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Research Article

REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION BY ACTIVATED CARBON PREPARED FROM WASTE BIOMASS

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ABSTRACT

Adsorption of Malachite Green (MG) on activated carbon obtained from *Azadiratcha indica* has been investigated by batch adsorption method. The percentage removal of dye has been optimized by studying the initial concentration of the dye, adsorbent dosage, adsorption time and pH. The experimental data were found to be well fitted to Langmuir isotherm. Among the various kinetic models described, the adsorption of MG can best be described by the Lagergren first order kinetic model. The present study indicates that activated carbon obtained from *Azadiratcha indica* is an effective adsorbent of MG dye.

Keywords: Activated Carbon, Kinetic Studies, Adsorption Isotherms, Malachite Green, Neem Carbon

1. INTRODUCTION

Malachite green (MG) is a popular dye and is used extensively. It also finds applications in medical sciences. MG is highly toxic to flora and fauna. It induces risk of cancer, acts as a liver tumor-enhancing agent and many other diseases. The dyes check the biological activity in aquatic lives. It has mutagenic and carcinogenic characteristics [1, 2]. It can cause severe effects on nervous system, reproductive system, liver, brain and kidney. Precipitation, coagulation, flocculation, ion exchange, biosorption, and adsorption are the conventional methods used for removal of dyes. Activated carbons are widely used as industrial adsorbents for separation, purification of solid and liquid phase, and as recovery processes due to their texture being highly porous and they have large capacity to adsorb pollutants but their large scale application is cost intensive [3,4]. The use of activated carbon for removal of malachite green has also been reported [5]. Commercial activated carbons are expensive and therefore, there is a need to search for effective adsorbents for economical wastewater treatment. Utilizing wastes and bio-wastes of environment as adsorbents for the removal of dyes from wastewater is of interest. Number of materials such as coconut coir, bagasse pith, rice husk, neem tree leaves, and orange peel has been used to prepare carbon from agricultural wastes as low-cost adsorbent materials for the removal of dyes from wastewater [6-10].

In the present studies, rice husk, a non conventional agricultural-waste material, has been indirectly used to prepare activated carbon for the removal of MG from its aqueous solutions.

2. MATERIAL AND METHODS

2.1. Adsorbate

The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42,000, chemical formula = $C_{52}H_{54}N_4O_{12}$, MW=927.00, λmax = 618 nm (measured value) was supplied by BDH (India).

2.2. Adsorbents

The Vembu tree (*Azadiratcha indica*) waste biomass material was collected from Thanjavur District, Tamil Nadu, the collected plant material was washed and air dried for 15-20 days. The dried material was cut into small pieces for further chemical modification. The ground material was mixed with equal amount of concentrated phosphoric acid and stirred for 30 min. The acid- plant material slurry was placed in a beaker and dried at 80^{o}C in a hot air-oven. After 24h, the thermo chemical reaction between acid and plant material, it was proceeding by raising the oven temperature to 120^{o}C for 90 min. After cooling, the resulting carbon washed with distilled water until a constant pH of the slurry reached. The wet carbon material was dried at 110^{o}C and sieved into discrete particle size and stored. The adsorbent after phosphoric acid treatment was designated as VPAC. A stock solution of dye with known concentration (1000 ppm) was prepared. It is diluted to get different required initial concentration of the dye and used in the adsorption experiments. The initial pH was adjusted with prepared 0.1M HCl or 0.1M NaOH. All the adsorption experiments were carried out at room temperature (30 ± 1°C).

2.3. Characterization of adsorbent

The surface morphology of the adsorbent were visualized via Scanning Electron Microscopy (SEM). The diameter of the composite range was 10 μm.

2.4. Malachite green dye solution

A stock solution of dye with known concentration (1000 mg/L) was prepared. It is diluted to get different required initial concentration of the dye and used in the adsorption experiments. The initial pH was adjusted with prepared 0.1M HCl or 0.1M NaOH. All the adsorption experiments were carried out at room temperature.

