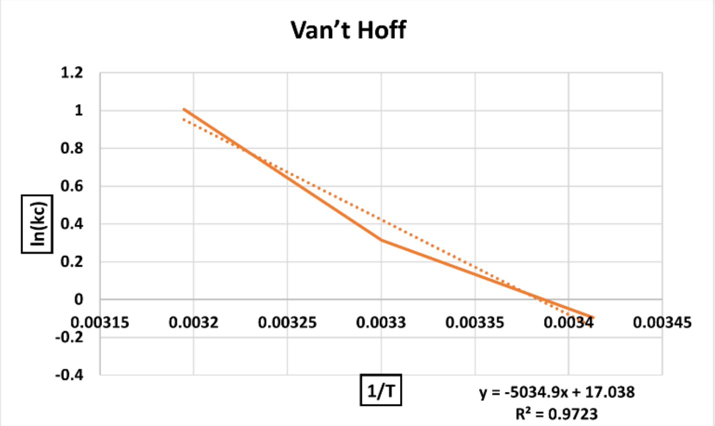

Fig 9 :- Plot of 1/T vs lnkc

The positive sign on enthalpy (ΔH),41.8kJ/molfor MB indicates that the process is endothermic. Higher temperature favours the adsorption as observed in experimental results. Change in Gibbs free energy (ΔG) – 400.7 kJ/mole for MB is negative suggesting that the adsorption is spontaneous. A positive entropy change (ΔS), 141.65 J/ mole K for MB indicates the dye binding is spontaneous and increase in the randomness at the solid/solution interface during the sorption of Methylene blue dyes onto Eucalyptus globulus leaf powder. The values are tabulated in table 3.

Table 3 :- Thermodynamic Parameter for adsorption of MB on Eucalyptus globulus leaf powder.

Temperature(°K)	ΔH°(kJ/mole)	ΔG°(kJ/mole)	ΔS°(J/mole K)
313	41.8	-400.7	141.65

CONCLUSION

The Adsorption equilibrium data best fitted to the Freundlich adsorption isotherm model for Methylene blue dye. Positive value of enthalpy and entropy describes endothermic and nature of adsorption and negative value of Gibbs free energy demonstrates the favourable and spontaneous nature of adsorption of MB. Adsorption kinetic data followed the pseudo-second order model. Thus, *Eucalyptus Globulus* leaf powder appears as a very prospective, effective and inexpensive adsorbent for the removal of Methylene blue.

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