

Removal of Malachite Green Dye by Adsorption Method using Activated Carbon (AC)

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Abstract:- The objective of this work is to study the adsorption of Malachite Green Dye using Activated Carbon (AC). This is a cheap and eco-friendly adsorbent. Liquid phase batch operations were carried out to observe the effect of various experimental parameters such as Contact Time, Adsorbate Dose, Initial Concentration along with Langmuir and Freundlich Isotherm models. Here, the optimum conditions for the Contact Time and the Dosage were evaluated using above adsorbent. This work is helpful to design a low cost adsorption columns for treating effluent water in industries or other adsorption processes.

1. INTRODUCTION

A dye is generally a substance that bears an affinity to the substrate to which it is being applied which is often applied in aqueous solution. It appears to be coloured because they absorb some wavelengths of light in particular than other. Various industries like chemical, refineries, textile, plastic and food processing plants discharge wastewaters. These wastewaters include dyes as residues which cause many hazards. Such residual dyes are non- biodegradable due to their complex molecular structures making them more stable and hard to biodegrade. They cause water pollution and also pose a serious threat to the environment. These coloured stuffs along with being aesthetically displeasing also inhibit sunlight penetration into water bodies and thus affect aquatic ecosystem. Many of them are also toxic in nature and can cause direct destruction or can affect catalytic capabilities of various microorganisms.

Textile industries are the main sources of discharge of dyes. They are used to colour the products. Today there are over 1,00,000 dyes for commercial use and around 700 tons of dyestuffs are produced annually. The types of dyes are mainly basic, acidic, direct, reactive, mordant, azonic, disperse, sulphur and vat dyes. Most of the dyes are toxic and have carcinogenic properties hence they make water bodies inhibitory to aquatic systems. They don't fade by water or sunlight owing to their complexity in structures. They can't be adequately treated in conventional treatment plants for waste waters.

Coloured water is not aesthetically acceptable to the general public though it may not be toxic. In fact, given a choice, consumers tend to choose clear, non coloured water of otherwise poor quality over treated potable water

with an objectionable colour. Highly coloured water is unsuitable for laundering, dyeing, paper making, beverage, textile, plastic, dairy and other food-processing industries. Recent reports suggest that colour-causing substances are microtoxic to aquatic biota. Colour acquired by a river through the discharge of coloured industrial effluents, inhibits growth of the desirable aquatic biota necessary for self- purification-oxygenation) by reducing penetration of sunlight and consequent reduction in photosynthetic activity and primary production.

There are various ways to remove dyes from wastewater discharges like adsorption, coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis, aerobic and anaerobic microbial degradation. Many of these processes are not so popular due to their economic disadvantages and inefficiency. Coagulations, chemical and electrochemical oxidations have low feasibility on large scale plants. There by Adsorption process is only preferred over these processes and is widely used due to its low cost and high performance. Some of the common adsorbents are activated carbon, alumina silica, saw dust, zeolite, char, metal hydroxides etc., Economic advantages, performance efficiencies and the environment are the main concerns when selecting any adsorbent. Due to this reason most of the researchers generally go for low-cost adsorbents.

2. MATERIALS AND METHODOLOGY

Activated Carbon (AC):

Activated carbon, also called activated charcoal, activated coal, or carboactivatus, is a form of [carbon](#) processed to have small, low-volume pores that increase the [surface area](#) available for [adsorption](#) or [chemical reactions](#). *Activated* is sometimes substituted with *active*. Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 500 m², as determined by gas adsorption. An activation level sufficient for useful application may be attained solely from high surface area; however, further chemical treatment often enhances adsorption properties. Activated carbon is usually derived from [charcoal](#) and increasingly, high-porosity [biochar](#).

Malachite Green dye

Malachite green was first prepared by Fischer in 1877 by condensing [benzaldehyde](#) and [dimethylaniline](#) in the molecular ratio 1:2 and in the presence of a [dehydrating agent](#).

