Equilibrium, Thermodynamic and Kinetic Studies on Biosorption of Malachite Green From Aqueous Solution Using Guava leaves.

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Abstract

In this work, batch biosorption experiments were carried out for the removal of malachite green dye from aqueous solution using guava leaf powder (GLP) as biosorbent. The effect of process parameters such as contact time, pH, biosorbent dosage, initial concentration and temperature were studied. Equilibrium data were represented well by a Langmuir isotherm equation with a monolayer sorption capacity of 39.29 mg/g, indicating that GLP can be used as an excellent low cost biosorbent. The thermodynamic parameters such as free energy change ΔG^0 *(kJmol*$^{-1}$*), enthalpy change (*ΔH^0 *= -13.984 kJmol*$^{-1}$*) and entropy change (*ΔS^0*= -0.0672kJmol-1K-1) were calculated and the bio-sorption was exothermic in nature.*

Key words: biosorption, dye, equilibrium studies, thermodynamic studies, kinetic studies

1. Introduction

Dyes are highly used throughout the world. For example, a textile industry utilizes about 10,000 different dyes annually. Dyes are a major cause of environmental problems dealing with marine life and as far as our drinking water as well. Their immense wastewater discharge, extremely high salinity, alkalinity, substantial pollution load, and heavy colored effluents are major ways in which the environment is being destroyed. These wastewaters are composed of high dye fluids. When these dye fluids are mixed with water, they cause severe problems such as increasing the chemical oxygen demand and reducing light penetration which pose negative effects on marine life. The textile industry has been condemned as being one of the world's worst offenders in terms of pollution because it requires a great amount of chemicals and water. It takes about 500 gallons of water to produce enough fabric to cover one sofa. Water is affected by the heat, its increased pH, and because it's saturated with dyes, de-foamers, bleaches, detergents, optical brighteners, equalizers and many other chemicals used during the process. Textile industries discharge millions of gallons of effluent each year consists full of chemicals which are significant causes of environmental degradation and human illnesses. There are various methods for treating wastewaters. The most common systems are physicochemical, chemical, and biological methods. These processes are really expensive. There's also another method which is the adsorption process, which is an attractive alternative treatment. One of the most popular adsorbent that has been used with success is granular activated carbon. The only problem with granular activated carbon is its difficult regeneration and disposal.

The agricultural and forestry waste products represent unused resources and also they are widely available and environmentally friendly, so they have a great potential to be used as bio-sorbents. A number of low cost agricultural materials including Arundodonax root[1], sugar cane dust [2], wheat bran [3], waste apricot [4], de-oiled soya [5], etc. have been used for the removal of MG from waters and wastewaters. The GLP was selected as an biosorbent for the removal of MG from aqueous solutions.

Guava or *Psidiumguajava* of Myrtaceae family is a tropical and semi tropical plant. It is common in back yards and waste places. Its seeds and leaves possess medicinal value and are traditionally used to treat a number of human ailments. The objective of the present study was to evaluate the potential usage of

GLP as a low cost adsorbent for the removal of one of the highly toxic dye, MG, from aqueous solutions. The effects of important experimental parameters such as contact time, pH initial MG concentration, biosorbent dosage etc. are studied. The adsorption mechanisms of MG onto GLP are evaluated in terms of thermodynamics and kinetics.

2. Materials and methods:

2.1. Preparation of biosorbent:

The GLP was collected from Andhra University College of engineering, Visakhapatnam, and it was washed with de-ionized water several times to remove surface impurities, and then dried in sunlight for 15 days. The dried GLP samples were ground in a domestic mixie and sieved to obtain a required particle size and stored in glass containers to be used for biosorption experiments.

2.2. Preparation of Biosorbate:

A cationic basic dye malachite green hydro chloride (C.I= 42,000, MF=$C_{23}H_{26}N_2Cl$, molecular weight 364.92); λ_{max} = 619 (measured value) was supplied by Merck, India.

One gram per liter of stock solution was prepared by dissolving accurately weighed amount of the dye in distilled water. The range of concentration of the prepared dye solutions varied between 20 and 100 mg/L. The solutions were prepared by diluting the malachite green stock solution, which were obtained by dissolving in de-ionized water.