2.5. Batch experiments

Batch experiments were conducted in bottles of 125 ml capacity. 100 ml of the solution containing predetermined concentration of the MG dye under investigation was taken in the bottles. After the addition of known amount of adsorbent, the bottles were equilibrated for a predetermined period of time in a mechanical shaker (120 rpm). At the end of the equilibration period, the dye solution is taken and the residual dye in solution was determined. The pH of the dye solution was adjusted by using digital pH meter.

2.6. Effect of initial aqueous pH on adsorption

The pH of the dye solution is the most important factor compared to the all other factors that affect the adsorption process. The influence of pH on dye adsorption was investigated by performing experiments taking 100 ml of 20 mg/l of MG dye solutions and equilibrating with 0.200 g VPAC after adjusting the solution pH varying from 5.0 to 9.0 range for 2 hours at room temperature. After equilibration time, the solutions were separated using filters and the supernatant was analyzed for residual concentration.

2.7. Effect of carbon dosage

The various concentration of adsorbent was taken in a 100 ml conical flask. MG dye concentration of 20 ppm was taken in that 100 ml conical flask The flask was put in a shaker at 115 rpm and 35 °C. Various amounts of concentration of adsorbent were taken inside 5 different conical flasks of 0.2, 0.4, 0.6, 0.8 & 1 gm respectively. Samples were kept in each conical flask for a period of 40 min. The % absorbance at 664 nm was found out using a UV-spectrophotometer. The amount of adsorbent dosage was varied in the given range 0.2 gm, 0.4 gm, 0.6 gm, 0.8 gm & 1 gm .

The amount of dye adsorbed at time t, q_t and at equilibrium q_e was calculated from the mass balance equation:

$$qt= \frac{(C_0\text{-}Ct)\ V}{m}$$

Where, q_t is the amount of dye adsorbed (mg/g) at time t, C_0 is the initial dye ion concentration (mg/L), C_t is the dye adsorbent (mg/L) at time t, V is the volume of solution (ml) and m is the mass of the adsorbent (g). When t is equal to equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of dye ion adsorbed at equilibrium, q_e, is calculated using equation [11].

2.8. Adsorption isotherms

Several models of adsorption isotherm are available. The most common among them are Freundlich and Langmuir isotherm. In the present study the data obtained were tested for these two isotherms to study the relationship between the amounts of dye adsorbed with the equilibrium concentration and to find out the possibility of monolayer or multilayer adsorption.

The linear logarithmic form of Freundlich isotherm is given by:

$$\log qe=\log k+1/n \log Ce$$

where, q_e = x/m is the amount of dye adsorbed, Ce the equilibrium concentration, k and n are the constants. When log q_e was plotted against logC_e a straight line was obtained with slope log$k$ and y -intercept.

The linear form of Langmuir isotherm is given by,

$$\frac{Ce}{Qe} = \frac{1}{q_0 b} + \frac{Ce}{qe}$$

where q_o is the equilibrium constant, b is monolayer capacity, C_e is the equilibrium concentration and q_e = x/m is the amount adsorbed per unit mass of the adsorbent [12].

2.9. Statistical analysis

The average values of duplicate runs were obtained and analysed. Error in data: ±1-2% for percentage removal ±0.005-0.01 mg/g for amount adsorbed.

3. RESULTS

3.1. FTIR analysis of activated carbon

The surface chemical characteristics of VPAC after the adsorption of MG were determined by Fourier Transform Infrared Spectroscopy (FTIR), and the spectrum is given in Fig. 1. The peak at 3406 cm^{-1} is attributed to the stretching vibration of O–H band and aliphatic, asymmetric C–H stretching vibration of methylene group. The peaks at 2935 cm^{-1} in the spectra are due to stretching vibration of C-H. The band at 1701 cm^{-1} represents the acidic carbonyl C=O stretching. The peaks around 1030–1308 cm^{-1} presents C-O stretching in phenols, alcohols, acids, ethers and esters. These groups participate in MG adsorption to VPAC. The surface of carbon materials is, in general, rich in a variety of surface functional groups among which the C–O type groups are predominant and they form in ethers, acids and esters. FTIR analysis confirmed the presence of phenolic surface group on the VPAC. There are hydroxyl groups (3406 cm^{-1}; O–H stretching mode) present in the IR spectrum of the functionalized VPAC.

