Efficiency of Water Hyacinth as Bio-Adsorbent to Uptake Methylene Blue from Wastewater

Shahanaz Parvin*, Md. Abdul Halim, Biplob Kumar Biswas, Al-Mamun, Md. Abdur Ruman, Md. Wasikur Rahman

Abstract — In the present study, the removal of methylene blue from aqueous solution by batch adsorption technique using low cost adsorbent was investigated. Water hyacinth was used as adsorbent to determine the adsorption efficiency. The influence of pH, initial dye concentration, adsorbent dosages and contact time of the removal process at different operating conditions were investigated. Adsorption process was found to be highly pH dependent. The optimum pH range for adsorption of methylene blue was found to be 8. The removal of methylene blue is proportionally steady to the adsorbent dosage. Kinetic studies were performed and the rate kinetics for the adsorption of methylene blue was best fitted with the pseudo-secod-order kinetic model. Langmuir adsorption isotherms were applicable to the adsorption process and Langmuir constant was evaluated. The adsorption capacity (q_{max}) calculated from the Langmuir isotherm and obtained value showed that the water hyacinth was the most effective adsorbent for the removal of methylene blue from the aqueous solution. Heat of the sorption process was estimated from Temkin isotherm model to be 7.51 J/mol and mass transfer of the process was studied. These results point out the suitability of the nearby available low cost adsorbents in the niche area of wastewater treatment and can be implemented in commercial dye enriched industrial effluent.

Index Terms: Waste water treatment, Adsorption, Water hyacinth, Methylene blue, kinetic study, Isotherm, Mass Transfer.

1 INTRODUCTION

Uncontrolled release of contaminants presents a serious problem and water quality, soil productiveness, aquatic organisms and ecosystem integrity are adversely exaggerated by toxic effluents which are discharged from various industries. Colouring material content of these discharges is one of the foremost problems which encountered mostly in the textile industry. The textile waste water is rated as the most polluting amongst all in the industrial segments [1, 2]. The textile industry turn out huge amount of dye contained waste water in dyeing and finishing processes. Mostly dyes are non-biodegradable and due to non-biodegradability, the components of dye substances create harsh problem not only to the ecosystem but also create toxicity to the biological life [3]. There are many physical and chemical treatment processes such as coagulation, flocculation, membrane filtration, irradiation etc from these processes good decolorizing efficiency can be achieved [4] but these processes are very costly and produce large amount of sludge material which require final disposal. From these points of view, adsorption is one of the most efficient methods of removing dyes from waste water [5, 6].

Adsorption is the method for separation of mixtures on a laboratory and industrial scale where it is a surface phenomenon that can be defined as the raise in concentration of a particular component at the interface between two phases. In this study, we want to represent that how can we remove dye from solution by using water hyacinth as bio-adsorbent. Water hyacinth is one of the worst weed in the world but by modifying this weed we can use this as bio adsorbent which is capable to remove various industrial dye such as methylene blue, congo red, crystal violet, malachite green from aqueous solution where maximum removal percentage were found 90%, 88%, 92% and 90% respectively [7]. In case of heavy metal removal from aqueous solution, water hyacinth has great potential. Water hyacinth can remove copper with an efficiency of 97.3% [8], cadmium, chromium, zinc from textile waste water with an efficiency of 94.87%, 94.78% ,96.88% [9, 10] respectively. Nowadays a large number of low cost adsorbents have been investigated for their capacity to remove dyes from aqueous solutions such as rice husk [11], wood dust [12], tree bark powder [13], peat [14], lignin [15] wheat bran [16] , brown sea weed [17], banana and orange peel [18], fly ash [19] , pineapple stem waste [20], tuberous pulp, sugarcane pulp, and coconut pulp [21] but the search for simple, economic, eco-friendly and highly effective adsorbents is still continuing. From these perspectives, we select water hyacinth as bio-adsorbent to remove dye from waste water.

