A
DISSERTATION REPORT
ON
"TO STUDY ADSORPTION OF METHYLENE BLUE DYE ON ACTIVATED RICE HUSK"

Submitted for partial fulfillment of the requirement for the award of the degree of

MASTER OF TECHNOLOGY

IN

PULP AND PAPER

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CANDIDATE'S DECLARATION

I hereby professed that the work which is being shown in this Dissertation Report titled **"To study Adsorption of Methylene Blue dye using NaOH activated Rice husk"** in partial completion of the requirement for the award of the degree of Master of Technology in Pulp and Paper, IIT Roorkee, Saharanpur campus, is a record of my own work carried out under the supervision of Dr. Satish Kumar, Professor, Department of Paper Technology, IIT Roorkee Saharanpur campus, Saharanpur.

The matter embodied in this Dissertation report has not been submitted by me for the award of any other degree.

Date: 12th June 2013

Place: Saharanpur

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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I take this occasion to express my sincere thanks to every person, who has directly or indirectly contributed in the development of this work. I am able to recall only a few, but the contribution made by all of them is sincerely acknowledged.

I feel appropriate to express my profound indebtedness, deep sense of gratitude and sincere thank to my Supervisor Dr. Satish Kumar Professor, Department of Paper Technology, IIT Roorkee, Saharanpur Campus, Saharanpur.

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Date: 12/06/2013 Wasim Sheikh

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INTRODUCTION

Many industries like pulp and paper, textile, food processing, etc. dye their goods. Dyeing of products consumes water and releases colored wastewater. Colored wastewater further goes into waterways, lakes, pools, etc. Wastewater comprises many man-made chemicals, refractory compounds and lethal substances. Colored wastewater disturbs the life of aquatic animals by obstructing the sunlight to pass through it. These chemicals go into body of aquatic animals and human being eats them. Thus, it enters into body of human being and causes toxicity.

Methylene blue dye has many adverse effects on human body like itchiness of skin, eyes and even oncogenic. Therefore, treatment of dyed wastewater is of huge concern. Many treatment practices has been used for the elimination of dyes like photo catalytic degradation, physic-chemicals treatments, ozonation , etc. But these techniques are too expensive. Adsorption process has got interest due to its easiness, being economical and has good dye elimination capacity. Activated carbon is the primary choice for adsorption but it has drawback of high-cost and reusability. So, search for substitute non-conventional adsorbent is continued.

I studied the adsorption of methylene blue dye on NaOH activated rice husk. I found good adsorption capacity of activated rice husk (4558 mg of dye/g of ARH). Secondly, it's very cheap, easily available and reusable.

EXPERIMENTAL

Rice husk has been purchased from rice mill. It has been properly cleaned and treated with 10% NaOH for activation. Main components of rice husk are cellulose, hemicellulose, lignin and Silica. It has negative charge on it and entices more preferably positively charged organic dyes thus gives a higher uptake of cationic dyes.

Methylene blue dye has been selected for adsorption studies. The concentration of aqueous solutions of dye has been assessed spectrophotometrically by drawing calibration curve at their λ_{max} .

Batch method has been adopted, because of its ease of assessment of adsorption parameters. 1 g of NaOH activated rice husk is equilibrated with 1000 mg/l of adsorbate solution. The residual dye concentration in solution is assessed spectrophotometrically. Adsorption isotherm has been drawn at temperature and pH studied

RESULTS

Adsorption Studies

The plot of MB dye elimination and time of contact indicates that the removal of dye occurred in two phases. Adsorption of MB dye was very fast in first 30 min i.e. 29.5 mg of dye adsorbed out of 30 mg/l and then it slow down and all the active sites were occupied after 3 h. Hence, equilibrium time of 3 h has been taken for further experiments.

Adsorption of MB dye increased with increasing concentration of dye. At 50 mg/l adsorbate concentration, adsorption was 49.8 mg/g of adsorbent. At 5000 mg/l adsorbate concentration, adsorption was 4558 mg/g of adsorbent. This shows that NaOH activated rice husk is excellent adsorbent for MB removal.

Adsorption of MB was minimum at pH 2.7 (673 mg/g). Adsorption increased with increasing pH and maximum adsorption was seen at pH 11.5 (987mg/g).

Adsorption of MB dye has been found to increases with increasing temperature. Hence, it is endothermic process. Adsorption was minimum at temperature 25 °C (458 mg/g) and maximum adsorption was seen at temperature 40 °C (906 mg/g).

Overall adsorption of MB dye increased, on increasing doses of NaOH activated rice husk. But, adsorption per gram of adsorbent decreased on increasing adsorbent doses.

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Due to rapid industrialization and many modern day activities led to the origination of enormous quantity of materials of small value. Such materials are generally studied as trashes and having problem of clearance. Utilization of such materials wherever possible and their safe disposal is being intensively looked into at all levels. Hazards from toxic wastes like metal salts, acids and radioactive material are quite well known. Besides this, agricultural, domestic, industrial and, cooling and rinsing activities generate waste water containing many pollutants.

1.2 WASTEWATER PROBLEM

Exhaustive exploitation of natural reserves has resulted in the worsening of the environment, making the healthy survival of mankind, a challenge. Water and air is the most important elements of life. As a result of intense use of fresh water, biological agents, the presence of toxic chemicals (inorganic and organic), and even heat and radiation in surface water is gradually increasing. The nature of these chemicals varies from place to place, industry-to-industry and level of advancement in domestic life. Thus, depending on activity, water may contain different pollutants.

Removal of toxic pollutants from water is a difficult task because of the diverse number of compounds and present in extremely low concentration. The standard of the quality of waste water effluent are gradually becoming more rigid. Stringent restrictions have been imposed on the concentration of these compounds in waste waters for safe discharge and new treatment methods are continuously being investigated.

1.3 POLLUTANTS

The term pollutants refer to materials that alter the natural feature of the environment by physical, chemical and biological ways. Some of the most common chemicals found in wastewater and considered as pollutants are detergent, poly-nuclear hydrocarbons, poly chlorinated biphenyls (PCBs), insecticides, phenols, dyes, pesticides, heavy metals, etc. They are toxic if present above a certain level.

1.3.1 Biological Agents

Biologically active agents are E.coli, shigella dysenteriae, vibrio comma, salmonella typhosa and Yersinia entrocolitica. Most of them are pathogen cause disease. These are generally present in effluent released from sewage.

1.3.2 Heat

Heat is also considered as pollutant. Elevated temperature of wastewater not merely effect aquatic life but is also known to trigger high corrosive activity and many chemicals and bacteriological reactions, such as creation of tri halo methane (THM).

1.3.3 Dissolved and non-dissolved chemical

The existence of hanged solids chokes canals, fills up dams and threat to water life in many ways. These include heavy metals, dyes, phenols, etc.

1.3.3.1 Heavy metals

Heavy metals are normally existent as pollutants in a wide variety of industrial effluents. They are deadly to aquatic plants and animals even at comparatively low strengths. Heavy metals include mercury, zinc, copper, chromium, cadmium lead, etc. These are released from various industries and extremely harmful for human beings. These heavy metals are essential at certain amount but harmful in higher concentration.

1.3.3.2 Phenols

Apart from metals, phenol is also reflected as significant contaminants (1) as they impart carbolic odor and bad flavor to water and toxic (2) to fish and human beings even at low concentrations. Phenol present in waste water are generated from pesticides, gas and coke manufacture, pulp and paper , chemical, paint, resin, and dyeing industries (3,4).

1.3.3.3 Dyes

Dyes are the coloring agents used in many industries. Effluent discharge from industries contains dye and enters into water bodies. Colored water indicates contamination. Many dyes are synthetic and extremely harmful and may be carcinogenic. Dye in wastewater inhibits penetration of sunlight in rivers, lakes and ponds. Thereby, inhibits photosynthetic activities of aquatic plants and algae. MB is the most commonly used substance for dying cotton, wood and silk. It can trigger eye injuries, skin irritation, and difficulty in breathing, nausea, vomiting and methamoglobinemia. Consequently, the treatment of run-off having such dye is of great concern due to its dangerous consequences on receiving waters.

1.3.3.4 Miscellaneous substances

Radioactive substances (5) are also dangerous pollutants released from research laboratories, hospitals, and nuclear power plants. Many adsorbents have been discovered to remove radioactive materials from wastewater.

1.4 TREATMENT METHODS

The type of process to be used depends on the nature of the pollutant. Some existing technologies like oxidative destruction via UV/Ozone treatment (6), dialysis (7), photo catalytic degradation (8), reverse osmosis (9), biological methods (10) , electrochemical reduction (11) etc. may have certain efficiency for the elimination of poisonous materials but their initial and functioning expenditures are high, that it is not easily affordable to dyeing and finishing industries(12).

Impurities in water vary in size and largely removed by sedimentation. Gravitation separation by sedimentation is an effective technique for the elimination of unstable suspended solids. Chemical precipitation and biological methods are the two commonly used processes for the treatment of colored waste water. But, these methods suffer from the disadvantage of sludge disposal and long term degradation respectively. Conventional treatment processes such as aerated lagoon and activated sludge processes are frequently used for removal of suspended solids and chemical oxygen demand (COD). But, it's not effective in decolorisation of waste water. Decolorisation of wastewater can be done using of membrane filtration, chemical oxidation, coagulation, coagulants oxidizing agents, ultra filteration, precipitation and electrochemical techniques, adsorption and ion exchange techniques (13).

These methods have their own shortcomings e.g. coagulation require pH control and causes further problem of sludge disposal. Ozonation removes color effectively but does not minimize COD. Some of these methods have been found to be quite efficient for removal of color but the cost factor inhibits their large-scale use for small scale industries. The cost of such processes, therefore, needs to be ascertained.

1.5 ADSORPTION

Adsorption is a famous process and an operative method for removal of pollutants from water [14]. Adsorption has an edge over other techniques in terms of cost and reversibility. It is very simple process, doesn't require large human labor. Adsorption technique can be used to remove variety of pollutants.

