

# Removal of Organic Dye from Artificially Contaminated Water System with Different Low Cost Naturally Available Bio-adsorbents

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## Abstract

The removal of organic dye (methylene blue) with naturally available low cost bio-adsorbents (water hyacinth, sawdust, duckweed, bindweed) from artificially contaminated water has studied with different experimental conditions (particle size, amount of adsorbents, adsorption time, concentrations of methylene blue, and pH). UV-visible spectrophotometer was used to determine the concentrations of methylene blue (MB). The removal efficiency of methylene blue in percentage increases with the particle size of the adsorbents. The adsorption equilibrium time for methylene blue surface is about 40 minutes. The percentage of adsorption increases with of the amount of adsorbents, and observes maximum at 100mg with 75 mgL<sup>-1</sup> MB concentration. The removal efficiency (%) decreases with the increasing concentrations of methylene blue. Whereas, the removal efficiency (%) increases with the increasing of the pH up to 7 and remains almost constant between 7 and 11. Overall, the removal efficiency of these bio-adsorbents follows the sequence: water hyacinth > sawdust > bindweed > duckweed.

**Key words:** Biomass, adsorption, methylene blue, industrial effluents, water treatment

## I. Introduction

Rapid urbanization and industrialization of the developing countries have great impact on the environment, especially on the water quality. Varieties of pollutants from different urban and industrial effluents destroy the natural aquatic system. Many industrial units are located along the banks of the rivers in many parts of the world, which provide transportation for incoming raw materials and outgoing finished products. These industries drained their wastes into the rivers without considering the environmental pollutions. For example, wastewaters from dye houses can have strong impacts on the aquatic environment, as they are carcinogenic and toxic, and poses a serious hazard to aquatic living organisms [1]. Now-a-days, the concern about the long term toxic effect of water containing dissolved pollutants has also increased. Dyes are the most difficult constituents in wastewater to treat, since they are recalcitrant organic molecules, resistant to aerobic digestion, and stable to light, heat and oxidizing agents [2]. This is also a major economical and environmental issue in the textile industries [3]. Therefore, a great deal of attention has been receiving for dye removal from industrial wastewaters in the recent years.

Several physical, chemical and biological methods have been reported to remove dyes from wastewaters [4]. Among the numerous techniques, adsorption is widely used method as it gives the best results to remove coloring dyes from wastewaters [5-9] with different adsorbents. Many non-conventional and low-cost adsorbents including natural as well as waste materials have been used [10-11]. The reported adsorbent materials for removal of dye are clay materials (bentonite, kaolinite), zeolites, siliceous materials (silica beads, alunite, perlite), agricultural wastes (bagasse, maize cob, rice husk, coconut shell, banana pith, wheat straw, tea leaves, cow dung, etc.), industrial wastes (carbon slurries, metal hydroxide sludge), bio-adsorbents (peat, biomass, sawdust, lignite) [12-13]. Bio-adsorbents have been receiving considerable attention as they offer the most economical and effective treatment methods [12]. The ability of removal of methylene blue with sawdust and chemically treated sawdust has already been reported [13]. From literature survey it also shows that there is not much

work done for the removal of organic dye with naturally available low cost bio-adsorbents like water hyacinth, duckweed and bindweed from wastewaters.

In this paper we are focusing on removal of methylene blue with four bio-adsorbents (water hyacinth, sawdust, duckweed and bindweed) at different experimental conditions (adsorbent size and amount, concentration of methylene blue, and pH) from aqueous system. Methylene blue has selected as a model compound as an attempt for using natural bio-adsorbents for removal of dye from wastewater. The goal of the study is to see the effectiveness of four bio-adsorbents in removing methylene blue, optimum conditions for adsorption, and suggest a low cost method for removal of organic dye from wastewater.

## II. Methods and Experimental

### Description of the Biomass

Water hyacinth, sawdust, bindweed and duckweed were used to remove methylene blue from artificially contaminated water. The idea was to remove colored dyes from the effluents of textile and other industries with naturally available, cost effective and efficient bio-adsorbents. Water hyacinth (*Eichornia crassipes*) is a wild fern belonging to the family Pontederiaceae, a native of South America. Sawdust is composed of fine particles of different woods collecting from local saw mills. Duckweed (*Lemna perpusilla*) is a wild fern belonging to the family araceae. Bindweed (*Ipomoea aquatica*) is also wild fern belonging to the family convolvulaceae. An aquatic and marshy trailing herb with cylindrical stems and funnel shaped pinkish white flowers grows all over the country in ponds and swamps.