Malachite green dye is basically a cationic dye and is an

[organic compound](#) that is used as a [dyestuff](#) and has emerged as a controversial agent in [aquaculture](#). Malachite green is traditionally used as a dye for materials such as [silk](#), [leather](#), and [paper](#). Although called malachite green, the compound is not related to the [mineral malachite](#) — the name just comes from the similarity of colour.



Fig A. Activated Carbon



Fig B. Malachite Green Dye Adsorption

Adsorption is a surface phenomenon which results out of binding forces between atoms, molecules and ions of adsorbate and the surface of adsorbent. It is the process of formation of a layer of solid or gas on the substrate. It involves separation of a substance from fluid phase by accumulation on the substrate of solid phase.

Factors affecting adsorption

1. Surface area of the adsorbent
2. Contact time
3. Particle size of the adsorbent
4. Solubility of the adsorbate in waste water
5. Degree of ionization of the adsorbate molecule
6. Number of carbon atoms
7. Size of molecule with respect to the size of the pores
8. Temperature
9. pH

out of which the following were studied along with adsorption isotherms

- a) Contact time
- b) Dosage
- c) Initial Concentration

Adsorption Isotherms

Adsorption isotherms help in describing how molecules of adsorbate interact with adsorbent surface. The adsorption processes are generally described by the Langmuir and the Freundlich isotherm models.

The Langmuir equation is based on the fact that there is no interaction between the adsorbate molecules and that the adsorption process is localized in a monolayer. It then assumes that once a dye molecule occupies a given site, no more adsorption can take place at that site. The Langmuir equation is commonly expressed as in the linear form

$$\frac{1}{q_e} = \frac{1}{b \cdot q_0 \cdot C_e} + \frac{1}{q_0}$$

where C_e is the equilibrium concentration of dye solution (mg L^{-1}), q_e is the equilibrium

capacity of dye on the adsorbent (mg g^{-1}), q_0 is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}) and is related to the free energy of adsorption.

The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Its linear form can be written as:

$$\ln q_e = \ln K_f + \frac{1}{n * \ln C_e}$$

where K_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicates the capacity and intensity of the adsorption, respectively.

Isotherms study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption is usually described by adsorption isotherms, such as Langmuir, Freundlich isotherms. These isotherms relate metal uptake per unit mass of adsorbent q_e , to the equilibrium adsorbate concentration in the bulk fluid phase C_e .

Experimental methodology:

In this experimental methodology, the experimental procedures are detailed in four phases. In Phase I - stock solution, in Phase II – determination of optimum time, in Phase III

– determination of optimum dosage, in Phase IV – initial dye concentration are described below.

Phase – I :Stock solution: It is prepared by diluting 1g of Malachite green dye in 1 litre of distilled water. And afterwards, it was diluted in distilled water as per our requirement. The entire experimental procedure was carried out with the concentration of 10ppm or 10mg/l.

Phase – II: Determination of optimum time

100 ml of dye solution with dye concentration (10mg/L) was prepared in a 250ml conical flask with adsorbent concentration (g/L) and placed on the shaker. The samples were withdrawn from the shaker (orbital shaker) at predetermined time intervals. Keeping the concentration (10mg/l) constant and varying the time from 0– 150 minutes, it was observed until it reached equilibrium to find the optimum time. The dye concentrations were measured after 1,3,5,10,15,30,60,90,120 and 150 minutes until equilibrium reached. The dye solutions were taken by the help of micropipettes and % absorbances were estimated by using Spectrophotometer (Lovibond PC) at the wavelength corresponding to maximum absorbance, ($\lambda_{\text{max}}=618$).

