# CHAPTER 1
# INTRODUCTION

# 1. Introduction

Dyes are usually soluble substances used to impart colour to textile fabrics, paper and leather, ceramic, plastic, cosmetics, food etc. and also they are used to prepare ink, paints and varnishes[1]. These compounds consist of chromophore and auxochrome groups attached to one or more benzene rings. Their characteristic colour is due to the chromophore group and dyeing affinities due to the auxochrome group. The chromophore groups may be azo, quinonoid, nitroso, nitro, carbonyl, vinyl, sulphonate and carboxyl group etc. General auxochrome groups include either electron donating groups such as amino, methyl amino, dimethyl amino, hydroxy, alkoxyl group etc., or electron accepting group such as nitro[2,4].

The dyes can be broadly classified into cationic dyes, anionic dyes and nonionic dyes. Cationic dyes are those, which dissociate in aqueous solution to give positively charged ions. All the basic dyes and some of the direct, azo and disperse dyes are cationic dyes. Anionic dyes are those, which dissociate in aqueous solution to give negatively charged ions. Some examples are the direct, acid and reactive dyes. Nonionic dyes are those, which do not ionize in aqueous solutions. All the disperse dyes are nonionic dyes.[13]

Dyes are the major constituents of the wastewater produced from many industries related to textile, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery etc., and also to the industries, which produces dyes. The presence of dyes in effluents even in very low concentration is highly visible and hence causes aesthetic pollution. The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water and thus causing reduction in photosynthesis and DO level in river. This may affect the aquatic life. Many of the dyes are carcinogenic, mutagenic and detrimental to the environment and aquatic life.[2]

Various treatment methods that industries used to adopt for removal of dye from the wastewater are coagulation (using alum. Lime, ferric chloride, ferric sulfate etc.), floatation, chemical oxidation (using chlorine and ozone), photo-oxidation (using UV light), membrane separation, biological treatment and adsorption.

Among the above mentioned treatment methodologies some are less efficient and some are too expensive. However, in a developing country like ours, the methods, which are less expensive and efficient, are very useful is obviously in our present consideration. In this context, biological treatment and adsorption are reckoned to be the two most economical as well as effective options for us[1]. Biological treatment is disadvantageous as it requires large land area and is constrained by sensitivity towards diurnal variation as well as toxicity of some chemicals and this method of treatment has less flexibility in design and operation. However, the second method i.e., adsorption has some advantages[1,6,7], viz

• Less land area (half to quarter of what is required in biological system)

• Lower sensitivity to diurnal variation

• Not being effected by toxic chemical(s).

• Greater flexibility in the design and operation

• Superior removal of organic contaminants.

Adsorption onto costly adsorbent e.g. onto commercially activated carbon has emerged as one of the most efficient and highly accepted method in eliminating dyes and other hazardous pollutants from water[14]. However, in a developing country like ours it is not commercially viable so the current emphasis is on exploring the possibilities of use of suitable low cost and locally available alternative adsorbents, which are efficient and cost effective and have the entire characteristic mentioned earlier[11]. In this regard industrial solid waste such as power plant fly ash, saw dust, agricultural waste (like rice husk ash, saw dust, sugarcane bagasse pith, activated carbon prepared from rubber wood, silk and cotton hull, used tea leaves, bamboo dust, coconut shell, and straw etc.), coconut coir pith, orange peel etc. Other carbonaceous adsorbents prepared from clay minerals, solid, algae, wood etc. has proven their efficiency as good low cost adsorbent[6,7].

Absorbability of a compound increases with increasing molecular weight, a higher number of functional groups, such as double bonds or halogen compounds, increasing Polaris ability of the molecule, and is related to electron clouds of the molecules etc[4].

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## 1.1 Objective of the Present Work

The present investigation has been carried out with the objective to explore the possible use of the sodium carbonate treated rice husk ash (NCRH) as an alternative low-cost adsorbents for removal of colour contributed by commonly applied industrial dye viz. Malachite green (MG)  from the aqueous solution i.e. simulated or synthetic wastewater

## 1.2 Scopes of the present work

The scopes of the present work considered for achieving the stated objective are given below:

1. The investigation has been made through fixed bed column study to explore the possibility of utilizing NCRH  for the adsorptive removal of MG from the wastewater.
2. The effect of such factors such as the initial pH value, flow rate, influent concentration and bed depth on MG  adsorption by husk bed column was investigated.

In practice the adsorption process can be either a batch process or continuous flow system. The continuous flow system in itself can be either fixed bed system or a moving bed one. Due to paucity of time and other constraints, the present study was limited to fixed bed column in a continuous flow system.

# CHAPTER 2
# LITERATURE REVIEW

## 2. LITERATURE REVIEW

This chapter deals with properties of malachite green, prevalent method of dye removal, feasibility of adsorption as method of dye removal, use of rice husk as low cost adsorbent and previous studies carried out on malachite green.
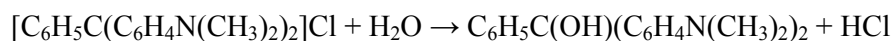
## 2.1 Malachite Green Dye

Malachite green is classified in the dyestuff industry as a triarylmethane dye. Formally, Malachite green refers to the chloride salt $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$, although the term Malachite green is used loosely and often just refers to the colored cation. The oxalatesalt is also marketed. The chloride and oxalate anions have no effect on the color. The intense green color of the cation results from a strong absorption band at 580 nm (extinction coefficient of $10^5\ M^{-1}cm^{-1}$). Malachite green is prepared by the condensation of benzaldehydeand dimethylaniline to give leuco malachite green (LMG):

$$C_6H_5CHO + 2\ C_6H_5N(CH_3)_2 \rightarrow C_6H_5CH(C_6H_4N(CH_3)_2)_2 + H_2O$$
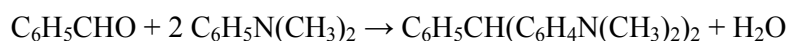
Second, this color lessl euco compound, a relative of triphenylmethane, is oxidized to the cation that is MG:

$$C_6H_5CH(C_6H_4N(CH_3)_2)_2 + HCl + 1/2\ O_2 \rightarrow [C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl + H_2O$$
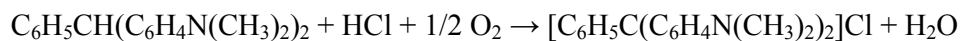
Hydrolysis of MG gives the carbinol form:[1,]

$$[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl + H_2O \rightarrow C_6H_5C(OH)(C_6H_4N(CH_3)_2)_2 + HCl$$

This alcohol is important because it, not MG, traverses cell membranes. Once inside the cell, it is metabolized into LMG. Only the cation MG is deeply colored, whereas the LMG and carbinol derivatives are not. This difference arises because only the cationic form has extended pi-delocalization, which allows the molecule to absorb visible light[15,17].

**Table 2.1:**Properties of malachite green[3]

| | |
|---|---|
| Synonyms | Anilene green<br>Basic green<br>Victoria green<br>Diamond green |
| Chemical name | 4-{[4-(dimethylamino)phenyl](phenyl)methylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride |
| Molecular formula | $C_{23}H_{25}ClN_2$ (chloride) |
| Molecular weight | 364.911g/mol |
| Appearance | Dark green |
| Water solubility | 10.8 g/l at $20^o$ C |
| Alcohol solubility | 138.7 g/l at $20^oC$ |
| Toxicology | Severe eye irritant<br>Harmful by inhalation<br>Ingestion and through skin contact |
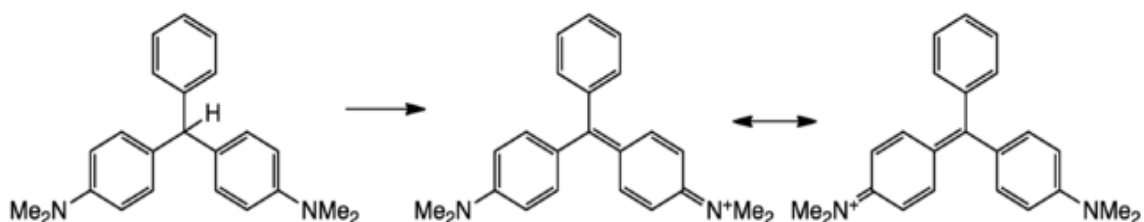


**Fig. 2.1 :Structure of malachite green(source: google)**

## 2.2 Methods of dye removal

Some of the methods which are prevalent in dye removal are as follows :

## 2.2.1 Coagulation-flocculation

Coagulation-flocculation is often applied in the treatment of textile-processing wastewater to partly remove chemical oxygen demand (COD) and colour from the raw wastewater before further treatment. The principle of the process is the addition of a coagulant followed by a generally rapid chemical association between the coagulant and the pollutants. The formed flocs are generally removed by sedimentation. Various inorganic coagulants are used, mostly lime, magnesium, iron and aluminium salts. Coagulation-flocculation with inorganic chemicals generates considerable volumes of useless or even toxic sludge that must be incinerated or handled otherwise. This presents a serious drawback of the process. Recently different organic polymers are being used for the removal of dye from wastewater. Most of the polymers used for colour removal are, however, cationic and may be toxic to aquatic life even at very low concentrations (less than 1 mg/l). Some cationic polymers have been found to inhibit the nitrification process.