### Collection and preparation of the adsorbents

All four adsorbents were collected from a village in Madaripur, Bangladesh. Water hyacinth, duckweed and bindweed were collected from different ponds in the village, and sawdust was collected from a local saw mill. All of them were thoroughly washed with clean de-ionized water several times. The biomasses were dried in sun light for seven days. The dried biomasses were crushed with a

crusher and sieved with 140, 355, and 425 $\mu\text{m}$  size. The crushed powdered of different sizes were preserved in different airtight container for further experiments.

#### Preparation methylene blue (MB) dye solution

Methylene blue (MB) has been used as a model compound for adsorption of organic pollutants and widely used in many textile industries for coloring agent [14-15]. It is a heterocyclic compound with molecular formula of  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}\cdot 3\text{H}_2\text{O}$ . Stock solution was prepared from commercially available methylene blue (Source: E. Mark, Germany). The methylene blue concentration was determined before and after of each adsorption experiment.

#### Adsorption experiments

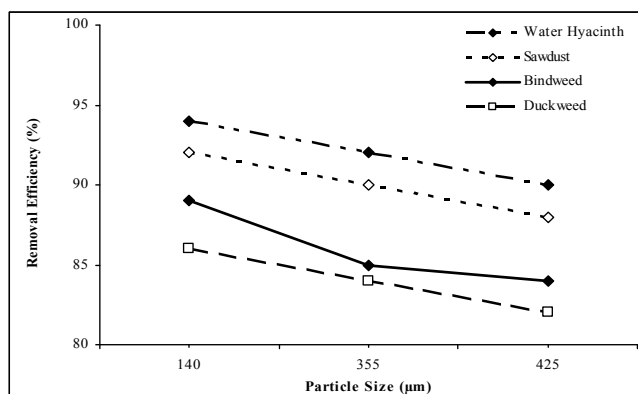
In each experiment, 50mL of methylene blue solution of known concentration was added to 100mg of adsorbent in a 250mL reagent bottle at 25 $^\circ\text{C}$ , and the mixture was shaking continuously at required times (varying from 0 to 120 minutes). The pH (Model HN-265, TOA, Japan) of the solution was adjusted with NaOH or HCl. After completion of the shaking the adsorbents were separated through filtration. The amounts of dye adsorbed on biomass were calculated from the difference of the concentrations in solutions before and after adsorption.

#### Determination of the methylene blue concentration

The methylene blue concentration was determined with UV-Visible Spectrophotometer (UV-160A, Shimadzu, Japan) before and after adsorption. It is a widely used method for the determination of methylene blue concentration [8,16]. The absorbance maxima of methylene blue at different concentrations and pH were determined, and found to be 665nm. However, all measurements for methylene blue were carried out at 665nm ( $\lambda_{\text{max}}$ ) to obtain maximum sensitivity. The concentration of methylene blue was calculated from a calibration curve of five known standard solutions.

#### Removal efficiency calculation

The removal efficiency of methylene blue (MB) with different bio-adsorbents was calculated in percentage by using this equation. **Removal efficiency (%)** =  $[(C_0 - C_e)/C_0] \times 100$ , Where,  $C_0$  = Concentration of MB before adsorption,  $C_e$  = concentration of MB after adsorption.

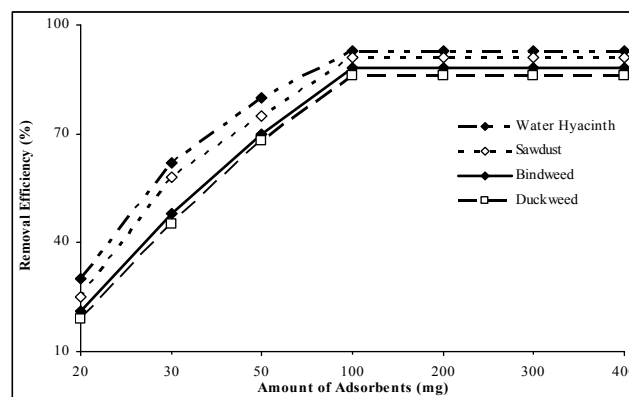


**Fig. 1.** Removal efficiency of methylene blue (%) with particle size. Experimental conditions: 100mg adsorbent, 75mgL $^{-1}$  methylene blue, 120 min adsorption time, with pH 7.0 at 25 $^\circ\text{C}$ .

