

## Removal of Methylene Blue (Mb) Dye from Aqueous Solution by Bioadsorption onto Untreated *Parthenium hysterophorous* Weed

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### Abstract

Nowadays, the application and search of alternative cheap and ecofriendly adsorbents to replace activated carbon was made. It has been a major focus for the removal of dyes from waste water. In this study untreated *Parthenium hysterophorous* weed (PHW) was used to remove a textile dye (Methylene Blue (MB)) from an aqueous solution by adsorption technique. The factors influencing the adsorption were also investigated. The MB dye removal by the PHW was significantly dependent on contact time, pH, dye concentration, adsorbent dose and pH. The optimum equilibrium conditions for removal of MB dye by PHW were; contact time of 2 hrs, at pH 8 and an adsorbent dose of 0.8 g. The adsorption data better fits Langmuir isotherm model well and the maximum adsorption capacity of the PHW was found to be 23.8 mg g<sup>-1</sup>. The results obtained in this study indicated that PHW will be an attractive candidate for removing cationic dyes from the dye wastewater.

**Keywords:** *Parthenium hysterophorous*; Weed; Adsorption; Methylene blue

### Introduction

Water pollution by dyes is a worldwide problem particularly in textile industry where large quantities of dye effluents are discharged from the dyeing process. Considering both volume and composition, effluent from the textile industry was declared as one of the major sources of wastewater in the world. Dyes are also widely used in many industries such as rubber, paper, plastic, cosmetic etc. There are more than 10,000 commercially available dyes with over  $7 \times 10^5$  tons of dyestuff being produced annually across the world [1]. The total dye consumption of the textile industry worldwide is more than 10<sup>7</sup> kg/year, and about 90% ending up on fabrics. Dye producers and consumers are interested in the stability and fastness of dyes and consequently, are producing dyestuffs which are more difficult to degrade after being used. It is estimated that 10-15% of the dye is lost during the dyeing process and released with the effluent [2].

So, it is vital to treat these polluted waste waters efficiently as well as effectively in terms of cost by using Bio-sorbents. Biomaterials that are available in large quantities may have a potential to be used as low cost adsorbents, because they represent unused resources that are widely available and environmentally friendly [3]. Today, many industries commonly used activated carbon as adsorbent agent for dye removal. Commercially available Activated Carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents [4,5].

A wide variety of carbons have been prepared from agricultural and wood wastes, such as bagasse [6], coir pith [7], banana pith [8], date pits [9], corn cob [10], maize cob [10], straw, rice husk [11,12], rice hulls, fruit stones and nutshells [13], pinewood, sawdust [12] and etc.

Moreover, the overlying cost of activated carbon and associated problems of regeneration has force a new research in order to find other alternative low cost adsorbents agent. Since preparation of activated carbon from bio-resources requires a great amount of energy and as well as regeneration of pollutants from the activated carbon poses a great deal of bulky process. In addition to biomaterials, microorganisms have also been used as metal sorbents. Bacteria, fungi, yeast and algae have been reported to remove heavy metals from aqueous solutions [14].

Nowadays, there are numerous numbers of low cost, commercially available adsorbents which had been used for dye removal. However,

as the adsorption capacities of the above adsorbents are not very large, the new adsorbents which are more economical, easily available, environmentally friendly and highly effective are still needed [15,16]. A variety of materials are used as adsorbents for dyes removal, and various studies have been published on its adsorption on activated carbon, starch xanthate, alumina, low-grade manganese ore, crushed coconut shell, fly ash, sawdust, rice husk carbon, wood charcoal, bituminous coal, and lignite.

Past recent research was still searching of an effective biosorbent that can be used to remove dyes from aqueous solution. However, study on *Parthenium hysterophorous* weed adsorbent is only few in this field. Hence there is a need to investigate dry *Parthenium hysterophorous* ability to MB from industrial waste waters. Therefore, the aim of this study was to investigate the potential of untreated *Parthenium hysterophorous* weed, as a non-conventional adsorbent in the removal of a Methylene Blue dye from aqueous solutions. Using these alien weeds as biosorbent can be an alternative way to monitor their spreading in the environment to some extent.

