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Equilibrium Studies of Malachite Green from Aqueous Solution Using Corn Cob as Adsorbent

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Abstract:-The objective of this work is the study of adsorption of dye solution which is a dye malachite green using corn cob. Removal of this dye from aqueous solution using corn cob has been investigated. Liquid phase adsorption experiments were conducted. Batch adsorption studies are Carried out by observing the effect of experimental parameters, namely, pH, and amount of adsorbents, contact time and initial concentration. Optimum conditions for dye removal are studied like pH value, contact time required, amount of adsorbent, initial concentration, etc. The results generated by this work can be used for determination of optimum conditions for adsorption of dye in aqueous solutions. Dye is present in mixture form in various Industrial effluents like Textile Industries, Sewage water, Water treatment plants. This work can have use in Design of adsorption columns for dyes removal. The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Adsorption increases with increase in pH. The adsorption of cationic dye is mainly influenced by the amount of negative charges in the solution which is actually influenced by the solution pH. At pH=2 there is net positive charge in the solution so adsorption is less whereas at pH=12there is increase in negative charges increasing adsorption of malachite green. Maximum adsorption was found to take place at pH=12. Adsorption tends to increase with contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Adsorption decreases at later stages till saturation is reached due to saturation of active sites. The optimum contact time for equilibrium was found to be 100 min.

Keywords:-corn cob, adsorption, malachite green, dye, adsorbent.

I. INTRODUCTION

A dye is generally a substance that bears an affinity to the substrate to which it is being applied. It is often applied in aqueous solution. It requires a mordant to improve its binding with the fabrics. It appears to be colored because they absorb some wavelengths of light in particular than other. Various industries discharge wastewaters like chemical, refineries, textile, plastic and food processing plants .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 environment. These colored 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. The main source of discharge of dyes is textile industries where they are used to color 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 dyes, acid dyes, direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulphur dyes .Most of the dyes are toxic and have carcinogenic properties so they make water bodies inhibitory to aquatic systems. They don't fade by water or sunlight and owing to their complexity in structures; they can't be adequately treated in conventional treatment plants for waste waters. There are innumerous harmful effects of dyes on ecosystem such as: (1) 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. (2) 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. (3) They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes. (4) They have complex molecular structures which makes them difficult to treat with common municipal treatment operations. (5) Consume dissolved oxygen and affect aquatic ecosystem. (5) 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. Many of these processes are not so popular due to their economic disadvantages and inefficiency. Coagulations and chemical and electrochemical oxidations have low feasibility on large scale plants. Adsorption is preferred over these processes and is widely used due to low cost and high performance. Common adsorbents are activated carbon,

alumina silica and metal hydroxides. Economic advantages, performance efficiencies and environment are the main concerns when selecting an adsorbent, thus researchers generally goes for using low-cost adsorbents like char from agricultural wastes and others.

II. MATERIALS AND METHODS

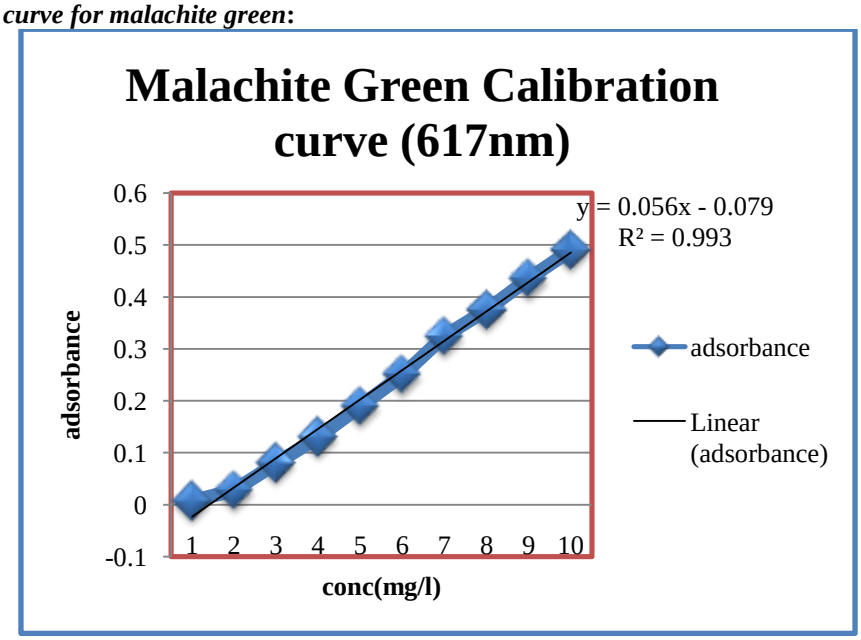
1.1. *Preparation of adsorbent*

Corn cob collected from local agricultural field and dried. Then the corn is grinded using grinder. Then the grinded powder is sieved at a size of 150 µm. Then it is washed with distilled water. Then it is dried using hot air oven at 100c for 5hrs. Now the corn cob absorbent is stored in vacuum desiccators.