### III. Results and Discussion

#### Effect of particle size of bio-adsorbents on removal of methylene blue

The effect of particle size on the methylene blue removal efficiency was studied with for four bio-adsorbents at three different particle sizes of 140, 355 and 425 $\mu\text{m}$  with 100mg adsorbent, 75mgL $^{-1}$  methylene blue concentration, pH 7.0 at 25 $^\circ\text{C}$ . Methylene blue removal efficiency was decreased with increasing of particle size (Figure 1) for all four biomass. The lower the particle size has the higher adsorption, though the difference was not so large (about  $\pm 5\%$ ). It can be explained that the smaller particles have relatively larger surface area and higher numbers of active sites, which increases the adsorption of dye on biomass surface of smaller particle. To get the maximum removal efficiency of methylene blue, 140 $\mu\text{m}$  of the particle size bio-adsorbent was chosen for the next set of experiments.



**Fig. 2.** Removal efficiency of methylene blue (%) with adsorbent amount. Experimental conditions: 140 $\mu\text{m}$  particle size, 75mgL $^{-1}$  methylene blue, 120 min adsorption time with pH 7.0 at 25 $^\circ\text{C}$ .

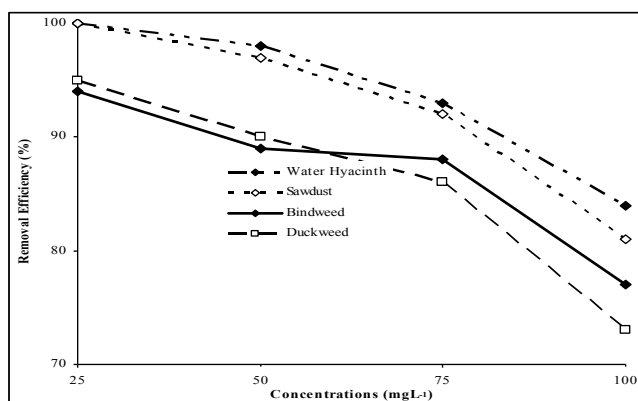
#### Effect of the variation of the amount of adsorbents

The effect of the variation of the amount of bio-adsorbent was studied at particle size of 140 $\mu\text{m}$  with 75mgL $^{-1}$  of methylene blue, 120 min adsorption time, and pH 7.0 at 25 $^\circ\text{C}$ . 20, 30, 50, 100, 200, 300 and 400mg of adsorbents were taken for each experiment. The uptake pattern of the adsorption of methylene blue was increasing with the amount of water hyacinth, sawdust, duckweed and bindweed. The removal efficiency was increased with the increasing amount of bio-adsorbent up to 100mg, and after that it attained a saturated condition (constant value) for each biomass (Figure 2). The maximum removal efficiency was 93, 91, 86 and 88% for water hyacinth, sawdust, duckweed and bindweed, respectively with 100mg of adsorbents. However, the sequence of removal efficiency of four bio-adsorbents are water hyacinth > sawdust > bindweed > duckweed.

#### Effect of variation of methylene blue concentrations

The effect of the variation of methylene blue concentration was studied at 140 $\mu\text{m}$  particle

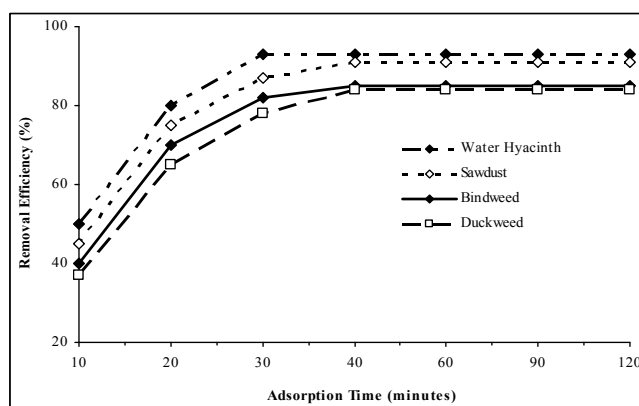
size, 100mg adsorbent, 120 min adsorption time, pH 7.0 at 25°C. Methylene blue concentrations were 25, 50, 75 and 100mgL<sup>-1</sup>. The percentage removal efficiency of methylene blue decreased with increasing of the methylene blue concentration for four bio-adsorbents, though the actual amount of methylene blue adsorption was increasing. The highest percentage of the removal efficiency was observed at 25mgL<sup>-1</sup> and followed by 50, 75, and 100mgL<sup>-1</sup> (Figure 3). We have chosen 75mgL<sup>-1</sup> methylene blue concentration for all experiments for better adsorption results. The removal efficiency with 75mgL<sup>-1</sup> methylene blue concentration was 93, 92, 86 and 88% for water hyacinth, sawdust, duckweed and bindweed, respectively. Evidence showed that sawdust could able to remove very high amount of methylene blue from aqueous solution [13]. They found that sawdust (4gmL<sup>-1</sup>) removed about 97% of methylene blue (at 100mgL<sup>-1</sup> concentration) from the aqueous solution at pH 7.0.