### Materials and Methods

#### Apparatus and instruments

All glassware (conical flasks, measuring cylinders, beakers, pipettes etc.) were manufactured by Borosil / Rankem. Whatman No-1(125 mm) filter paper, Sieve to get 1mm particle size and all the instruments used in the experiment are listed below: (Table 1)

#### Chemicals and reagents

Analytical grade reagents; Methylene blue (C.I. 52015, S.D. Fine Chemicals) were used to prepare standard solutions of the adsorption studied. HCl and NaOH (Blulux Laboratories (p) Ltd- 121001) used to

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Instrument	Manufacturer
Electronic Balance	OHAUS, Switzerland
pH meter	Jenway/(MP 220)
Oven	Shivaki(Contherm 260M)
Shaker	Orbital shaker SO1, UK
Spectrophotometer	Sanyo (Uv/Vis-65)
Electrical mill	(IKA WERKE), UK

Table 1: List of all instruments used

adjust pH and buffer solutions (E. Merck) used to calibrate pH meter.

### Experimental site

The adsorbent (*Parthenium* weed) was collected from the Arba Minch City, Ethiopia in randomly sampling technique and the collected samples were mixed to prepare adsorbent composite sample.

### Biosorption study

**Adsorbent collection and preparation:** Adsorbent is the material upon whose surface the adsorption takes place is called an adsorbent. For this study *Parthenium hysterophoresis* weed was used as a low cost biosorbent. The collected weed adsorbent was then washed with distilled water for several times to remove all the dirt particles. The washed materials were cut into small pieces (1-3 cm) and dried in a hot air oven at 60°C for 48 hr. Then ground and finally screened to obtain a particle size range of 1 mm size sieve and then stored in plastic bottles for further use.

**Adsorbate:** The basic dye, methylene blue (C.I. 52015, S.D. Fine Chemicals, 85% dye content, chemical formula C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl, FW 319.86, nature basic blue, and λ<sub>max</sub> 665 nm) has been used in this study. The MB was chosen in this study because of its known strong adsorption onto solids. An accurately weighed quantity of the dye was dissolved in double distilled water to prepare the stock solution (1000 mg/L). Experimental solutions of desired concentration were obtained by successive dilution (Figure 1).

### Batch adsorption studies

Batch mode adsorption studies for individual parameters were carried out using 250 ml Erlenmeyer flask. The effects of different parameters such as adsorbate concentration, adsorbent dose, contact time and pH were studied. The Erlenmeyer flasks were pretreated with the respective adsorbate for 24 hours to avoid adsorption of the adsorbate on the container walls. Standard solutions of the MB dye were mixed with the *Parthenium hysterophoresis* adsorbent and agitated at different agitation rate on a mechanical shaker. This was carried out by varying the MB dye concentration. Finally, the resulting suspension of each of the dye was filtered using a Whatman No.1 filter paper and the filtrate was analyzed for the corresponding MB dye concentration. Removal efficiency was finally calculated by using the relationship.

$$\text{Adsorption (\%)} = (C_o - C_e) / C_o \times 100$$

Where C<sub>o</sub> = the initial concentration (mg/L) and C<sub>e</sub> = final concentration (mg/L) of the MB dye being studied. The adsorption capacity of the *Parthenium hysterophoresis* is the concentration of the MB dye on the adsorbent mass and was calculated based on the mass balance principle.

$$q_e = (C_o - C_e) \times V / m$$

Where q<sub>e</sub> = adsorption capacity of *Parthenium hysterophoresis* (mg/g)

V = the volume of reaction mixture (L)

m = the mass of adsorbent used (g)

C<sub>o</sub> = the initial concentration (mg/L) of the MB dye and

C<sub>e</sub> = final concentration (mg/L) of the MB dye

**Effect of contact time:** Contact time is one of the most important parameters for the assessment of practical application of adsorption process.