1.2. *Preparation of dye solution*

Stock solution of malachite green was prepared by dissolved 500mg of dye in 1Lt of distilled water to give concentration of 500mg/L. The pH of dye
Solution were adjusted with o.1 normal NaOH or H2So4 using a pH meter.

2.*3Calibration curve for malachite green*:



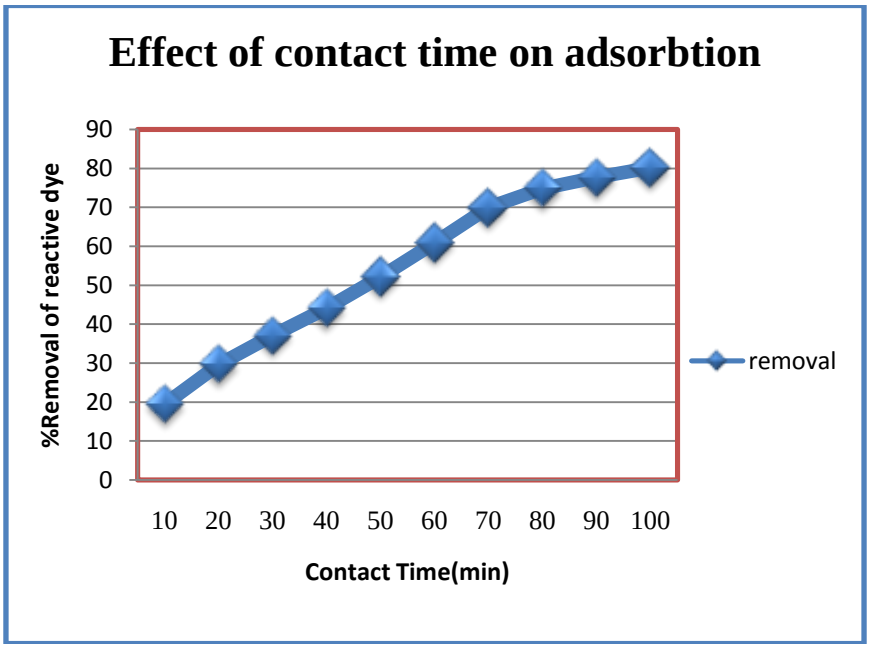
2.4. Batch adsorption experiment

Batch mode experiment were carried out in orbital shaker at a constant speed of 120rpm at 30c using 250ml conical flask containing 50mg of adsorbent with 10ml of dye solution after predetermined time intervals sample were withdrawn from the flask. The adsorbent were separated from the solution by centrifuge (REMI make) at 6000rpm for 5 min.The dye concentration was determined spectrophotometric ally using Ellico make UV visible spectrophotometer at λ_{max} =617nm.

