

Adsorption Capability of *Gmelina arborea* Bark using Crystal Violet

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Abstract. The adsorption capability of *Gmelina arborea* (*G.a*) bark was investigated using batch adsorption of crystal violet (CV) in aqueous solution. Two *G.a* bark types were considered, Acid treated (bark A) and untreated/controlled (bark B). Adsorption studies results were computed from the absorbance detected by UV-VIS spectrophotometer at maximum wavelength of 590 nm after agitating preselected bark quantities and solution concentrations until equilibrium. Highest adsorption capacities recorded were evident at 100ppm solution concentration when 1.0g of bark A and 1.0g of bark B were used. Values were 4.9943 and 4.9819 (mg CV/g) for bark A and B, respectively. Further studies examined the behavior of the bark with the effects of temperature and agitation time using 1.0g bark dose and 10ppm solution concentration. Results revealed that as temperature and agitation time are increased, percent adsorption of CV decreases. Thermodynamic parameters were evaluated and negative enthalpy and free energy results suggest an exothermic nature of adsorption which took place spontaneously, with an increasing randomness at the adsorption sites boundary (positive entropy).

Keywords: *Gmelina arborea*, Crystal violet, Color adsorption, Low cost adsorbent, Adsorption isotherms

1. Introduction

Because *G.a.* is a fast growing tree purposefully planted for industrial source of logs which are used for many products, the tree is considered the second most widely available and the most abundant (Industrial Tree Planting Species) ITPS in the 2007 Philippine Timber Licensees Report of the Forest Management Bureau of the Department of Environment and Natural Resources. The use of log generates solid wastes including the barks. The Philippines and many other regions like India, Malaysia, Pakistan (Report on Southern African Regional Commission for the Conservation and Utilization of Soil [1], where textile industries are located, can benefit from this study. This study is to establish another low cost, readily available color adsorbent alternative and that is the *G.a.* bark.

Generally, color is one of the most obvious indicators of water pollution and in some cases is itself harmful compound that can originate dangerous by-product and metabolites that are toxic, mutagenic and carcinogenic [2 – 8]. The exact amount of synthetic organic dyes produced in the world is unknown, although financial reports estimate their continuous increase in the worldwide market up to about US\$11 Billion in 2008 with a production dyestuffs over 7×10^5 tons [9,10]. However, sad and real stories are happening, some of these dyes cause effluents to fail the quality standard and pollutants are spilled off and discharged to the creeks and streams of waters. Thus, researches and studies for the effective method of color removal are continuously developed.

The present study is devoted to the investigation of adsorption capacity of two *G.a* bark types: acid treated *G.a* bark (bark A) and untreated (controlled) bark (Bark B). Further adsorption studies focused on the effects of initial adsorbent dose, temperature and agitation time in the adsorption of CV dye. Resulting adsorption data were tested for fit in adsorption isotherms Linear, Langmuir, Freundlich, and Tempkin

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Models. All figures and graphical presentations of data and analysis were achieved with the aid of Minitab Software. Finally, thermodynamic parameters were explored to understand conditions that favour CV adsorption process. Mechanism of CV adsorption, desorption study, column adsorption tests and CV recovery were not included but will be stated as recommendations.

2. Adsorption Study

2.1. Materials and Methods

Crystal Violet (CV) is requested from the Chemical Preparation Room of Mapua Institute of Technology (MIT). The working solutions were prepared by taking the required weights of CV diluting to volume with distilled water to achieve the desired concentrations. The physical and chemical properties of CV are presented in Table 1. Other chemicals such as 37% formaldehyde and sulfuric acid were supplied by MIT Chemical Preparation Room and used as is. *G.a.* bark was taken from freshly cut branch in a plantation at Purok 4 Brgy. Laguerta, Calamba, Laguna and allowed to stay outside for three weeks allowing natural elements (sun, air, and day and night moisture) to interact for some time, a simulation of forest wastes being left for a time after logging. Barks are milled in Wiley mill at MIT pilot plant laboratory, passed through 4.0mm and retained in 250 mesh sieve and oven dried using Quincy Lab Inc. Model 30 GC oven of MIT Environmental Research Lab at 100°C for four hours [12]. One half of the dried bark was packed in a plastic zip lock labeled “Bark B” (controlled bark) while the other half was treated with formaldehyde (37%) in acidic medium (2:1 bark to formaldehyde mass ratios), mixture was stirred and heated at 80°C for 2 hours, filtered washed with cold distilled water until the filtrate’s pH was 4 or close to neutral, (in this case at pH 5.48) [11], drained then dried [12], packed in zip lock, labeled “Bark A” (acid treated bark) and were stored in dessicator until use.