In the present work, naturally available low–cost adsorbent such as water hyacinth has been used as adsorbent for methylene blue dye removal from aqueous solution. The effect of the experimental parameters such as initial pH, concentration of dye, adsorbent dosage and contact time has been investigated. The results of these experiments are analyzed using Langmuir adsorption isotherm and the experimental results

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International Journal of Scientific & Engineering Research, Volume 9, Issue 6, June-2018
ISSN 2229-5518

suggest that water hyacinth is capable to take away dye from textile waste water.

2 Materials and methods

2.1 Materials

Water hyacinths were collected from the pond of Jessore University of Science and Technology, Jessore, Bangladesh. The chemical substances which included methylene blue dye, HCl and NaOH were purchased from Merck, Germany. Stock solution of methylene blue was prepared by dissolving 319.85 g/mol in doubled distilled water and different concentrations (25, 50,100, 200, 300, 400 and 500 ppm) were made by dilution of the stock solution.

2.2 Preparation of adsorbent

The sample of water hyacinth was carefully washed by doubled distilled water to remove the dirt and mud. It was then sun dried and acid washed to eliminate the soluble impurities. Then acid washed sample was dried again in an oven at 105°C for 2 hrs to leave out the moisture from it. The dried adsorbent were crushed in a grinding machine and converted into fine powder which were used to uptake methylene blue dye in whole experiment.

2.3 Adsorbent Characterization and analysis

UV-1650 spectrophotometer (SHIMADZZU Co., Japan) was used to measure the concentration of solution where maximum absorbance wavelength was 450 nm. pH of the solutions were studied over the range from 4 to 10 through pH meter.

2.4 Adsorption experiments

The batch experiments were run out to investigate the influence of various parameters including contact time (0 to 210 minutes), pH (4 to 10), adsorbent dosages (0.5 to 5g/L). In this study, 250 ml conical flasks were used to keep 100 ml adsorbate solution of variable concentrations (25, 50,100, 200, 300, 400 and 500 ppm) and known amount of adsorbent was added into each flask at different condition which shaken continuously at a constant oscillation of 211 osc/min for 3.5 h. After agitation time, the solution was filtered and remaining sample was analyzed to determine the adsorption percentage of methylene blue which computed by the following equation (1):

$$\%\ \text{Removal of MB} = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

Where, C_o is the initial concentration (mg/L) and C_t is the concentration at time t. The amount of methylene blue adsorbed per unit mass of the adsorbent, q_e (mg/g) was evaluated by the following mass balance equation (Eq.2):

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

Where, C_o and C_e are the concentrations (mg/L) of methylene blue (MB) at initial and at equilibrium, respectively. V is the volume (L) of the solution and m is the adsorbent mass (mg).

2.5 Adsorption Isotherm

2.5.1 Langmuir Isotherm

The linear Langmuir isotherm model was expressed by the following equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \qquad (3)$$

Where, C_e is the concentration of adsorbate at equilibrium (mg/L), q_e is amount of dye adsorbed at equilibrium (mg/g), q_{max} is maximum adsorption capacity (mg/g).

2.5.2 Temkin model

Temkin and Pyzhev [22] clearly think about the interactions between adsorbing species and adsorbate on adsorption isotherms and this equation can be expressed in linear form as follows (4):

$$q_e = B\ \text{In}K_T + B\ \text{In}\ C_e \qquad (4)$$

Where, K_T is the Temkin equilibrium binding constant (L/mg) and B = RT/b is related to the heat of adsorption (J/mol).

2.6 Adsorption Kinetics

Adsorption kinetics is one of the most significant characters which govern the rate of adsorption. To represent the adsorption kinetics of methylene blue on water hyacinth, two different kinetic models i.e; second order kinetic model [23] in equation (5), intra-particle diffusion model [24] in equation (6) were used to fit kinetics data.

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^{\,2}} + \frac{t}{q_e} \qquad (5)$$

$$q_t = K_{ip} t^{1/2} + \emptyset \qquad (6)$$

Where, q_t and q_e are the amounts of methylene blue adsorption at time t (min) and at equilibrium (mg/g) respectively and k_2 (g/mg/min) and k_{ip} (mg/g/min$^{1/2}$) are the rate constant of pseudo second order and intra-particle diffusion model respectively.