A survey of literature has revealed that amongst the many methods used for removing pollutants from waste water, the adsorption of impurities from solution onto solid material is widely used because it is cheap, effective, efficient, as well as versatile as it remove broad range of assorted pollutants. It has evolved as the frontline of defense to the removal of pollutants, which is difficult to remove by other techniques. Adsorption process can be used to remove heavy metals, dyes and color, phenolic compounds, refractory organics and other non-biodegradable materials.

1.6 ADSORBENTS

Adsorbents are the materials onto which adsorbates fix. Important property of adsorbents is having pores and roughness. Porosity is directly proportional to adsorption capacity of adsorbent. Surface area also increases on increasing porosity increases. Good adsorbents also have less contact time as it represents faster kinetics.

1.6.1 Activated Carbon

Activated carbon is a carbon containing material having enormous internal surface area and spongy structure. The surface area contains mostly micro pores with pore diameters smaller than 2 nm [15]. This makes activated carbon a popular adsorbent for large number of applications.

Activated carbon is first choice for adsorption of pollutants. It has been extensively exercised for the adsorption of heavy metals, dyes, chlorinated carbon, pesticides and recalcitrant. Activated carbon is produced from carbonaceous material. Wastewater has been treated since long time using activated. Activated carbon is generated by treating carbonaceous material in oxygen-less environment and then, carbonized material is activated by hot steam at very high temperature. This result, a highly porous structure called activated carbon. In spite of excellent adsorption capacity, its application has been restricted to higher cost and problem of regeneration. Therefore, research is continuing for low cost adsorbent for adsorption of pollutants. Many low cost adsorbents have been found. Low-cost adsorbents from agricultural rests are economic and recyclable. A large number of low-cost adsorbents have been established from waste materials using agricultural as well industrial and municipal wastes.

1.6.2 Other Adsorbents

A large number of materials have been greatly searched as adsorbent for wastewater treatment. It includes silica gel, activated alumina, zeolites and activated carbon, etc.

Regular density silica gel has extremely spongy structure and well suited for adsorption of contaminants. Activated alumina has poriferous solid structure and has good adsorption capacity. Zeolites-based materials are tremendously multipurpose adsorbents. Zeolite is a good adsorbent for water, carbon dioxide and hydrogen sulfide.

1.6.3 Low-cost alternative adsorbents

Agricultural material containing cellulose shows good potential for adsorption. These materials contain cellulose hemicellulose, lignin, silica and other material that have many functional groups and, proved to be good adsorbents. These material are easily available, cheap and doesn't results pollution

Rice husks, wheat husk, waste tea leaves, shells, fly-ash, peels of orange and banana, Bagasse pith, waste newspaper, etc., are waste material that shows good adsorption for wide range of pollutants. [16].

1.6.4 Adsorbents for Dyes

Industry uses dyes for coloring their products. As a result, dye appears in wastewater and causes water pollution. Wastewater of dye adversely affects aquatic life and human being. So, elimination of dyes from wastewater is of concern. Many adsorbents have been searched for the elimination of dyes from wastewater.

Large number of low cost material (rice husk, husk and cotton waste, teak wood bark, bentonite, clay,) can be used as adsorbents for the elimination of acidic, basic, disperse and direct dyes (17). Sawdust from Sagaun can be used for the eliminaiont of basic dyes from liquid solutions (18). Other than above mentioned adsorbents, large number of agricultural and industrial waste products has also been searched as adsorbents for dye exclusion. An agricultural waste of rice mills, rice husk ash, has been studied (19) as an adsorbent for the exclusion of acidic dyes from liquid solutions and result was good.

Banana and orange coverings also proved to be good adsorbent for dyes (20). Rhodamine B and Methylene blue can be eliminate by bagasse fly-ash (21). Exclusion of Methylene blue and Malachite green using high and low carbon content fly ash has been done (22).Waste-tyre rubber (23) has been examined for the adsorption of organic compounds.

1.6.5 Rice Husk

Rice is one of most eaten food throughout the world. It has been produced all over the world. Rice husk is the by-product of rice. Rice husk is easily available and very cheap. Rice husk is found to possess good adsorption capacity for wide range of pollutants.

1.7 THE PROBLEM

Review of literature dealing with various alternative adsorbents for the removal of dyes. Many alternative adsorbents have been studied, but their adsorption capacity as compared to activated carbon is considerably less. Therefore, Search for alternative adsorbent having higher adsorption capacity, lower initial cost and potentially greater ease of regeneration is continued, so that, they can be used to replace activated carbon.

1.8 AIM AND OBJECTIVES

The work has been divided into three chapters. The first chapter deals with general introduction describing the status of work.

The second chapter of this thesis deals with the materials and various experimental techniques (methods) used in this study.

The third chapter deals with the adsorption of Methylene blue dye on NaOH activated rice husk. The studies have been performed by batch process under different conditions of dye concentration, pH, temperature, etc.

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CHAPTER-2

2.1 EXPERIMENTAL MATERIALS AND METHODS

2.1.1 Dye

Methylene dye is purchased from Vishwani Chemicals Ltd. Roorkee (India).It's practical grade methylene blue having molecular formula $C_{16}H_{18}ClN_3S \cdot 3H_2O$, molecular weight 373.90, and C.I. 52015.

2.1.2 Other Chemicals

Chemical used were NaOH and HCl solution. These were used without further purifications. Solution of dye was prepared in distilled water.

2.1.3 Rice Husk

Rice husk was obtained from nearby rice mill.

2.2 Instrumentation

Measurement for pH determinations were made with Toshniwal pH meter. For the spectrophotometric work, Systronic UV/VIS Spectrophotometer-118 has been used.

2.3 ADSORBENT MATERIAL AND PREPARATION OF ACTIVATED CARBON

Rice husk was purchased from nearby rice mill. Rice husk was cleaned constantly with double distilled water to exclude dust. Then, it was dehydrated at 70 °C for 3 h. Rice husk kept in 10% Sodium hydroxide solution and then, it was autoclaved at 10 psi for 15 min. Alkali solution was Separate out. Washing of treated rice husk has been done using distilled water. Dehydrated treated rice husk in sunlight. After drying the rice husk was kept in sealed glass container. This rice husk was used in all experiments.

Rice Husk

2.4 Estimation of dye

Methylene blue displays maximum absorbance at 664 nm. Therefore, spectrophotometer was adjusted at 664 nm wavelength for determining absorbance of methylene blue solution.

2.5 Calibration Curves

Aqueous solution of the methylene blue dye of different dilute concentrations was prepared. The absorbance of methylene blue solutions was measured at λ_{max} value. Calibration curve were constructed between absorbance v/s concentrations. Calibration curve was linear. This calibration curve was used for the determination of the residual concentration of MB dye upon adsorption.

2.6 Sorption Study

2.6.1 Batch Method

Outcome of various factors on adsorption has been done using Batch method. Batch method is comparatively simple and easy to analyze. Stock solutions of MB dye of concentration 3000 mg/l was made and further water down to get required concentrations. Calibration curve for MB dye was prepared. HCl and NaOH solution was used for pH safeguarding. and measurement of pH was done using a Toshniwal pH meter. Thermostat shaker was used to shake the MB solution. The effect of experimental parameters such as concentration of MB dye, contact time, pH, temperature and adsorbent doses on MB adsorption was studied.

Adsorption experiments were conducted and effect of following parameters were analysed-

2.6.1.1 Contact Time

1g of activated Rice husk was added into a series of 250 ml Erlenmeyer flask, which are filled with 100 ml of MB solution having each initial concentration (30 mg/l), pH (9) and temperature (25 °C). Thermostatic shaker bath is used for shaking and shaking has been done. Activated carbon was separated from the solution at different time interval by centrifugation at 3000 rpm for 5 min and Systronic uv/vis spectrophotometer-118 has been used to measure absorbance of clarified supernatant. The amount of adsorbed Methylene blue was calculated and equilibrium time was determined.

2.6.1.2 Concentration of Adsorbate

1g of NaOH activated carbon was added into a series of Erlenmeyer flask and 100 ml of experimental MB solution was added with each initial pH(9) and temperature (25 °C) and initial concentration of MB was varied. All vessels have been covered and shaken to equilibrium in a thermostatic shaker. Activated carbon was separated by centrifuging at 3000 rpm for 5 min and Systronic uv/vis spectrophotometer-118 has been used to measure absorbance of clarified supernatant. The amount of adsorbed Methylene blue was calculated.

2.6.1.3 Amount of Adsorbent

Varied amount of adsorbent (activated rice husk) was added into a series of Erlenmeyer with 100 ml of experimental MB solution with each initial concentration of MB solution (1000 mg/l), pH (9) and temperature (25 °C). All vessels have been covered and shaken to equilibrium in a thermostatic shaker. Activated carbon was separated by centrifuging at 3000 rpm for 5 min and Systronic uv/vis spectrophotometer-118 has been used to measure absorbance of clarified supernatant. The amount of adsorbed Methylene blue was calculated.

2.6.1.4 Effect of pH

1g of NaOH activated carbons was added into a series of Erlenmeyer with 100 ml of experimental MB solution having varied pH and with each initial concentration (1000 mg/l) and temperature (25 °C). All vessels have been covered and shaken to equilibrium in a thermostatic shaker. Activated carbon was separated by centrifuging at 3000 rpm for 5 min and

Systronic uv/vis spectrophotometer-118 has been used to measure absorbance of clarified supernatant. The amount of adsorbed Methylene blue was calculated.

2.6.1.5 Effect of Temperature

1g of NaOH activated carbon was added into a series of Erlenmeyer with 100 ml of experimental solution having varied temperature and with each initial concentration (1000 mg/l) and pH. All vessels have been covered and shaken to equilibrium in a thermostatic shaker. Activated carbon was separated by centrifuging at 3000 rpm for 5 min and Systronic uv/vis spectrophotometer-118 has been used to measure absorbance of clarified supernatant. The amount of adsorbed Methylene blue was calculated.

