

ADSORPTIVE SEPARATION OF METHYLENE BLUE DYE USING BANANA PEEL

A dissertation submitted in partial fulfillment of the requirements

for the award of the Degree of

BACHELOR OF TECHNOLOGY

in

CHEMICAL ENGINEERING

by

R. Sunil Kumar Reddy (16001A0856)

S. Firoz (16001A0817)

A. Vikranth Kumar (16001A0829)

R. S. Sowmya (16001A0826)

Under the esteemed guidance of

Dr. DILIP KUMAR BEHARA

Department of Chemical Engineering

JNTUA College of Engineering (Autonomous)

Anantapuramu



JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR

COLLEGE OF ENGINEERING (AUTONOMOUS)

ANANTAPURAMU -515002

2020

i

DEPARTMENT OF CHEMICAL ENGINEERING
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR
COLLEGE OF ENGINEERING (AUTONOMOUS)
ANANTAPURAMU -515002

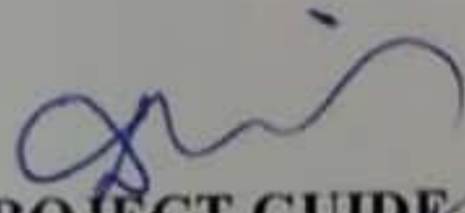


CERTIFICATE

This is to certify that the dissertation entitled “*Adsorptive Separation of Methylene Blue Dye using Banana Peel*” is the bonafide work done and submitted to Jawaharlal Nehru Technological University Anantapur College of Engineering (Autonomous), Anantapuramu during the academic year 2019-2020 in partial fulfilment of the requirements for the award of the Degree of Bachelor of Technology in Chemical Engineering by

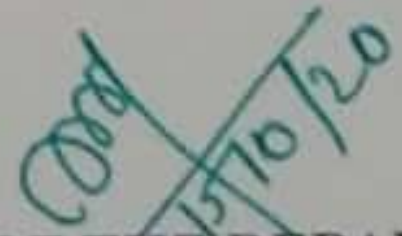
R. Sunil Kumar Reddy	(16001A0856)
S. Firoz	(16001A0817)
A. Vikranth Kumar	(16001A0829)
R. S. Sowmya	(16001A0826)

The contents of this report have not been either partially or fully submitted to any other Institute for the award of either any other degree or diploma.


PROJECT GUIDE

Dr. DILIP KUMAR BEHARA

Assistant Professor
Department of Chemical Engineering
JNTUA College of Engineering
Anantapuramu


HEAD OF THE DEPARTMENT

Dr. Lt. S. SHARADA

Assistant professor
Department of Chemical Engineering
JNTUA College of Engineering
Anantapuramu

ACKNOWLEDGEMENTS

This satisfaction and euphoria that accompanies the successful completion of any task would be incomplete without the mention of the people who made it possible, whose constant guidance and encouragement crown all the efforts with success.

First of all, we take this opportunity to express our deepest gratitude to our project guide Dr. DILIP KUMAR BEHARA, Assistant Professor, Department of Chemical Engineering, JNTUA College of Engineering, Anantapuramu, for giving us this opportunity to work under his esteemed guidance. We are greatly indebted to him for his kindness, generosity, consistent involvement and encouragement throughout our project work.

Our sincere thanks to Dr. Lt. S. SHARADA, Head of the department for providing us with the facilities for completion of our project.

We also express our sincere thanks to Dr. S. V. Satyanarayana, Dr. Subba Rao, Dr. T. Balanarasaiah, Mr. M. Kalyan Kumar and other teaching faculty for their valuable teaching and necessary encouragement throughout the course.

We also convey our thanks to all the Non-Teaching Staff of the department who have helped us in several ways in completion of our project successfully.