2.3. Batch Experimentation:

Bio sorption experiments were performed at room temperature (30 ± 1^0C) in a rotary shaker at constant agitation speed containing 30 mL of different dye concentrations using 250 mL Erlenmeyer flasks. After 90 minutes of contact time (according to the preliminary sorption dynamics tests), with 0.1 g GLP leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5minutes. The dye content in the supernatant was determined using UV Spectrophotometer. The amount of dye adsorbed and percentage of color removal by GLP was calculated. The same procedure was repeated for different concentrations of dyes and at different temperature.

3. Results and discussion:

3.1 Effect of contact time:

Time course profiles for the bio-sorption of Malachite green for a solution of 20 mg/L to 100 mg/L are shown in Fig-1. It showed that a contact time of 90 minutes for malachite green was required to achieve an optimum bio-sorption and there was no significant change in concentration of the dye solution with further increase in contact time. Therefore, the uptake and unadsorbed malachite green concentration at the end of 90minits are given as the equilibrium values, q_{eq} (mg/g) and C_{eq} (mg/L).

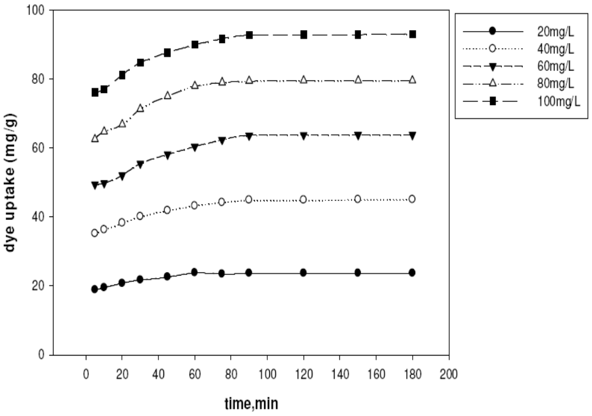

Fig.1. Effect of contact time on uptake of MG by *Psidiumguajava* for various dye concentration at 0.02g/30mL of bio-sorbent concentration

3.2. Effect of pH:

pH is an important parameter on biosorption of dye from aqueous solutions. *Psidiumguajava* presents a high content of ionizable groups (carboxyl groups) on the cell wall polysaccharides, which makes it very liable to the influence of the pH. As shown in Fig-2, the uptake of malachite green depends on pH. The biosorption of malachite green was observed to increase with an increase in pH up to a value of 5. With further increase in pH, the amount of dye adsorbed decreased slowly. The maximum amount of dye (92.85mg/g) was adsorbed at a pH of 5. As the pH increased, the ligends such as carboxylate groups in GLP would be exposed increasing the negative charge density on the biomass surface, which in turn increases the attraction of dye ions with positive charge and allowing the biosorption onto the cell surface.

In this study, the dye ion at around pH 5 was expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for MG bio-sorption was found as 5 and the other adsorption experiments were performed at this pH value.

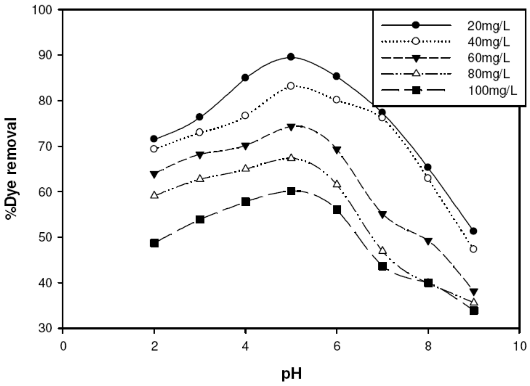

Fig.2. Effect of pH on % dye removal of MG by *Psidiumguajava* for various concentrations of dyes 0.1g/30 mL of biosorbent

3.3. Effect of initial concentration:

Experiments are undertaken to study the effect of initial dye concentration (20mg/L–100mg/L) on malachite green removal from the solution. The results obtained are shown in Fig-3. The obtained curves showed that the dye uptake increases with an increase in initial concentration of malachite green while the percentage biosorption of malachite green dye decreases with an increase in initial malachite green concentration. The increase of dye uptake is result of the increase in the driving force i.e. concentration gradient, with an increase in the initial dye concentrations (from 20 to 100 mg/L). However, the percentage biosorption of malachite green on *Psidiumguajava* was decreased from 89.5 to 79.3% and dye uptake increased from 5.37mg/g to 23.79mg/g. At lower concentrations, all malachite green present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher initial malachite green concentrations. The percentage of color removal was calculated by using the simple equation

$$\%biosorption = \frac{(C_i - C_{eq})}{C_i} \times 100 \quad \text{------- (1)}$$

