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ADSORPTIVE REMOVAL OF METHYLENE BLUE DYE FROM AN AQUEOUS SOLUTION USING WATER HYACINTH ROOT POWDER AS A LOW COST ADSORBENT

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ABSTRACT

Adsorbent prepared from roots of water hyacinth; an aquatic weed was used to remove the Methylene blue from an aqueous solution. The batch adsorption study was carried out by varying the parameters such as pH adsorbent dose, initial concentration of dye, and contact time to obtained removal kinetic data. At optimum experimental condition maximum 95% removal of dye was achieved. Equilibrium data were best represented by both Langmuir and Freundlich isotherms. The maximum dye uptake was found to be 8.04 mg/g.The adsorption kinetic data are adequately fitted to the pseudo second order kinetic model. On the basis of experimental results WHRP was found to be an excellent adsorbent for the MB removal from wastewater.

Keywords: Adsorption, Dye, Methylene blue, Water hyacinth, Batch study, Adsorption isotherm

1. INTRODUCTION

Color is the first contaminant to be recognized in wastewater (1). The presence of very small amounts of dyes in water is highly visible and undesirable (1, 2). The decolorization of waste water is a major environmental concern. Synthetic dyes have been extensively excreted in the waste water from different industries particularly from textile, paper, rubber, lather, cosmetic, food and drug industries which used dyes to color their products. It is reported that over 100000 commercially available dyes exist and the global annual production of synthetic dyes is more then 7x 10^5 metric tons (3). Colored effluent from dyes consuming industries give undesirable perspective to the water streams where as some dyes and their metabolites pose toxic, carcinogenic, mutagenic and teratogenic effects. Dyes also prevent light penetration and reduce photosynthetic activities of water streams and disturb aquatic equilibrium. Methylene blue (MB) is the most common among all other dyes of its category. It is generally used in dying textile specially cotton and silk and in some medical treatments. Though MB is not strongly hazardous it can cause some harmful effects. It can cause eye injury for both human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia (4, 5). Acute exposure to MB can cause increased heart rate, vomiting, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans (6). Thus, the removal of MB from industrial effluents has become one of the major environmental concerns.

A range of conventional treatment technologies including biological, physical and chemical methods have been employed for the treatment of colored effluent. Due to structure complexity and low biodegradability conventional biological method are not very effective thus it is usually treated with either by physical or chemical processes. However these processes are very costly and can not effectively be used to treat the wide range. Therefore, adsorption process provides an attractive alternative for the treatment of colored water (2). Adsorption process can treat high flow wastewater with good final quality and no harmful substance production (7). Activated carbon is quite effective adsorbent for wastewater treatment but the large scale application of activated carbon is restricted due to its higher cost and regeneration problem. At present there is a growing interest of researchers in using other low cost adsorbents for dyes removal. Many materials like coir pith (8), sun flower stalks (9), corn cobs and barley husk (10), rice husk (6), neem leaves (11), mango seed kernel (12), modified saw dust (13,14), giant duck weed (15), peanut hulls (16), peanut shells (17), pineapple stem (18), treated wood shavings (19), banana pith (20), orange peel (21), guava leaf (22), wheat shell (23) and wheat bran (24) have been used as low cost dye adsorbents.

In this study water hyacinth root powder (WHRP) has been tested for their potential to adsorb Methylene blue (MB) dye from synthetic wastewater by adsorption.

2.0 MATERIALS AND METHOD

2.1 Adsorbent Preparation: Water hyacinth was collected from local river Kshipra, Ujjain. The roots of collected water hyacinth plant were separated and extensively washed with tape water to eliminate soil dust and earthy materials. Finally roots were washed several time with distilled water and sliced in pieces manually. It is then dried over night at 50 ^{0}C in oven. The dried roots then creased sieved and stored in air tied container for further use.

2.2 Adsorbate and Chemicals: All the chemicals used in this study were of analytical grade. MB was supplied by Merck India private limited. The general characteristics of MB ($C_{16}H_{18}N_3SCl$) are molar mass = 319.86, C.I. No. = 52015, λmax = 664 nm. Stock solution of dye was prepared by dissolving accurately weighted 1gm MB dye in 1000 ml distilled water. Latter it was diluted by using distill water according to concentration required. pH was adjusted by adding 0.1 M NaOH and 0.1 M HCl solution.

