

## **THE SEED OF BURMESE GRAPE (BACCAUREA RAMIFLORA) AS LOW-COST BIO-ADSORBENT FOR REMOVAL OF METHYLENE BLUE FROM WASTEWATER**

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### **ABSTRACT**

Treatment of the industrial wastewater containing dyes is becoming the concern of many conservationists. As dye containing effluent from industries has biological and environmental hazards, techniques for the removal of dyes from waste has been growing rapidly. Bio-adsorbent from divergent sources has been used as promising agent for removing the contaminants in wastewater due its availability, low-cost, biodegradability and nontoxicity. In this study the capacity of Burmese grape seeds as a low-cost bio-adsorbent for the removal of methylene blue from aqueous solution was explored. Batch adsorption experiments were performed with varying process parameters (pH, contact time and initial dye concentration) at ambient temperature. UV-vis spectrum analysis was performed to determine the change in concentrations of dye. Changes in adsorption capacity with varying pH was noticed and maximum sorption of methylene blue was found to be at pH 8. The adsorption rate was rapid for first 10 minutes of contact time and at 40 minutes the equilibrium condition was achieved and no further change was observed in concentrations with contact time. Kinetic studies showed good correlation coefficient ( $R^2=0.999$ ) for a pseudo-second order kinetic model over the selected range of contact time (10-40 minutes). The removal mechanism was described by Langmuir isotherm model with a good fit ( $R^2=0.983$ ). Maximum sorption capacity was calculated by Langmuir isotherm model and found to be 163.93 mg/g. So, the results showed that if the process variable can be optimized, Burmese grape seeds can be a very effective adsorbent and have the potential to remove a significant amount of dye from industrial wastewater.

**Keywords:** *Dye, Burmese grape, Bio-adsorbent.*

## 1. INTRODUCTION

Rapid growth of textile industries in Bangladesh has led to economic growth but caused a serious problem to the adjacent water sources such as rivers. The disposal of dye waste water into fresh water as an effluent from textile industries causes severe damage to the aquatic environment (Hassaan et al. 2017; Gita et al. 2017). Furthermore, these dyes cause allergic reactions, dermal irritation and genetic mutation as a result of their toxic property (Daciana 2010). Several physico-chemical methods like coagulation/flocculation, membrane separation, electrochemical process, adsorption, ion exchange, irradiation, biological treatment and many others are used for removing dyes from wastewater (Chidambaram et al. 2015; Verma et al. 2012; Nidheesh et al. 2018; Gupta, 2009; Mohammed et al. 2014). Among these, adsorption is as an efficient and cost effective process as its initial cost and energy consumption is far less than other processes.

In recent years many adsorbents are used to remove dye from wastewater such as activated carbon, alumina composite, activated clay, kaolin, bentonite, red mud and many others (Adaket al. 2005; Kannan et al. 2001; Özcan et al. 2005; Nandi et al. 2008). Though they work very well the cost of these adsorbents are quite high. To make the process cost effective recently the focus of researchers is devoted to bio-adsorption process bio-adsorbents are found in vast amount. Moreover, bio-adsorbents are more selective and can reduce the dye concentration to ppb level (Mustafa et al. 2014). Some of the reported bio-adsorbents are jute fibre carbon (Senthilkumaar et al. 2005), coconut husk based activated carbon (Tamai et al. 1996), baker yeast (Yu et al. 2009), wheat straw (Batziatas et al. 2009), living biomass (Yu et al. 2000), algal biomass (Vilar et al. 2007) etc.

In this study, for the first time the feasibility of Burmese grape seed powder as bio-adsorbent for removal of methylene blue was investigated. Burmese grape (*Baccaurea ramiflora*) is a plant belongs to the family phyllanthaceae, most commonly cultivated in Burma, Bangladesh and India. The flesh of the fruit is eaten and the seeds are thrown away. These seeds can be used as potential adsorbent for dye removal. The implementation of this bio source must bring obvious social and economic benefit.

The research results on the removal of methylene blue from wastewater using Burmese Grape seeds are presented in this work. The effects of various parameters of adsorption such as contact time, initial pH, and dye concentration were monitored and optimal experimental conditions were determined. Moreover, the kinetic study based on pseudo second order kinetic model was done and the isotherm data were analysed using Langmuir isotherm model. The adsorption property of Burmese Grape seeds towards methylene blue is executed for the first time and this defines the novelty of this work.