The amount of dye adsorbed by GLP was calculated from the differences between dye quantity added to the biomass and dye content of the supernatant using the following equation:

$$q_{eq} = \frac{V(C_i - C_{eq})}{1000\,w} \quad \text{---------- (2)}$$

Where q_{eq} is the dye uptake (mg/g); C_i and C_{eq} the initial and final dye concentrations in the solution (mg/L), respectively; V the solution volume (mL); w the mass of bio sorbent (g).

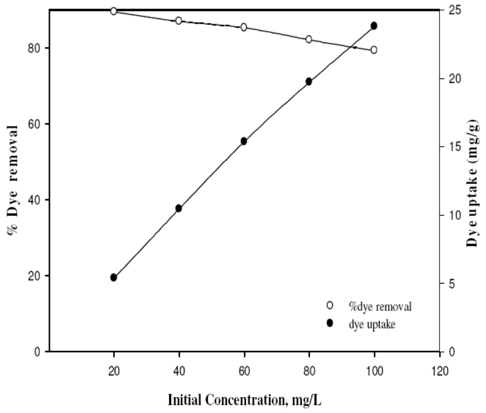

Fig.3. Effect of concentration on % dye removal of MG by *Psidiumguajava* for various concentrations of dyes 0.1g/30 mL of bio-sorbent

3.4. Effect of bio-sorbent dosage:

For studying the effect of biosorbent dosage on removal of malachite green, the bio-sorbent dosage was changed from 0.02 to 0.1 g, fixing other parameters like initial concentration at 20 mg/L, pH 5 and particle size 75µm. The biosorption plot of Fig-4 shows that with an increase in bio-sorbent dosage, the % bio-sorption increases and the dye uptake was decreases. This is because of the availability of more binding sites for complexion of dye ions.

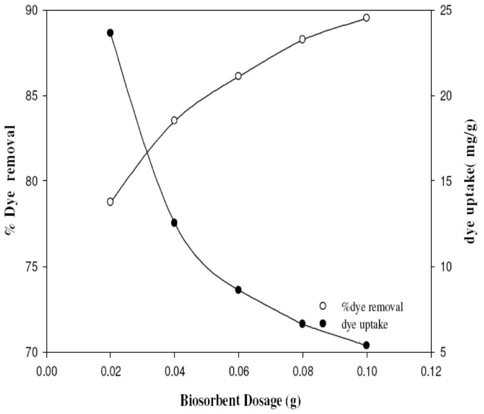

Fig.4. Effect of GLP dosage on % dye removal and uptake of MG dye for 20mg/L of initial dye concentration

3.5 Sorption equilibrium:

The capacity of a biomass can be described by equilibrium sorption isotherms which express the surface properties and affinity of the biomass. In this study, the biosorption isotherms were investigated using four equilibrium models, which are namely the Langmuir [6], Freundlich [7], Redlich Peterson [8] and Temkin [9]isotherm models. The linearized Langmuir, Freundlich, Redlich and Temkin adsorption isotherms obtained at room temperature are shown in Fig.5 the regression values and isotherm constants were given in Table.1.

Table-1: Langmuir, Freundlich, Redlich-Peterson, and Temkin models Estimated from the fittings of experimental points of Malachite green

Biosorption:

Langmuir model	**Freundlich model**	**Redlich-Peterson model**	**Temkin model**
q_{max} = 39.296 k_a = 0.0724 r^2 = 0.9959	m = 0.655 K_f = 1.711 r^2 = 0.9926	g = -1.365 B = 15.96 r^2 = 0.392	b_T = 312.48 A_T = 0.8199 r^2 = 0.9821