CHAPTER-3

ADSORPTION OF MB DYE ON NaOH ACTIVETED RICE HUSK

3.1 INTRODUCTION

Dyes are normally used for dyeing industrial products. Some are natural dyes while others are synthetic dyes. Most of the industries use synthetic dye for coloring their stuffs. Most of the synthetic dyes are dangerous and lethal. Methylene blue is the basic dye used in paper, textile and other industries. Effluent of these industries contains methylene blue dye. This imparts dark blue color to wastewater. MB dye adversely affects aquatic life and human beings. It inhibits photosynthetic activities of aquatic plants and micro-organisms in water bodies. It causes skin irritation, and carcinogenic to human beings.

Adsorption is one of the most popular and effective process for the removal of wide variety of pollutants including dyes, heavy metals and organic compounds. It has advantage of low cost, easy operation and regeneration of adsorbents. It doesn't result sludge formation.

Activated carbon is most popular and commonly used adsorbent (1). It has high surface area and adsorption capacity. But, its application at industrial scale has been restricted due to high cost and problem of regeneration.

Rice husks have been found to have good potential for adsorption of wide variety of pollutants including dyes, heavy metals, recalcitrant, etc. Secondly, it's very cheap and easily available and can be reuse. All these points make it very suitable for adsorption of pollutants and can be employ at large scale.

This chapter describes the investigations on the sorption of Methylene blue dye on NaOH activated rice husk. It includes the sorption equilibrium, various adsorption models, factors affecting adsorption, some preliminary investigations undertaken to fix up necessary parameters for studying the sorption equilibrium by batch process and the results on the sorption of the Methylene blue dyes under different conditions of temperature, pH, etc.

3.2 EQUILIBRIA AND KINETICS

The suitability of the process of adsorption, as a unit operation, for the treatment of wastes can be determined in terms of two aspects viz., the equilibria and the kinetics of adsorption. The mechanism of the adsorption process involves three steps:

1. Transfer of the adsorbate molecules through a surface film to the exterior of the adsorbent (film diffusion).
2. Dispersion of the adsorbate into pores of the adsorbent (pore diffusion).
3. Adsorption of solute at the interior surfaces and to the capillary spaces of the adsorbent (intraparticle diffusion).

The overall rate of the process of adsorption relies on the slowest step. For a batch process, 'pores diffusion' and for continuous flow system 'film diffusion' are the most likely rate controlling factors.

The occurrence of adsorption, in general, includes ion-exchange, physical adsorption and chemical adsorption. Ion exchange or exchange adsorption is the reversible exchange of ions between two phases. Physical adsorption is adsorption occurring as a result of vander waal's forces (dispersion forces). Mostly it's reversible and non-specific in nature. Chemical adsorption is a result of specific interactions between the sorbing species and sorbent material. In most cases, it's irreversible in nature and is effective at high temperature.

When adsorption is irreversible, solute molecules cannot be eluted from the sorbent material. In reversible adsorption the solute is adsorbed at the surface and then moves towards interior of the adsorbent. This process continues till the equilibrium distribution of the solute between solid and solution phase occurs. In this type of adsorption recovery of solute is possible.

3.3 FACTORS AFFECTING SORPTION

Many factors influence the rate of adsorption and extent to which a particular adsorbate can be adsorbed. The parameters that have been investigated for optimizing the use of ARH wastewater treatment are:

3.3.1 Nature of Adsorbate

Solubility of solute in solvent is one of the deciding factor in adsorption of solute onto adsorbent. Adsorption is not favorable if solution is lyophilic and vice-versa. Normally, solubility of organic compounds decreases with increase in length of carbon chain and consequently adsorption increases with ascending homologous series. Other factors of importance, which have profound influence on the extent of adsorption, are molecular size, structure and polarity of adsorbate molecules present in wastewater and their concentration.

3.3.2 Nature of Adsorbent

As adsorption is a surface phenomenon, portion of the total surface available for adsorption depends on the particle size and shape of the adsorbent material. The adsorption capacity for a non-porous or a porous adsorbent varies as the inverse of the particle diameter but for highly porous adsorbents, the adsorption rate is independent of particle diameter. Apart from this, the chemical nature of adsorbent material is also of interest that determines the rate of adsorption.

3.3.3 Method of Contact

The uptake of adsorbate material also depends on the type and the time of contact i.e., the rate of adsorption may be different in "Batch mixing" or "Continuous flow system".

3.3.4 Adsorbate Concentration

Initially active sites on adsorbents are vacant. So, if adsorbate concentration is increase, it enhances movement of dye molecules towards adsorbent and vacant sites on adsorbents start filling and adsorption is very fast. But, after some time, adsorption slow-down and become almost constant. This is due engagement of vacant sites on adsorbents with dye molecules

3.3.5 Adsorbent Dose

Varying adsorbent doses gives an idea about the effectiveness of an adsorbent It also determines minimum dose of adsorbent for removing particular adsorbate concentration. This analysis is good from economical point of view. Usually, adsorption of dye increases with increase in adsorbent doses. It's due to increase in binding sites on adsorbents. But adsorption of dye per gram decreases due to insufficient exposure of binding sites.

3.3.6 Contact Time

Contact time is also an important factor from the design point of view. Adsorption of adsorbate species is faster in the initial stages of contact period, reflects faster kinetics and become slow near equilibrium (2-4, 5). Contact time required to attain equilibrium is a function of particle size, pH, rate of agitation, temperature, etc. Pretreatment of adsorbent also influences the equilibrium time. It was found that if contact time is less, efficiency decreases

3.3.7 pH

Surface charge of adsorbents depends upon the pH of adsorbate solution. Surface charge determines adsorption of adsorbate on adsorbent. Therefore, pH of solution strongly affects adsorption. Dissociation of functional groups on the adsorbate and adsorbent occurs due to change in pH (6).

In general, adsorption of cationic dyes increases with increasing pH of solution because $-OH^-$ ions attaches to the functional group on adsorbents. Thus pass on negative charge on it and attracts cationic dyes. For acidic dyes, adsorption reduces on increasing pH. Because at basic condition, the OH^- ions in the solution increases and due to which adsorbent surface appears negatively charged. This results in repulsion between acidic dye molecule and adsorbent. Hence, adsorption of acidic dye decreases at high pH.

3.3.8 Temperature

Nature of adsorption process is fixed by effect of temperature of adsorbate solution. It indicates whether adsorption process is exothermic or endothermic. If the adsorption is promoted on increasing temperature, then it is an endothermic process. Because, kinetic energy of adsorbate molecule increase on increasing temperature of solution and supports adsorption process. This also creates active sites on the adsorbent for the adsorption with increasing temperature [7]. If on increasing temperature of solution adsorption reduces, indicates adsorption is exothermic [8].

3.4 ADSORPTION MODEL

During adsorption the solute goes to the boundary till equilibrium is attained between that in bulk phase and that at the surface, at constant temperature. At the position of equilibrium, there is a defined distribution of solute between two phases. The plot between amount of adsorbate adsorb per unit weight of adsorbent v/s remaining concentration of adsorbate in solution at equilibrium i.e. equilibrium concentration, at constant temperature. An expression of this type is termed as "Adsorption isotherm".

For decades the Langmuir and the Freundlich theories have been used to model the adsorption behavior of dye at equilibrium. The sorption process is then discussed in terms of constants that are characteristics for the individual system. The type of isotherms followed by a system can be any, or a combination of the following models:

3.4.1 Langmuir Adsorption Model

It is valid for monolayer adsorption. It is based on the assumptions that:

a) This model is applicable when adsorbate forms monolayer on adsorbent surface.

b) Energy of adsorption is distributed uniformly at the surface.

c) No transmigration of solute molecules in the plane of the surface is assumed.

The Langmuir isotherm is expressed as :

$$q_e = \frac{Q^o . b . C_e}{1 + b . C_e}$$

where:

C_e = equilibrium concentration of adsorbate remained in solution

q_e = amount of solute adsorbed per unit weight of adsorbent

Q^o = Maximum adsorption capacity for forming monolayer

b = Langmuir constant related to the free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$)

The expression can also be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q^o.b} + \frac{C_e}{Q^o}$$

Thus, a plot of C_e/q_e vs. C_e results in straight line. $1/Q^o$ is the slope and $1/Q^o$ b is intercept. The assumptions of Langmuir model are not true for most systems of wastewater treatment, yet this equation is very useful for the treatment of adsorption data. For example, the value of Q^o for organic wastes on activated carbon doesn't represent monolayer formation but a fractional limiting capacity for adsorption, which is also a factor of practical utility.

3.4.2 Freundlich Adsorption Model

It's applicable for adsorption on solid surface. It is applied when surface energies on adsorbent is heterogeneous. Freundlich equation can be represented as:

$$q_e = K_f.C_e^{\frac{1}{n}}$$

data is usually fitted to the logarithmic form of equation:

$$\log q_e = \log K_f + \frac{1}{n}.(\log C_e)$$

Where 'K_f' and 1/n is system specific constant. K_f indicates adsorption capacity while 1/n represents intensity of adsorption. The plot of log q_e vs. log C_e is linear with slope of 1/n and an intercept equal to log K_f.

This isotherm does not predict any saturation of the adsorbent surface and can only be applied in the low to intermediate concentration range.

3.4.3 B.E.T. Adsorption Model

Derived by Brunauer, Emmert and Teller is indicative of sequential multilayer adsorption and is represented by the equation:

$$q_e = \frac{A.\ C_e.Q^o}{C_s - C_e.[1 + (A+1).\frac{C_e}{C_s}]}$$

where,

q_e and C_e are the same as above,

C_s = saturation concentration of solute

Q^o = Maximum adsorption capacity for forming monolayer.

A = a parameter related to the binding intensity for all layers.

