

Removal of Dyes Using Leaves of *Morinda Pubescens* as a Low Cost Green Adsorbents

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ABSTRACT : The present study, investigated the potential use of low cost green adsorbent *Morinda pubescens* leaves for decolourisation of waste water containing a mixture of dyes. Three dyes namely Malachite green (MG), Crystal Violet (CV) and Congo Red (CR) have been used for imparting colour, in the representative samples of waste water. Batch experimental studies were performed to evaluate the influence of various experimental parameters like adsorbent dose, effect of pH, initial dye concentration at different temperature, and different contact time. The equilibrium of adsorption was modelled by using Langmuir and Freundlich isotherm models. The objective of the present study suggests the *Morinda pubescens* leaves used as a low cost green adsorbent for the removal of Malachite green (MG), Crystal Violet (CV) and Congo Red (CR) dyes from aqueous solution.

KEYWORDS : Adsorption, Dyes, Activated Carbon, *Morinda pubescens* and adsorption isotherms.

I. INTRODUCTION

Water resources are the critical importance to both natural ecosystem and human development. But in recent years, there is a drastic increase in water pollution and the quality of water deteriorating day by day due to many industrial activities [1]. The discharge of large quantities of dyes from the textile industries poses serious environmental problems [2]. Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics etc. There are more than 100000 commercially available dyes with over 7×10^5 tonnes of dye stuff produced annually [3]. It is estimated that 2% of dyes produced annually is discharged in effluents from associated industries [4]. Discharge of dye bearing waste water into natural streams and rivers poses severe problems to the aquatic life, food web and cause damage to the aesthetic nature of the environment. Dyes are persist for long distances in flowing water, retards photosynthesis, inhibit growth of aquatic biota by blocking out sunlight and utilising dissolved oxygen. Some dyes may cause allergic dermatitis, skin irritation, cancer and mutation in man.

Many treatment processes have been applied for the removal of dye from waste water such as adsorption, electro coagulation, biodegradation, Fenton process, nano filtration, ultra filtration, electrochemical oxidation, membrane filtration process [5-7]. Among the various treatment processes of waste water, adsorption is more effective method due to the flexibility, easy operation and no/lesser sludge disposal problem [8]. Activated carbon is most widely used adsorbent for dye removal because of its extended surface area, micro – pore structure and high adsorption capacity [9]. However, commercial activated carbon is very expensive and high regeneration cost while being exhausted. Therefore, their use in waste water treatment may be economically not feasible. There is, therefore a need to identify and study the adsorptive characteristics of low cost alternatives.

Recently, a number of low cost adsorbents like pearl millet husk, coconut shell, pine bark, saw dust, rice husk, plant leaves and jack fruit peel have been used for removal of dyes from waste water [10-12]. The present study is to evaluate the efficiency of *Morinda pubescens* leaves as an adsorbent for the removal of Malachite Green (MG), Crystal Violet (CV) and Congo Red (CR) dyes from aqueous solution. The effect of adsorption parameters such as adsorbent dose, effect of pH, initial dye concentration at different temperature, and different contact time also have been studied.

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II. EXPERIMENTAL METHODS

ADSORBENT MATERIAL

The leaves of *Morinda pubescens* (Fig.1) were collected from agricultural land area and carbonized with con. sulphuric acid in the weight ratio of 1:1 (W/V). Heating for 12 hrs in a furnace at 400°C for complete carbonization and activation. The resulting carbon was washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for 4 hrs at 100°C in a hot air oven. The dried material was ground well to a fine powder (Fig.2) and sieved to 0.2mm by using a standard mesh. The activated carbon prepared was characterized by conventional chemical and physical methods [13] and the important characteristics are given in table 1.



Fig. 1 *Morinda pubescens* leaves



Fig. 2 Activated carbon prepared from leaves

ADSORBATE MATERIAL

All the chemicals including the dyes (Malachite green (MG), Crystal Violet (CV) and Congo Red (CR)) used were of high purity commercially available analytical grade (AR – sd fine - India). Stock solutions of 1000mg/L of the different dyes were prepared using double distilled water. From this stock solutions, we used for adsorption studies.