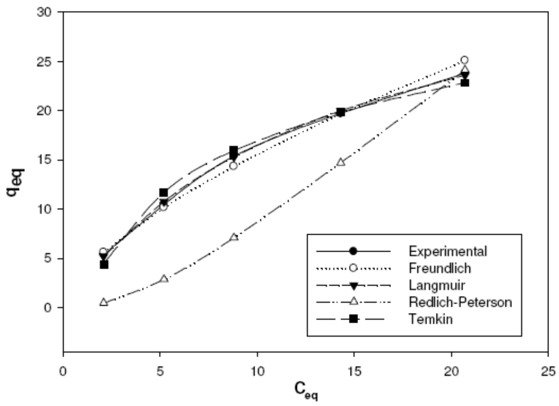

Fig.5. Equilibrium curves for Malachite Green

3.6. Effect of temperature:

The rate of biosorption is a function of initial dye ion concentration as well as its temperature. The percentage bio-sorption of malachite green onto guava leaves was decreased from 89.5 to 76.94% as the temperature increased from 303 to 333K at 20mg/L. The percentage of color removal at higher temperature levels gives a decreasing trend because at lower temperatures, all the dye ions present in the solution could interact with the binding sites and thus the percentage of color removal is higher than those at higher temperatures. This happens because of more interaction of the ions with solution due to convection. At higher temperatures, lower adsorption yield is due to the mobilization of ions with solution because of highly energized ions. As a result, the purification yield can be increased by reducing the temperature. A similar observation was previously reported by [10] for the sorption of Acid red 274 from waste water by Spirogyra rhizopus.

3.6.1 Thermodynamic studies:

Temperature (K)	**k_a(L/mg)**	**ΔG°(kJ /mol)**	**ΔH°(kJ/ mol)**	**ΔS°(kJ/ mol K)**
303	0.0724	6.397	-13.985	-0.0673
313	0.0691	7.061	-13.985	-0.0672
323	0.0590	7.733	-13.985	-0.0672
333	0.0435	8.406	-13.985	-0.0672

The thermodynamic parameters for the adsorption process, ΔH, ΔS and Δ*G*, were evaluated using the equation [11- 12] :

$$\ln K_a = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{----------------}\ (3)$$

Here K_a, known as the distribution coefficient of the adsorbate, is equal to (q_e/C_e). ΔH and ΔS values were determined using the slope and intercept of liner plot between ln K_a and 1/T.

These values could be used to compute Δ*G* from the Gibbs relation, ΔG= ΔH– T ΔS at constant temperature. All these relations are valid when the enthalpy change remains constant in the temperature range.

Of the thermodynamic point of view the data in Table 2 and of the Fig.6 shows that the adsorption process of the MG on GLP was exothermic and that occur a decrease of the entropy probably associated to the organization of the dye adsorbed on surface of the adsorbent.

Table-2: Thermodynamic parameters for adsorption of malachite green on *PsidiumGuajava*:

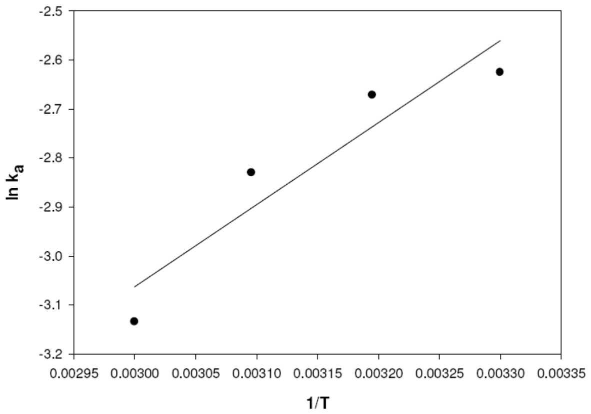

Fig.6. Plot of lnK_a vs. 1/T for the estimation of thermodynamic parameters for bio-sorption of MG onto *Psidiumguajava*

3.7. Adsorption kinetics:

The prediction of bio-sorption rate gives useful information for designing batch bio-sorption systems. In order to clarify the bio-sorption kinetics of MG by *Psidiumguajava* leaves two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second –order model were applied to the experimental data. All these models correlate equilibrium uptake, which are important in designing the reactor volume. These models are explained as follows:

3.7.1. Pseudo-first order model:

The possibility of bio-sorption data following [13] pseudo-first order kinetics is given by:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{K_I}{2.303}t \qquad \text{--------------------- (4)}$$