Phase – III: Determination of optimum dosage

100 ml of dye solution with dye concentration (10mg/L) was prepared in a 250ml conical flask with adsorbent concentration (g/L) and placed on the shaker (orbital Shaker). The samples were withdrawn from the shaker at predetermined time intervals (RPM=120, temp=(27 ± 1) °C). Keeping the time constant (optimum time) and varying the dose from 2– 4.5 mg/100ml, it was observed until it reached equilibrium to find the optimum dosage and % absorbances were measured by using Spectrophotometer at the wavelength corresponding to maximum absorbance, ($\lambda_{\text{max}}=618$). The dye solutions were taken by the help of micropipettes. The dye concentrations were measured after 2.0, 2.5, 3.0, 3.5, 4, 4.5 and 5mg/100ml until equilibrium was reached.

Phase – IV: Initial dye concentration

Eleven solutions of dye in distilled water were prepared in conical flasks with varying concentrations of dye - 2, 4, 6, 8, 10, 15, 20, 25, 30, 40 and 50mg/l. Accurately weighed adsorbent was put into the solutions in the conical flasks at optimum dosage and were placed on the shaker (RPM=120, temp=(27 ± 1) °C) until optimum time was reached. Their % absorbances were determined using spectrophotometer ($\lambda_{\text{max}}=618$) and the removal efficiency was calculated. The dye solutions were taken by the help of micropipettes. The dye concentrations were measured at every 2,4,6,8,10,15,20,25,30,40 and 50mg/l respectively.

Calibration Curve:

Dye solutions were prepared with concentrations required and their % absorbances were found out by UV spectrophotometer ($\lambda_{\text{max}}=618$) with these values a standard calibration curve was plotted. The equation of the curve was used to calculate the concentrations for various % absorbances of all the adsorbents. Calibration Curve is shown below.

Table 1.0: Dye Concentrations and Absorbance Values

Conc. of dye(mg/L)	%Absorbance
0	0.000
2	0.320
4	0.632
6	0.946
8	1.261
10	1.565
15	2.351
20	3.131
25	3.912
30	4.724
40	6.263
50	7.826

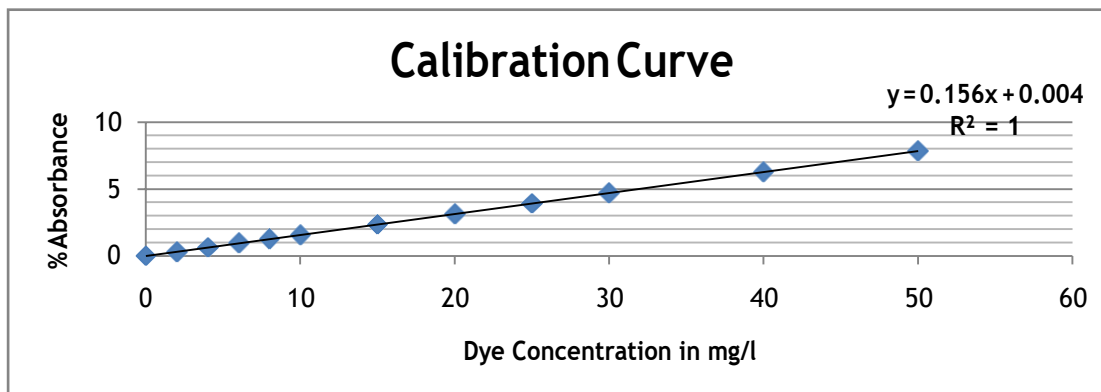


Fig 1.0 : Standard calibration curve

Equation from the above graph is $y = 0.156x + 0.004$ which is of the form $y = mx + c$. Now from this equation, concentrations can be calculated.

Where x = concentration, y = % absorbance

Moreover, according to Beer Lambert's law, absorbance is the product of slope and concentration.

The Removal Efficiency (RE) was determined as follows: Removal efficiency (%) = $(C_0 - C_e) / C_0 \times 100$

The amount of adsorption at equilibrium q_e (mg/g) was calculated by the following equation: $q_e = (C_0 - C_e) \times V / m$ where,

C_0 is the initial dye concentration (mg/L),

C_e is the equilibrium (or) final dye concentration (mg/L),

V is the volume of the solution (L) and m is the amount of adsorbent used (g).