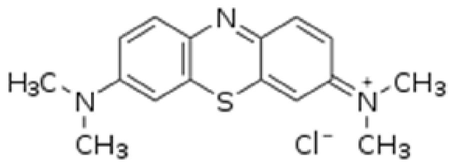

Fig.1. Structure of Methylene Blue

2.3 Batch adsorption Experimentation:

Batch experimentation were carried out at room temperature to study the effects of important parameters such as effect of pH, contact time, initial concentration and amount of adsorbent. The concentration of MB solution before and after adsorption were estimated by measuring absorbance at 664 nm with help of UV-visible spectrophotometer (Systronics 2105).

A fixed amount of WHRP adsorbent was placed in 250 ml flasks containing 100 ml of dye solution (concentration 20 to 100 mg/l) at pH ranging from 2 to 10. Then flasks were shaken in orbit shaker with a speed of 60 rpm at room temperature for 10 to 120 minutes. After filtration final concentration of dye solution were analyzed by UV-visible spectrophotometer. The amount of equilibrium uptake of dye is calculated by using equation

$$q_e = (C_0 - C_e)\ V/\ W$$

Where, q_e is the dye up taken by adsorbent mg/g, C_0 is the initial MB concentration, C_e is the MB concentration (mg/l) after the batch adsorption process, W is the Mass of adsorbent (gm), V is the Volume of dye solution taken (l).

The percentage removal of dye is defined is the ratio of difference in dye concentration before and after adsorption ($C_0 - C_e$) to the initial concentration of the dye of the aqueous solution of the dye (C_0) and was calculated by using equation

$$\text{Percentage removal} = (C_0 - C_e)\ x100/C_0$$

3.0 RESULTS AND DISCUSSION

3.1 Effect of pH:

The interaction between dye molecule and adsorbent is basically a combined result of charges on dye molecules and the surface of the adsorbent (25). Figure 2 shows that pH of the solution has significantly affect adsorption of MB on WHRP. Water hyacinth root powered achieved its optimum adsorption capacity for MB at pH=8. It is evident that uptake of dye increased consistently with pH. The adsorption of MB onto adsorbent surface is influenced by the surface charge on the adsorbent and the initial pH of the solution (26). As the pH of the solution increases, the number of negatively charged site increased. Strong electrostatic attraction exists between the positively charged cationic dye molecules. As a result a negatively charged surface on the adsorbent favours the adsorption of the dye (27). Several investigations have reported that MB adsorption usually increases as the pH is increased (28-30).

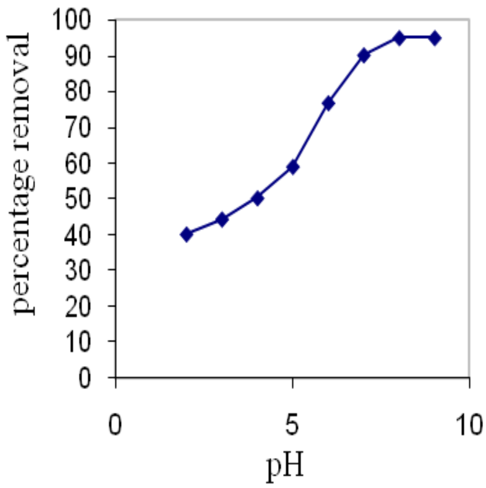

Fig.2: Effect of pH on percentage removal of MB (20mg/l) at room temperature.

3.2 Effect of Adsorbent Dose:

Adsorbent dose is representing of important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate. Effect of adsorbent dose on removal of MB was monitored by varying adsorbent dose from 0.1 g/100ml to 1.5 g/100ml. The adsorption of dye increased with the adsorbent dosage and reached on equilibrium value after 1.0 g of adsorbent (figure 3) as one was accepted, the percentage of dye removal increased with increasing amount of WHRP, however the ratio of dye adsorbed to WHRP (mg/g) decreased with increasing amount of adsorbent WHRP.