In order to obtain the rate constant, the straight-line plot (Fig-7) of log (q_{eq}-q) versus time (t)was made for *Psidiumgaujava* for initial Malachite green concentrations, 20 mg/L to 100mg/L. The intercept of the above plot should be equal to log q_{eq}. However, if q_{eq} from intercept does not equal to the equilibrium malachite green dye uptake then the reaction is not likely to be first order, even this plot has high correlation coefficient with the experimental data. The correlation coefficient was found to be 0.9901, but the calculated q_{eq} is not equal to experimental q_{eq}, suggesting the insufficiency of Pseudo-first-order model to fit the kinetic data for the initial malachite green concentration examined.

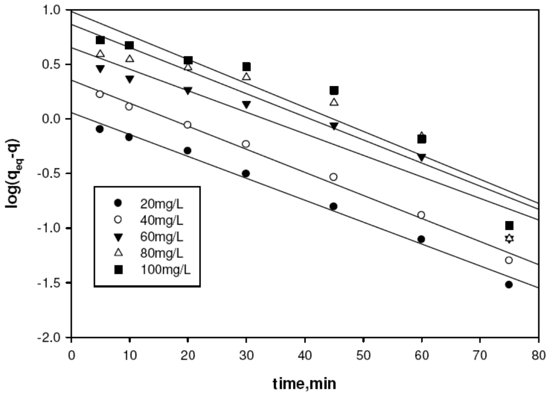

Fig.7. Pseudo-first-order for bio-sorption of MG by *Psidiumguajava* for 20 mg/L of dye concentration at 0.1g/30mL of bio-sorbent

3.7.2. Pseudo-second order model:

A pseudo-second order model proposed by Ho and McKay [14] was used to explain the sorption kinetics. This model was developed based on the assumption that the bio-sorption follows second order chemisorption. The pseudo-second order model can be expressed as

$$\frac{dq}{dt} = K_{II}(q_{eq} - q)^2 \qquad \text{----------------- (5)}$$

Separating the variables in Eq. (5) gives:

$$\frac{dq}{(q_{eq} - q)^2} = K_{II}\,dt \qquad \text{----------------- (6)}$$

Integrating Eq. (6) for the boundary conditions q=0 to q=q at t=0 to t=t, Eq. (6) simplifies to:

$$\frac{t}{q} = \frac{1}{K_{II}q_{eq}^{\ 2}} + \frac{1}{q_{eq}}t \qquad \text{-------------------- (7)}$$

Where t is the contact time (min), q_{eq} (mg/g) and q (mg/g) are the amount of dye adsorbed at equilibrium and at any time, t. The correlation coefficients were found to be 0.9995 for initial concentrations 20 mg/L to 100mg/L.

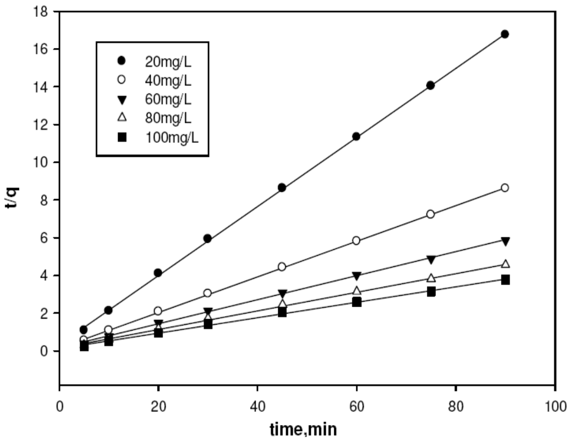

Fig.8. Pseudo-second-order for bio-sorption of MG by *Psidiumguajava* for 20 mg/L of dye concentration at 0.1g/30mL of bio-sorbent

Conclusions:

Bio-sorption equilibrium was better described by the Langmuir isotherm model than the other three models. The bio-sorption capacity of GLP for MG was found to be 39.296 mg/g at pH 5 and 0.1 g biomass dosage, 90 min equilibrium time and 30^{O}C.The thermodynamic parameters such as free energy change, enthalpy change and entropy change shows that the bio-sorption process was exothermic and the reaction is feasible and spontaneous.The kinetics of the bio-sorption of malachite green on *Psidiumguajava* can be better described with second-order kinetics.

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