50 ml of the working solution which is 50 mg/L concentration was put in each different conical flask. An adsorbent dose of 0.2 g/50 ml and an initial pH of 8 were used. All the flasks were put in the shaker at 150 rpm and 25°C for a predetermined time period ranging from 20 to 140 minutes, on a 20 minutes interval. Other parameters were kept constant. Then, flasks were withdrawn from the shaker, solution was filtered and absorbance of the solutions was measured. A graph was plotted with % Q vs. contact time.

**Effect of adsorbent dose:** 50 ml of the working solution was put in each different conical flask. Then, different adsorbent dose from (0.1, 0.2, 0.4, 0.6, 0.8 and 1 gm) was added in each flask other parameters are constant. And all the flasks were kept inside the shaker at 150 rpm and 25°C for 100 min.

After 100 minutes, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbents by using filtration. The absorbance of all the solutions was then measured. A graph was plotted with percent removal (%Q) vs. adsorbent dose. %Q is expressed as,

Where,

%Q = percentage of dye adsorbed

C<sub>o</sub> = initial dye concentration (mg/lit)

C<sub>e</sub> = equilibrium time solution concentration (mg/lit)

The amount of dye adsorbed onto *Parthenium hysterophorous*, q<sub>e</sub> (mg/g), was calculated as follows:

$$q_e = \frac{(C_o - C_e) V}{W}$$

Where, C<sub>o</sub> and C<sub>e</sub> are the initial and equilibrium time solution concentrations of the dye (mg/L), respectively, V the volume of the solution (L) and W the weight of the dry adsorbent used (g).

**Effect of initial pH:** 50 ml of the 50 ppm methylene blue dye solution was put in each different conical flask. The optimum adsorbent dose as obtained from the above study (0.8 gm) was put in each flask. The pH of each flask was adjusted in the range of 2-10 with dilute HCl (0.1 M) and NaOH (0.1 M) solution by the use of pH meter. Then, all the flasks were kept inside the shaker at 150 rpm and 25°C for 100 minutes. After that, flasks were withdrawn, solution was filtered and absorbance of the solutions was measured. A graph was plotted with % Q vs. initial pH.

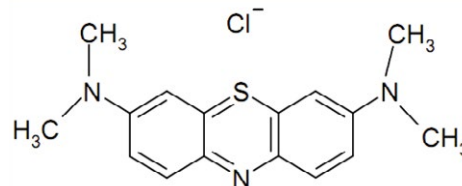


Figure 1: Structure of methylene blue dye

**Effect of adsorbate concentration:** 50 ml of the methylene blue dye solution with concentration ranging from 10 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L was put in each different conical flask. The optimum contact time, adsorbent dose and pH as obtained from the above studies was put in each flask. Then, all the flasks were kept inside the shaker at 150 rpm and 25°C. After that, flasks were withdrawn, solution was filtered and absorbance of the solutions was measured. A graph was plotted with % Q vs. adsorbate concentration.

Each experiment result was an average of three independent adsorption tests. Blank runs with only the adsorbents in 50 mL of double distilled water and 50 mL of dye solution without any adsorbent, were conducted simultaneously at similar conditions to account for any color leached by the adsorbent and adsorbed by the glass containers. Each experimental point is the average of three independent runs and all the results were reproducible with  $\pm 3$  error limit.

### Data analysis

The data generated were analyzed by using Microsoft Excel to compute the mean, standard deviation and linear regression values.

## Results and Discussion

### The effect of contact time on the removal of MB dye

The effect of contact time on the removal of unmodified *Parthenium hystrophorous* at different equilibration time is given in Figure 2. It indicates that the rate of color removal increased depending on the contact time. For the first 60 minutes, the percentage removal for MB dye by the adsorbent was rapid and thereafter it proceeds at a slower rate and finally attains saturation at different contact time for different initial concentration of the dye.

