A Comparative Study on Removal of Malachite Green Dye from Waste Water Using Different Low Cost Adsorbents

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Abstract - **In this present study the adsorption comparison have been investigated on the removal of malachite green dye using different low cost adsorbents. Adsorbents were play efficient role for removal of dyes from waste water. Dyes and colours are frequently used in industries and textile and pulp and paper industries are reported to utilize large quantities of a number of dyes. According to an estimate more than 1,00,000 commercially available dyes with over $7X10^5$ tonnes of dyestuff are produced and used annually. Batch adsorption experiments were carried out for the removal of malachite green from aqueous solutions onto different activated carbons, such as Rice husk, Thespesia Populnea Bark, Calatropis gigantis bark, Corn cob, Neem bark and Mango bark, Root powder of water hyacinth (Eichhornia crassipes), Araucaria cookii bark. Seaweed Enteromorpha. The influence of operating parameters such as contact time, pH, temperature, adsorbent dosage and initial dye concentration on the sorption of malachite green were analyzed using response surface methodology. Equilibrium isotherms were analyzed by the Langmuir, Freundlich and Tempkin isotherm models. Removal of malachite green dye from industrial effluents using different bio sorbents found to be very efficient and satisfactory.**

Keywords: Waste water treatment, malachite green, response surface methodology, , pollution control, different adsorbents, adsorption.

INTRODUCTION:

Dyes and colours are frequently used in industries and textile and pulp and paper industries are reported to utilize large quantities of a number of dyes. According to an estimate more than 1,00,000 commercially available dyes with over 7X105 tonnes of dyestuff are produced and used annually. The discharge of effluents from these applications is one of the potential sources of their contamination and pollution.[1] The textile, paper and leather industries consume large quantities of water and produces large volume of waste water from different steps in the dyeing and finishing process.[2] Some dyes can cause allergic dermatitis, skin irrigation, cancer and mutation in man. Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters. Wastewaters from dyeing industries released in to nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes, recognizing the economic drawback of commercial activated carbon.[3] There are in numerous harmful effects of dyes on ecosystem such as: (a) they pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes. (b) They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities. (c) They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes. (d) They have complex molecular structures which makes them difficult to treat with common municipal treatment operations. (e) Consume dissolved oxygen and affect aquatic ecosystem. (f) Sequester metal ions which produce micro toxicity to aquatic lives. There are various ways to remove dyes from wastewater discharges like coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation.[4]Activated carbon is the most popular adsorbent, which is capable of adsorbing many dyes with a high adsorption capacity.[5] the use of Activated carbon to decolorizes the effluent is not only economical technique but also reduces problems associated with water hyacinth plants[6] Activated carbon is the most widely used adsorbent with great success due to its large surface area, micro porous structure, high adsorption capacity, etc. However, its use is limited because of its high cost. This has led to research for cheaper substitutes.[7] Many botanical materials of a very low price have directly been used as sorbent for dye adsorption from waste water.[8] The objective of the present study is adsorption comparison have been investigated on the removal of malachite green dye using different low cost adsorbents. The effects of important experimental parameters such as contact time, initial malachite green concentration, adsorbent concentration, pH and temperature were studied. The adsorption isotherms were described by using the Langmuir, Freundlich and Tempkin isotherm models.

MATERIALS AND METHODS:

The dye, malachite green was supplied from India. The stock solution (1000 mg L-1) of malachite green was

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 6 Issue 04, April-2017

prepared by dissolving accurately weighed amount of the dye in distilled water. All the chemicals used throughout this study were of analytical- grade. All working solutions of desired concentrations were obtained by diluting the stock solution with distilled water. The pH of the solutions was adjusted with 0.1 mol L-1 HCl or 0.1 mol L-1 NaOH. Characterization: SEM analysis was carried out on the ACB to study its surface texture before and after malachite green biosorption. FTIR spectroscopy was used to identify the chemical present in the biosorbent. Infrared spectra of the samples (ACB before biosorption of malachite green) and the malachite green loaded samples were obtained using a FTIR spectrophotometer. Experimental design by response surface methodology (RSM): The effect of various process parameters such as temperature (x1), pH (x2), dosage (x3) and initial dye concentration (x4) on color removal was studied by using central composite design (CCD). A CCD with 26 experiments was used for the optimization of process parameters for removal of malachite green dye from synthetic solution. All independent variables were coded to four levels as Xi according to eqn. 1.