BATCH EQUILIBRIUM METHOD

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60°C temperatures. The known weight of adsorbent material was added to 50ml of the dye solution with initial concentration of 10mg/L to 50mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120rpm. The solution was then filtered at preset time intervals and the residual dye concentration was measured using UV-spectrometer [14].

The amount of dye adsorbed per gram of adsorbent i.e q_e at a time t , has been calculated by using the following formula [15],

$$q_e = \frac{(C_0 - C_e)}{w} V \quad \text{-----(1)}$$

Where, q_e is the amount of dye adsorbed, C_0 and C_e (mg/L) are the liquid phase concentrations of dye at initial and equilibrium respectively.

The percentage of dye removed was calculated by the following formula [15],

$$\% \text{ of dye removed} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad \text{-----(2)}$$

EFFECT OF VARIABLE PARAMETERS

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant. In order to determine the rate of adsorption, experiments were conducted with different

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initial concentration of dyes ranging from 10 to 50mg/L. All other factors were kept constant. The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by various time intervals and keeping particle size, initial concentration dosage, pH and concentration of other ions constant. Adsorption experiments were carried out at pH 2,4,6,8 and 10. The acidic and alkaline pH of the medium was maintained by adding the required amount of dil.HCl and NaOH solutions. The parameters like particle size dye concentration, dosage of adsorbent and concentration of other ions are kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter (Systronics model). The adsorption experiments were performed at four different temperatures viz 30, 40, 50 and 60°C in a thermostat attached with a shaker. The constancy of the temperature was maintained with an accuracy $\pm 0.5^\circ\text{C}$.

III. RESULTS AND DISCUSSION

Activated carbon widely used as an adsorbent due to its high adsorption capacity, high surface area micro structure and high degree of surface respectively. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico – chemical properties of morinda pubescens activated carbon (MAC) are presented in Table 1.

Table 1 Characteristics of an adsorbent

Properties	MAC
Particle size	0.2mm
Density (g/cc)	0.5281
Moisture Content (%)	2.6 %
Loss of Ignition (%)	83.8 %
Acid insoluble matter (%)	8.5 %
Water soluble matter (%)	0.22 %
pH of the solution	7.1

The results of adsorptions of Malachite Green (MG), Crystal Violet (CV) and Congo Red (CR) dyes on the activated carbon prepared from leaves of Morinda pubescens were determined and the effect of various parameters also analyzed.

Effect of initial dye concentration and contact time

From the results it showed that, the percentage of adsorption decreases with increase in initial dyes concentration, but actual amount of dyes adsorbed per unit mass of carbon increased with increase in dyes concentration. This showed that, the adsorption is highly dependent on initial dye concentration. It is because that at lower concentration, the available surface area is low, subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage of removal of dyes gets decreased with increase in initial concentration [16,17] (Fig.3).

The effect of contact time between the adsorbent and adsorbate is presented in Fig.(4). Based on the fig.4, the adsorption of dye increased with increasing shaking time and attained a constant value at equilibrium after a specific time (75min.). It was also observed that the uptake of the dye was fast at the initial stages of contact time and thereafter becomes slower near equilibrium and reached a steady value at the equilibrium. Further, in fig.4, the curves are single and continuous, leading to saturation, suggesting the possible monolayer coverage of dye on the carbon surface [13].