With gratitude

R. Sunil Kumar Reddy	(16001A0856)
S. Firoz	(16001A0817)
A. Vikranth Kumar	(16001A0829)
R. S. Sowmya	(16001A0826)

ABSTRACT

Water pollution has become the greatest menace due to the discharge of effluent water from various industrial branches, mainly from the dye manufacturing industries. Adsorption techniques employing solid sorbents are widely used to remove chemical pollutants such as dyes from water. One such cheap and eco-friendly solid adsorbent has been used for removal of Methylene Blue dye from aqueous solution. Liquid phase semi continuous operations were carried out to observe the effect of various parameters such as contact time (50 min - 500 min), initial adsorbate concentration (10mg/l,20mg/l) and adsorbent dosage (0.5g,1g).

The objective of this project work is to study the removal of Methylene Blue from waste water using banana peel powder as an adsorbent. Adsorption tends to increase with increase in contact time, but after some time, it gradually approaches a constant value, denoting attainment of equilibrium. The dye removal efficiency increases from 12.5% to 67.5% in case of 15 mg/l and 9.1% to 72.72% for banana peel powder by varying contact time from 50 min to 300 min.

As initial concentration of the dye increases, percentage removal of the dye decreases. As adsorbent dosage increases, percentage removal of the dye increases. Study of Freundlich, Langmuir, Temkin adsorption isotherms were carried out and best fitting models for adsorption isotherms were suggested as Langmuir Isotherm. The isotherms were simulated using python. Study of Pseudo First order and Pseudo Second order rate kinetics were carried out and the process of adsorption with treated bio-sorbent follows Pseudo First order kinetics than Pseudo Second order kinetics.

LIST OF CONTENTS

Title	Page No.
Certificate	ii
Acknowledgments	iii
Abstract	iv
List of figures	vi
List of tables	vii
Nomenclature	viii
CHAPTER 1. INTRODUCTION	1-7
CHAPTER 2. LITERATURE REVIEW	8-15
CHAPTER 3. EXPERIMENTAL WORK	16-22
CHAPTER 4. RESULTS AND DISCUSSION	23-33
CHAPTER 5. CONCLUSIONS	34
CHAPTER 6. REFERENCES	35-37

LIST OF FIGURES

Fig No.	Title	Page No.
1.1	Structure of Methylene Blue dye	03
3.1	Banana Plant	16
3.2	Peel and Fibre Powders	16
3.3	Weighing Balance	18
3.4	UV-Spectrophotometer	19
3.5	Collected samples for calibration chart	19
3.6	Experimental setup	21
3.7	Collected samples	22
4.1	Calibration plot for Methylene Blue	23
4.2	Effect of Contact time on % removal of Methylene Blue	25
4.3	Effect of Adsorbent dosage on % removal of Methylene Blue	26
4.4	Effect of Initial Dye concentration on % removal of Methylene Blue	26
4.5	Freundlich isotherm curves	27
4.6	Langmuir isotherm curves	28
4.7	Temkin Isotherm	29
4.8	Python plots of adsorption isotherms	31
4.9	The Pseudo First order kinetics	32
4.10	The Pseudo Second order kinetics	33

LIST OF TABLES

Table No.	Title	Page No.
4.1	Effect of Contact time on % removal of Methylene Blue	24
4.2	Effect of Adsorbent Dosage on % removal of Methylene Blue	25
4.3	Effect of Initial Dye Concentration on % removal of Methylene Blue	26
4.4	Freundlich isotherm values	27
4.5	Langmuir isotherm values	28
4.6	Temkin isotherm values	29
4.7	Kinetic Constants for Bio-Sorbents	29
4.8	Estimated parameters of Kinetic models	33

NOMENCLATURE

UV Spectrophotometer = Ultra-Violet spectrophotometer

MB = Methylene Blue

T = time(min)

q_e = Equilibrium capacity of dye on adsorbent (ml/L)

q_t = Adsorption capacity at time (mg/g)

C_e = Equilibrium concentration of dye solution (ml/L)

q_0 = Monolayer adsorption capacity of the adsorbent (mg/g)

C_0 = Initial Dye Concentration(mg/L)

k_F = (Dimensionless constant) Freundlich Adsorption Constant indicates Capacity of Adsorption

n = (Dimensionless Constant) Freundlich Adsorption Constant indicates intensity of Adsorption

CHAPTER-1

INTRODUCTION

The need to maintain a cleaner environment for the survival of both aquatic and terrestrial lives including human beings is very crucial and is a subject of increasing concern to the environmentalist. Pollution caused by agents such as heavy metals and dyes are amongst the list which rendered the environment unwholesome and posed serious health concern to the populace. Effluents from industries such as dyestuff, textiles, leather, paper, printing, plastic and food contain various dyestuffs.