$$X_i = x_i - x_{0i} / \Delta x_i \ (i=1,2\ldots\ldots k)$$

where xi is dimensional less value of an independent variable, xi is the real value of an independent variable, xoi is the real value of the independent variable at the center point and Δxi is step change. A polynomial (eqn. 2) was developed to estimate the behaviour of the percentage removal of color.

Y = b0 + b1x1 + b2x2 + b3x3 + b4x4 + b11x12 + b22 x22 + b33x32 + b44x42 + b12x1x2 + b13x1x3 + b14x1x4 + b23x2x3 + b24x2x4 + b34x3x4 (2)

where Y is the predicted response; x1, x2, x3 and x4 are independent variables; b0 is an offset term; b1, b2, b3 and b4 are linear effects; b11, b22, b33 and b44 are squared effects and b12, b13,b14, b23, b24 and b34 are interaction terms.

Experimental procedure: Biosorption studies were mainly carried out by batch technique to obtain rate and equilibrium data. The experiments were performed to observe the effect of important parameters like initial pH (2, 3 4, 5, 6,7, 8, 9, 10, 11), initial malachite green concentration (20, 40, 60, 80 and 100 mg L-1), biosorbent dosage (0.02, 0.04, 0.06, 0.08 and 0.1 g per 30 mL of synthetic solution), contact time (1-45 min) and temperature (303, 308, 313, 318, 323 K) on the adsorptive removal of malachite green. For each experimental run, 30 mL of malachite green solution of known concentration, pH and a known amount of the biosorbent were taken in a 100 mL stoppered conical flask. The mixture was agitated in a temperature controlled orbital shaker at a constant speed of 180 rpm at 30 ± 1 ºC. Samples were withdrawn at appropriate time intervals. All the samples were centrifuged at 5000 rpm for 10 min to settle down suspended particles. After centrifugation clear supernatant samples were obtained and their residual dye concentration was analyzed by using UV spectrophotometer. The above procedure was repeated for different pH values, initial dye concentration, dosage of biosorbent, contact time and temperatures. All experiments were performed triplicate and reported values are average of three. The percentage color removal of dye and dye uptake were calculated using the following relationships:

Color removal (%) $= C_i - C_f / C_i \ \ 100$……………………(3)

Dye up take(q) $= C_i - C_r \ V/M$…………………………(4)

where Ci is the initial sorbent concentration (mg/L), Cf is the final sorbent concentration (mg/L), v is the volume of the solution (L) and m is the mass of the biosorbent (g).

RESULTS AND DISCUSSION:

Effect of initial concentration:

It was observed that with increase in the initial dye concentration, the percentage biosorption decreased for different adsorbents . This decrease in the percentage biosorption can be attributed to the decrease in the driving force available for biosorption. This can be attributed to the fact that for a given mass of adsorbent, the active sites are fixed and as the concentrations goes on increasing the active sites will not be abundant as when compared to lower dye concentrations .The increase in the biosorption observed with the increasing temperature.