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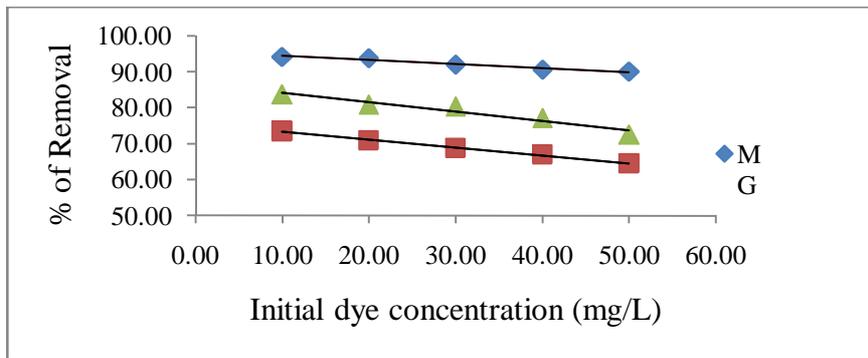


Fig.3 Effect of initial dye concentration on the removal of dyes at 30°C, adsorbent dose 2mg/L, pH = 7.

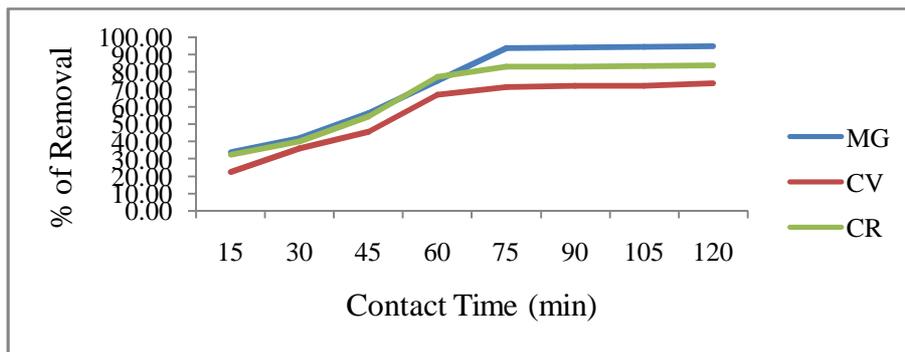


Fig.4 Effect of contact time on the removal of dyes (Conc. 30mg/L) at 30°C, adsorbent dose 2mg/L, pH = 7.

Effect of adsorbent dosage

Adsorption dose is an important parameter because, it determines the capacity of an adsorbent for a given initial concentration of adsorbate. The adsorption of dyes on carbon was studied by varying the concentration (20 – 200mg/ml) for 30mg/L of dyes concentration. This study showed that, the percentage of adsorption increased with increase in the dosage of adsorbent (Fig.5). The increase in adsorption with adsorbent dosage can be attributed to an increase in the adsorption surface and availability of more adsorption sites [18-20].

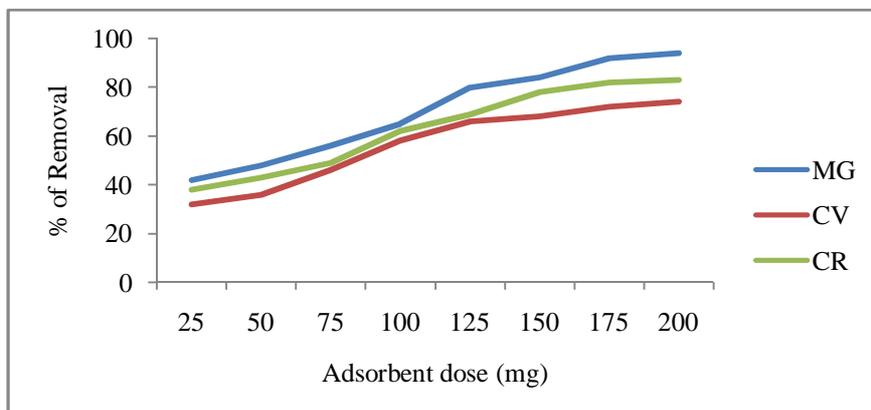


Fig.5 Effect of adsorption dose on the removal of dyes (Conc. 30mg/L) at 30°C, Contact time 60min, pH = 7.