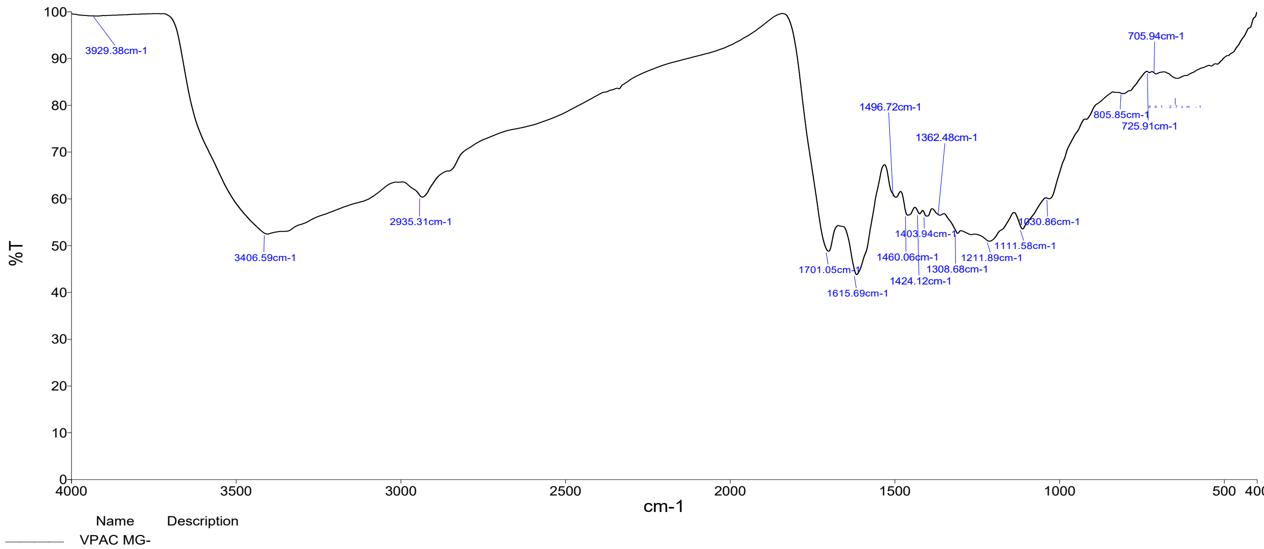

Fig.1: IR spectrum of VPAC after the adsorption of MG dye

3.2. Scanning Electron Microscope analysis of activated carbon

The SEM micrograph of VPAC before adsorption is shown in Fig. 2. It is seen that VPAC has a highly porous structure.

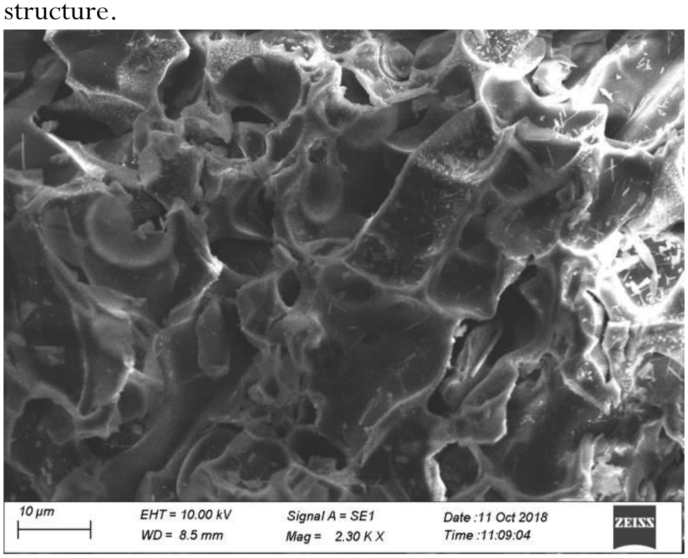

Fig.2: SEM image of VPAC before adsorption of MG

3.3. Effect of initial aqueous pH on adsorption

In VPAC system, the increase of pH of the solution increases the adsorption of dyes from solution (Fig.3).