2.7 Mass Transfer Analysis

Mass transfer analysis [25] for adsorption of methylene blue on the water hyacinth was carried out using the following equation (7):

$$ln\left(\frac{c_t}{c_o} - \frac{1}{1+MK_{bq}}\right) = ln\left(\frac{MK_{bq}}{1+MK_{bq}}\right) - \left(\frac{1+MK_{bq}}{MK_{bq}}\right)\beta S_s t \qquad (7)$$

Where, M is the mass of the adsorbent per unit volume (g/L), K_{bq} is the constant obtained by multiplying q_{max} and b which are defined in 2.5.1 section , S_S is the external surface area of the adsorbent per unit volume (m^{-1}), β is the mass transfer coefficient (cm/min) and t is the contact time (min).

The plot of $ln\ \{(C_t/C_o-1)/\ (1+MK_{bq})\}$ versus t is carried out. The

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ISSN 2229-5518

values of mass transfer coefficient, β were determined graphically from the slope $\{(1+MK_{bq})/MK_{bq}\}\beta Ss$ of the individual plots.

3. Results and Discussions

3.1 Removal properties of methylene blue (MB)

3.1.1 Effect of pH

The variation of adsorption with pH can be discussed over pH ranges 4 to 10 where optimum concentration 100 ppm, adsorbent dosage 1.0 g/L, contacts time 150 min.

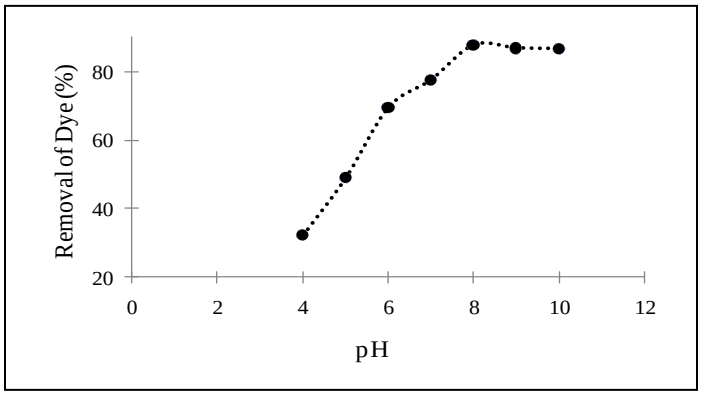

Fig.1: Effect of pH on the adsorption of methylene blue (MB) by the adsorbents at optimum concentration 100 ppm, adsorbent dosage 1.0 g/L, contact time 150 min.

The removal of methylene blue improved remarkably as the pH of the solution increased and lower adsorption of methylene blue at acidic pH was accounted. In this study, MB dye was highly adsorbed at pH 8 shown in Figure 1.

3.1.2 Effect of Adsorbent Dosage

The results of methylene blue dye removal where initial concentration 100 ppm, contact time 150 min and optimum pH 8 with varying amount of adsorbent dosages is depicted in Figure 2.

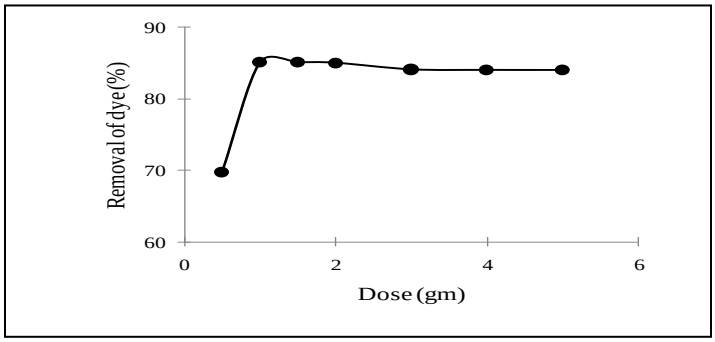

Fig. 2: Effect of adsorbent dosage on MB dye removal (%) by adsorption where initial dye concentration 100 ppm, Time 150 min, pH 8.