**Fig. 3.** Removal efficiency of methylene blue (%) with the variation of the initial concentrations. Experimental conditions: 140 $\mu$ m particle size, 100mg adsorbent, 120 min adsorption time with pH 7.0 at 25°C.

#### Determination of the equilibrium time

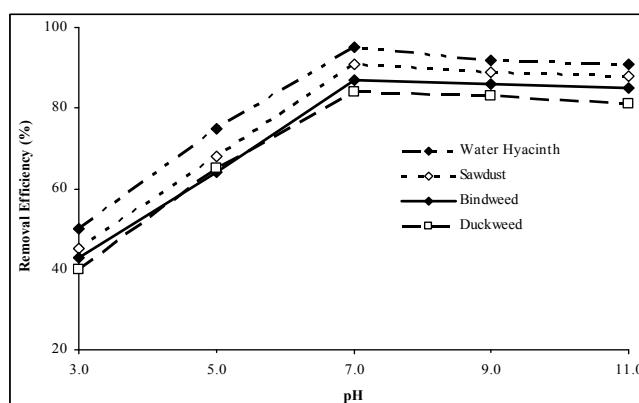
The effect of adsorption time variation was studied at particle size of 140 $\mu$ m, 100mg of adsorbent with 50mL of 75mgL<sup>-1</sup> methylene blue, pH 7.0 at 25°C. The adsorption study was done for 10, 20, 30, 40, 60, 90, and 120 minutes for each of four bio-adsorbents. The removal efficiency of methylene blue was increasing with increasing of adsorption time for water hyacinth, sawdust, duckweed, and bindweed, respectively (Figure 4). About 93, 87, 78 and 82% methylene blue was removed within 30 minutes of adsorption time. The maximum adsorption of methylene blue on adsorbent surface was 30 minutes for water hyacinth (93%), and 40 minutes for sawdust (91%), duckweed (84%) and bindweed (85%). After the maximum adsorption of methylene blue on adsorbent surface, the adsorption curves remain almost constant (Figure 4). However, the equilibrium adsorption time was 40 minutes for each of the four bio-adsorbents within the current experimental conditions.



**Fig. 4.** Removal efficiency of methylene blue (%) with adsorption time. Experimental conditions: 140 $\mu$ m particle size, 100mg adsorbent, 75mgL<sup>-1</sup> methylene blue with pH 7.0 at 25°C.

#### Effect of pH on the removal of methylene blue

The effect of pH variation was studied at particle size of 140 $\mu$ m with 50mL of 75mgL<sup>-1</sup> methylene blue, 100mg adsorbent, 120 min adsorption time at 25°C. The adsorption experiments were carried out at pH 3, 5, 7, 9 and 11 for each adsorbent. The removal efficiency of methylene blue was increasing with the increasing of pH for water hyacinth, sawdust, duckweed, and bindweed (Figure 5). When initial pH of the methylene blue was increased from 3 to 7, the percentage of removal efficiency has gradually increased. The increasing trend of the removal efficiency of the methylene blue with increasing of pH was dependent on the nature of the adsorbent. The maximum adsorption occurred at pH 7.0; i.e. 95% for water hyacinth, 91% for sawdust, 84% for duckweed, and 87% for bindweed. Interestingly, at pH higher than 7.0, the trend of the removal efficiency was reversed (Figure 5). It may be explained that different adsorbents contain different percent of cellulose materials. Therefore, at lower pH, most of the hydroxyl of the cellulose is protonated resulting lower interactions between the cationic dye and the positive surface of the adsorbent. On the other hand, de-protonation occurs with increasing pH. As a result, at higher pH, the cationic dye molecules can easily interact with the hydroxyl group of the cellulose network.



**Fig. 5.** Removal efficiency of methylene blue (%) with pH. Experimental conditions: 140 $\mu$ m particle size, 100mg adsorbent, 120 min adsorption time, 75mgL<sup>-1</sup> methylene blue at 25°C.

#### IV. Conclusion

This study is an attempt for the treatment of organic dye contaminated water system with naturally available low cost bio-adsorbent. Water hyacinth, sawdust, duckweed and bindweed were used as adsorbents and methylene blue as a model organic dye. Our report revealed that they are very efficient in removing methylene blue under the current experiments conditions. However, the textiles and other color producing industrial effluents could be treated with these naturally available low cost biomasses.

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