## 2.2.2 Oxidation

Dye can be removed from wastewater by oxidation using different oxidizing agents like ozone, hydrogen peroxide etc. Using catalysts like $Fe^{2+}$, UV radiation, $TiO_2$ etc., the efficiency of oxidation can be increased. These processes are called advanced oxidation processes (AOPs). AOPs are based on the generation of highly reactive radical species (especially the hydroxyl radical, HO) that can react with a wide range of compounds, also with compounds that are difficult to degrade, e.g. dye molecules. The dyes can also be removed by electrochemical oxidation methods using Ti/Pt as anode and stainless steel as cathode. In this process strong oxidants like hydroxyl radical, ozone etc. are produced. The oxidation processes are very costly and hence not feasible in developing countries.

## 2.2.3 Photocatalytic Degradation

Photocatalytic degradation is like oxidation process. The degradation of dye bearing wastewater is possible by irradiation under highly intense light source. If

simple solar radiation is used, lot of time is required for the degradation which is not favourable. UV radiations with different semi-condactors like $TiO_2$ as catalysts are used. In this process, semi-conductors first absorb radiation energy and then dissociate water molecules to hydroxyl ions. These hydroxyl ions are responsible for the degradation of dyes. The presence of high dissolved oxygen increases the degradation efficiency. Application of this method in the field is very difficult and expensive also.

### 2.2.4 Membrane Process

Membrane process can be applied as main or post treatment processes for separation of salts and larger molecules including dyes from dye bath effluents and bulk textile-processing wastewaters. Membrane filtration is a quick method with low spatial requirement. Another advantage is that the permeate, as well as some of the other concentrated compounds, including non-reactive dyes, can be reused. The disadvantages of membrane techniques are flux decline and membrane fouling, necessitating frequent cleaning and regular replacement of the modules. Another important drawback is that the generated concentrate must be processed further. The capital costs of membrane filtration are therefore generally high.

### 2.2.5 Biological treatment

Biological treatment is the best way of treating any waste. Biological dye removal techniques are based on microbial biotransformation of dyes. As dyes are designed to be stable and long-lasting colorants, they are usually not easily biodegraded. Many researches have demonstrated partial or complete biodegradation of dyes by pure and mixed cultures of bacteria, fungi and algae. This process cannot work at higher dye concentration and in presence of toxic substances. Maintaining operation conditions for biological process is also very difficult.

### 2.2.6 Adsorption

Adsorption is widely used for the removal of dyes from the wastewater due its low cost and simplicity in operation. Activated carbon is highly efficient adsorbent for removal of organics from water environment. But from regeneration point of view it is not suitable. Various other (mostly low-cost) adsorbents have therefore been investigated as an alternative to activated carbon. These adsorbents include non-

modified cellulose (plant) biomass, maize stalks, wheat straw, linseed straw, rice husks, wood chips, sawdust, banana pith, bagasse pith, peat, sand, silica, natural clay, bentonite clay, diatomite clay, montmorillonite clay, wood charcoal, bone charcoal, perlite, fly ash etc. Most of the low cost adsorbents are suitable for low dye concentration. It has been found in the column study for these adsorbents, that the breakthrough comes earlier and the adsorbents are not used upto their maximum efficiency. Their regeneration is not effective and they show uncertainty in their performance. Thus there is need for the development of good adsorbents for wastewater treatment.

## 2.3 Adsorption as a method of waste water treatment

Adsorption is an effective, economical and efficient method for the removal of metal ions from wastewaters. The most commonly used solid sorbent is activated carbon but it is expensive and requires chelating agents (for metal containing effluents) to enhance its performance, which results in increases of its cost. Because of high cost of activated carbon, there is a need to explore less expensive cleanup methodology for the eradication of metal ions from aqueous systems[1,4].

Research in the recent years has indicated that some natural biomaterials including agricultural products and by-products can accumulate high concentration of heavy metals. Adsorbent generated from these biomass are cost effective and efficient[13]. Low-cost agricultural products and by-products have been reported to be effective in removing heavy metals. Adsorption process of heavy metals present in aqueous solution by low-cost adsorbents from plant wastes can be carried out with or without chemical modifications. In general, chemically modified plant wastes exhibit higher adsorption capacities than unmodified forms.[7]

In our continued study on the use of low-cost material for the removal of organic and organic pollutants from water and wastewater we investigated rice husk as a sorbent for the removal of crystal violet dye. Some simple and low-cost chemical modifications resulted in increasing the sorption capacity of raw rice husk. The highly efficient low cost and the rapid uptake of Cd(II) by NCRH indicated that it could be an excellent alternative for the removal of heavy metal by sorption process.

Rice husk consists of cellulose (32.24%), hemicelluloses (21.34%), lignin (21.44%) and mineral ash (15.05%) as well as high percentage of silica in its mineral ash, which is approximately 96.34%.[3] Rice husk is insoluble in water, has good chemical stability, has high mechanical strength and possesses a granular structure, making it a good adsorbent material for treating heavy metals from wastewater [6].Rice husk, an abundant agricultural product, is capable of removing heavy metals and can be considered as an efficient and low-cost adsorbent for heavy metals.In recent years, attention has been taken on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants. The present study has been undertaken to report the Crystal Violet adsorption in the fixed bedcolumn process.

## 2.4 Rice Husk

Study carried out using rice husk as a low cost adsorbent due to following reasons :

### 2.4.1 Rice husk as a potentially low-cost biosorbent dye removal

Various techniques have been employed for the removal of dyes from wastewaters. Conventional physical and chemical methods are either costly, e.g., activated carbon, or produce concentrated sludge, e.g., Fenton's reagent, or may not capable of treating large volumes of effluent without the risk of clogging, e.g., membrane filtration..The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Many carbonaceous materials such as bark, coal, lignite, coconut shells, wood, dead biomass, seaweed, pecan shell and peat are used in the production of commercial activated carbons[1]. However, the review presented here concerns the use office husk for the removal of heavy metals and of water-soluble dyes present in wastewater. Rice husk, an agricultural waste, contains about 20% silica, and has been reported as a good sorbent of many metals and basic dyes. These rice husks, as the commodity waste, can be made into activated carbons which are used as adsorbents in water purification or the treatment of industrial wastewater. It would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons. The removal of heavy metals by agricultural waste or by-products has been extensively reviewed by Bailey et al.. However, they only reported little information on rice husk being a low cost sorbent. Sorption depends heavily on individual experimental conditions such as pH, metal

concentration, temperature, contact time, competing ions and particle size. It is advised that the reported sorption capacities should be taken as an example of values that can be achieved under a specific set of conditions and not as maximum sorption capacities. The authors strongly recommend that the reader should refer to the original articles for information on experimental conditions. The report will also review those effects on the adsorption using rice husk and mechanisms. It also covers the methodology on modification of rice husk in order to enhance sorption capacities for metal ion and dyes.

## 2.4.2 Properties of Rice Husk

From the statistical data of the Food and Agriculture Organisation, 1995, there is an estimated annual rice production of 500 million tonnes in developing countries; approximately 100 million tonnes of rice husk is available annually for utilization in these countries alone. However, the amount of rice husks.