The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions [17]. After a certain period, only a very low increase in the dye uptake was observed because there are few active sites on the surface of sorbent. From the contact time studied, it was revealed that 120 minutes of agitation time is sufficient to reach equilibrium when 50 mg/L of dyes concentration was employed. Therefore, equilibrium time of 2 hours was selected for the adsorption of both dyes for further studies. A similar observation was reported for the adsorption of MG on oil palm trunk fiber [18].

### Effect of adsorbent dosage

The percentage removal of dyes was studied by varying the adsorbent dose between 0.1 g and 1.00 g at a dye concentration of 50 mg/L. An attempt to enhance MB dye removal was evaluated by examining the effect of adsorbent dosage. As shown in Figure 3, it is apparent that the removal percentage of MB dye increases as the adsorbent amount increases and then becomes constant. The removal increased with increased amount of adsorbent dose up to a maximum efficiency (>90%), after which an increase in adsorbent dosage does not further improve the dye removal, implying that a complete dye removal could not be achieved even though using large amount of the adsorbents. An adsorbent dose of 0.8 g was selected for subsequent studies equilibrium studies. When too much adsorbent was added into the dye solution, the transportation of dye ions to the active adsorption sites will be limited as well, hence reduced the adsorption efficiency [15].

### Influence of initial pH

The effect of initial pH on bio-adsorption percentage of MB dye was examined over a range of pH values from 2 to 10 and the results

are presented in Figure 4. As elucidated in Figure 4, the dye removal was minimum at the initial pH 2. The dye adsorbed increased as the pH was increased from pH 2 to 7. Incremental dye removal was not significant beyond pH 8. For this reason, pH 8 was selected for future equilibrium studies.

After adsorption experiments, it was found that at low pH, the dyes become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites results in decreased adsorption. Higher adsorption at increased pH may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent; which facilitates the diffusion process and provides more active sites for the adsorbent. These findings obtained in this study are in line with the results obtained by the following scholars [15].

### Effect of adsorbate concentration

The adsorption of the dyes on carbon was studied by varying the carbon concentration (10–400 mg/L). The percentage of adsorption increased up to dye concentration of 50 ppm as the carbon concentration increased shown in Figure 5. This is attributed to increased weed's surface area and availability of more adsorption sites. It is apparent that the percent removal of MB dye increases rapidly with increase in the concentration of the MB dye weed due to the greater availability of the exchangeable sites or surface area at higher concentration of the sorbent.

But it gradually decreases as result of less available sites for adsorption as depicted in Figure 5. According to Anjaneya et al. [19], lower decolorization percentage at high dye concentration was reported and it was expected to happen because the inhibitory effects of high dye concentrations which have been observed in this study. Initial concentration provides a significant driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases and thus, this suggests that initial dye concentration affected dye decolorization percentages.

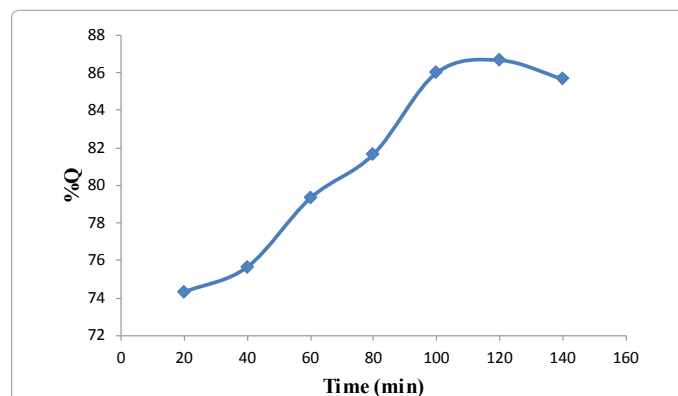
### Adsorption isotherm

The Langmuir and Freundlich equation were employed to study the adsorption isotherms of dye.