Table 1. Experimental conditions of adsorption experiment for the removal of MG by Different adsorbents at 30ºC

S.NO	ADSORBENTS	Initial dye concentration (mg/l)	Dose (g /1)	Contact time (min)	Initial pH	Particle size of absorbents (µm)	Rpm	Per cent (%) Removals of MG dye from waste water.
1	Rice husk	60-100	60	40	7	150	150	94.91
2	Thespesia Populnea Bark	50-250	50	40	6	150	120	90
3	Calatropis gigantis bark	10-50	50	40	6	150	120	82
4	Co r n cob	0-500	50	100	12	150	120	83
5	Neem bark and Mango bark	10-150	50	120	5and 2	150	400	85.45 and 91.5
6	water hyacinth (Eichhornia crassipes)	80-100	0.5-5	10-300	2-10	100	120	99.33
7	Araucaria cookii bark	80-100	3.3	15	3	150	180	98.5
8	Seaweed Enteromorpha	50-350	50	30-180	1-7	0-63	180	94.74

Effect of contact time:

The effect of contact time for the removal of malachite green by the different adsorbents at different concentrations for 0.1 g of biosorbent (Fig. 1) showed rapid adsorption of dye in the first 15 min and, thereafter, adsorption reached equilibrium. Further batch experiments were conducted for 15 min contact time with shaking speed of 180 rpm.A large number of vacant surface sites are available for adsorption during the initial stage and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

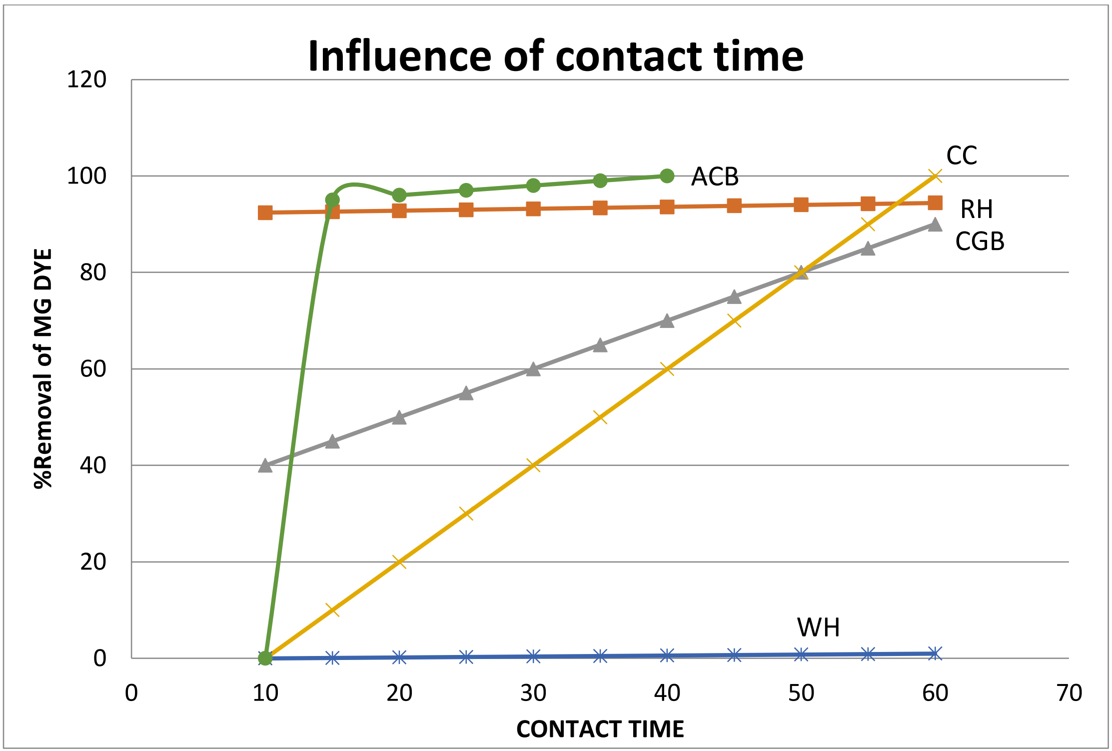

Fig (1) Influence of contact time

Effect of dose of adsorbent :

Study of the effect of biosorbent dosage gives an idea of the effectiveness of a biosorbent and the ability of a dye to be adsorbed with a minimum dosage, so as to identify the ability of a dye from an economical point of view. Fig. 2 explains the influence of biosorbent dosage on % color removal of malachite green. Usually the percentage of dye removal increases with an increase in biosorbent dosage, where the number of sorptionsites at the adsorbent surface will increase by increasing the dosage of the adsorbent24 and as a result increase in the percentage of dye removal from the solution.