## 2. EXPERIMENTAL METHODS

### 2.1 Adsorbent and Chemicals

Burmese Grape seeds were collected from local market and all other chemicals were of analytical grade. 100ppm methylene blue solution was prepared using methylene blue and diluted further using distilled for adsorption experiments. 0.1 mole/L HCl and 0.01 mole/L NaOH were used to adjust Ph.

### 2.2 Adsorbent Preparation

The collected Burmese Grape seeds were washed repeatedly with distilled water to remove dust and insoluble impurities. The seeds were air dried for 2 days and followed by microwaving at 600Hz for 4 minutes to ensure the removal of water. Then the seeds were grounded to fine particles for using in adsorption experiments.

### 2.3 Equilibrium Adsorption Studies

#### 2.3.1 Effect of pH

This investigation was done to determine the optimum P<sup>H</sup>. for methylene blue removal from water using seed of Burmese Grapes. In this study, 0.01 g of adsorbent was contacted with 50ml 10 ppm dye

solutions for 40 minutes for different PH.(5, 6, 7, 8 and 9). The PH. value was adjusted using HCl and NaOH solution. The mixture was centrifuged to separate the adsorbent and the supernatant solutions were analysed using UV-vis spectrophotometer.

### 2.3.2 Effect of Contact Time

Methylene blue removal capacity using the seeds was determined as a function of time to determine the optimum contact time. For this purpose, 50 MI 20ppm methylene blue solution was contacted with 0.01 g adsorbent. The samples were collected at different time intervals (10, 20, 30, 40, 50 minutes) from the solution and centrifuged to separate the adsorbent with a view to analysing the samples.

### 2.3.3 Effect of Initial Concentration

It is well known fact that the adsorption capacity of adsorbent changes with the initial concentration of dye. To investigate this 0.01 g of adsorbent was contacted with methylene blue solutions, concentration ranging from 5 to 70 at regular intervals for 40 minutes. Then the treated water was centrifuges and analysed.

For adsorption experiments the removal capacity and adsorption capacity were calculated by equation 1 and 2 respectively,

$$\text{Removal percentage} = (C_0 - C_e) / C_0 \times 100\%$$

$$\text{Adsorption capacity} = (C_0 - C_e) \times V / m$$

where  $C_0$  and  $C_e$  is initial concentration(mg/L) and equilibrium concentration(mg/L) respectively, V is the volume of solution(L) and m is the mass of adsorbent(g).

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of pH.

Figure 1 illustrates the effect of Ph on methylene blue removal using Barmese Grapes seed as adsorbent. There was a rapid increase in the adsorption capacity with the increase of Ph from 5 to 8 and later decreased at 9. At Ph 8, the adsorption capacity was highest with the value of 34.8 mg/g. At lower Ph the surface of the adsorbent was surrounded by  $H^+$  ions and these ions blocked the dyes from being captured by the adsorbent. At higher Ph the competition was decreased as the number of  $H^+$  ions decreased with the increase in Ph.

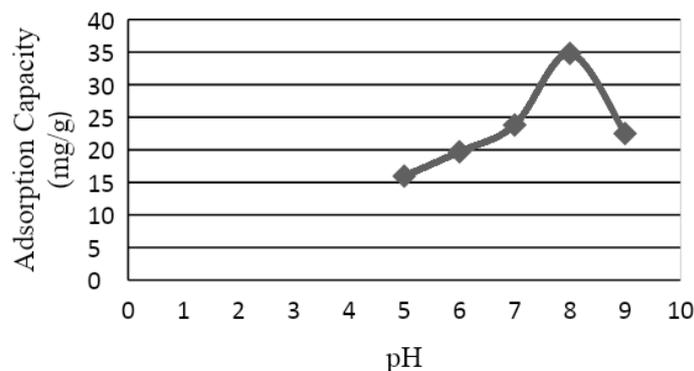


Figure 1: Effect of pH on the adsorption of methylene blue

### 3.2 Effect of Contact Time and Adsorption Kinetics

From figure 2, it can be seen that the adsorption rate was higher for first 10 minutes. Then the adsorption rate decreased with time as the available surface for dye was reducing with time. At 40 minutes the equilibrium condition was found and no further change was observed with time. Therefore, 40 minutes was chosen as the optimum adsorption time for dye removal.