Table 1: The Physical and Chemical Characteristics of Crystal Violet (CV) Dye

Parameters	Values
Generic Name	C.I. Basic Violet (10BV 10)
Molecular Formula	C ₂₅ H ₁₀ N ₃ Cl
Molecular Weight	407.99
λ _{max} (nm)	Reject
Color index number	42555

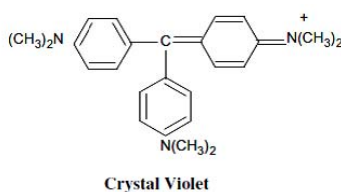


Fig. 1 : Crystal Violet Chemical Structure

Initial adsorption studies were carried out at 30°C at pre-selected solution concentrations and bark weights. Calibration curve of the solution were made by analyzing the known concentrations of the C.V. solutions in the Perkin-Elmer Lambda 40 Spectrophotometer. Perkin-Elmer Lambda 40 Spectrophotometer gave a calibration curve equation shown below:

$$y = 1.340677e^{-1} * x - 1.03944e^{-3} * x^2 \quad (1)$$

Using different bark concentration (0.5g increments) in predetermined solution concentrations, samples were withdrawn and separated using Whatman paper (No.41) and analyzed for the remaining CV content. The percent removal of dye from solution was calculated by the following equation:

$$\% \text{ removal} = \frac{(C_o - C_i)}{C_o} \times 100 \quad (2)$$

where C_o is the initial concentration of dye and C_i is the final concentration of dye.

Isotherm studies were recorded by agitating preset bark concentration for different solution concentrations until equilibrium. Concentrations of CV in the solutions were computed using the calibration curve equation. After determination of the solution concentration, CV concentrations in the bark were computed using the following equation as also used by Monash et al. (2009) and Ahmad, (2009):

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (3)$$

where q_e is the adsorption capacity equal to the amount of dye adsorbed at equilibrium (mg/g), V is the volume of the solution (ml), m is the mass of the adsorbent (g), C_o and C_e are the initial and the equilibrium solution concentrations, respectively.

The effects of agitation time were investigated using one fixed initial dye concentration (10ppm) by adding 50ml of solution in 1.0g of the barks and agitated at for 30°C, 45°C and 60°C temperatures. At a predetermined time intervals, samples were taken and the concentrations analyzed. The amount of CV adsorbed q_t at time t was determined by the following equation, as also used by Monash et. al. (2009) and Ahmad (2009):

$$q_t = \frac{(C_o - C_t) \times V}{m} \quad (4)$$

where q_t is the amount of dye adsorbed at time t (g/g), V is the volume of the solution (ml), m is the mass of the bark (g), C_o and C_t are the concentrations of the dye at initial time ($t = 0$) and at time t , respectively.

2.2. Results and Discussions

2.2.1. Effect of Initial Bark and Dye Concentrations

Both initial solution and adsorbent concentrations definitely affected adsorption behaviour of the dye. Effects were recorded from the experiments conducted using solution concentration range of 5ppm to 100ppm, adsorbent dosage of 0.5g increments and at room temperature. The absorbance for barks A and B were recorded and percent removal computed. Fig 2 graphically reveal the trends of percent adsorption as solution concentration is increased for both barks A and B respectively. Similar observations were noted from the works of Ahmad (2009), Mittal (2010) and Somasekhara Reddy (2006). As the initial concentration of solution increases from 5ppm – 100 ppm, percent CV removal increases for both barks.