The B.E.T. model has been linearized to yield the following equation:

$$\frac{C_e}{q_e}.(C_s - C_e) = \frac{1}{A.Q^o} + \left(\frac{A-1}{A.Q^o}\right).\left(\frac{C_e}{C_s}\right)$$

The constants A and Q^o can be evaluated by plotting C_e / q_e. (C_s-C_e) vs. C_e/C_s.

3.5 HEAT OF ADSORPTION

The process may be exothermic or endothermic. The exact nature of the process can only be determined by the values of heat of adsorption. Calculation of adsorption's isosteric heat is done by:

$$Q = R.\left(\frac{T_1.T_2}{T_1 - T_2}\right).\log\left(\frac{C_1}{C_2}\right)$$

Where, for the same amount of adsorption:

C_1 = solute concentration in solution corresponding temperature T_1 at equilibrium

C_2 = solute concentration in solution corresponding temperature T_2 at equilibrium.

R = Universal gas constant

3.6 RESULTS AND DISCUSSION

3.6.1 Evaluation of Sorption Parameters

The parameters to be fixed up for investigating the equilibrium by batch process are:

a) Concentration of adsorbate in solution

b) Equilibrium time of adsorbate and adsorbent

c) Quantity of adsorbent

d) pH and temperature

A moderate concentration of adsorbate 50-1500 mg/l has been chosen for running of adsorption isotherm. This has been decided; keeping in view, dye concentration generally present in wastewater.

The equilibrium time and quantity of adsorbent for optimum adsorption have been determined experimentally by observing the effect of the time of contact at a fixed adsorbate concentration (30 mg/l). The quantity of adsorbent has been decided after making a few trial runs. Finally, 1 g of adsorbent per 100 ml of solution has been maintained for all the adsorption experiments

The results of these experiments depicted in Fig 1. This has been plot between adsorption of Methylene blue (mg/g) and time of contact (h). The nature of plot indicates that the adsorption of methylene blue occurs in two phases. In the first phase, the uptake of solute is fast while in second phase rate of removal becomes quite slow and subsequent removal of solute continues over longer period time.

The uptake of methylene blue is very in first 30 minutes and till 3 h adsorption was almost constant. After this, adsorption occurs almost negligible. So, all sorption determinations have been made after equilibrating the solution with adsorbent for three hours.

3.6.2 ADSORPTION OF METHYLENE BLUE

3.6.2.1 Scanning electron microscope (SEM) analysis

SEM analyzes the surface properties of adsorbent like pores, active sites, roughness and surface area of adsorbents. Fig. 1a shows the surface of untreated rice husk. Fig. 1b shows the change of surface active sites and roughness of NaOH treated rice husk. It shows that surface of adsorbent is changed. Pores, ridges and roughness is clearly seen on activated rice husk. The average diameter of surface cavities was 10 μm. These cavum are sufficient for the adsorption of dye molecules.

3.6.2.2 **Effect of Contact time**

Fig. 2 and 3 shows the effect of contact time on adsorption of MB dye. Initially, adsorption was very fast till 30 minutes, after this adsorption slows down and became almost negligible after 3 h. It indicates that, vacant sites of adsorbents filled very fast in 30 min. After this, adsorption takes place at internal pores, thus adsorption slowdown. After 3 h all the sites of adsorbent saturated with adsorbate.

3.6.2.3 **Effect of Initial dye concentration**

Fig. 4 shows the variation of adsorption onto NaOH activated rice husk on varying initial dye concentration. Adsorption increased on increasing initial dye concentration from 50 mg L^{-1} to 1500 mg L^{-1} indicated completion of single layer. Adsorption again increase with increasing dye concentration. Maximum adsorption was found to be 4558 mg of dye/ g of ARH. Because, driving force is generated as adsorbate concentration increase, which helps dye molecules to avoid resistance for adsorption. Langmuir adsorption model has been fitted in concentration range of 50-1500 mg/l. As concentration increased above 2000 mg/l, adsorption again increased, indicating formation of second layer of adsorbate on adsorbent. But I couldn't reach to saturation point (Cs) due to error in measurement of concentration of MB dye due to very high concentration of dye.

3.6.2.4 **Effect of Adsorbent Doses**

On varying amount of adsorbent (Activated rice husk), it was found that adsorption per gram was decreased as its amount increased. But overall adsorption was increased on increasing amount of adsorbent. Adsorption per gram was maximum at 0.5 g amount of activated rice husk and was lowest at 4 g of activated rice husk as it is shown in table 4.This might be due to decrease in exposed surface area of ARH as adsorbent is increased. Exposed surface was maximum when adsorbent dose was 0.5 g.

3.6.2.5 **Effect of temperature**

Fig. 8 illustrates, change in adsorption of MB dye with respect to temperatures. This indicates, whether adsorption is endothermic or exothermic. From the figure, it is seen that adsorption of MB dye increases on increasing temperature. Adsorption was minimum at 25 ^{o}C and maximum at 40 ^{o}C. This shows adsorption of MB on NaOH rice husk is endothermic in nature. It is due to creation of active sites on adsorbents and increase in mobility of MB dye molecules, adsorption increased on increasing temperature.

3.6.2.6 **Effect of pH**

The effect of pH on adsorption process has been studied. The variation of solution pH is reported to significantly affect the dye adsorbed i.e. the system is strongly pH dependent. The experimental results indicate that the adsorption of MB dye first increased from pH 2.7 to 4.55 (673 mg/g to 962.9 mg/g ARH). After this, adsorption decreased continuously till pH 8 and again increased on increasing pH. The adsorption was maximum at high pH (11.5).

At very low pH (2) protonation of functional group occurs on adsorbent surface. Adsorbent surface becomes positively charged and hence, adsorption reduces. As the solution becomes less acidic, deprotonation of adsorbent's functional group occurred and repulsion between cationic MB dye and adsorbent decreased, and adsorption increased. H^+ ions reduced on increasing pH, which compete with MB dye cat ions for appropriate sites on adsorbent. At high pH, this competition weakens and dye cat ions replaces. Hence, cationic MB dye replaces H^+ ions. This lead to increase in adsorption at high pH.

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Table - 1

Effect of Contact time on adsorption of Methylene blue on ARH at 25 °C

pH = 9

Volume = 100 ml

Adsorbate concentration = 30 mg/l

ARH = 1 g

Time (h)	Adsorption (mg dye/g ARH)
0.5	29.5
1	29.7
1.5	29.75
2	29.76
2.5	29.78
3	29.828
4	29.83

Table - 2

Adsorption of Methylene blue dye on NaOH activated Rice husk (ARH) at 25 °C

pH = 9

Total volume = 100 ml

ARH added = 1 g

S. N.	Initial concentration (Co) mg/l	Equilibrium concentration (Ce) mg/l	Adsorption (Qe) mg/g ARH
1	50	0.2	49.8
2	100	0.8	99.2
3	150	1	149
4	200	1.2	198.8
5	250	1.4	248.6
6	300	2	298
7	350	3	347
8	400	4	396
9	450	5	445
10	500	6	494
11	550	7.5	542.5
12	600	10	590
13	1000	127	873
14	1400	410	990
15	1500	525	975
16	1900	930	970
17	2000	781	1219
18	2500	231	2269
19	3000	225	2775
20	3500	301	3199
21	4000	548	3452
22	4500	430	4070
23	5000	442	4558

Table - 3

Effect of pH on the adsorption of Methylene blue on ARH at 25 °C

Volume = 100 ml

Initial Concentration = 1000 mg/l

ARH added = 1 g

S.N.	pH	Adsorption (Qe) mg/g ARH
1	2.7	673
2	4.55	963
3	6	945
4	7.1	961
5	8	790
6	10	823
7	11.5	987

Table - 4

Effect of Adsorbent doses on adsorption of Methylene blue at 25 °C

pH = 9

Volume = 100 ml

Methylene blue = 1000 mg/l

S.N.	Adsorbent doses (g)	Adsorption Qe (mg/g ARH)
1	0.5	706 (mg/0.5 g)
2	1	978
3	1.5	660
4	2	427
5	4	247

Table - 5

Effect of Temperature on adsorption of Methylene blue onto ARH

pH = 9

Volume = 100 ml

Adsorbent doses = 1 g

M B dye Concentration = 1000 mg/l

S.N.	Temperature (^{o}C)	Adsorption (mg/g)
1	25	458
2	30	867
3	35	900
4	40	906

Table - 6

Values of Langmuir constants for adsorption of MB onto ARH

pH = 9

Temperature = 25 °C

S.N.	1/Ce	1/Qe	Q°	B
1	5	0.02	1219.5	0.3075
2	1	0.0067	1219.5	0.06735
3	0.86	0.005	1219.5	0.12023
4	0.714	0.00402	1219.5	0.2787
5	0.4878	0.003356	1219.5	0.1770
6	0.3846	0.002878	1219.5	0.2647
7	0.27	0.002523	1219.5	0.1865
8	0.207	0.002246	1219.5	0.1677
9	0.1618	0.002025	1219.5	0.12525
10	0.134	0.00184	1219.5	0.1730
11	0.10256	0.001694	1219.5	0.1417
12	0.00786	0.001146	1219.5	0.03268
13	0.00244	0.0010	1219.5	0.030
14	0.002	0.000998	1219.5	0.00324
15	0.001818	0.00095	1219.5	0.00334