III. RESULT AND DISCUSSION

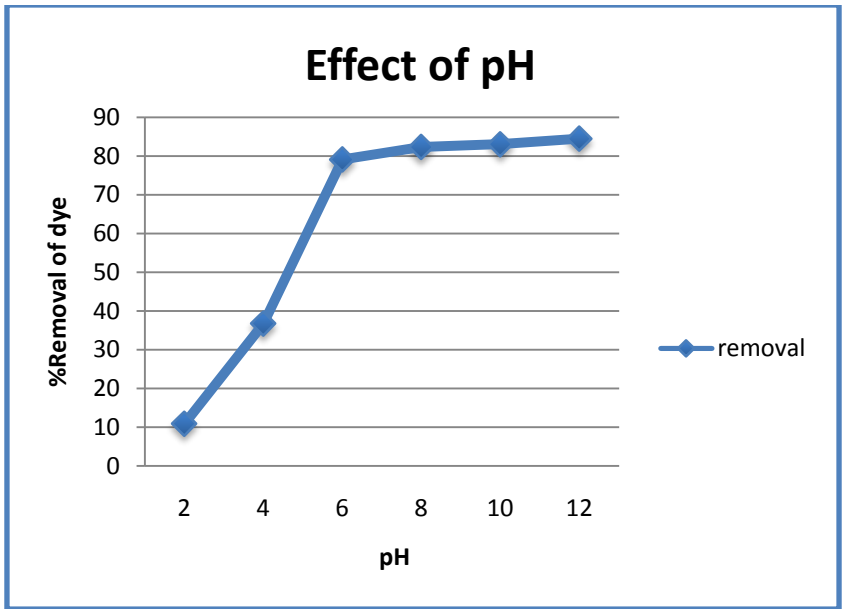
3.1. Effect of contact time

The study of effect of contact time on adsorption uptake, dye solution with initial concentration 10mg/L was agitated with 50mg of adsorbent. In this case the solution pH was kept natural without any pH adjustments. The experimental results of adsorption of dye onto adsorbent at constant initial concentration or showed in fig.1. As shown in fig.1, the contact time needed for dye solution to reach equilibrium was 100min. The results indicated that there was no change in adsorption capacity after 100min.



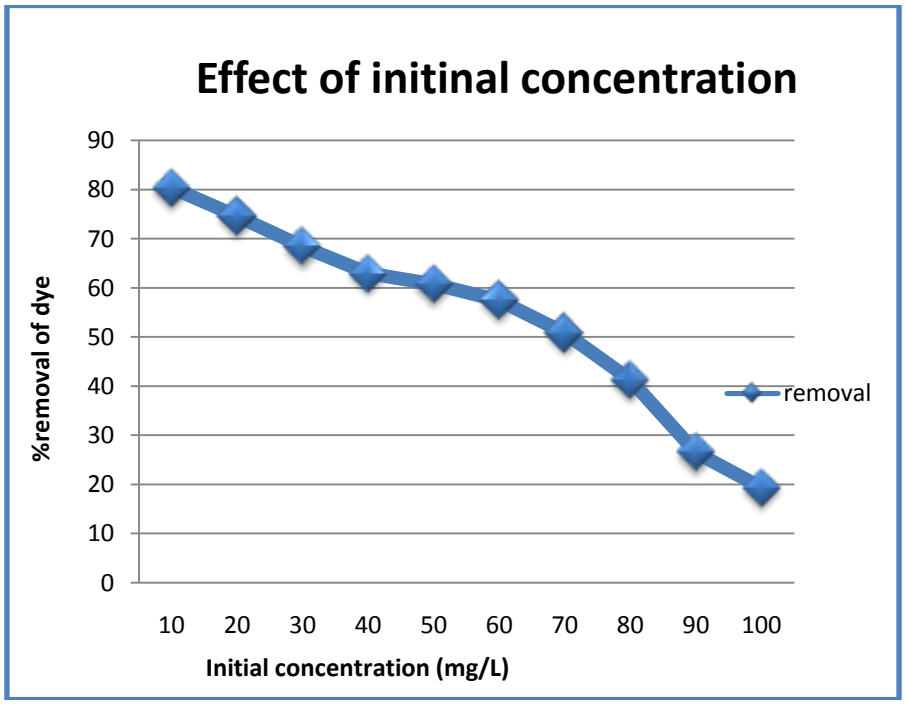
3.2. Effect of pH

The effect of pH was investigated by employing initial concentration of dye 10mg/L. The initial pH values were adjusted with 0.1N H2So4 and 0.1N NaOH to form a series of pH from 2 to 12. The result shows that there was no significant change in the present removal of dye over the entire pH range. This indicates that either H+ or OH- ions could not influence the dye adsorption onto adsorbent.