**Table 2.2**: Typical composition office husk[3]

| Composition | Percent |
|---|---|
| Cellulose | 32.24 |
| Hemicellulose | 21.34 |
| Lignin | 21.44 |
| Extractives | 1.82 |
| Water | 8.11 |
| Mineral ash | 15.05 |

**Table 2.3:** Chemical composition in mineral ash[3]:

| Composition | Percent |
|---|---|
| $SiO_2$ | 91.34 |
| $K_2O$ | 2.31 |
| $MgO$ | 0.45 |
| $Fe_2O_3$ | 0.20 |
| $Al_2O_3$ | 0.41 |
| $CaO$ | 0.41 |

**Table 2.4:** Reported physicochemical characteristics of rice husk[3]

| Characteristic | Values |
|---|---|
| Bulk density (g/ml) | 0.73 |
| Solid density (g/ml) | 1.5 |
| Moisture content (%) | 6.62 |
| Ash content (%) | 45.97 |
| Particle size (mesh) | 200-16 |
| Surface area (m2/g) | 272.5 |
| Surface acidity (meq/gm) | 0.1 |
| Surface basicity (meq/gm) | 0.45 |

## 2.5 Studies on MG as an Adsorbate

The ability of five low cost adsorbents – rice husk, cotton, bark, hair and coal – to adsorb two basic dyes, namely, Safranine and malachite green, has been studied by **G. Mckay et al. (1998)**. Equilibrium isotherms have been determined and analyzed using the Langmuir equations. A limited number of fixed bed column studies have been performed and the bed depth service time for each dye adsorbent system has been determined. The study has shown that bark, rice husk cotton waste have a high adsorption capacity for Safranine and malachite green dyes. equilibrium studies showed that bark had monolayer equilibrium adsorption capacities, based on a Langmuir analysis for Safranine and malachite green respectively. A series of fixed bed column studies were carried out and bark has a service of over 100 hr shows 50% breakthrough for both dyes.

A comparative study was carried out by **Nagarethinam Kannan et al. (2001)** In this study, The kinetics and mechanism of malachite green adsorption on commercial activated carbon (CAC) and indigenously prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw, have been investigated. The effects of various experimental parameters have been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry. The extent of dye removal increased with decrease in the initial concentration of the dye and particle size of the adsorbent and also increased with

increase in contact time, amount of adsorbent used and the initial pH of the solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and first order kinetic equations. The kinetics of adsorption were found to be first order with regard to intra-particle diffusion rate. The adsorption capacities of indigenous activated carbons have been compared with that of the commercial activated carbon. The results indicate that such carbons could be employed as low cost alternatives to commercial activated carbon in wastewater treatment for the removal of colour and dyes.

Basic dye removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste was investigated the potential use of Indian Rosewood (Dalbergia sissoo) sawdust, pretreated with formaldehyde and sulphuric acid, for the removal of methylene blue dye from simulated wastewater by **V.K. Garg et al. (2003).** Dyes are usually present in trace quantities in the treated effluents of many industries. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal alternative to other expensive treatment methods.. The effects of different system variables, viz., adsorbent dosage, initial dye concentration, pH and contact time were studied. The results showed that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of methylene blue. Optimum pH value for dye adsorption was determined as 7.0 for both the adsorbents. Maximum dye was sequestered within 30 min after the beginning for every experiment. The adsorption of malachite green followed a first order rate equation and fit the Lagergren equation well. Similar experiments were carried out with commercially available activated carbon to compare the results. Sulphuric acid treated sawdust or 10 formaldehyde treated sawdust of Indian Rosewood can be attractive options for dye removal from dilute industrial effluents.

The dye, malachite green, was adsorbed on an adsorbent prepared from mature leaves of the Neem tree (Azadirachta indica). A batch adsorption study was carried out by **Krishna G. Bhattacharyya et al. (2004)** with variable adsorbate concentration, adsorbent amount, pH, and temperature. Ninety three percent of the dye could be removed by 2 g of the Neem leaf powder from 1 L of an aqueous solution containing 25 mg of the dye at 300 K. A possible mechanism of adsorption was suggested on the basis of concurrently operating surface adsorption and pore

diffusion. The experimental data yielded excellent fits with Langmuir and Freundlich isotherm equations. The results indicated that the dye, malachite green, strongly interacts with a biomass-based adsorbent, the Neem leaf powder. In this paper the Kinetics and thermodynamics of malachite green adsorption on Neem (Azadirachta indica) leaf powder was represented.

Equilibrium data, isotherm parameters and process design for partial and complete isotherm of malachite green onto activated carbon was investigated by **K. Vasanth Kumar et al. (2005)**. Equilibrium data for the adsorption of malachite green onto activated carbon was reported. The equilibrium data were splitted to different data sets to have an idea on the partial and complete isotherm. The equilibrium data were analyzed using Freundlich, Langmuir and Redlich–Peterson isotherm. The influence of partial isotherm and complete isotherm on the equilibrium parameters in isotherm expression were estimated. Equilibrium data covering the complete isotherm is the bestway to obtain the parameters in isotherm 11 expressions. Present investigation showed that for successful batch sorber design, equilibrium data with partial isotherm is not sufficient, instead equilibrium data that covers complete isotherm is required.

The removal of malachite green (MG) dye from aqueous solution present as a pollutant material in textile waste water was studied at 298 K in terms of its adsorption behaviour. Local sand sample was used as an adsorbent in this work by **Saeed B (2006)**. The textural properties of the sand including surface area, mean pore radius and total pore volume were examined from the low-temperature adsorption of nitrogen at 77 K. The conditions for maximum adsorption of the dye on sand were optimized. It was seen that under optimized conditions, up to 92% dye could be removed from solution onto the sand surface. The adsorption data were fitted to Freundlich and Dubinine-Raduushkevich equations for the calculation of various adsorption parameters. The Freundlich constants n and A were determined as 0.9682 and 0.639 mol/g, respectively. The sorption energy calculated by the Dubinine-Raduushkevich equation was found to be 1.22 kJ/mol. The adsorption behaviour of the dye was also investigated in terms of added cat ions and anions. It was found that the dye adsorption decreased considerably in the presence of thiosulphate, potassium, nickel and zinc ions. Redlich–Peterson isotherm is a special case of Langmuir when the constant 'g' equals unity.

Adsorption of basic dye (malachite green) onto activated carbon prepared from rattan sawdust was studied by **B.H. Hameed et al. (2006).** Activated carbon prepared from non wood forest product waste (rattan sawdust) has been utilized as the adsorbent for the removal of malachite green dye from an aqueous solution. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the Langmuir model with maximum monolayer adsorption capacity of 294.14 mg/g. The dimensionless factor, RL revealed the favourable nature of the isotherm of the dye activated carbon system. The rates of adsorption were found to conform to the pseudo second- order 12 kinetics with good correlation. The kinetic parameters of this best-fit model were calculated and the results are discussed.

Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw was studied by **Renmin Gong et al. (2006)**. In this article, rice straw was chemically modified by means of phosphorylation, and then the phosphoric acid modified rice straw was further loaded with sodium ion in order to yield potentially biodegradable cationic sorbent. The feasibility of the modified product as cationic dye sorbent for removing basic dyes from aqueous solution was investigated. Two basic dyes, basic blue 9 (BB9) and 13 basic red 5 (BR5), were used as sorbates. The effects of various experimental parameters (e.g. initial pH, sorbent dosage, dye concentration, ion strength, contact time) were examined and optimal experimental conditions were decided. The BB9 and BR5 removal ratios came up to the maximum value beyond pH 4. The 1.5 g/l or more sorbent could almost completely remove BB9 and BR5 from 250 mg/l of dye solution. The ratios of BB9 and BR5 sorbed were kept above 96% over a range from 50 to 350 mg/l of dye concentration when 2.0 g/l of sorbent was used. Increase in ion strength of solution induced decline of BB9 and BR5 sorption. The isothermal data fitted the Langmuir model. The sorption processes followed the pseudo-first-order rate kinetics. The results in this research confirmed that the phosphoric acid modified rice straw was an excellent basic dye sorbent.

Adsorption of malachite green from aqueous solution by rice husk in a fixed-bed column was studied by **Runping Han et al. (2006)**. In this study, the ability of rice husk to adsorb malachite green (MG) from aqueous solution was investigated in a fixed-bed column. The effects of important parameters, such as the value of initial pH, existed salt, the flow rate, the influent concentration of MG and bed depth, were

studied. The Thomas model was applied to adsorption of MG at different flow rate, influent concentration and bed depth to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design using non-linear regression. The bed-depth/service time analysis (BDST) model was also applied at different bed depth to predict the breakthrough curves. The two models were found suitable for describing the adsorption process of the dynamic behavior of the rice husk column. All the results suggested that rice husk as adsorbent to removal MG from solution be efficient, and the rate of Adsorption process be rapid.

Adsorption of malachite green from aqueous solution by fallen phoenix tree's leaves was studied by **Runping Han et al. (2006)**. A new adsorbent, the fallen phoenix tree's leaf, has been investigated in order to remove malachite green (MG) from aqueous solutions. 14 Variables of the system, including contact time, leaf dose, solution pH, salt concentration and initial MG concentration, were adopted to study their effects on MG Adsorption. The results showed that as the dose of leaf increased, the percentage of MG sorption increased accordingly. There was no significant difference about the quantity of MG adsorbed onto leaf as the pH was within the range 4.5–10.0. The salt concentration has negative effect on MG removal. The equilibrium data were analyzed using the Langmuir and the Freundlich isotherms. The results of non-linear regressive analysis are that the Langmuir isotherm is better fit than the Freundlich isotherm at different temperature according to the values of determined coefficients. The thermodynamics parameters of MG/leaf system indicate spontaneous and endothermic process. It was concluded that an increase in temperature be advantage to adsorb MG onto leaf.