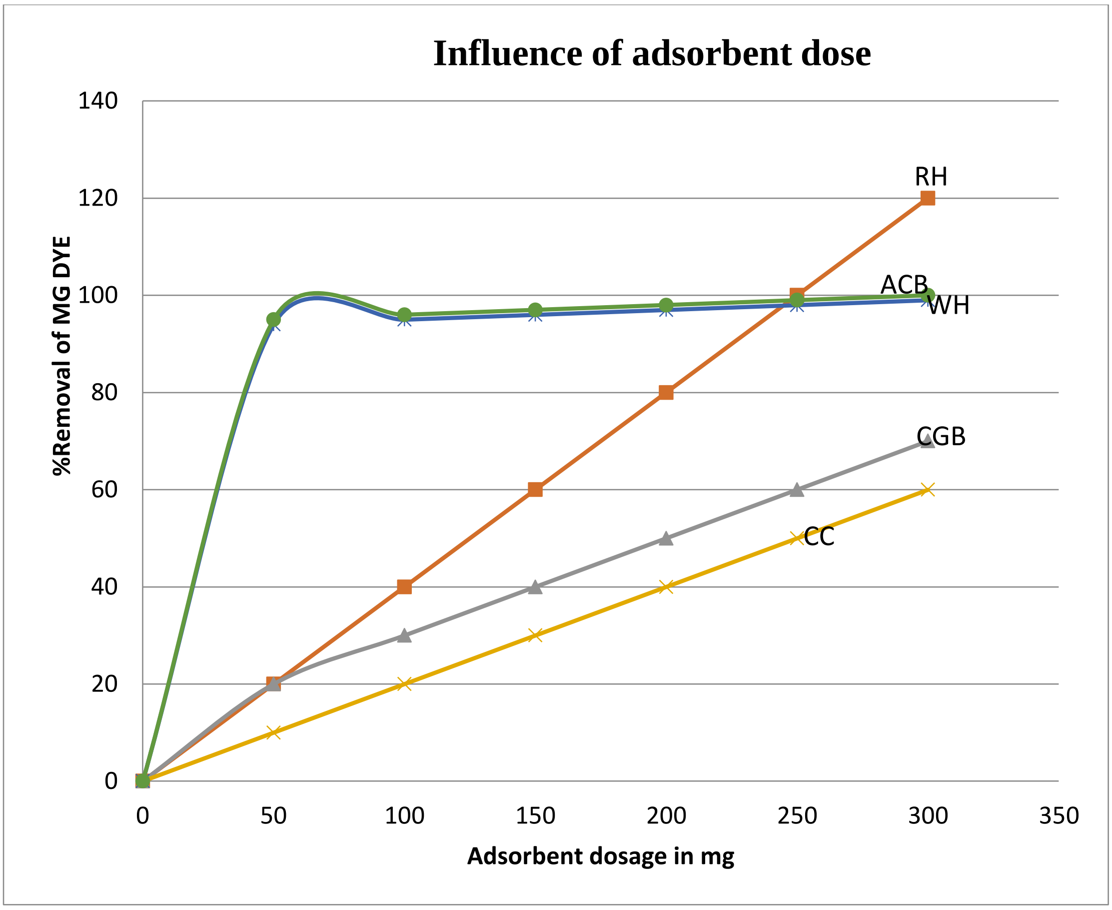

Fig (2) Influence of adsorbent dose

Effect of initial pH :

At higher pH the percentage biosorption values were low. The low biosorption capacity under alkaline conditions could be mainly attributed to that the increasing number of negative charge on the surface of the different adsorbents could result in electrostatic repulsion between the adsorbent and dye molecules17 and that the existence of excess OH– ions may compete with the cationic dyes for the decreasing number of positively charged sites on the different adsorbents as the pH increased.