The linearized form of the Langmuir equation [20] is as follows

$$C_e / q_e = 1 / (aQ_m) + C_e / Q_m$$

where  $C_e$  (mg/L) is the concentration of the dye solution at



**Figure 2:** Effect of contact time on the removal of MB dye on bio adsorption of MB by the *Parthenium hystrophorous* weed (0.2 g/50 mL; particle size: <250  $\mu$ m; pH 8)

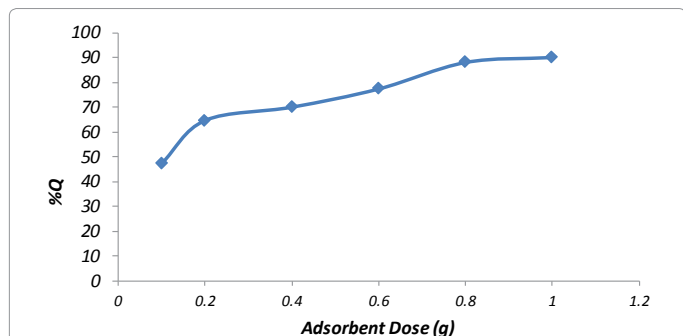


Figure 3: Effect of adsorbent dosage on bio adsorption of MB by *Parthenium hystrophorous* weed (pH 8; particle size: <250 m; contact time: 2 h, 50 mg/L)

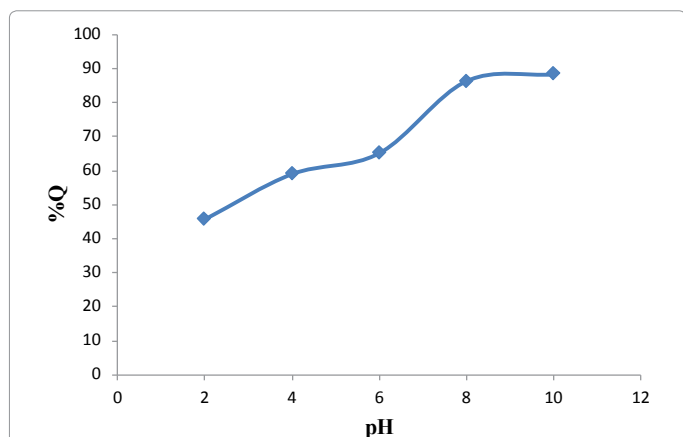


Figure 4: Influence of initial pH on bio adsorption of MB by *Parthenium hystrophorous* weed (adsorbent dose: 0.8 g/50 mL; particle size: <250 m; contact time: 2 h)

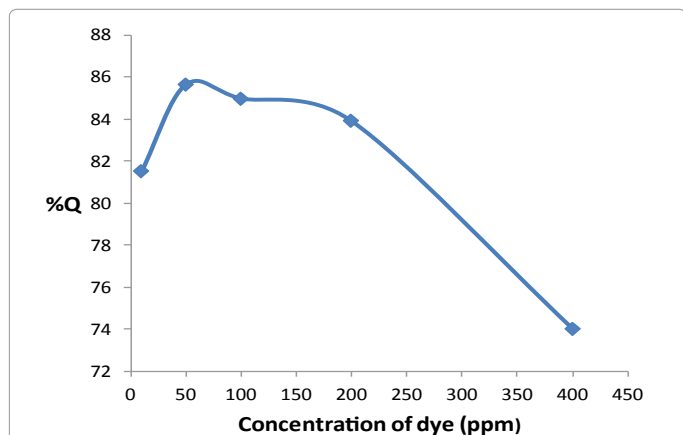


Figure 5: Effect of contact time on the removal of MB Dye on bio adsorption of MB by *Parthenium hystrophorous* weed (0.8 g/50 mL; particle size: <250 m; contact time: 2 h; pH 8)

equilibrium,  $q_e$  (mg/g) is the amount of dye adsorbed at equilibrium,  $Q_m$  is the maximum adsorption capacity and represents a practical limiting adsorption capacity when the adsorbent surface is fully covered with monolayer adsorbent molecule and  $a$  is Langmuir constant. The  $Q_m$  and  $a$  values are calculated from the slopes ( $1/Q_m$ ) and intercepts ( $1/aQ_m$ ) of linear plots of  $1/C_e$  versus  $1/q_e$  as shown in Figure 6.