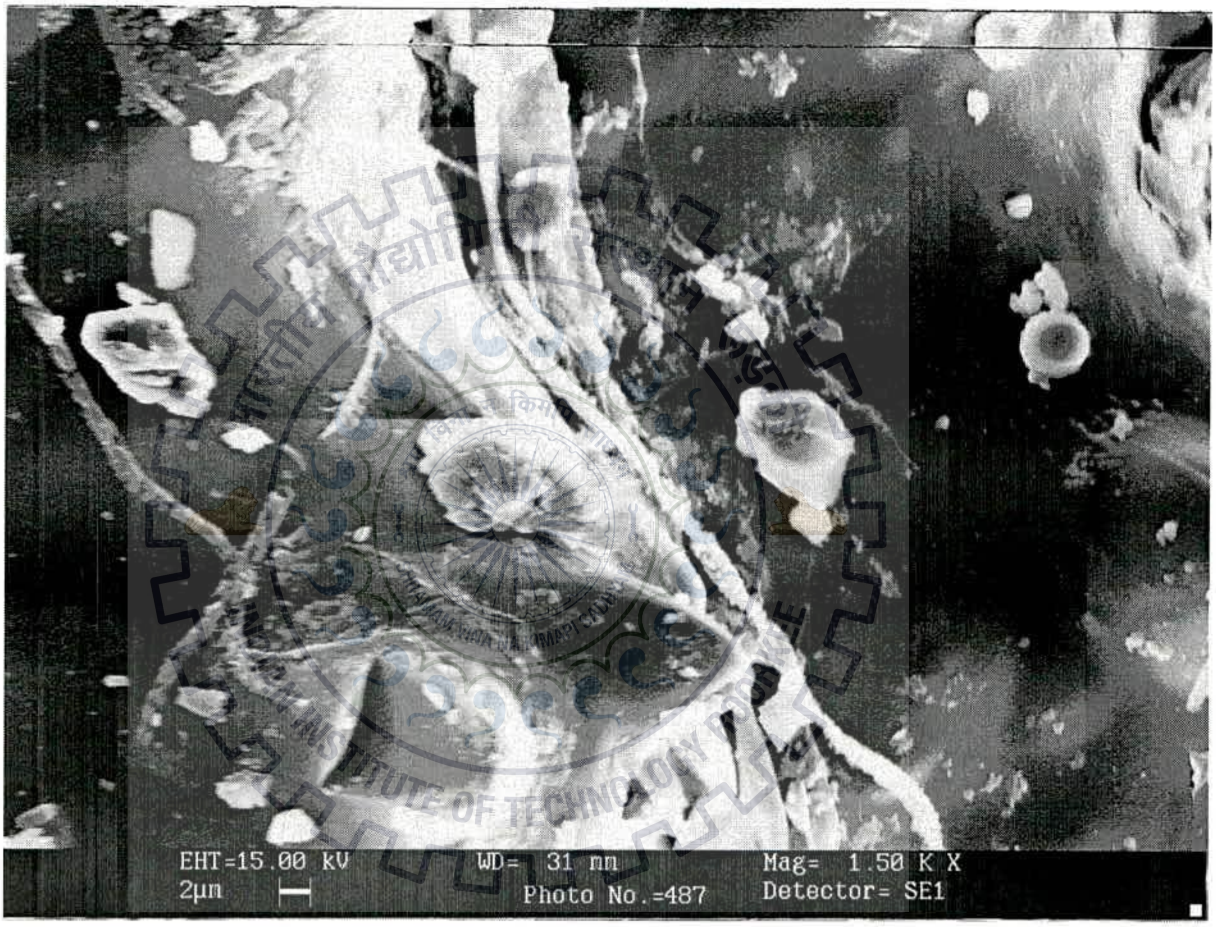

Fig. 1a –SEM image of untreated Rice Husk

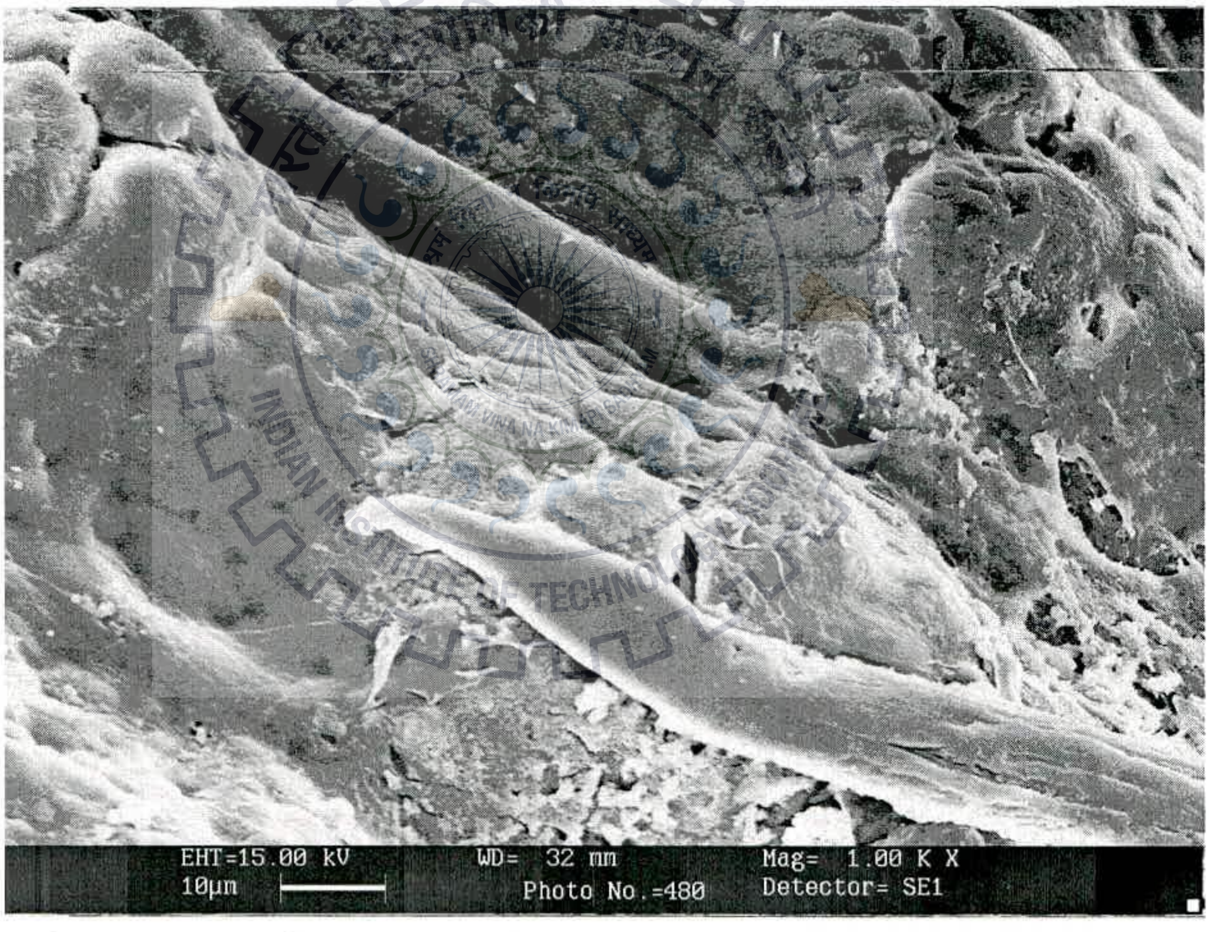

Fig 1b – SEM image of NaOH treated Rice husk

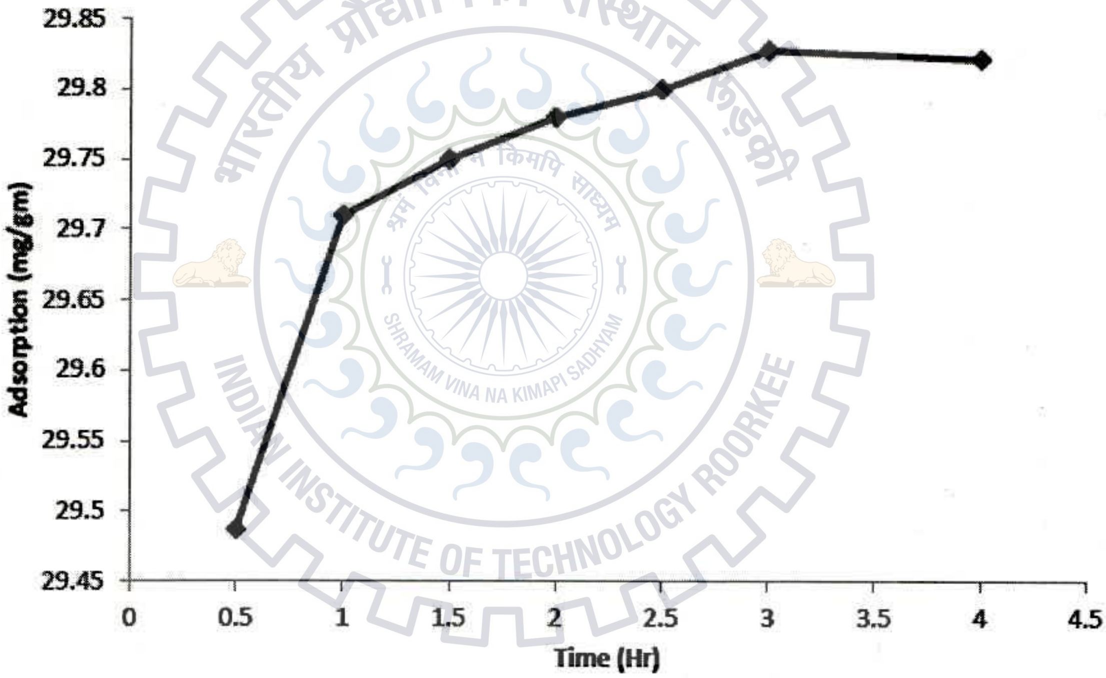

Fig. 2- Adsorption of MB dye as a function of time