From the Figure 2, it can be seen that adsorption of dye increased from 69% to 85% with increasing adsorbent dose from 0.5 g/L to 1.0g/L. After that when we increased the adsorbent dose, the dye removal % falls. This is due to the fact that some of the adsorption sites stay unsaturated. Similar result was found from lead ion removal by bamboo based activated carbon which is reported in [26]. Thus 1.0 g/L of adsorbent dose was taken as an optimum dose for accompanying experiments.

3.1.3 Effect of Dye Concentration and contact time on methylene blue (MB) Removal percentage

These studies were performed by changing the initial dye concentration in the range of 100 to 300 ppm with optimum conditions received from previous experiment which graphically shown in Figure 3.

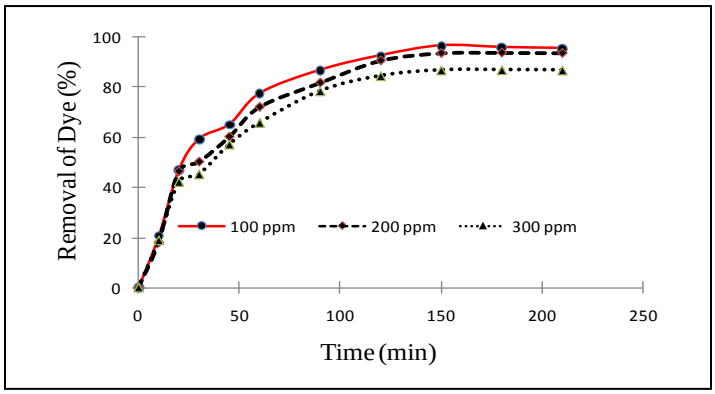

Fig. 3: Effect of dye concentration and contact time on MB dye removal (%) where Adsorbent dose 1.0 gm/L and pH 8.

From the figure, it can be observed that the dye removal percentage increased with decreasing initial methylene blue dye concentration from 300 to 100 ppm. This is due to that for fixed adsorbent dosage, at higher initial dye concentration, the number of active adsorption sites of adsorbent become fewer [27]. On the other hand, it was seen that percentage of adsorption increases with increasing contact time at all initial dye concentration and equilibrium is attained at 150 min. Similar types of results were reported by various researchers in [28, 29].

3.2 Adsorption Isotherm Study

3.2.1 Langmuir Isotherm

In the present study, the plot of $1/q_e$ against $1/c_e$ gives straight line shown in Figure 4 with a slope of $1/q_{max}\, b$ and intercept of $1/q_{max}$.

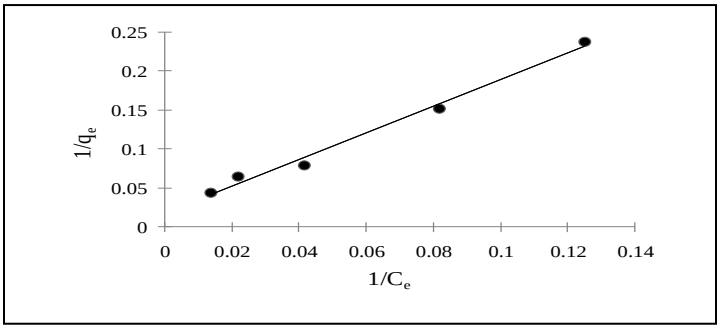

Fig. 4: Langmuir plot for the adsorption of methylene blue (MB) dye by the adsorbent where pH 8, adsorbent dosage 1.0 g/L, contacts time 150 min.

From the plot, it can be seen that the value of regression correlation co-efficient (R^2) is 0.9879 which is very close to 1 and indicates that the obtained data are well fitted in Langmuir

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ISSN 2229-5518

isotherm model and also implies that monolayer sorption exists under the experimental condition. The adsorption capacity (q_{max}) of adsorbent is 54.76 mg/g. The maximum adsorption capacities of water hyacinth for the removal of methylene blue for the different investigations are reported in Table 1.