Removal of basic dye (malachite green) from wastewaters utilizing beer brewery waste was studied by **Wen-Tien Tsai at al (2007)** . In the work, the beer brewery waste has been shown to be a low-cost adsorbent for the removal of basic dye from the aqueous solution as compared to its precursor (i.e., diatomite) based on its physical and chemical characterizations including surface area, pore volume, scanning electron microscopy (SEM), and non-mineral elemental analyses. The pore properties of this waste were significantly larger than those of its raw material, reflecting that the trapped organic matrices contained in the waste probably provided additional adsorption sites and/or adsorption area. The results of preliminary adsorption kinetics showed that the diatomite waste could be directly used as a

potential adsorbent for removal of malachite green on the basis of its adsorption–Adsorption mechanisms. The adsorption parameters thus obtained from the pseudo-second-order model were in accordance with their pore properties. From the results of adsorption isotherm at 298K and the applicability examinations in treating industrial wastewater containing basic 15 dye, it was further found that the adsorption capacities of diatomite waste were superior to those of diatomite, which were also in good agreement with their corresponding physical properties. From the results mentioned above, it is feasible to utilize the food-processing waste for removing dye from the industrial dying wastewater.

Removal of malachite green from wastewater using fly ash as an adsorbent by hydrocyclone was studied by **K. Rastogi et al. (2008)**. The excessive release of color into the environment is a major concern worldwide. Adsorption process is among the most effective techniques for color removal from wastewater and fly ash has been widely used as an adsorbent. Therefore, this study was carried out to understand the adsorption behavior of malachite green from aqueous systems onto fly ash using the continuous mode. Continuous mode sorption experiments were carried out to remove malachite green from its aqueous solutions in hydrocyclone equipment. The experiments were performed at constant temperature and dimensions of hydrocyclone with variation of flows through the equipment, concentrations of malachite green solutions and fly ash concentration, respectively.

# CHAPTER 3
# MATERIAL AND METHODOLOGY

# 3. Material and Methods

This chapter deals with the equipment, material and chemical used during the work. It also explain the procedure of preparation of adsorbent and dye solution and the experimental methodology.

## 3.1 Equipments and Chemicals:

All chemicals used were of analytical grade (BDH, India). Stock solutions of 1000 mg/l were prepared malachite green, which were diluted with distilled water to prepare working solutions. A standard pH meter was used for the measurement of pH of the solution. A peristaltic pump was also used for providing constant flow of metal and desorbing solution in the fixed bed column. The malachite green concentrations in the solution were analyzed using UV spectrophotometer. CV was measured by spectrophotometric method at its maximum wavelength 580 nm at neutral pH.

**Table 3.1 :** Instruments used

| INSTRUMENT | MANUFACTURER / TYPE | FUNCTION |
|---|---|---|
| Electronic weight balance | Sartorius | To measure weight |
| Oven | Shivaki | To dry the samples / to maintain the temperature |
| pH meter | μpH System 361, M/S Systronics India Ltd., India | To measure pH |
| Spectrophotometer (UV/ Vis) | Jasco ( V 530) | Absorbance |
| Peristaltic pump | | To maintain the flow rate |
| Scanning Electron Microscope((SEM) | JEOL JSM-6480 LV | Morphology |
| Sieve | | To maintain the size of particle |

## 3.2 Preparation of adsorbent:

Fresh rice husk was obtained from a local rice mill and was passed through different sieve size. The fraction of particle between 425 and 600 micron (geometric mean size: 505 micron) was selected. The rice husk was washed thoroughly with distilled water. It was dried at 60°C. The sorbent thus obtained was designated Raw Rice Husk (RRH). Rice husk was treated with 0.1 M sodium carbonate solution at room temperature for 4h. Excess of sodium carbonate was removed with distilled water and the material was dried at 40°C. This material was designated as sodium carbonate treated rice husk (NCRH).
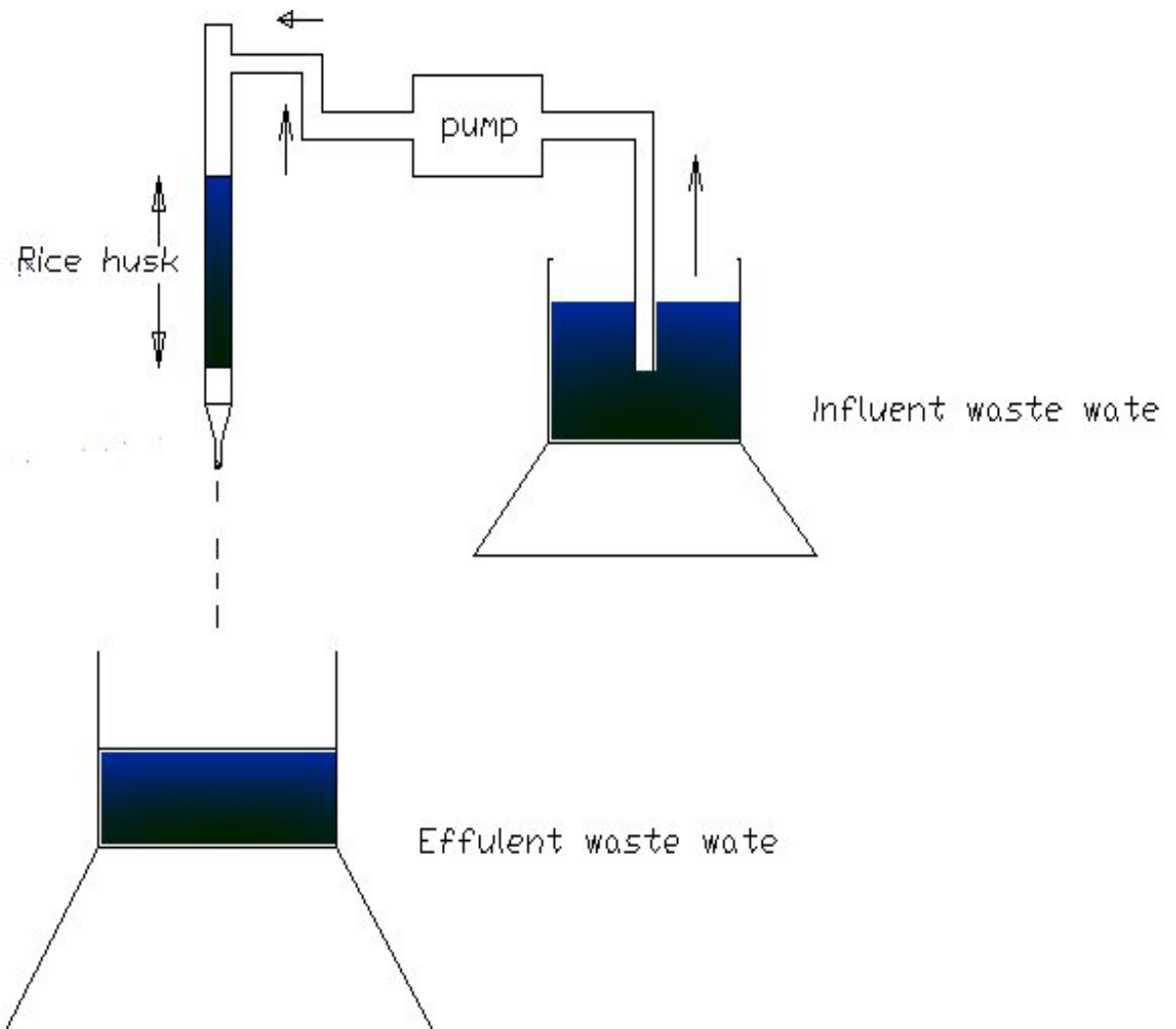


**Fig. 3.1 : Schematic diagram fixed bed column experimental set up**

**Fig.3.2 : Instrumental setup for experiment**



**Fig.3.3 : sample collection**

**Fig. 3.4 : spectrophotometer reading**

## 3.3 Procedure of the tests for MG removal:

Fixed bed column study for removal of Malachite Green from wastewater by NCRH was conducted using a column of 2.5 cm diameter and 45 cm length. The column was packed with NCRH between two supporting layers of pre-equilibrated glass wool. The bulk density of NCRH packed in the column was 0.110 g/cm$^3$. The column bed depth was kept 10, 20 & 30 cm respectively in the three sets of experiments. The schematic diagram of column study is shown in figure 3.1. The study was conducted at temperature of $28 \pm 2^o$C and the pH of the malachite green solution as 8.0 for the present study. The column was charged with malachite green bearing wastewater with a volumetric flow rate of 9 to 11 ml/min. The initial concentration of malachite green was 50 mg/l and 100 mg/l. The samples were collected at certain time intervals and were analyzed for malachite green using UV spectrophotometer.