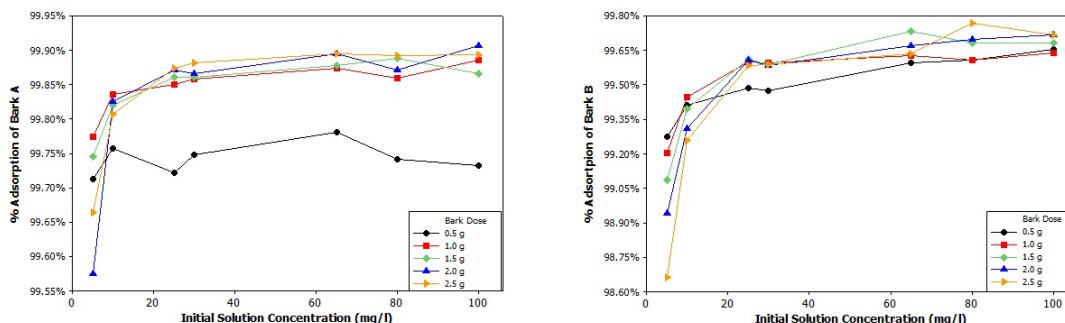


Fig. 2: Effects of initial solution and initial bark concentrations (Bark A and B)

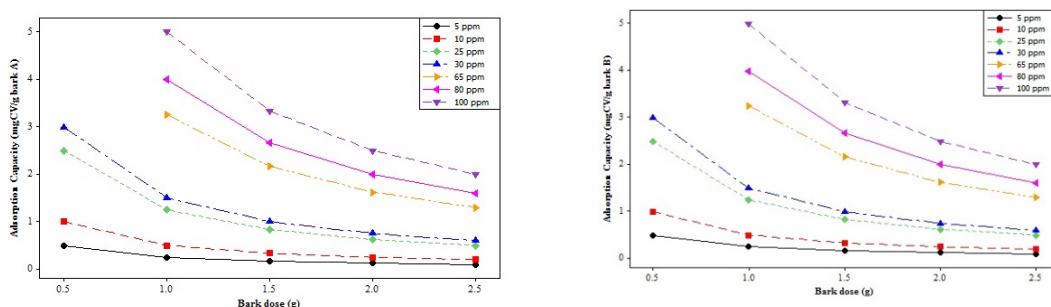


Fig. 3: Effect of Initial adsorbent dose and solution concentration in the adsorption capacities

Fig 3 show the decreasing trend of adsorption capacities as adsorbent dose is increased at different initial solution concentrations.

2.2.2. Adsorption Isotherms

The equilibrium between the concentration of CV in the liquid phase and its concentration in the solid phase resembles somewhat the equilibrium solubility of a gas in a liquid. The concentration in the solid phase is expressed as q_e , (mg adsorbate (CV)/ g adsorbent (Bark)), and in the fluid phase (liquid) as C_e , (mg adsorbate (CV)/l fluid) [13]. The data were plotted for the adsorption isotherm and is fitted for various models using ANOVA in MINITAB software. Results were shown in Table 2.3.1.

Table 2: Lack of fit test for different isotherm models

Isotherms	R ² Values		Lack of Fit Test		Decision
	Bark A	Bark B	Bark A	Bark B	
Linear Model	79.0%	76.0%	Possible lack of fit		Used in current studies (dilute solution)
Langmuir Model	53.9%	42.8%	Possible lack of fit		Reject
Freundlich Model	86.9%	75.8%	No evidence of lack of fit		May be use in future studies
Tempkin Model	68.9%	52.2%	Possible lack of fit		Reject

2.2.3. Thermodynamic Parameters

For the thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:

$$K_c = \frac{C_{ac}}{C_e} \quad (5)$$

$$\Delta G^\circ = -RT \log K_c \quad (6)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (7)$$

where K_c is the equilibrium constant, C_{ac} and C_e are the equilibrium concentrations (mg/l) of the dye in adsorbent and in solution, respectively, T is the temperature in Kelvin and R is the gas constant ($R = 8314.47 \text{ J/kgmol.K}$). Log of K_c vs $1/T$ for both bark types were plotted to obtain value for equations (5)-(7) and to compute the thermodynamic parameters using bark A and B's line equations. Table 2.2.3.1 summarizes the values of the parameters.

Table 3: Summary of Thermodynamic parameters for Bark A and B's CV adsorption

Temp (°C)	Bark A			Bark B		
	ΔG° (kJ/mol)	ΔS° (kJ/mol)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	ΔS° (kJ/mol)	ΔH° (kJ/mol)
30	-7.1645			-5.7293		
45	-7.5547	0.0480	-2.0067	-5.8998	0.0257	-5.4084
60	-7.7849			-6.0640		

The negative free energy (ΔG°) for both bark A and B indicated a spontaneous adsorption process. The positive values for entropy (ΔS°) proved that there was an increasing randomness at the interface of the adsorbents and the solution for both bark types. The negative value for enthalpy (ΔH°) was proving that adsorption process for both bark types proceeded in an exothermic nature.