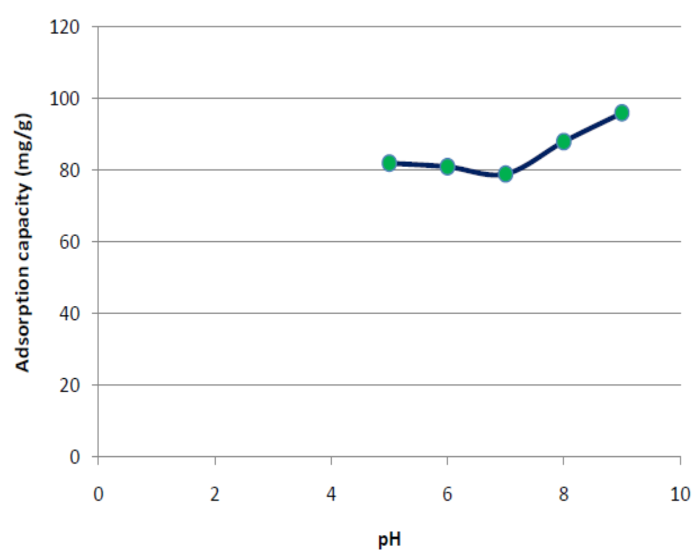

Fig.3: Effect of pH for VPAC-MG system

3.4. Effect of carbon dosage

It was observed from the graphs that increasing the dosage increases the % removal of MG (Fig.4). As there was no drastic increase in the adsorption rate on increasing the dosage of adsorbent beyond 1.0 gm of activated carbon, hence, from economic point of view, 1.0 gm was taken as optimum dosage for removal of MG. It can be attributed to the increase in adsorbent sites for more adsorption of the dye at the fixed 20 ppm.

3.5. Adsorption Isotherms

When log q_e was plotted against log*Ce* a straight line was obtained with slope log*k* and y-intercept. From the Fig.5, Freundlich isotherm is less fitted to the present adsorption study due to the less correlation coefficient value of 0.755. A plot of C_e/q_e against C_e over the entire concentration range is a straight line with a slope of $1/q_0$ and the intercept of $1/q_0b$. A straight line was obtained when C_e/q_e was plotted against C_e with a correlation coefficient (R^2) of 0.963 indicating that the present study of data follow Langmuir isotherm (Fig.6).