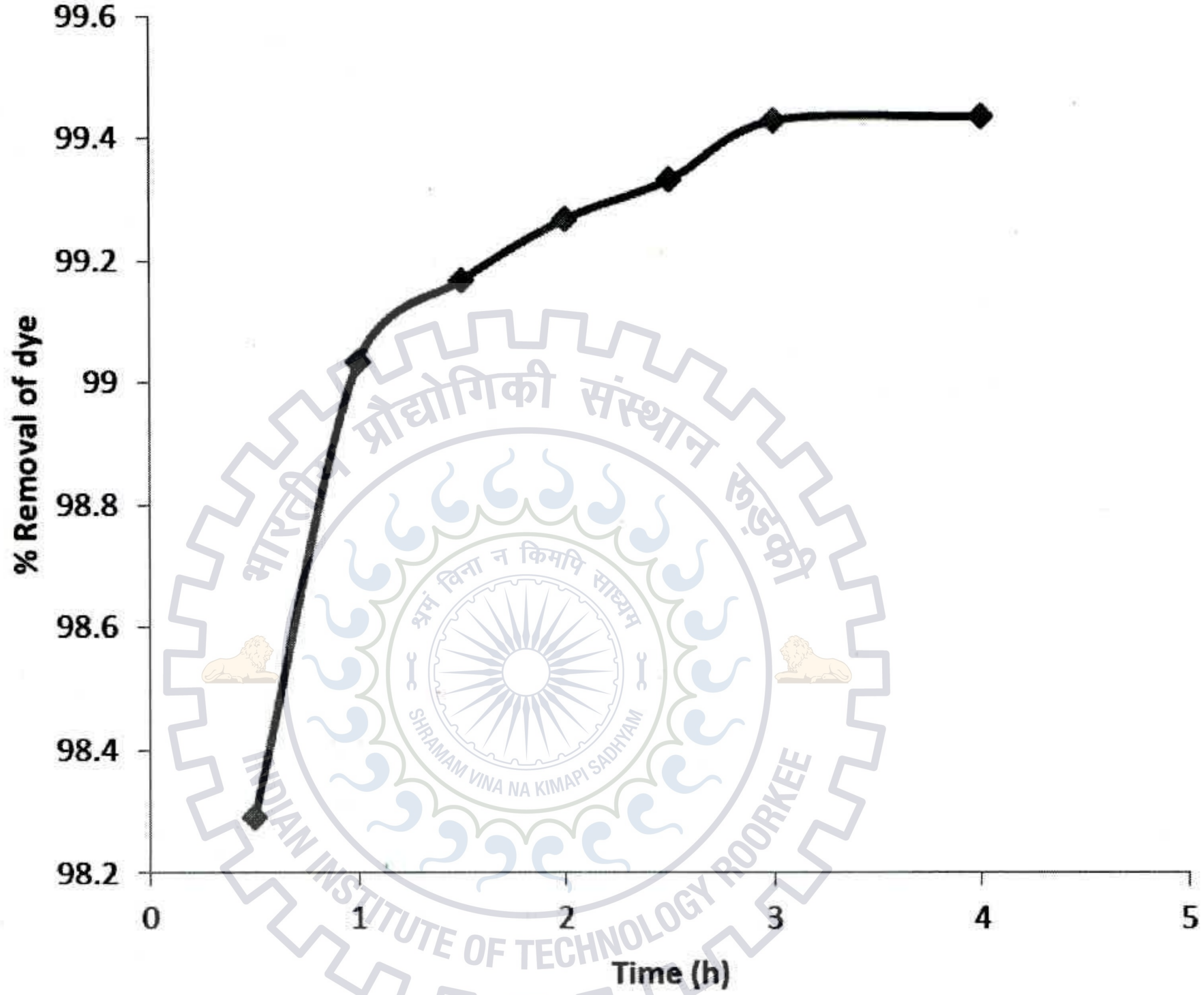

Fig. 3- Percent removal of MB dye as a function of time

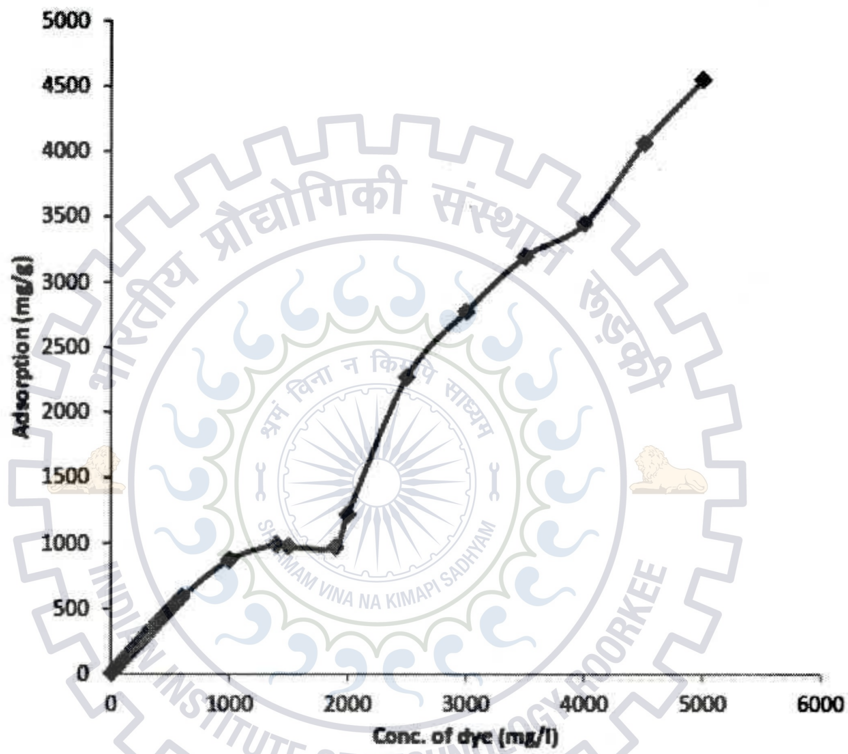

Fig. 4- Adsorption of dye as function of initial concentration of dye

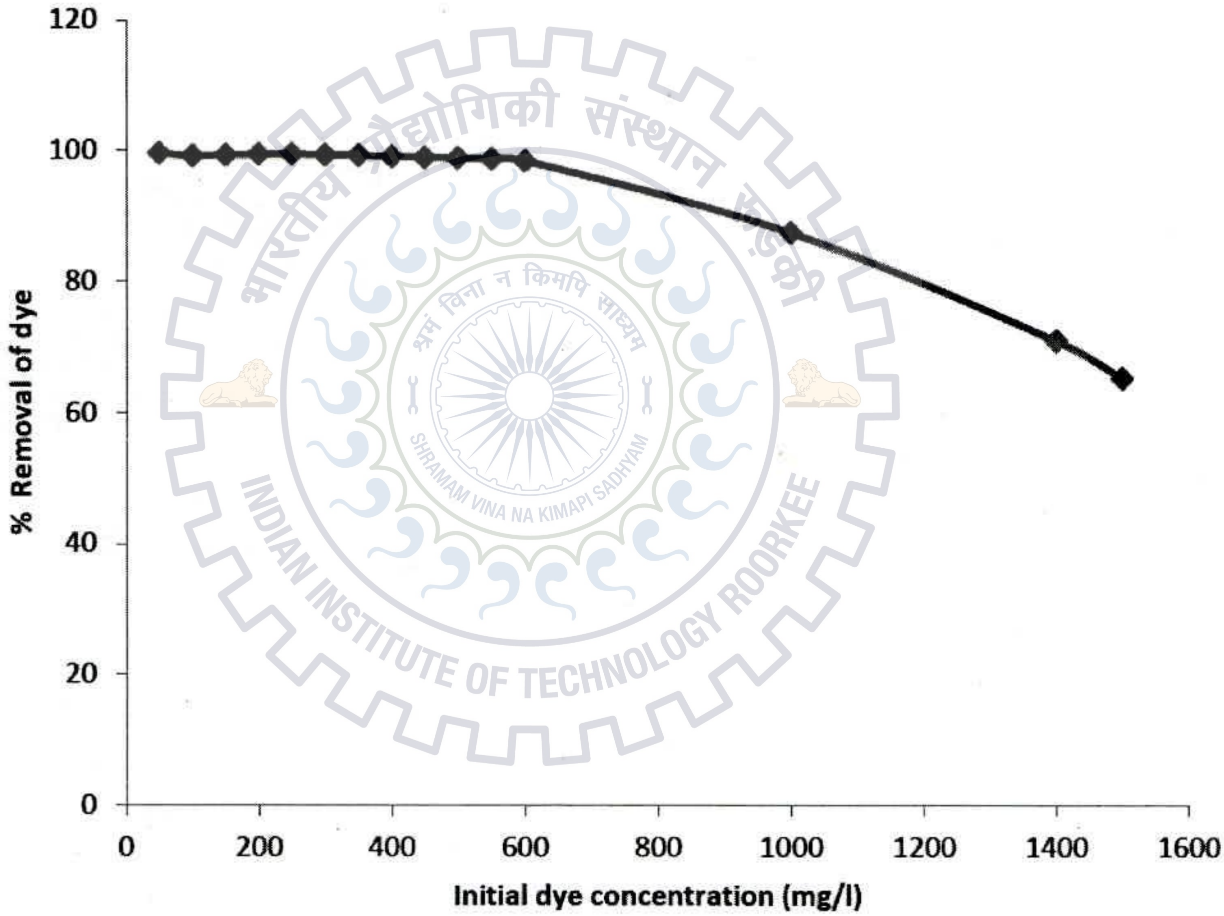

Fig. 5- Percent Removal v/s Initial dye concentration