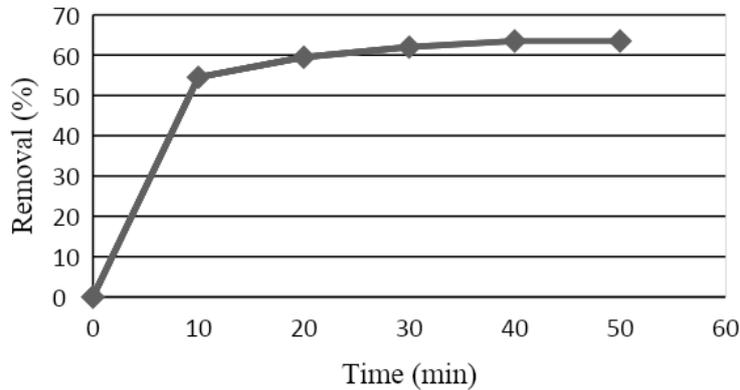


Figure 2: Effect of time on adsorption of methylene blue

Pseudo second order equation was used to analyse the kinetics of the adsorption process

$$t/q_t = (1/k_2 q_e^2) + (t/q_e)$$

where  $q_t$  and  $q_e$  are the adsorption capacity (mg/g) at time  $t$  and at equilibrium respectively, and  $K_2$  is the pseudo-second-order equilibrium rate constant ( $L \text{ mg}^{-1} \text{ min}^{-1}$ ). The graphical interpretation of the data for pseudo second order kinetic model is shown in figure 3. A good fit of data ( $R^2=0.999$ ) was observed which indicates that the adsorption process followed pseudo second order model and the process was chemisorption. The value for  $k_2$  and  $q_e$  were determined from the slope and intercept of the plot shown in fig. 3. The theoretical value of adsorption capacity ( $q_e$ ) at equilibrium was 66.67 mg/g which is quite near to the value 63.5 mg/g, found from experimental procedure.

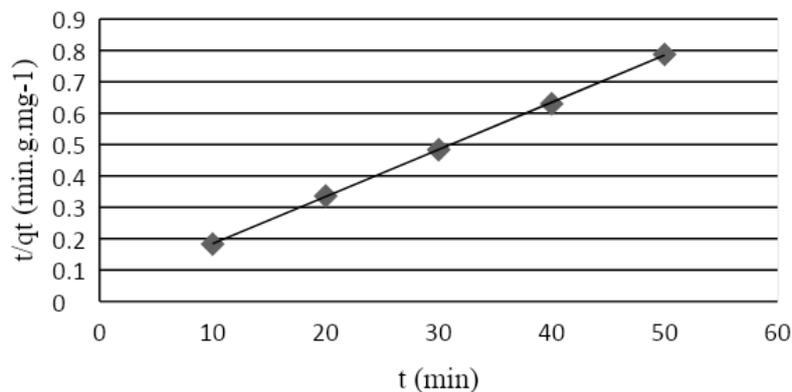


Figure 3: Pseudo-second order plot

### 3.3 Effect of Initial Concentration and Adsorption Isotherm

The effect of initial concentration of dye on adsorption performance was evaluated by varying the dye concentration. From figure 4 it can be inferred that the adsorption capacity increases with initial concentration to a certain point and after that point there was no change in adsorption capacity with the change in initial dye concentration. This can be explained by the fact that the concentration gradient increases with the increase in initial concentration and this forces the adsorbent to capture more dye before reaching equilibrium. After a certain point the adsorption capacity reaches to its peak point. After that increase in initial concentration does not affect the adsorption capacity. The maximum adsorption capacity reaches at dye concentration of 60 mg/L and the experimental value is 148.5 mg/g.

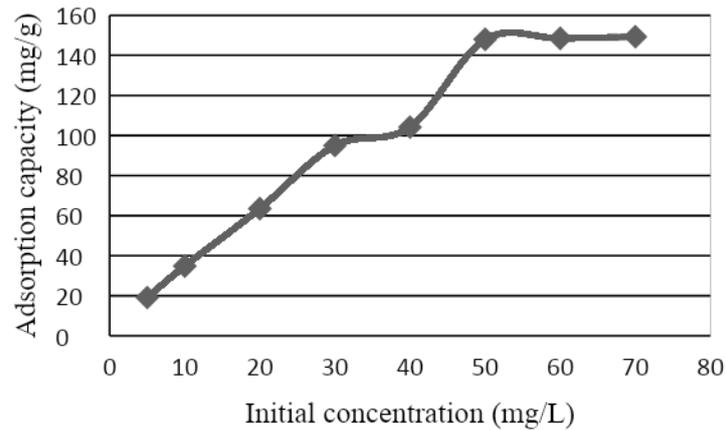


Figure 4: Effect of initial concentration on adsorption capacity

In this study the adsorption isotherm was analysed using the Langmuir isotherm, which is most commonly used. The linear form of Langmuir isotherm is expressed by,

$$1/q_e = 1/q_m + (1/C_e)(1/K_L q_m)$$

where  $K_L$  is the Langmuir constant,  $C_e$  is equilibrium concentration of dye solution (mg/L),  $q_e$  is adsorption capacity (mg/g) at equilibrium and  $q_m$  is the maximum adsorption capacity (mg/g). Figure 5 shows that experimental data fitted well with the Langmuir isotherm model as the regression value was close to unity ( $R^2=0.983$ ). The value of  $q_m$  was found to be 163.93 mg/g, which is closer to the maximum adsorption capacity determined experimentally.