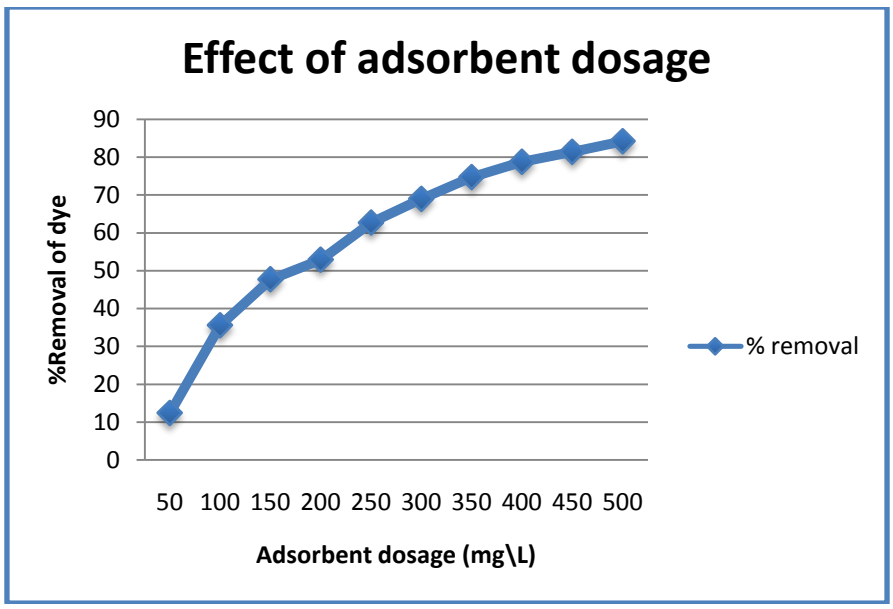
3.3. Effect of initial concentration

The adsorption experiment was carried out. The initial concentration of dye increased from 10mg/L to 100mg/L it is because of the fact that at lower concentration the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However at higher concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentrations.



3.4. Effect of adsorbent dosage

The effect of adsorbent dosage on removal of dye at constant concentration 10mg/L were investigated by agitating with different adsorbent dosage over the range 50 to 500mg. The study reveals that percentage of adsorption increases with increasing the adsorbent dosage. This attributes the increased corn cob powder surface area and availability of more adsorption sites.



3.5 Adsorption studies

The prologue investigations were carried out in batches at different conditions of pH, concentration, and time, amount of adsorbent and to check the tendency of adsorption process. In each experiment 250 mL measuring flasks containing 100 mL of dye solution of known concentration was mixed with known amount of adsorbent and mixture was sporadically shaken (100 rpm) and then kept for different time intervals (min) for saturation. The supernatant was harvested by centrifugation at 10000g for 20 min and amount of dye adsorbed was determined spectrophotometric ally at the λ_{max} 617 nm.

3.5.1 Equilibrium isotherms

3.5.2 Langmuir isotherm

The linear form of Langmuir isotherm assumes monolayer adsorption onto a surface Containing a finite number of adsorption sites of uniform strategies of adsorption Without interaction between adsorbed molecules commonly expressed as (Uma et al., 2013; Hameed, 2009).

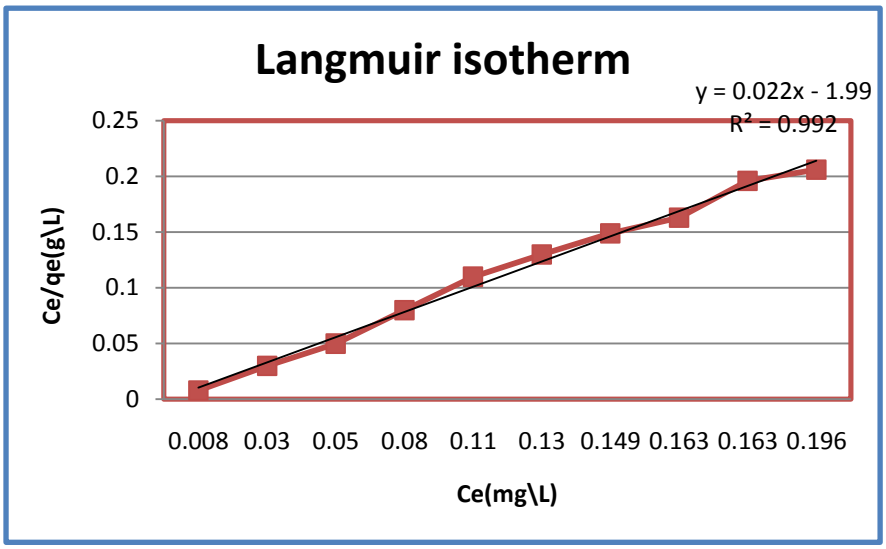
$$Ce/qe=1/bQo+Ce/Qo$$

Where,

Qo is a constant related to adsorption capacity (mg/g) b is Langmuir constant related to energy of adsorption (mg/L) Ce is equilibrium constant of dye (mg/L)Qe is amount of dye adsorbed at equilibrium (mg/g)

The linear plot of Ce/qe versus Ce .the constant Qo and b can be calculated from slop and intercept of the plot. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption and is expressed as $R_L=1/ (1+bC0)$. R_L value indicates the nature of adsorption process as given below.