# CHAPTER-4

# RESULT AND DISCUSSIONS

# 4. Results and Discussions

Continuous flow Adsorption experiments were conducted in a column (2.5cm internal diameter and 45cm height)with two sets of solutions of Malachite green solution with concentrations of 20 mg/l and 50 mg/l at three sets of bed depths of 10 cm, 20 cm and 30 cm respectively (maintaining a constant flow rate between 9-11 ml/min).. A series of experiments were conducted with the dye solutions of different concentrations, pH, flow rate and also different height of NCRH packed column. The experiments were conducted at room temperature.Samples were collected at every 10 minutes interval after passing through the column in downward direction by peristaltic pump. The concentration of MG was analyzed through digital spectrophotometer for getting necessary breakthrough curve.

## 4.1 Observations:

### Part (a)

- Depth 10 cm

- $C_o$ = 50 mg/L

- ph(i) = 8.0

- Lamda = 580 Nm

- Flow - 11ml/min

- Total Vol = 3500 ml

**Table 4.1 :** Values of C/Co with respect to time

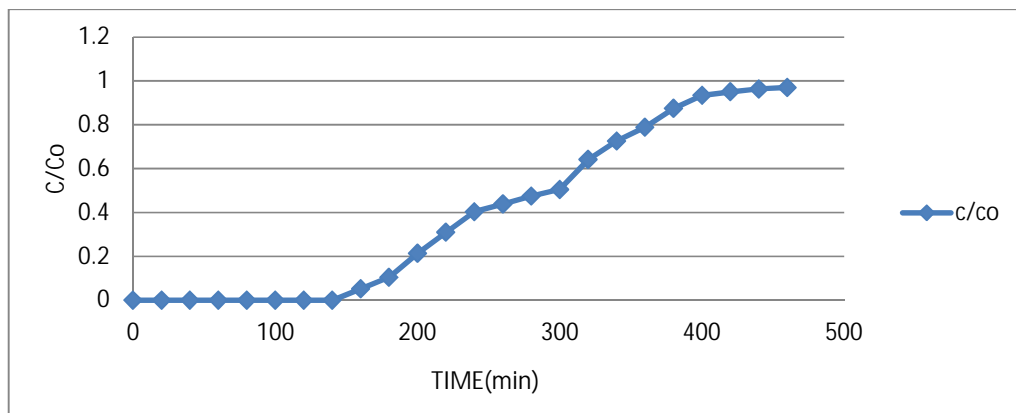| Time (min) | Concentration | c/co |
|---|---|---|
| 0 | 0 | 0 |
| 10 | 0 | 0 |
| 20 | 0 | 0 |
| 30 | 0 | 0 |
| 40 | 0 | 0 |
| 50 | 0 | 0 |
| 60 | 0 | 0 |
| 80 | 0.76 | 0.0152 |
| 90 | 0.9 | 0.018 |
| 100 | 1.12 | 0.0224 |
| 110 | 1.3 | 0.026 |
| 120 | 2.7 | 0.054 |
| 130 | 3.1 | 0.062 |
| 140 | 3.7 | 0.074 |
| 150 | 4.5 | 0.09 |
| 160 | 7 | 0.14 |
| 170 | 8.5 | 0.17 |
| 180 | 9.6 | 0.192 |
| 190 | 11.5 | 0.23 |
| 200 | 13 | 0.26 |
| 210 | 14 | 0.28 |
| 220 | 15 | 0.3 |
| 230 | 15.9 | 0.318 |
| 240 | 22 | 0.44 |
| 250 | 22.6 | 0.452 |
| 260 | 30 | 0.6 |
| 270 | 36.5 | 0.73 |
| 280 | 48.5 | 0.97 |
| 290 | 50 | 1 |
| 300 | 50 | 1 |
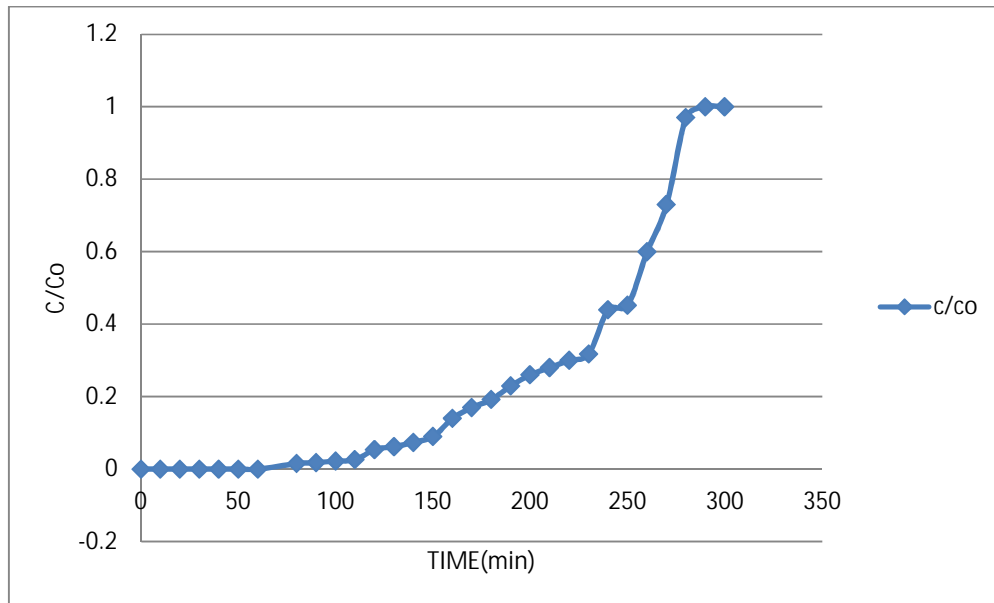
**Fig. 4.1:** Relationship between time & C/Co

**Part (b)**

- Depth 20 cm

- Co = 50 mg/L

- ph(i) = 8.0

- Lamda = 580 Nm

- Flow – 10.5ml/min

- Total Vol = 4520 ml

**Table 4.2** Values of C/Co with respect to time

| Time (min) | Concentration | c/co |
|---|---|---|
| 0 | 0 | 0 |
| 20 | 0 | 0 |
| 40 | 0 | 0 |
| 60 | 0 | 0 |
| 80 | 0 | 0 |
| 100 | 0 | 0 |
| 120 | 0 | 0 |
| 140 | 0 | 0 |
| 160 | 2.6 | 0.052 |
| 180 | 5.25 | 0.105 |
| 200 | 10.7 | 0.214 |
| 220 | 15.5 | 0.31 |
| 240 | 20.2 | 0.404 |
| 260 | 21.95 | 0.439 |
| 280 | 23.75 | 0.475 |
| 300 | 25.25 | 0.505 |
| 320 | 32.1 | 0.642 |
| 340 | 36.3 | 0.726 |
| 360 | 39.45 | 0.789 |
| 380 | 43.75 | 0.875 |
| 400 | 46.7 | 0.934 |
| 420 | 47.5 | 0.95 |
| 440 | 48.15 | 0.963 |
| 460 | 48.5 | 0.97 |