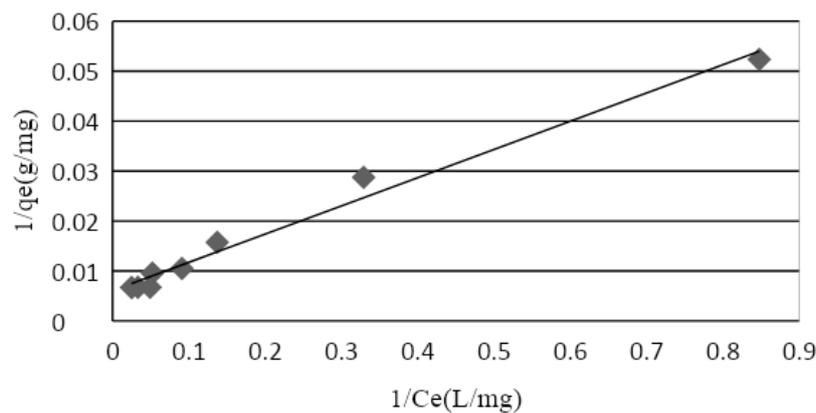


Figure 5: Adsorption isotherm

### 3.4 Comparison With Other Bio-adsorbents

Comparison of different bio-adsorbents on removing methylene blue is shown in table 1. Previously various bio-adsorbents were used to remove dye such as dead fungus *Aspergillus niger* and dead *Streptomyces rimosus* while their adsorption capacity were 18.54 mg/g and 34.34 mg/g respectively. Study reported the use of algal waste with the adsorption capacity of 104 for removing methylene blue. Fruit peels were also used for the same purpose. Among the shown adsorbents Burmese grapes show the highest adsorption capacity of 163.93 mg/g, which implies the feasibility of using this in large scale.

Table 1: Adsorption capacities of bio-adsorbents

Adsorbents	Adsorption capacity (mg/g)	Sources
Algal waste	104	Vilar et al. 2007
Unmodified baker's yeast	51.5	Yu et al. 2009
Green alga <i>Ulva lactuca</i>	40.2	Sikaily et al. 2006
The brown alga <i>Cystoseira barbatula</i> Kutzing	38.61	Caparkaya, et al. 2008
Dead <i>Streptomyces rimosus</i>	34.34	Nacera et al. 2006
Dead fungus <i>Aspergillus niger</i>	18.54	Fu et al. 2000
<i>Posidonia oceanica</i> (L.) fibres	5.56	Ncibi et al. 2009
<i>Caulerpa racemosa</i> var. <i>cylindracea</i>	5.23	Cengiz et al. 2008
Orange peel	18.6	Annadurai et al. 2002
Banana peel	20.8	Annadurai et al. 2002
Oak saw dust	29.94	Ferrero et al. 2007
Burmese grape seed	163.93	This study

## CONCLUSIONS

Removal of dyes from industrial effluents by bio-adsorbent has been growing soberly due to its large availability and low cost. Besides, this branch offers an embarking opportunity to transform waste to useful materials. Adsorption of methylene blue from aqueous solution by Burmese grape seeds has been explored in this study. Effectiveness of Burmese grape seeds for the removal of methylene blue from aqueous solution was sumptuous. It panopies higher adsorption capacity than traditional bio-adsorbents at optimum condition. Adsorption process shows pH sensitivity and pH 8 was found to be the optimum pH for maximum removal. Equilibrium was achieved after 40 minutes of contact time while first 10 minutes shows expeditious adsorption. Kinetic study shows that the adsorption process followed pseudo second order kinetics while the isotherm study suggests that the isotherm data fit with Langmuir isotherm. Maximum adsorption was found to be 163.93 mg/g .The potential use of Burmese grape seed for dye removal is established through this study. Yet there is scope of further works such as finding its adsorption capacity after alkaline treatment, it can be concluded that the locally available, low cost Burmese grape seed can be used for methylene blue removal from wastewater in an eco-friendly manner.

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