Effect of Time

The effect of contact time was studied at 1, 3, 5, 10, 30, 60, 90, 120 and 150 minutes. Fig

2.0 shows the relationship between contact time and colour removal efficiency. Observation reveals that the removal of colour improved by increasing the contact time. The percentage colour removal approached equilibrium 90 minutes. Further increase in contact time does not show significant change in colour. This might be due to the fact that a large number of vacant surface sites is available for the adsorption during the initial stage and with the passage of time. After some time, repulsive forces between solute molecules on solid phase and liquid phase create difficulty for the solute molecules to occupy remaining vacant surface sites.

Table 2.0 : Data for the effect of contact time on colour removal by AC

AC		
Time(min)	C_e (mg/l)	% Removal
1	8.324	16.76
3	7.564	24.36
5	4.231	57.69
10	3.048	69.52
30	2.336	76.64
60	1.506	84.94
90	1.077	89.23
120	1.063	89.37
150	1.071	89.29

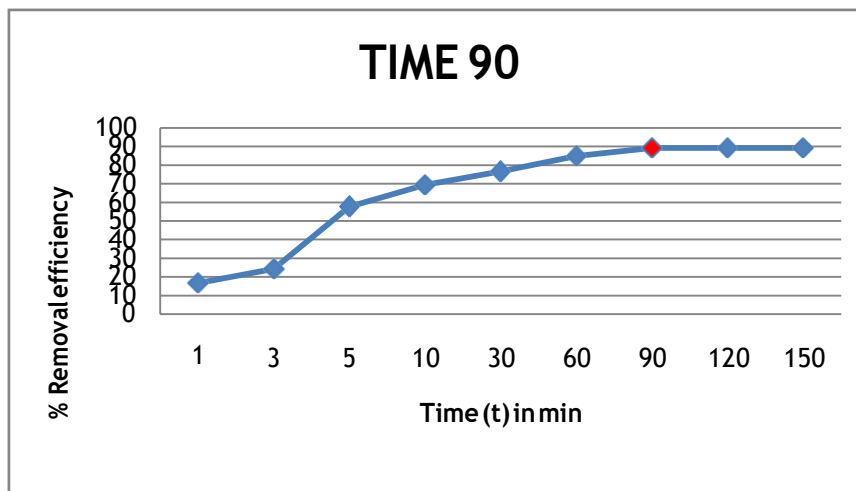


Fig 2.0: Removal Efficiency Vs Contact Time of AC

Effect of Dose

The effect of the adsorbent dose on colour removal is shown in Fig 3.0. Adsorbent dose was varied between 2 and 4.5 mg/100mL and it was indicated that the removal efficiency of colour improved by increasing the adsorbent dose up to 3mg/100mL where further dose increase yields negligible adsorption. Greater availability of exchangeable sites at higher concentration of adsorbent is the reason for the increase in colour removal with the increase in adsorbent dose. That's why beyond 3mg/100mL, the adsorption found to be constant. At fixed optimum time, the optimum dosage found was 3 mg/100mL. The percentage removal of colour at various mix dosages for an initial dye concentration 10mg/L by Activated Carbon is given by following table followed by a graph.

Table 3.0 : Data for the effect of adsorbent dose on colour removal by AC

AC		
Dose (mg/100ml)	Ce (mg/l)	% Removal
2	1.851	81.49
2.5	1.589	84.11
3	1.295	87.05
3.5	1.282	87.18
4	1.268	87.32
4.5	1.264	87.36