The linearized form of the Freundlich equation [21] is as follows:

$$\ln Q_e = \ln K + (1/n) \ln C_e$$

Where  $Q_e$  is the amount of dye adsorbed at equilibrium,  $C_e$  is the concentration of the dye solution at equilibrium and  $1/n$  is empirical constant and indicate adsorption capacity and intensity, respectively. Their values were obtained from the intercepts ( $\ln K$ ) and slope ( $1/n$ ) of linear plots of  $\log Q_e$  versus  $\log C_e$  as shown in Figure 7 [22].

The  $Q_m$  and  $a$  values in the Langmuir equation, the  $K$  and  $1/n$  values in the Freundlich equation are given in the Table 2 and Figures 6 and 7. From the results in Table 2, it could be concluded that the adsorption of MB followed the Langmuir model.

## Conclusion

This study confirmed that the bioadsorbent prepared from *parthenium hystrophorous*, a low cost agricultural weed, could selectively remove MB from an aqueous solution. The amount of MB dye adsorbed was found to be dependent on solution pH, adsorbent concentration, initial dye concentration, and contact time. The basic MB dye adsorption decreased at low pH values in accordance with a presupposed ion-exchange mechanism of the adsorption. The optimal pH for favorable adsorption of dye was 8. The change adsorbent dose had an effect on the bioadsorption of MB dye. The adsorption equilibrium was reached in approximately after 2 hours. From this study the adsorption equilibrium data fitted the Langmuir isotherm equation. Even though the removal efficiency of PHW is equivalent to conventional bio-adsorbents and so it is cheaply available. By using this invasive weed as economically and cheap friendly adsorbent

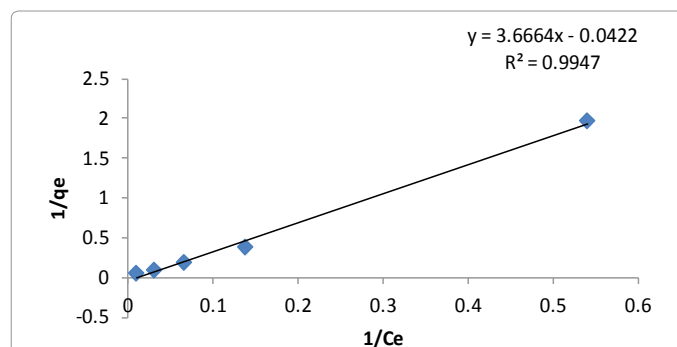


Figure 6: Langmuir adsorption isotherms of MB dye using *Parthenium hystrophorous*

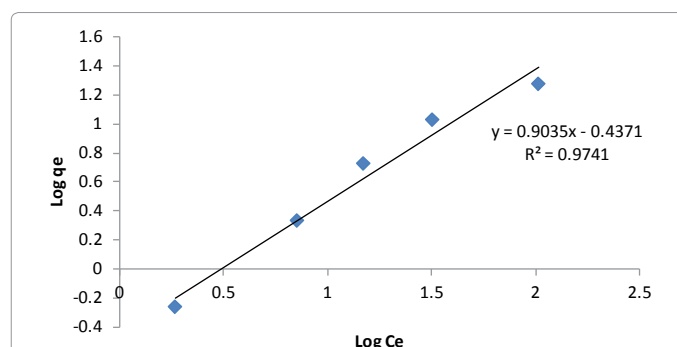


Figure 7: Langmuir Adsorption isotherms of MB dye using *Parthenium hystrophorous*

Langmuir		Freundlich	
Qm (mg/g)	a	K	1/n
23.8	3.66	2.28	0.903

Table 2: The  $Q_m$ ,  $a$  values in the Langmuir equation, the  $K$  and  $1/n$  values in Freundlich equation

considerable dye removal from industrial effluents can be achieved. So it can be substituting other expensive bio-adsorbents. With the experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the dye removal from industrial effluents by PHW. So as it poses killing two birds with one stone which is removing the invasive weed and dye simultaneously will be a novel adsorbent.

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