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Effect of pH

pH factor is very crucial in adsorption studies especially dyes adsorption. The pH of a medium controls the magnitude of electrostatic charges which are imparted both by the ionized dye molecules and the charges on the surface of the adsorbent. The effect of pH of the solution on the adsorption of three dyes (Malachite Green, Crystal Violet and Congo Red) on *Morinda pubescens* carbon were determined. The result is shown in fig.6.

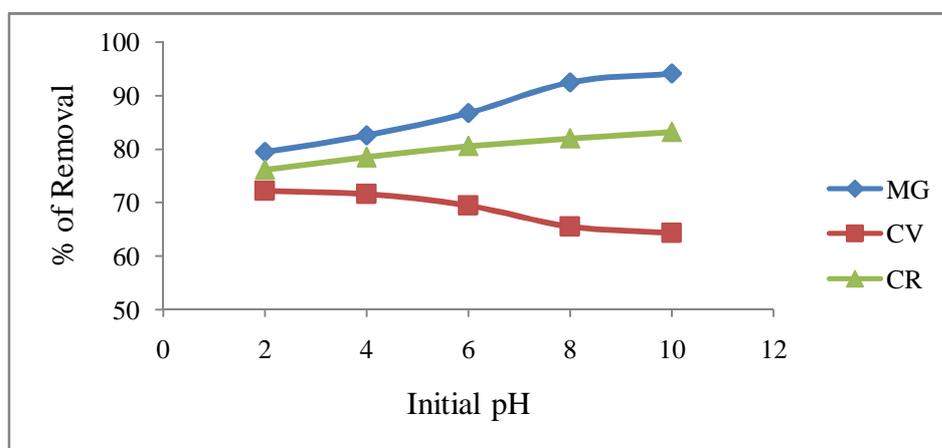


Fig.6 Effect of pH on the removal of dyes (Conc. 30mg/L) at 30°C, Contact time 60min, adsorbent dose 2mg/L.

This behaviour can be explained on the basis of zero point charge of the adsorbent ($pH_{zpc} = 6.0$). At higher pH above this point, the OH^- ions compete effectively with the acidic dye Congo Red (CR) causing a decrease in percentage of these removal. But the percentage of dye increased with increase in pH for basic dyes Malachite Green (MG) and Crystal Violet (CV) (fig.6). Similar type of study was carried out by Arivoli *et al* [21].

Adsorption Isotherm

The experimental data were analyzed by the linear form of the Langmuir [22] and Freundlich [23] adsorption isotherm. It is represented by

$$C_e / q_e = 1/Q_m b + C_e / Q_m \quad \text{-----(3)}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of dyes adsorbed.

Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption respectively. The linear plots of C_e / q_e versus C_e (Fig.7) suggest that, the applicability of Langmuir isotherm. The values of Q_m and b were determined from slope and intercept of the plot. From the results it is clear that, Q_m and b are increases on increasing temperature. From these values, we can conclude that, the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy. Similar type of study was carried out by Shanmugam Arivoli *et al* [24].

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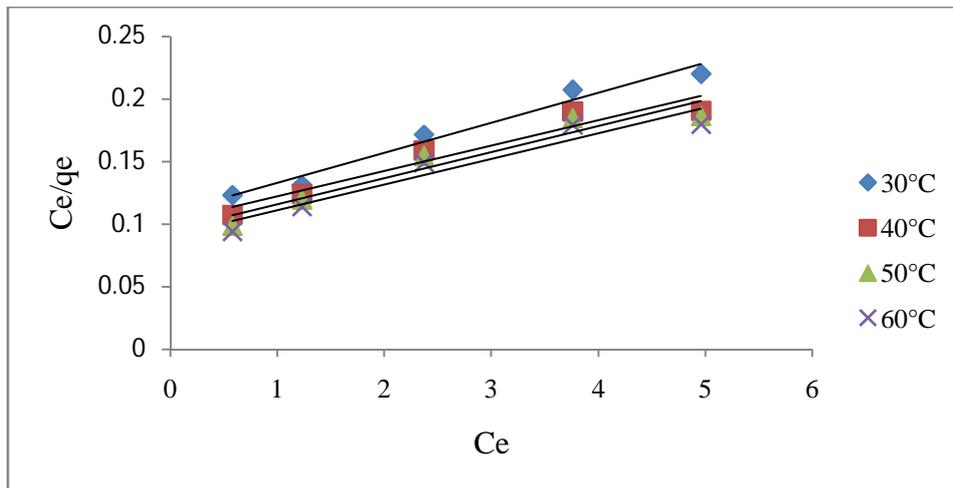