**Fig. 4.2:** Relationship between time & C/Co

**Part (c)**

- Depth 30 cm

- Co = 50 mg/L

- ph(i) = 8.0

- Lamda = 580 Nm

- Flow – 9.5ml/min

- Vol = 5710 ml

**Table 4.3**  Values of  C/Co with respect to time

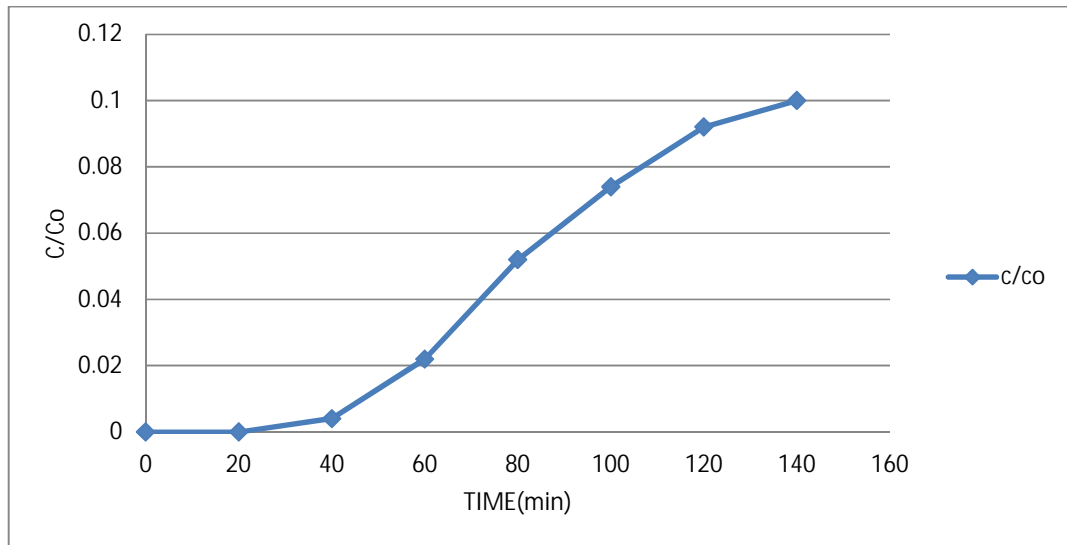| Time (min) | Concentration | c/co |
|---|---|---|
| 0 | 0 | 0 |
| 20 | 0 | 0 |
| 40 | 0 | 0 |
| 60 | 0 | 0 |
| 80 | 0 | 0 |
| 100 | 0 | 0 |
| 120 | 0 | 0 |
| 140 | 0 | 0 |
| 160 | 0 | 0 |
| 180 | 0 | 0 |
| 200 | 0 | 0 |
| 220 | 0 | 0 |
| 240 | 0 | 0 |
| 260 | 0 | 0 |
| 280 | 0 | 0 |
| 300 | 0 | 0 |
| 320 | 1.3 | 0.026 |
| 340 | 4.05 | 0.081 |
| 360 | 5.15 | 0.103 |
| 380 | 7.55 | 0.151 |
| 400 | 8.9 | 0.178 |
| 420 | 9.55 | 0.191 |
| 440 | 11.5 | 0.23 |
| 460 | 15.5 | 0.31 |
| 480 | 19.5 | 0.39 |
| 500 | 23 | 0.46 |
| 520 | 29 | 0.58 |
| 540 | 34.85 | 0.697 |
| 560 | 39.55 | 0.791 |
| 580 | 41.5 | 0.83 |
| 600 | 42.5 | 0.85 |
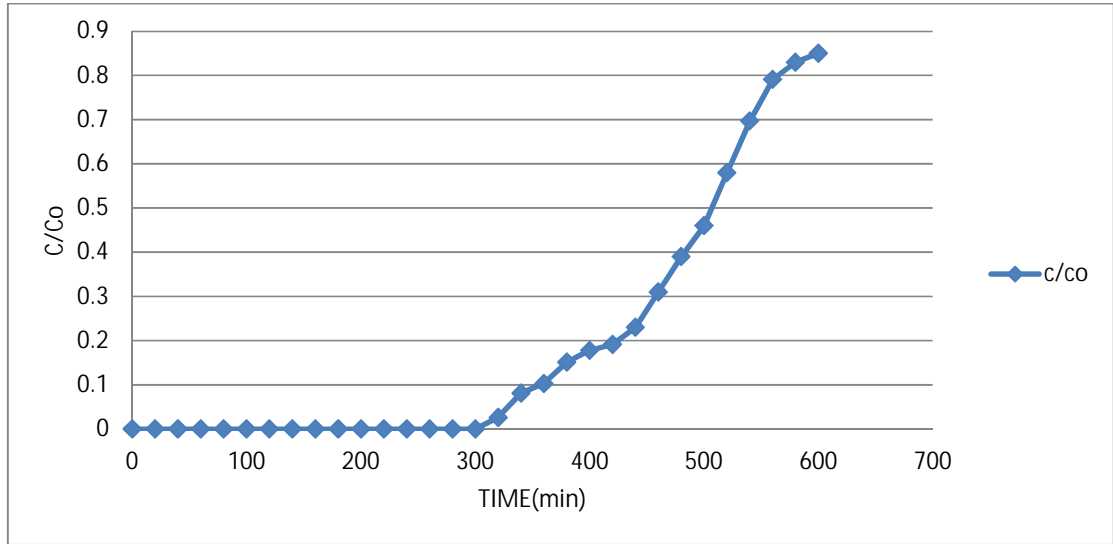
**Fig. 4.3 :** Relationship between time & C/Co

**Part (d)**

- Depth= 10 cm

- Co = 50 mg/L

- ph(i) = 8.0

- Lamda = 580 Nm

- Flow - 20ml/min

- Total Vol= 1940 ml

**Table : 4.4** Values of  C/Co with respect to time

| Time (min) | Concentration | c/co |
|---|---|---|
| 0 | 0 | 0 |
| 20 | 0 | 0 |
| 40 | 0.2 | 0.004 |
| 60 | 1.1 | 0.022 |
| 80 | 2.6 | 0.052 |
| 100 | 3.7 | 0.074 |
| 120 | 4.6 | 0.092 |
| 140 | 5 | 0.1 |

**Fig. 4.4 :** Relationship between time & C/Co

## Part(e)

- Depth= 30 cm

- Co = 100 mg/L

- ph(i) = 8.0

- Lamda = 580 Nm

- Flow – 9.5 ml/min

- Total Vol= 4000 ml

**Table 4.5** Values of C/Co with respect to time

| Time | Concentration | $C/C_0$ |
|---|---|---|
| 0 | 0 | 0 |
| 20 | 0 | 0 |
| 40 | 0 | 0 |
| 60 | 0 | 0 |
| 80 | 0 | 0 |
| 100 | 0 | 0 |
| 120 | 0 | 0 |
| 140 | 0 | 0 |
| 160 | 0.001 | 0 |
| 180 | 0.054 | 0.005 |
| 200 | 1.35 | 0.0135 |
| 220 | 2.87 | 0.0287 |
| 240 | 5.85 | 0.0585 |
| 260 | 7.26 | 0.0726 |
| 280 | 10.35 | 0.1035 |
| 300 | 14.75 | 0.1475 |
| 320 | 19.87 | 0.1987 |
| 340 | 25.85 | 0.2585 |
| 360 | 32.37 | 0.3237 |
| 380 | 39.93 | 0.3993 |
| 400 | 45.74 | 0.4574 |
| 420 | 47.16 | 0.4716 |
| 440 | 49.63 | 0.4963 |
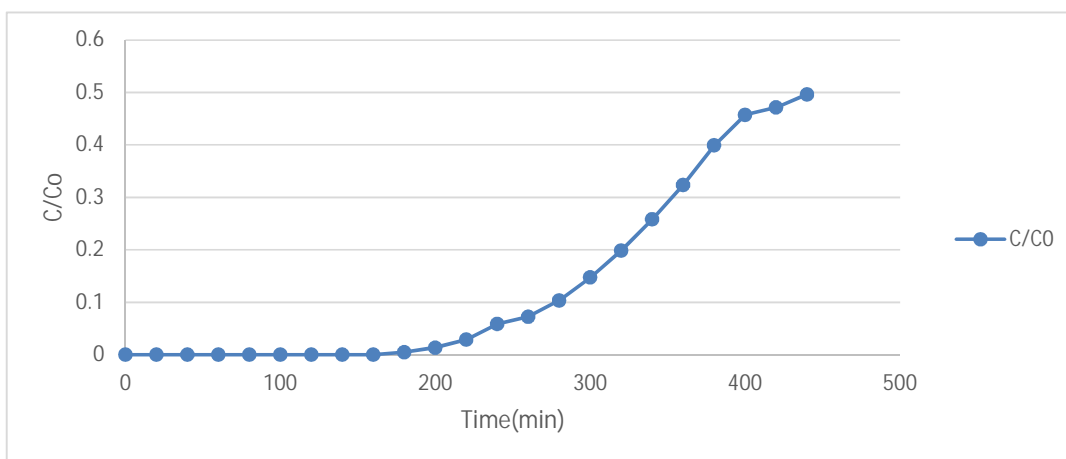
**Fig. 4.5 :** Relationship between time & C/Co

The details of the experimental results and their discussion are depicted below.

## 4.2 .The effect of different bed depth :

It was seen that as the bed height increased, MG had more time to contact with the rice husk that resulted in higher removal efficiency of MG. So the higher bed column resulted in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone. Higher uptake was observed at the highest bed height due to an increase in the surface area of the biosorbent, which provided more binding sites for the sorption.