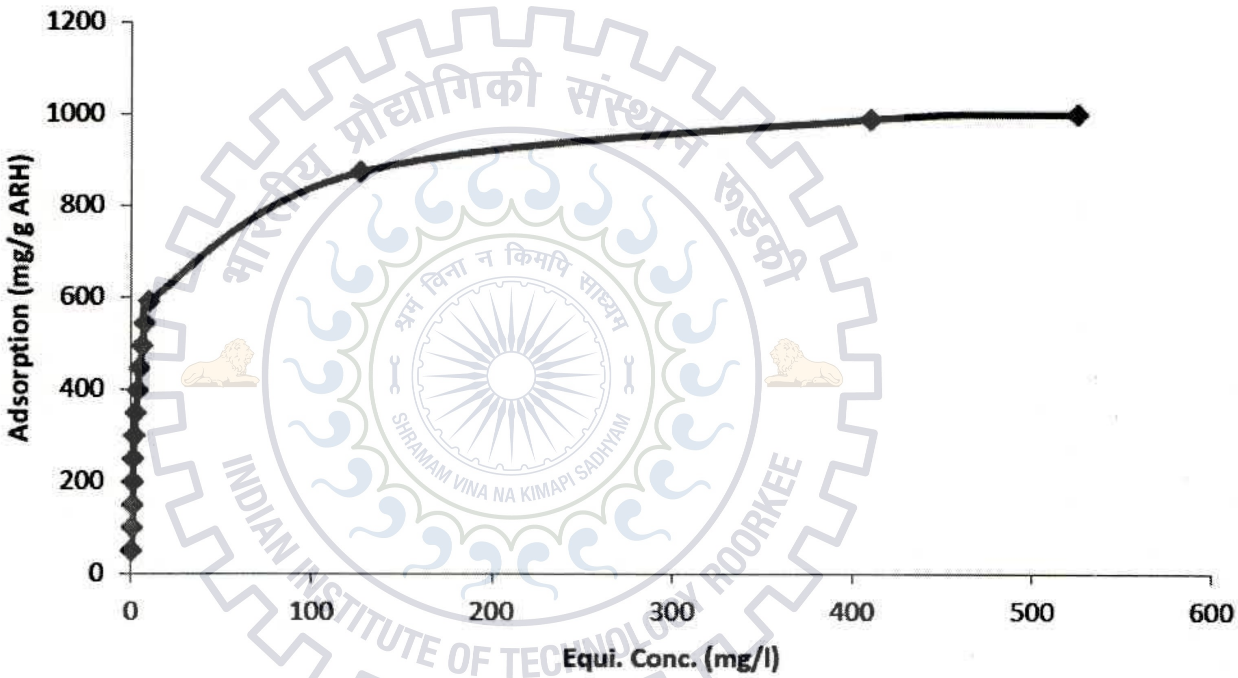

Fig. 6- Adsorption isotherm of MB

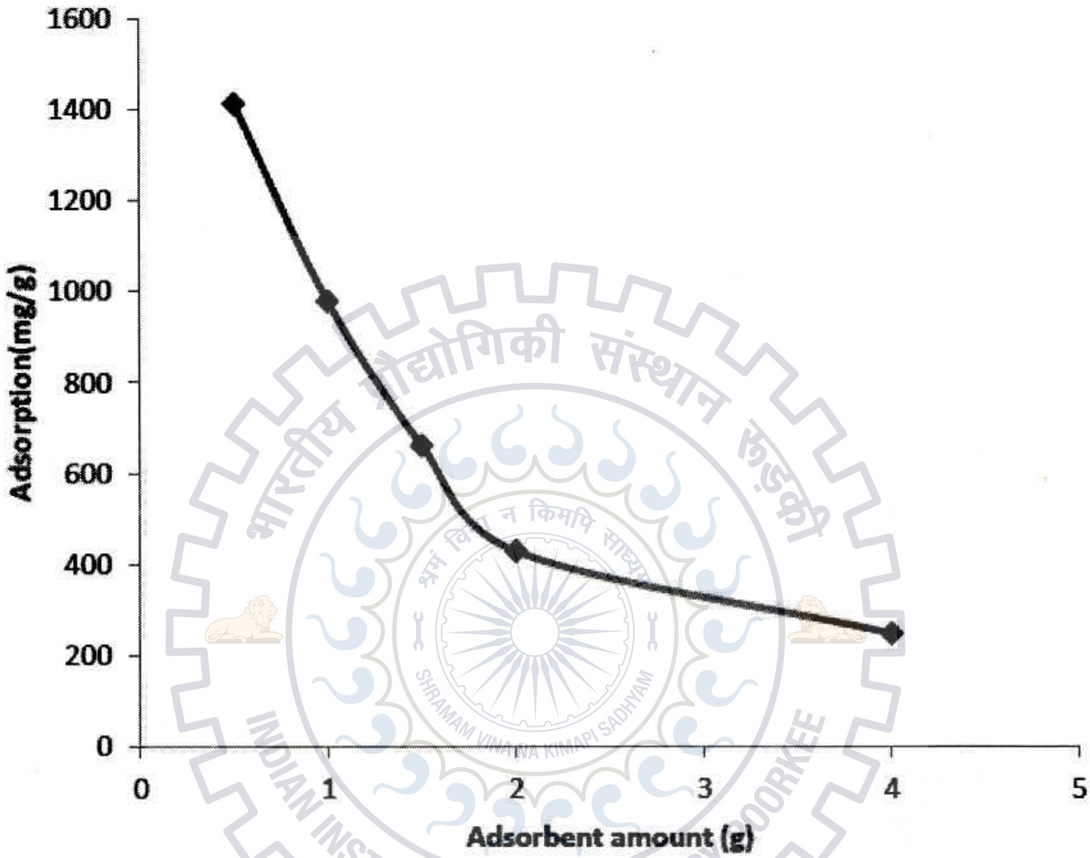

Fig. 7- Adsorption v/s Adsorbent (ARH) doses

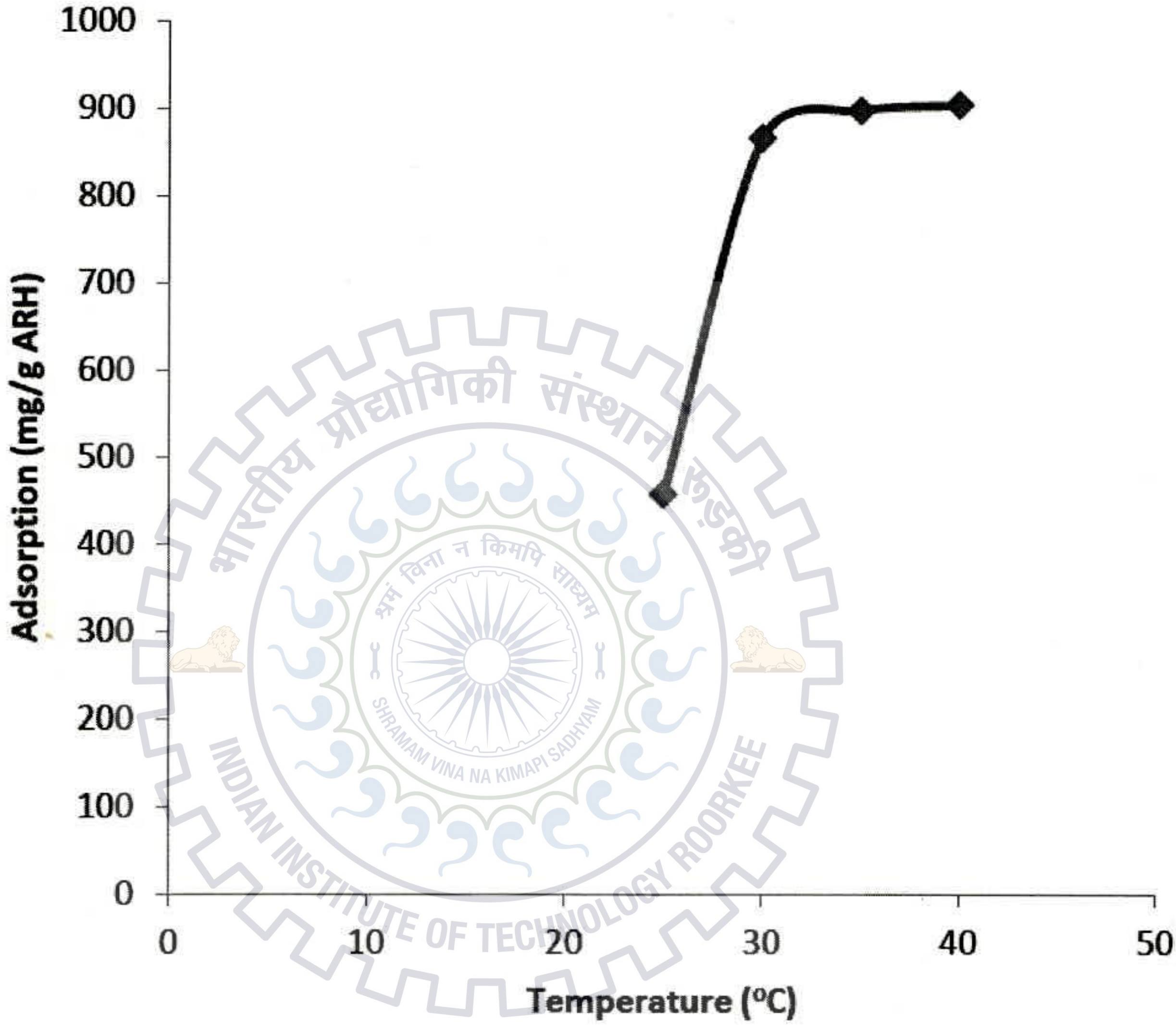

Fig. 8- Adsorption v/s Temperature (^oC)