Fig.7 Langmuir isotherm plot for the adsorption of MG onto Morinda pubescens carbon at different temperatures.

The Freundlich equation was employed for the adsorption of dyes onto the adsorbent. The Freundlich isotherm was represented by

$$\log q_e = \log K_f + 1/n \log C_e \text{ -----(4)}$$

Where q_e is the amount of dyes adsorbed (mg/g), C_e is the equilibrium concentration (mg/L) and K_f is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent and 'n' a dimensionless constant, which can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent respectively. The values of K_f and n are calculated from the intercepts and slopes of the plot $\log q_e$ versus $\log C_e$ (Fig.8). From the Freundlich adsorption, it showed that the n value is greater than one for the adsorption of the dye at all temperatures and decrease with increase in temperature. This explains that the amount of dye adsorbed increased with rise in temperatures.

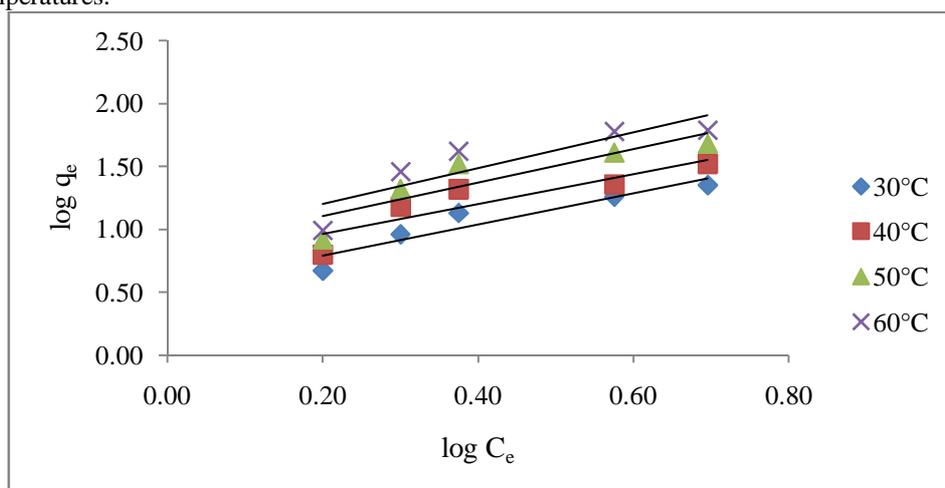


Fig.8 Freundlich isotherm plot for the adsorption of MG onto Morinda pubescens carbon at different temperatures.

IV. CONCLUSION

The present study shown the effectiveness of using activated carbon prepared from the leaves of Morinda pubescens in the removal of three dyes. Morinda pubescens leaves has a great role in modern life to clean environment. An adsorption test has been carried out for industrial pollutants (Dyes) under different experimental condition in batch

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mode. The adsorption of dyes was dependent on adsorbent surface characteristics, adsorbent dose, dyes concentration, initial pH, contact time and temperature. The experimental data are correlated reasonably well by the Langmuir and Freundlich adsorption isotherms. The objective of the present study suggests the *Morinda pubescens* leaves used as a low cost green adsorbent for the removal of Malachite green (MG), Crystal Violet (CV) and Congo Red (CR) dyes from aqueous solution.

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