**Table 4.6 Effect of different bed depth**

| Bed depth (cm) | 10% Breakthrough time (hr) | 90% Breakthrough Time(hr) | Treated volume (lts) | Total mass of NCRH (gm) | Mass per litre (gm/l) |
|---|---|---|---|---|---|
| 10 | 2.5 | 4.6 | 1.65 | 20.54 | 5.868 |
| 20 | 2.9 | 6.5 | 1.87 | 42.15 | 9.325 |
| 30 | 6 | 10 | 3.43 | 63.35 | 11.094 |

## 4.3 .The effect of flow rate on breakthrough curve

It was seen from fig 4.6 that breakthrough curves generally occurred faster with higher flow rate. Breakthrough time for reaching saturation was increased significantly with a decrease in the flow rate. When at a lower rate of influent, MG had more time to contact with rice husk and resulted in higher removal of MG in the column. The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. The reason is that at higher flow rate, the rate of mass transfer tends to increase. The amount of dye adsorbed onto the unit bed height (mass transfer zone) increased with increasing flow rate leading to faster saturation at a higher flow rate.
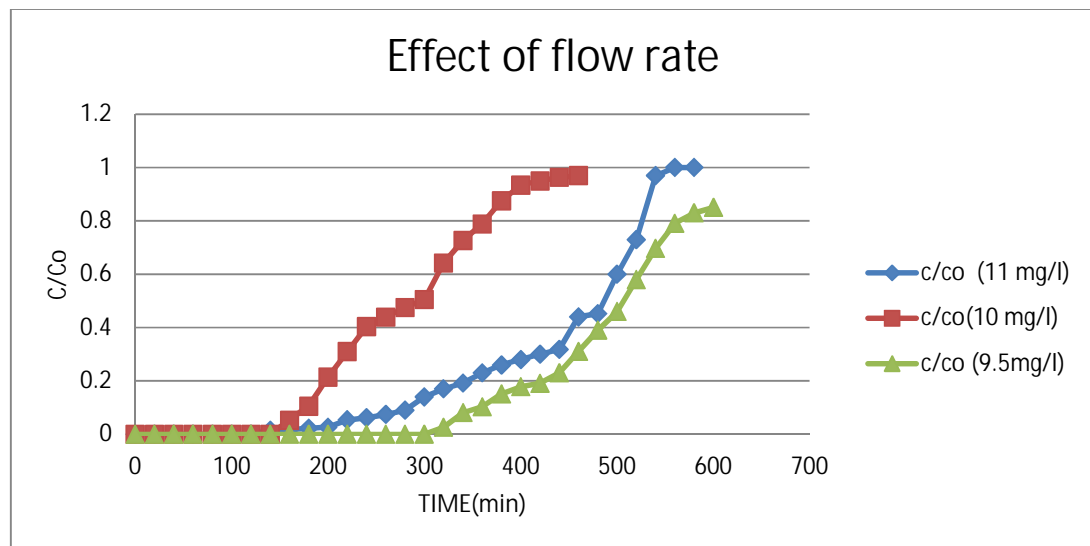


**Fig. 4.6** Effect of flow rate on breakthrough curve

## 4.4 .The effect of initial concentration on breakthrough curve

It was also illustrated in Fig 4.7 that the breakthrough time decreased with increasing influent MG concentration. At lower influent MG concentrations, breakthrough curves were dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrated that the change of concentration gradient affected the saturation rate and breakthrough time (Goel et al., 2005). This can be explained by the fact that more adsorption sites are being covered with the increase in MG concentration. The larger the influent concentration, the steeper the slope of the breakthrough curve and smaller

the breakthrough time. These results demonstrated that the change of concentration gradient affected the saturation rate and breakthrough time, or in other words, the diffusion process was concentration dependent. As the influent concentration increases, MG loading rate increases, so does the driving force for mass transfer, which results in a decrease in the adsorption zone length.
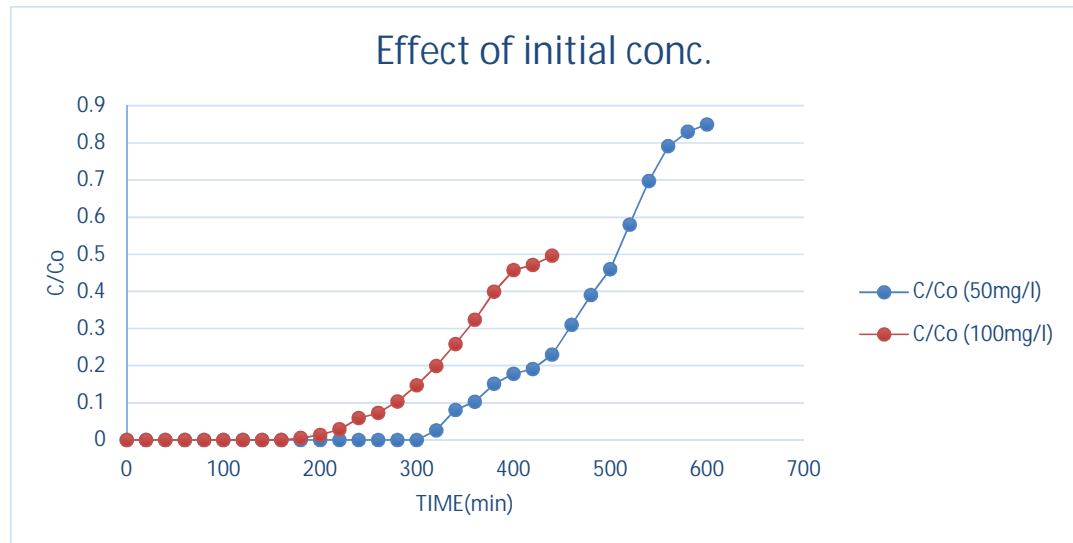


**Fig. 4.7 :**The effect of initial concentration on breakthrough curve

## 4.5 The effect of initial solution pH on breakthrough curve

In order to examine the pH variation as well as its effect on MG Adsorption in columns, MG adsorption experiments were done at different values of pH 4, 6.5 and 8. In the fig-4.8, shows the effect of pH values on adsorption of MG onto rice husk ash using a plot of dimensionless concentration (Ct/Co) versus time(t). Obviously, with an increase of pH in the influent, the breakthrough curve shifted from left to right, which indicates that more MG can be removed. It would spend more time reaching the saturation and the efficiency of Adsorption was much higher. The results suggested that with the increasing of pH in experimental condition, the adsorption capacities increase. So the removal of MG from aqueous solution was more efficient at higher initial pH value.

Several reasons may be attributed to MG adsorption behavior of the sorbent relative to solution pH. The surface of rice husk may contain a large number of active sites and MG uptake can be related to the active sites and also to the chemistry of the

solute in the solution.. At higher pH the surface of rice husk particles may get negatively charged, which enhances the positively charged dye cations through electrostatics forces of attraction.
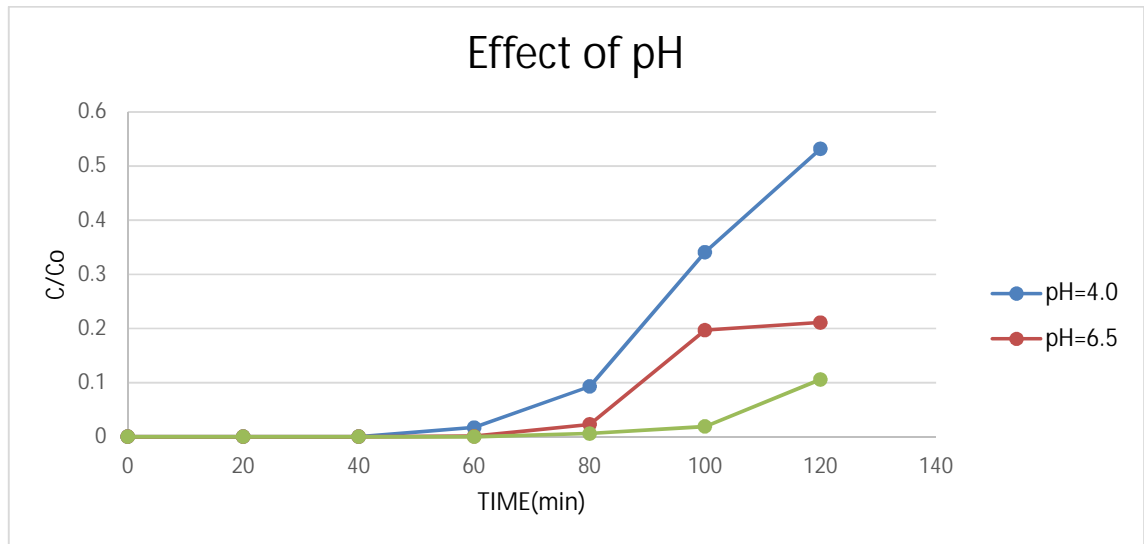