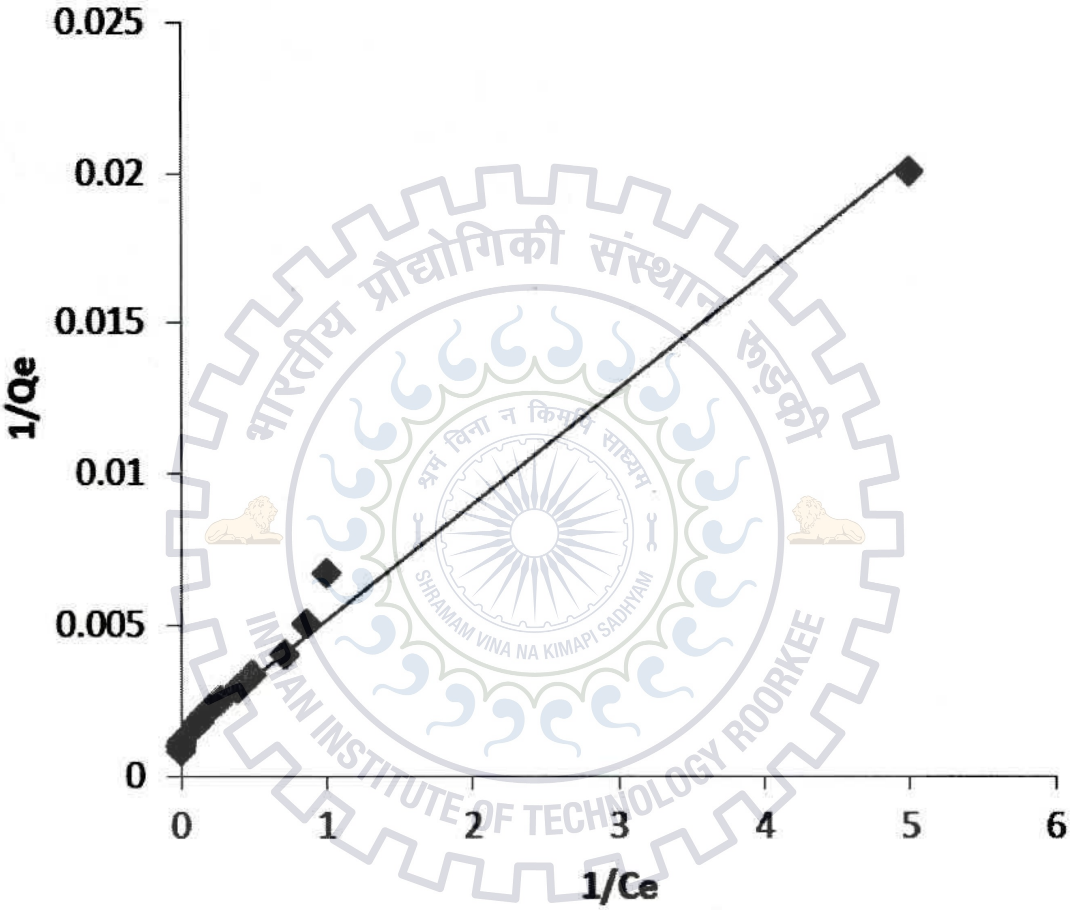

Fig. 9- Langmuir plot for MB at 25 °C

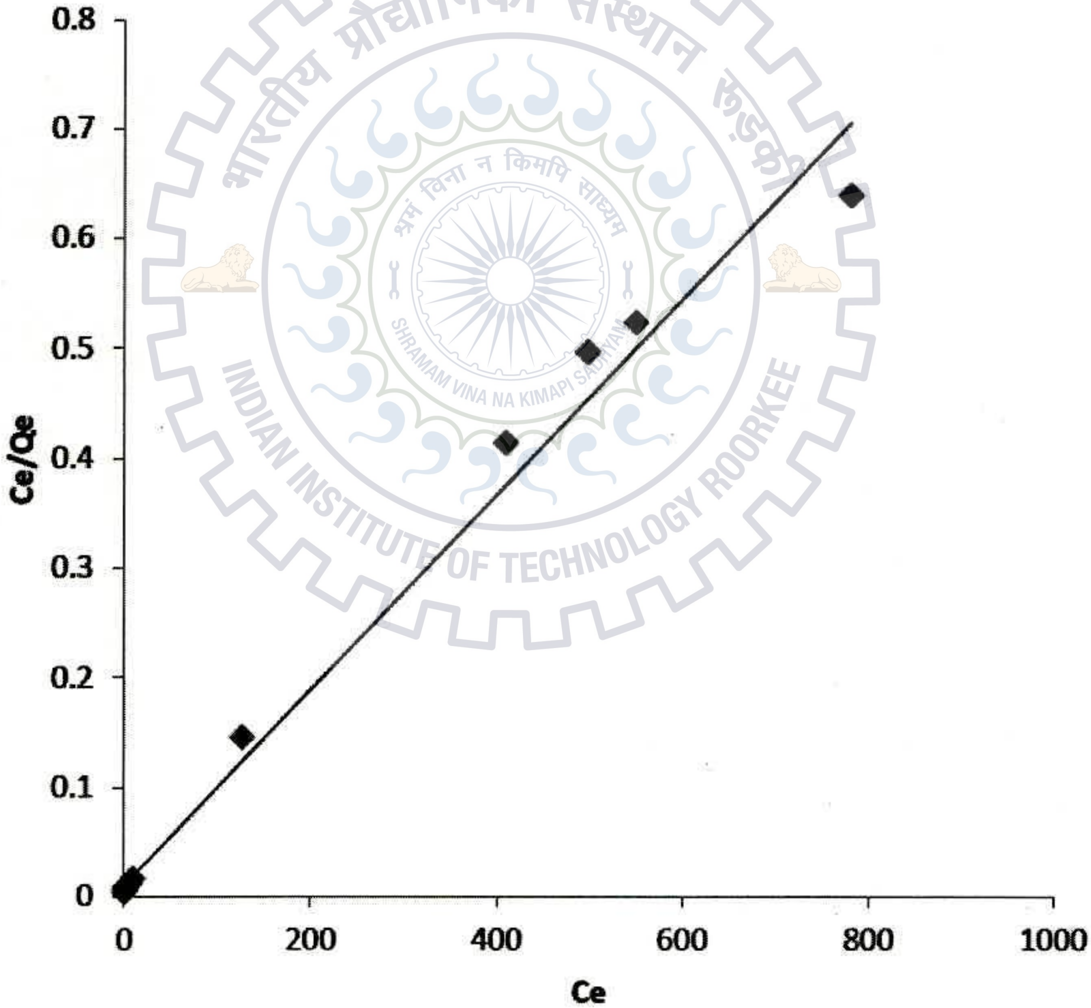

Fig. 10– Langmuir plot for MB at 25 °C

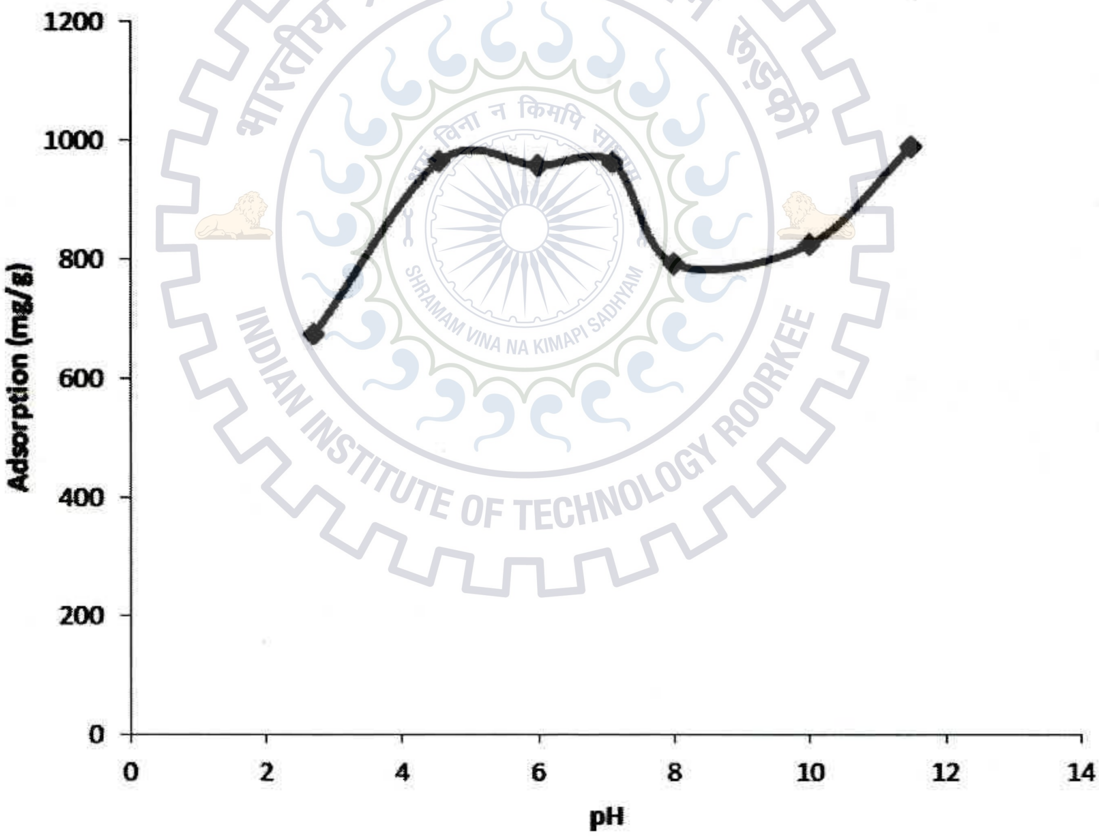

Fig. 11- Adsorption of MB as function of pH

CONCLUSIONS

Inferences drawn from the study are as follows:

1. Results show that rice husk can act as a good adsorbent for removal of Methylene blue dye. It is conceivable to eliminate 4558 mg of MB dye from aqueous solution of concentration 5000 mg/l in 3 h, using 1 g of NaOH activated rice husk.
2. Adsorption of Methylene blue dye increases with increasing temperature, adsorbent doses, and pH.
3. Adsorption data of Methylene blue dye fits into the Langmuir model till concentration range of 50-1500 mg/l at temperature and pH studied.

From above mentioned inferences it is proved that NaOH activated rice husk has excellent potential as an adsorbent for the elimination of Methylene blue dye from water or wastewater.