TABLE 1
MAXIMUM ADSORPTION CAPACITIES OF WATER HYACINTH (WH) AS BIO-ADSORBENT

Adsorbents	Adsorption capacity(mg/g)	Type of Dye	sources
WH	54.76	Methylene blue	Present study
WH root Aq. soln	42.55	Methylene blue	[30]
WH root	8.04	Methylene blue	[31]
Alginate fixed WH	86.2	Methylene blue	[32]

3.2.2 Temkin Isotherm

The plot of q_e versus lnC_e shows a straight line and the value of B is determined from the intercept of this plot which are shown in figure 5.

The calculated values of B indicates the physical adsorption of the process and similar result represented in [33] where physical sorption of Zn^{2+} take places unto phosphoric acid modified rice husk at 25.34 J/mol.

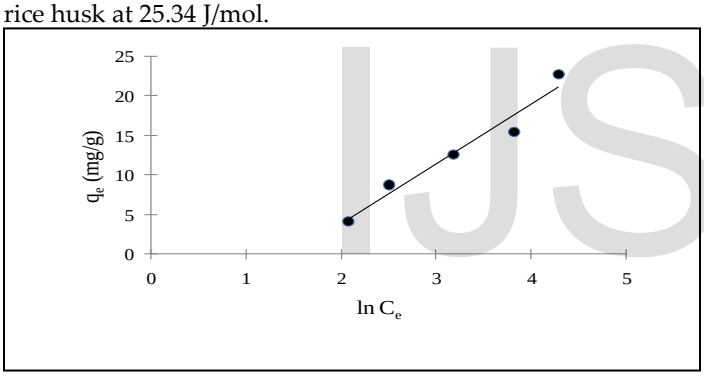

Fig. 5: Temkin isotherm plot for the adsorption of methylene blue (MB) by the adsorbents where pH 8, adsorbent dosage 1.0 g/L, contacts time 150 min.

3.3 Adsorption Kinetics

Pseudo second order kinetic model was studied at optimized operating condition such as concentration 100 ppm, pH 8 and the results were shown in Figure 6.

TABLE 2
KINETICS PARAMETERS FOR ADSORPTION OF METHYLENE BLUE (MB) ONTO WATER HYACINTH

Pseudo second order				Intra –particle diffusion	
K_2(g/mg)	q_e(mg/g)		R^2	K_{ip} (g/mg/min$^{1/2}$)	Ø (mg/g)
1.78×10^{-3}	Exp.	Calc.	0.9865	0.9512	7.8938
	8.75	20.22			

The figure of t/q_t versus t gives linear plot from which the value of q_e and k_2 were calculated [Table 2].

The result reveals that R^2 value is close to 1 and linearity of this curve indicate that the kinetic data fitted well with the pseudo second order model and similar results are found in [34].

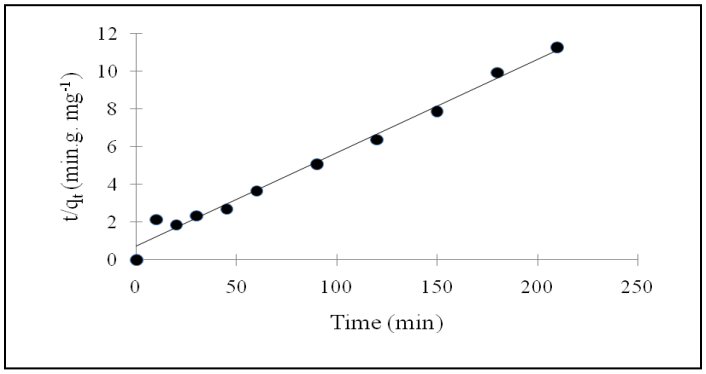

Fig. 6: Pseudo second order kinetic model for the removal of methylene blue (MB) using water hyacinth at pH 8.