RL value	Adsorption
$R_L>1$	Unfavorable
$R_L=1$	Linear
$0<R_L<1$	Favorable
$R_L=0$	Irreversible



b =22.93, C=1.99

RL =1/1+b*C0

RL =0.0214

In the present investigation the RL value less than one which shows the adsorption process was favorable.

3.5.3 Freundlich isotherm

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces result of the assumption that the adsorption occurs and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place (Freundlich, 1885). The linear form of the isotherm can be represented as: The Freundlich isotherm is based on multilayer adsorption on heterogeneous surface. Linear from of Freundlich equation islog qe=logkf+1/n log Ce

Where,

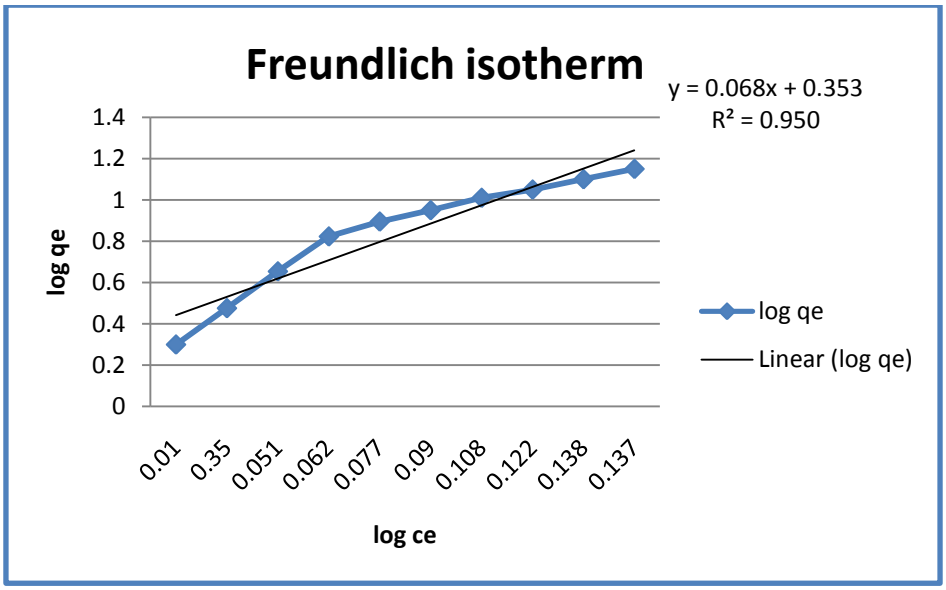
qe is dye concentration is solid at equilibrium (mg/g)

Ce is dye concentration in solution at equilibrium (mg/L)

Kf is measure of adsorption capacity (mg/g)

n is adsorption intensity

The values of 1/n and kf can be calculated from the slop and intercept respectively and the result are given below .When 1/n is>1.0, the change in adsorbed dye concentration is greater than the change in the concentration in solution.



Slope=1/n=0.353
Intercept=logkf =0.068

MODELS	ISOTHERM CINSTANTS		
Langmuir isotherm	Q_m(mg/g)	b	R^2
	45.45	22.93	0.992
Freundlishisotherm	K_f(mg/g)	n	R^2
	0.068	0.353	0.950

IV. CONCLUSIONS

Removal of malachite green from aqueous solutions by adsorption with Corn Cob has been experimentally determined and the following observations are made. The percentage of colour removed increase with increasing adsorbent dosage, increase. With increasing contact time and varied with dye solution pH.The adsorption rates increases with increasing initial concentration. Optimum contact time for equilibrium to be achieved is found to be 100 min. It is basically due to saturation of the active site which does not allow further adsorption to take place. For malachite green maximum adsorption found to be at pH = 12.The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. The Langmuir equation assumes that there is no interaction between the adsorbate molecules and that the sorption is localized in a monolayer. It is then assumes that once a dye molecule occupies a site, no further adsorption can take place at that site. The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Adsorption increases with increase in pH. The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Adsorption increases with increase in pH. The adsorption of cationic dye is mainly influenced by the amount of negative charges in the solution which is actually influenced by the solution pH. At pH=2 there is net positive charge in the solution so adsorption is less whereas at pH=12there is increase in negative charges increasing adsorption of malachite green. Maximum adsorption was found to take place at pH=12. Adsorption tends to increase with contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Adsorption decreases at later stages till saturation is reached due to saturation of active sites. The optimum contact time for equilibrium was found to be 100 min.

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