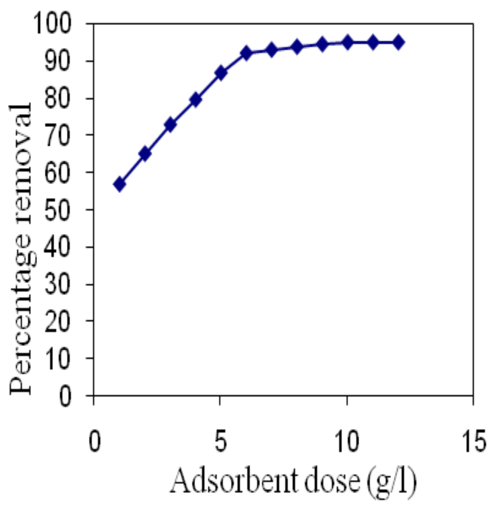

Fig.3: Effect of adsorbent dose on removal of MB for concentration 20mg/land 80 minutes agitation time at pH 8

Similar results were reported by Patil et al. (31). Many factors can attribute to this adsorbent concentration effects. The most important factor is that adsorption site remains unsaturated during the adsorption reaction. This decrease in adsorption capacity with increase in adsorbent dose is mainly attributed non saturation of the adsorption sites during the adsorption process (32, 33). The ratio of dye adsorbed to WHRP was started to reach equilibrium at 1.0 g adsorbent. When the WHRP further increases after 1.0 there is no significant change in adsorption thus 1.0 g WHRP adsorbent dose was chosen for study other parameters.

3.3 Effect of Initial Concentration and Contact Time:

The effect of contact time and initial concentration (20 to 100 mg/l) of MB adsorption on to WHRP is presented in figure 4.

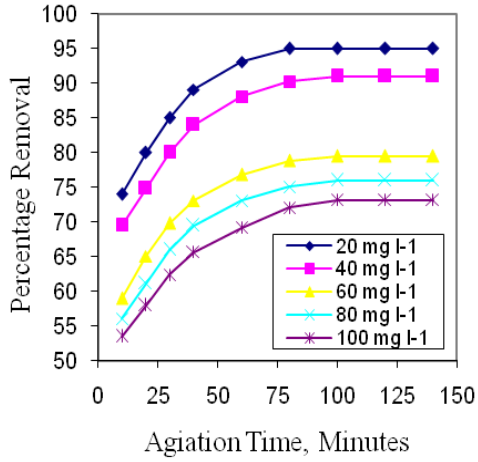

Fig.4: Effect of Initial Concentration and Contact Time on percentage removal of MB onto WHRP

A rapid removal is observed at the initial stages and it then proceeds slowly until reached equilibrium. This may be due to the availability of number of vacant adsorption sites at initial stage. The equilibrium adsorption capacity of WHRP is increased from 1.90 mg/g to 7.32 mg/g as increasing concentration from 20 to 100 mg/l. It was significant different with percentage removal that decreased from 95.0% to 73.2% as initial concentration increased. At lower dye concentration, the available adsorption sites are relatively high and consequently the dye species can find easily the accessible adsorption sites (6). However, at higher concentrations the available site of adsorption become fewer and consequently the dye ions take more time in order to reach the last available sites (34). Furthermore, the adsorption dynamic profile shows that equilibrium has been reached in 80 minutes.

3.4 Isotherm modeling

The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of adsorbate remained in the solution at equilibrium time (35). Langmuir and Freundlich isotherms were used to describe the equilibrium adsorption. Langmuir isotherm (36) refers to homogeneous monolayer adsorption where as the linear form of the Freundlich isotherm (37) model is derived by assuming a heterogeneous surface of adsorption capacity and adsorption intensity with a non uniform distribution of heat of adsorption. The equation for these models are given as

Langmuir isotherm

$$C_e/q_e=1/q_{max}K_L + (1/q_{max})\ C_e$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium(mg/g), C_e is the equilibrium concentration(mg/l) and q_{max} and K_L are the Langmuir isotherm constants related to free energy. The above equation can be linearized to get the maximum capacity, q_{max} by plotting a graph of C_e/q_e Vs C_e.

Freundlich isotherm

$$q_e=K_f\ C_e^{1/2}$$

On rearranging this equation we get

$$\log q_e= \log K_f +1/n \log C_e$$

where K_f and $1/n$ are freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively .A plot of $\log q_e$ vs $\log C_e$ yields a straight line with a slop of 1/n and intercept $\log K_f$.

The Langmuir and Freundlich adsorption isotherms of MB on WHRP are shown in figure 5 and 6. Table 1 gives the values of parameters and correlation coefficient of the Langmuir and Freundlich equations. The experimental results indicated that the adsorption isotherms of MB adsorption on WHRP followed both Langmuir and Freundlich models. Uddin et al. (38) also reported the same observation for MB.

Table 1: The values of parameters and correlation coefficient of Langmuir and Freundlich equations.