Ø (mg/g) is the intercept of the intra-particle diffusion model whose value gives the information about the thickness of the boundary layer [35]. If the plot of q_t versus $t^{1/2}$gives a straight line that pass through the origin which indicates the intra-particle diffusion model contributes in the rate determining step [36].

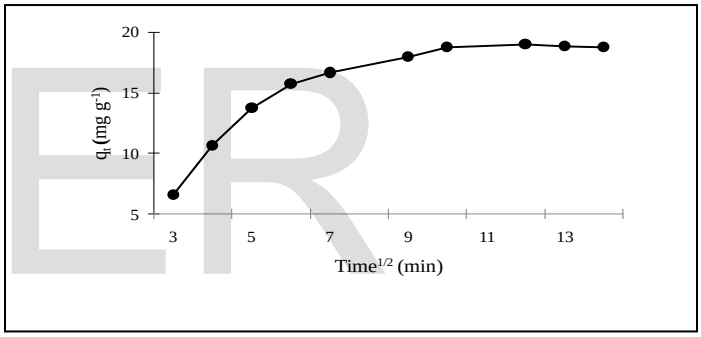

Fig. 7: Intra-particle diffusion kinetic model for the removal of methylene blue (MB) onto water hyacinth.

In Figure 7, this linear relationship does not pass through the origin that implies the intra-particle diffusion model was not rate controlling step and the value of Ø signify that boundary layer diffusion control the adsorption process to some degree [35]. The value of intercept is almost same [Table 2] with the q_e (exp.) which proved that in this experiment, the larger surface adsorption was occurred [37].

3.4 Mass transfer analysis

The plot of *ln {(Ct/Co −1)/(1+MKbq)}* versus *t* consequenced a straight line which seen in Figure 8 representing the applicability of the model.

The value of mass transfer coefficient *(β)* were determined graphically from the slope *{(1+MKbq/MKbq) βSs}* of the individual plots and presented in Table 3.

The values found from the experimental investigation show that the velocity of the adsorbate methylene blue for transporting from bulk i.e. solution phase to solid phase was moderately good [38].

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ISSN 2229-5518

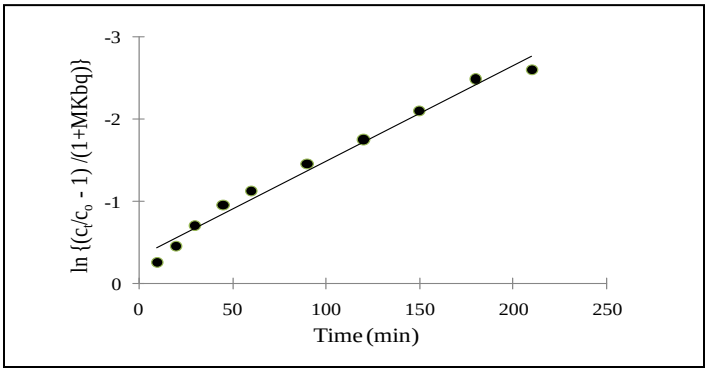

Fig. 8: Mass transfer plot for the adsorption of methylene blue (MB) by selected adsorbents where pH 8, initial concentration 100 ppm, and adsorbent dosage 1.0 g/L.

TABLE 3
MASS TRANSFER ANALYSIS FOR ADSORPTION OF METHYLENE BLUE (MB)

Adsorbent	Mass transfer constant, β (cm/min)	Correlation coefficient (R^2)
Water Hyacinth	52.39×10^{-12}	0.9625

4. Conclusion

In this study, Methylene blue dye was removed from aqueous solution by water hyacinth using as bio-adsorbent. The effect of various parameters like pH, adsorbent dosage, initial dye concentration and contact time were evaluated on the uptake competence of the adsorbent. The maximum uptake capability of the water hyacinth (97%) was achieved within 150 min at pH of 8. The maximum monolayer adsorption capacity was obtained equal to 54.76 mg/g and heat of adsorption of the process is 7.51 J/mol. The consequences showed that the experimental facts were followed pseudo second order kinetic model.

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