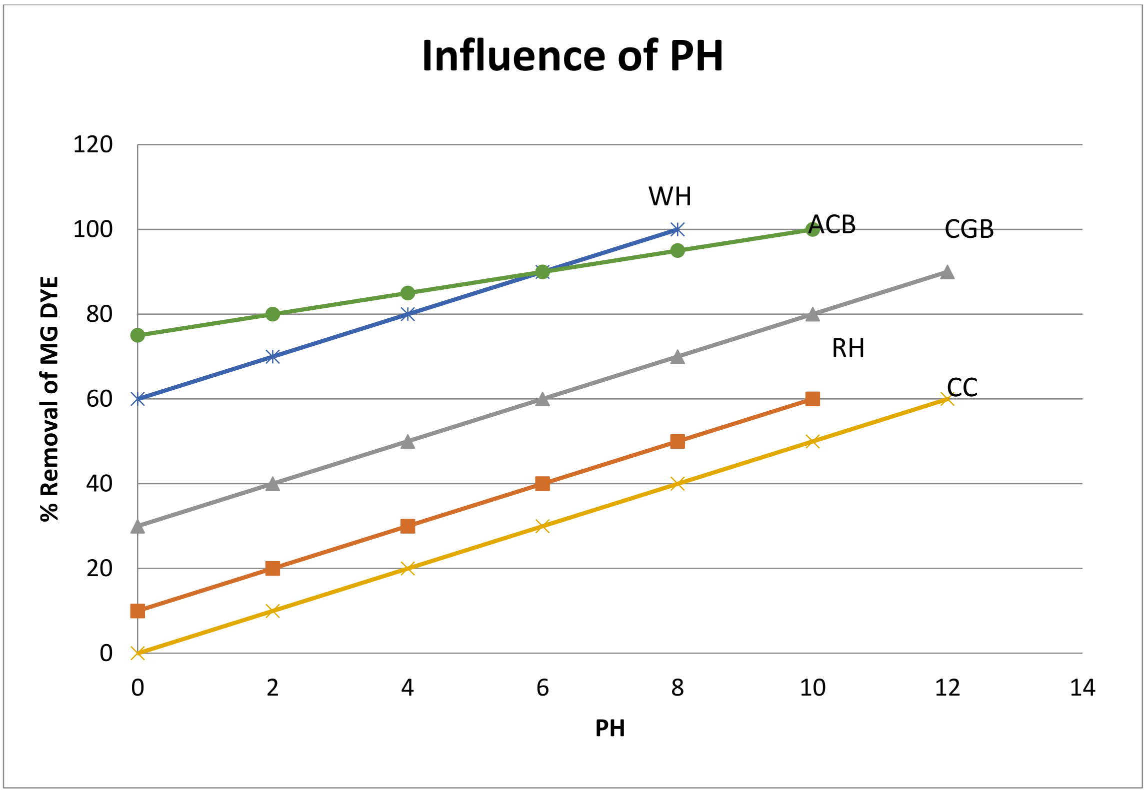

Fig (3) Influence of PH

CONCLUSIONS:

This work has proved that different adsorbents can be employed as effective bio sorbent for removal of malachite green. The maximum percentage of colour removal malachite green dye from different adsorbents were 94.91,90,82,83,85.45,99.33,98.5,94.74 respectively. Optimized parameters like temperature, pH, dosage and initial dye concentration using response surface methodology were found to be satisfactory. Adsorption equilibrium is consistent with Freundlich model and the adsorption kinetics fits the pseudo second order equation, indicating that the adsorption is interaction rather than diffusion controlled. Thermodynamic analysis of the adsorption suggests that the process is exothermic and spontaneous as well as predominant in chemisorption.

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