Langmuir			Freundlich		
q_{max}	K_L	r^2	K_f	1/n	r^2
8.04	0.20	0.9538	1.98	0.3846	0.9776

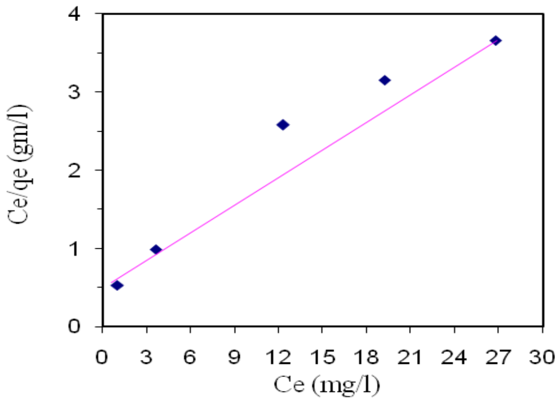

Fig.5: Langmuir isotherm for adsorption of MB on WHRP.

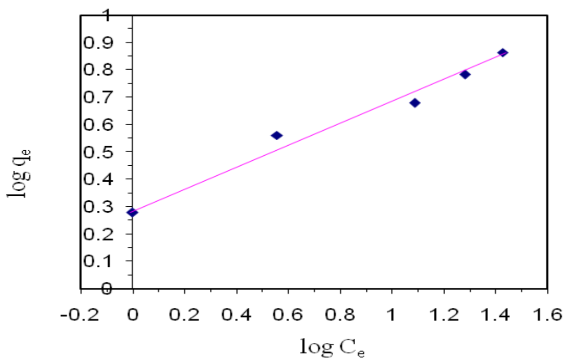

Fig.6: Freundlich isotherm for adsorption of MB on WHRP at room temperature.

3.5 Adsorption Kinetics

The kinetic adsorption data were processed to study the dynamics of the adsorption process in expression of the order of rate constant. Kinetic data were analyzed with the pseudo first order and pseudo second order kinetic models (39).

Equation for pseudo first order model is

$$\ln (q_e - q_t) = \ln q_e - K_1 t$$

Where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at time t(mg/g) and K_1 is the pseudo first order rate constant(min^{-1}).

Equation for pseudo second order model is

$$t/q_t = 1/ K_2 q_e^2 + 1/ q_e t$$

Where K_2 is pseudo second order rate constant ($g\ mg^{-1} min^{-1}$).

A straight line for pseudo second order model was obtained and it indicates the applicability of this kinetic model. The second order rate constant K_2 values were calculated from the slop of the line in figure 7. The pseudo second order reaction rate model adequately described the kinetics of dye adsorption with high correlation coefficient for all range of dye concentrations studied.

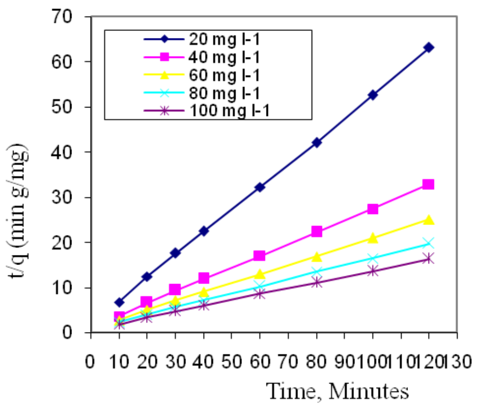

Fig.7: Pseudo second order plot for the removal of MB onto WHRP.

Table 2: Adsorption rate constant and coefficient of correlation associated with the pseudo second order kinetic model.

S.no	C_0 (mg/l)	q_e (mg/g)	K_2	r^2
1.	20	1.90	0.133	0.9997
2.	40	3.64	0.059	0.9997
3.	60	4.77	0.042	0.9998
4.	80	6.08	0.030	0.9998
5.	100	7.32	0.023	0.9994

4.0 CONCLUSION

Adsorption technology, utilizing natural materials or industrial and agricultural waste to passively remove dyes from aqueous media offers an efficient and cost effective alternative compared to traditional chemical and physical remediation and decontamination techniques. The goal of this work is to explore the potential of WHRP as low cost adsorbent to remove MB dye from aqueous solutions. Water hyacinth is easily available waterweed in local river kshipra. WHRP as low cost adsorbent may be appropriate for the treatment of dye effluent released from small scale industries. Data reported here should be useful for the design of batch or stirred tank flow reactors which can be used in small dyeing industries for a direct solution.

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