**Fig. 4.8 :** The effect of initial solution pH on breakthrough curve

## 4.6 Scanning electron microscope (SEM) analysis

SEM analysis is a useful tool for the analysis of the surface morphology of an adsorbent. SEM images of untreated and treated rice husks are shown in Fig. 4.9 a–b. The micrographs in Fig. 4.9(a) and (b) represent an un-even surface and porous structure of both untreated and treated rice husk. However, as seen in Fig. 4.9(b), the surface roughness of rice husk changed significantly after treatment with alkali. These include wearing of asperities and particle cracking. Pores and cavities of various dimensions are also clearly evident on the surface of treated rice husk. Further, the pores on the surface of the adsorbent are highly heterogeneous. The heterogeneous pores and cavities provided a large exposed surface area for the adsorption of MG. The presence of pores indicates that there was a good possibility for the dye molecules to be trapped and adsorbed onto the surface of the adsorbent. The mean size of surface cavities was measured on the image and the average diameter was less than 10 μm. These cavities are large enough to allow the dye molecules to penetrate into the lignocellulosic structure and interact therein with the surface groups.
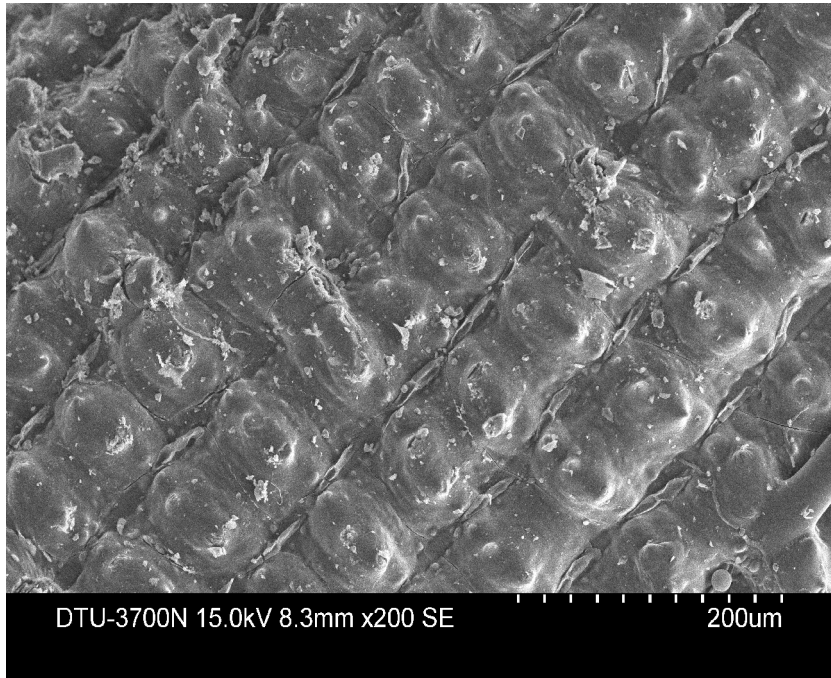
**Fig4.9 (a) SEM of untreated rice husk**
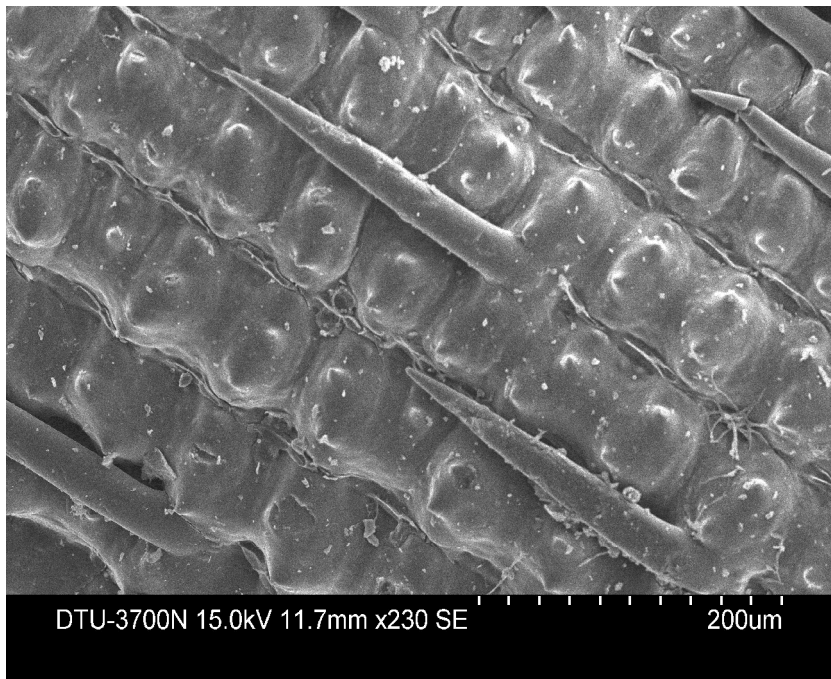


**Fig 4.9 (b) SEM of treated rice husk**

## 4.7. Column Regeneration and Reuse

Besides that, by using data from adsorption breakthrough curve, the studies on column regeneration and reuse can also be done as reported by also **Kumar and Bandyopadhyay (2005)**.It was observed that, at about 10 h the column was exhausted. Desorption was carried out by 0.01 mol/l HCl solution through the bed in the downward direction at a flow rate of 8.5 mL/min. The application of counter - current operation generally reduces regeneration costs and regenerant volume as well as increases effluent quality. It has also been noted that, the flow rate of eluting solution must be slightly less that the adsorption flow rate so that volume of regenerant is less which helps in easy handling and high in concentration so that economical solute recovery is possible.

It is therefore in theoretical aspect suggested that, the studies under continuous flow conditions are more useful compared to batch conditions, due to its suitability to be applied in large scale wastewater treatment. On top of that, continuous flow studies can also provide useful information on the adsorption process before extending it to commercial systems. Therefore, it can be concluded that, the studies under continuous system is much more practical and easily adopted in real industrial environment.

# CHAPTER 5
# CONCLUSIONS

# 5. CONCLUSIONS:

- Rice husk can be used as an inexpensive and highly effective adsorbent for the recovery and removal of malachite green from water environment.

- Sodium carbonate treated rice husk (NCRH) as developed in the laboratory, is an efficient and low cost option for MG dye removal. The rapid uptake and low cost simple pretreatment for NCRH makes it attractive.

- The increasing of pH in experimental condition, the adsorption capacities increased. The removal of MG from aqueous solution was more efficient at higher pH value. The percentage removal of MG was higher at pH 8 for NCRH  compare to lower pH 4 for NCRH. After a no. of trial it is found that the percentage uptake is better in pH greater than 7(7.5-9.5) and uptake is better in distilled water in comparison to tap water.

- Breakthrough time reaching saturation was increased significantly with the decreased flow rate. It was estimated that saturation time increased from 60 to 80 minutes with the decreased flow rate from 11 to 9 ml/mints in case of MG.

- The breakthrough time both the dyes for different influent concentrations like 50, 100 mg/l was decreased with the increase in concentration.

- The higher bed column yielded better performance in respect of removal of solute from the influent concentration at the same time. The breakthrough time increased from 80 to 100 minutes with the increased bed depth from 10cm to 30 cm in case of MG adsorption onto NCRH.

- BDST model is the best fit for MG adsorption onto NCRH. Thomas model showed better performance in case of MG adsorption onto NCRH. Overall performances of Thomas model and BDST model were excellent to predict the experimental data for all the coMGination of adsorption. The Yoon-Nelson model cannot be fit for predict the experimental data and therefore, it was not preferred in the present study.

- The entire column study has been conducted with a variation of room temperature from 22  to 30 C. The better removal was observed during higher temperature time.

- The optimum condition for MG Adsorption onto NCRH at flow rate 9.5ml/mint at bed depth 30 cm with influent concentration 50 mg/l.

- Percentage MG uptake increased with the increase of sorbent dose.

## Future Scope of Study

The present investigation can be extended to undertake more detailed study on colour removal by NCRH and like other low-cost adsorbent. The under mentioned works formulate the future directions in the fields of reaches.

- The result of the present study are based on the laboratory experiments using MG dye with distilled water samples. However, a parallel comparison using naturally polluted water (e.g. effluent from dying and bleaching industries, textiles industries and colour and pigment manufacturing industries etc.) is desirable.

- Fixed beds desorption and regeneration studies must be conducted.

- A comparative study may be tried to gather knowledge about NCRH as effective low-cost adsorbent to remove all kinds of dyes from aqueous solution (as textile industry effluents, dying and bleaching industry effluents are basically contains number of different dyes in the solutions)

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# CHAPTER-6
# REFERENCES

# 6. REFERENCES

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