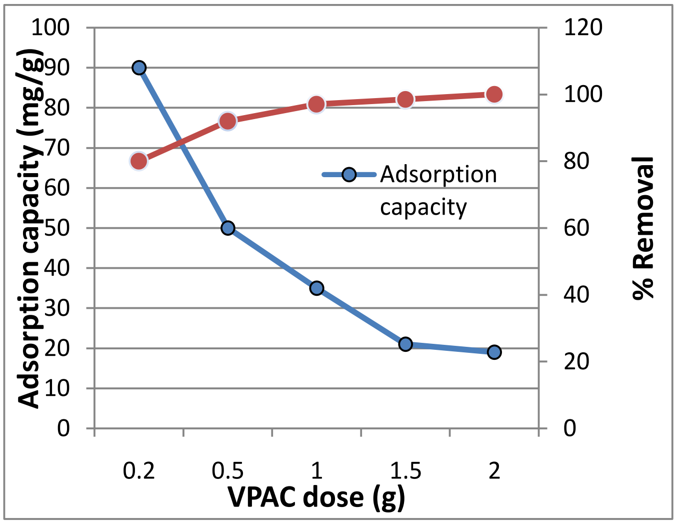

Fig.4: Effect of carbon dosage

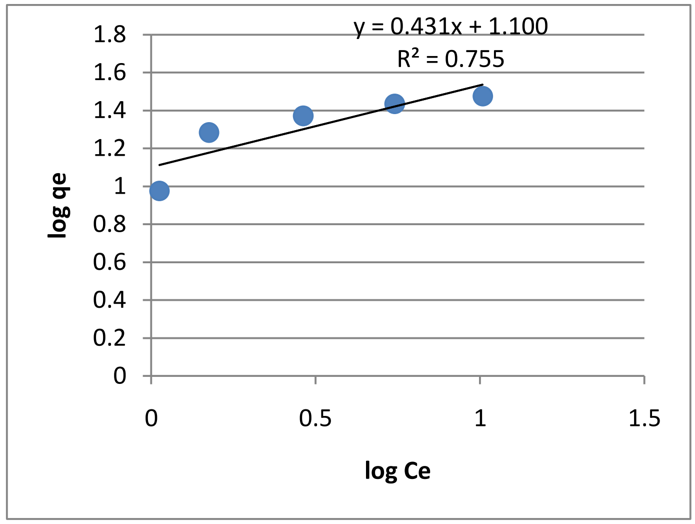

Fig.5: Freundlich adsorption isotherm

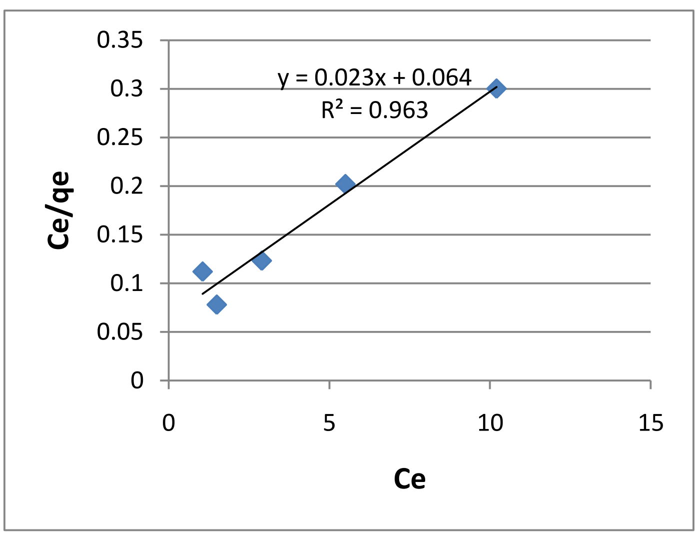

Fig.6: Langmuir Adsorption Isotherm

4. DISCUSSION

Malachite green is a distinctive example of a basic and cationic dye, that has been widely used in medicine, fisheries, food and directly as a dye in the wood, silk, leather and paper industries. However, high concentrations of MG are toxic if discharged into the aqueous environment, with carcinogenic effects on human beings and causing suffocation of aquatic plants [13, 14]. In the present study, *Azadiratcha indica* carbon was selected as a local, cheaper and readily available adsorbent for the removal of malachite green from the aqueous solution. From the Fig.3, the initial rate of adsorption is mainly decided by the protons release from carbon surface due to ion exchange process, which is confirmed by the measurement of pH of the solution after the adsorption process. At acidic pH, the adsorption of the dye is low up to pH 7 and then the adsorption capacity of VPAC is found to be higher at pH 9. At higher pH the protons are neutralized with OH ions, so the adsorption process increases. From the Fig. 4, it was observed that the percentage adsorption of MG dye using VPAC is increased with an increase of the carbon dosage due to the increase of the activated sites available for adsorption. In VPAC, the increase in initial concentration of dye solution increased the absorption capacity. From the Fig.5 and Fig. 6, it is very clear that adsorption of basic dye-MG on VPAC follows Langmuir model. Among the Freundlich and langmuir model studied, the correlation coefficient (R^2) value is 0.963 which is very close to 1 indicating that the adsorption follows the Langmuir isotherm. This confirms that the removal of basic dyes from aqueous solution by activated carbon obtained from *Azadiratcha indica* bio mass. This study confirmed that the VPAC has comparatively high adsorption capacity and can be used as cost effectiveness natural absorbent.

5. CONCLUSION

The present study indicates that activated carbon obtained from *Azadiratcha indica* waste biomass is an effective adsorbent of MG dye. The extent of adsorption decreases with increase in initial dye concentration, increases with increase in adsorbent dosage, adsorption time and pH. For adsorption isotherm, Langmuir Isotherm is more accurate because regression coefficient was $R^2 = 0.963$ as comparison to $R^2 = 0.755$ for Freundlich Isotherm. Hence after carrying out rigorous experiments we finally came to conclusion that activated carbon prepared from *Azadiratcha indica* biomass can be effectively used for the removal of malachite green effectively.

6. ACKNOWLEDGEMENT

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