2.2.4. Effect of Contact Time

Study on the influence of agitation time on the adsorption of CV to the bark was conducted using fixed amount of bark (1.0g) and dye concentration (10ppm). The consequence of further increasing contact time lowers the available adsorption sites or the "approaching-to-equilibrium and/or exhaustion" state of the bark. In the current study, the effects resulted in a no significant increase in percent adsorption at 30 minutes and longer periods, an evidence that equilibrium may already been attained. This is observed to both bark types. And throughout the study, bark A exhibits higher adsorption capacity than bark B.

2.2.5. Effect of Temperature

The study was carried out at temperatures 30°C, 45°C, and 60°C, at constant bark dose (1.0 g) and solution concentration (10 ppm). It was observed that highest adsorptions were recorded at 30°C temperature

for both Barks A (99.8741%) and B (99.5179%), while the lowest is at 60°C for both barks A (99.8345%) and B (99.2165%).

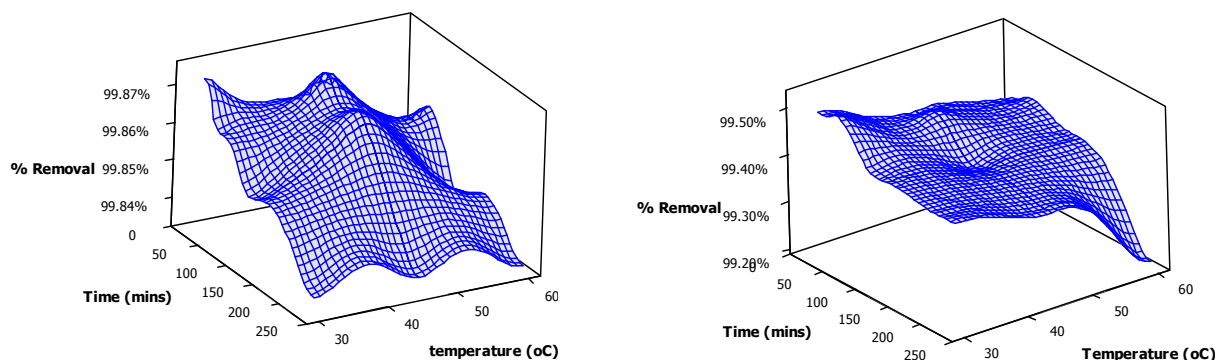


Fig. 4: Effect of temperature and contact time in the adsorption (%removal) of Bark A and B

The best explanation was relating adsorption behaviour to the thermodynamic parameter ΔG° with the negative value, which indicated spontaneous reaction at room temperature. Also, the negative value for ΔH° explicated that energy was liberated by the system during adsorption process and adding external heat, such in the case of CV solution at 60°C, suspended spontaneity and therefore lowered the adsorption values. A similar case was reported in the CV adsorption studies of Monash (2009), but opposing cases were noted in the works of Ahmad (2009), Mittal (2010) and Somasekhara Reddy (2006).

2.3. Conclusion

The present study proved *Gmelina arborea* bark is a potential low cost adsorbent for CV even without treatment. *G.a.* bark was capable of adsorbing as high as 4.9943 mg C V/g bark A and 4.9819 mg CV/g bark B. Capacities of the two bark types did not differ significantly in values, however, bark A's % CV adsorption (99.91%) was probably significantly higher compared with bark B (99.77%). The equilibrium isotherm examination considered Linear Model because the advance studies (effect of contact time and temperature) considered a dilute solution systems in which linear model proved to be useful [13]. Effects of agitation time revealed equilibrium is attained at less than or equal to 30 minutes agitation time. Adsorption at room temperature was favorable than at higher temperature. Finally, thermodynamic parameters suggested that CV adsorption process proceeds spontaneously in an exothermic nature.

2.4. Recommendation

In the course of this study, there are areas which are of interest, as such are the need for further studies on adsorption of *G.a.* bark using other dyes, further studies on the effects of agitation time and temperature to test hypothesis that it is proceeding to a negative adsorption (possibilities of a desorption effect), adsorption at a higher solution concentrations (higher than 100ppm) to examine mechanism and effect of particle structure of the two types of bark in CV adsorption, investigate fit of Freundlich Isotherm, and study adsorption and desorption kinetics for both bark types in batch and column methods including the regeneration could also be an interesting topic.

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