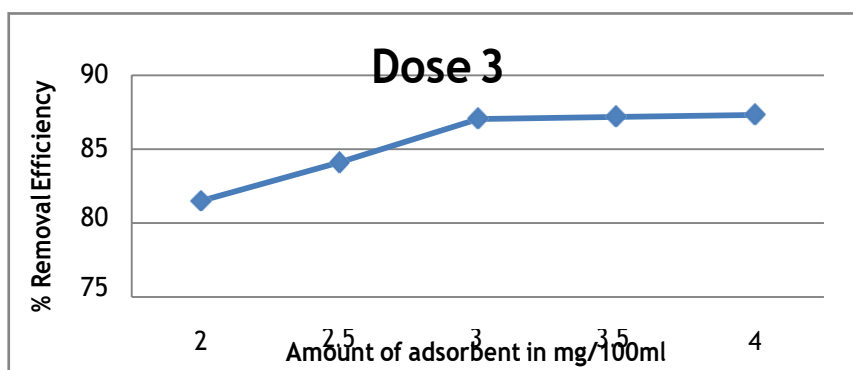


Fig 3.0: Removal Efficiency Vs Dosage of AC Effect of Initial Concentration

The effect of the Initial Concentration of the dye on colour removal is shown in Fig 4.0 . The initial concentration was varied between 2 and 50 mg/l and it was indicated that the removal efficiency decreases by increasing the initial dye concentration.

Table 4.0: Data for the effect of initial concentration on colour removal by AC

AC		
Initial Conc(mg/l)	Final Conc.(mg/l)	% Removal
2	0.681	93.19
4	0.724	92.76
6	0.785	92.15
8	0.828	91.72
10	1.002	89.98
15	1.525	84.75
20	1.948	80.52
25	2.356	76.44
30	2.803	71.97
40	3.397	66.03
50	3.876	61.24

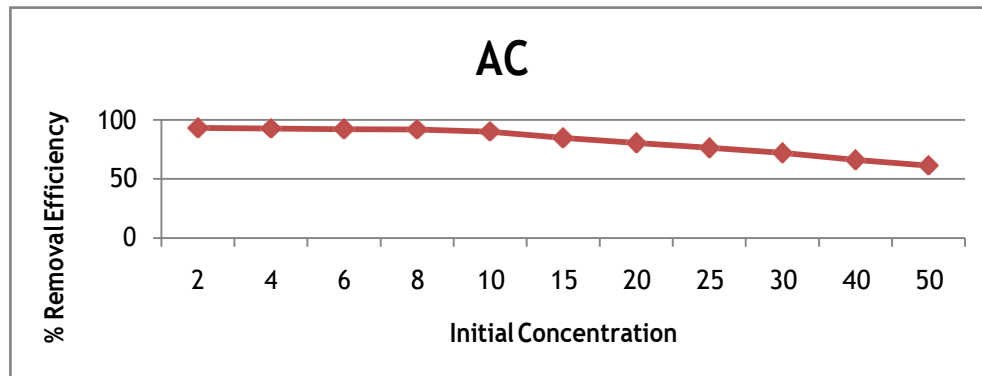


Fig 4.0: Effect of initial dye concentration on colour removal by AC

Isotherm Models

Langmuir & Freundlich Isotherms of AC are shown in the graphs along with the values in the table below.

Table 5.0: Data for Langmuir & Freundlich Isotherms of AC

Dose	Ce	qe	1/ce	1/qe	log ce	log qe
2	1.851	407.45	0.540249	0.002454	0.267406	2.610074
2.5	1.589	336.44	0.629327	0.002972	0.201124	2.526908
3	1.295	290.1667	0.772201	0.003446	0.11227	2.462648
3.5	1.282	249.0857	0.780031	0.004015	0.107888	2.396349
4	1.268	218.3	0.788644	0.004581	0.103119	2.339054
4.5	1.264	194.1333	0.791139	0.005151	0.101747	2.2881

A curve $1/q_e$ vs $1/C_e$ is plotted, the intercept gives the q_0 value and slope gives the K_L value

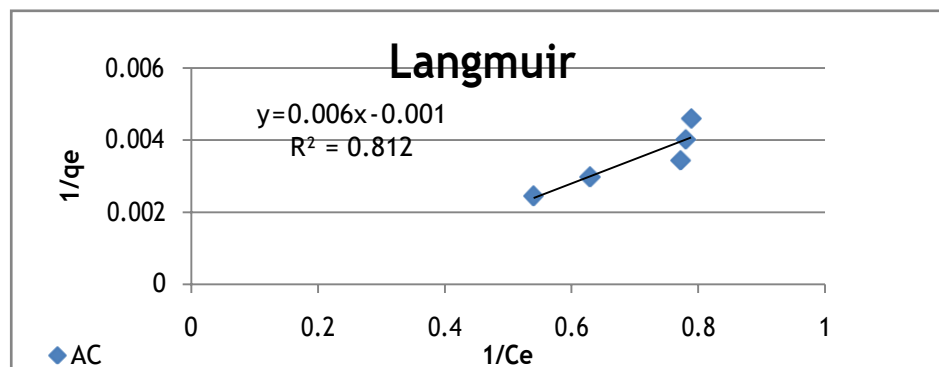


Fig 5.0: Langmuir isotherm curve of AC

The observed values of R^2 , q_0 and K_L of AC from the following plot that are 0.812, 166.67 and 0.0012 respectively. A curve $\ln(q_e)$ vs $\ln(C_e)$ is plotted, the slope gives $\frac{1}{n}$ value and intercept gives K_f value.

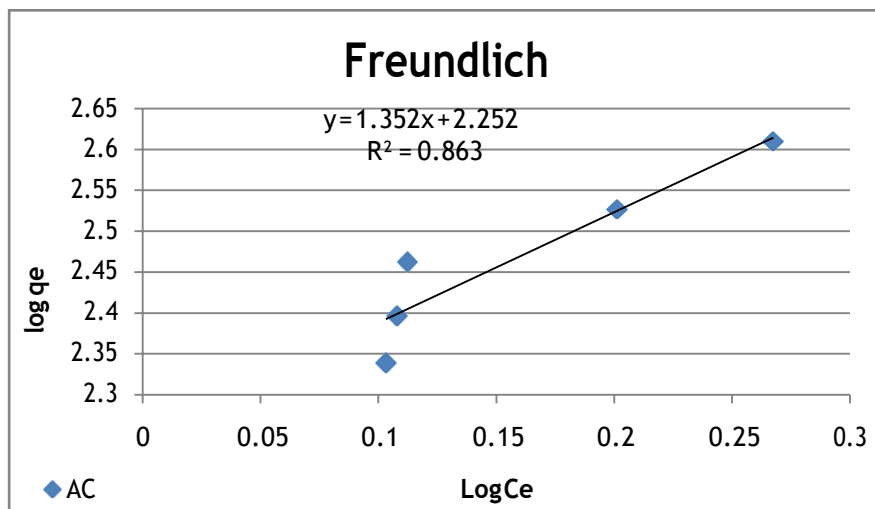


Fig 6.0: Freundlich isotherm curve of AC

The observed values of R^2 , n and K_L of AC from the following plot that are 0.863, 0.739 and 0.2529 respectively.

3. RESULTS AND CONCLUSIONS

Experimental studies were conducted to remove M.G dye using Activated Carbon (AC) as an adsorbent and it can be extended for the different adsorbents for future scope.

1. The maximum removal efficiency of the adsorbent AC was found to be 89% when treated for contact time.
2. The maximum removal efficiency of the adsorbent AC was found to be 87% when treated for adsorbent dosage.
3. The maximum removal efficiency of the adsorbent AC was found to be 89% when treated for initial dye concentration.
4. The minimum and maximum removal efficiencies of the adsorbent AC were found to be 61% and 93% respectively.
5. The removal efficiency increased with time and adsorbent dosage but it decreased with the increase in initial dye concentration.
6. Removal efficiency was found to be increasing till it reached the optimum time and the optimum dosage. Since then, it was found to be negligible.
7. We observe that both Isotherm curves fit well with the adsorption system as their R^2 values are quite near and both gives reasonable values of rate constants. However, Freundlich isotherm model fits well as its correlation coefficients R^2 values are higher than the Langmuir.

4. REFERENCES

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