1.1. Environmental Pollution:

One of the greatest problems that the world facing is Environmental pollution. It has been increasing with every passing year causing grave and irreparable damage to the earth. There are five basic types of pollution in environmental pollution namely air, water, soil, noise and light pollution. In the present study we are concerned with the water pollution caused by Synthetic dyes, its effects and methods of treatment.

1.2. Water Pollution:

Water pollution caused by the release of industrial waste products into lakes, rivers, and other water bodies, has made marine life no longer safe. Humans pollute water with large scale disposal of garbage, flowers, ashes and other household waste. The pollution of water due to effluents from textile dyeing industries has been a serious concern and is the point of discussion in the present study.

1.3. Dyes:

Dye, a highly coloured and synthetic substance contain at least one chromophore (colour bearing group) and auxo chromes (colour helpers) which impart intense colours to them and are undesirable and disgusting in wastewater. Water soluble dyes are characterized by their biodegradable ability and conventional treatment techniques such as flocculation, chemical oxidation, and membrane separation are not suitable. Nevertheless, adsorption has proven to be potentially powerful because of its imaginable opportunity to design the chemical composition of the adsorbent surface.

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc to colour their products. The dyes are left as a major waste from the industries. Colour is one of the characteristics of an effluent which is easily detected and readily traced back to source.

Today more than 100000 commercial dyes are available in market and nearly one million tonnes per annum are produced, whereas 10% of dyes are released in environment and natural resources as dyestuff waste. This production is increased day by day to meet the needs of growing population also increases the release of dye effluent.

Many dyes are organic compounds. These may be natural and synthetic. Dyes are classified according to their solubility and chemical properties. The classification includes Acidic dyes, Basic dyes, Vat dyes, Reactive dyes and Disperse dyes. Some of the dyes also find their importance in food industries which are known as food additives. The discovery of manmade (synthetic) dyes started from 19th century because of the less adhesive characteristic of natural dyes. This reason made us to select one of the synthetic dyes namely **Methylene blue** because of its adverse effects on humans and aquatic life.

Applications of various types of dye:

Azoic: Lighter colouring dyes that fade quickly but are cheap to use.

Acid: Acid-based dyes are used mostly on nylons and wools.

Sulphur: These dyes are combined with caustic soda and water to colour clothing, but they lighten quickly.

Reactive: These dyes used mostly in dye as a reaction to certain fibres, and are best used on silk, wool and acrylics.

Oxidation: these dyes start off without colour and are combined with specific chemicals to create new colours. This type of dye is used in a lot of hair colouring.

Mordent: this is a chrome-based dye that has to be blended with different types of acid to colour wools and cotton.

Solvent: this dye is usually used in organic dyeing processes, because it can be used with organic compounds.

Vat: these dyes require four steps of processing, starting off in a vat, and then combined with certain chemicals.

1.4. Health Effects:

Dyes may affect the photosynthetic activity in aquatic life due to decreased light penetration and may also be toxic to some aquatic life due to presence of metals, aromatics etc. It can also cause severe damage to human beings such as disfunction of kidney, reproductive system, liver, brain and central nervous system.

1.5. Methylene Blue:

Methylene blue, also known as **methylthioninium chloride**. Methylene blue (or MB) is a basic aniline dye with the molecular formula $C_{16}H_{18}N_3SCl$ and chemically named as 3,7bis(Dimethyl amino)-phenothiazin-5-ium chloride or Tetra methyl thionine.

Methylene blue is a dye that was the earliest synthesized antimalarial drug having first been tested at the end of the nineteenth century. Methylene blue is used as a dye or staining agent to make certain body fluids and tissues easier to view during surgery or an x-ray or other diagnostic exam.

As a dye, Methylene blue can cause eye burn which may be responsible for permanent injury to the eyes of human as well as aquatic animals. It can also cause irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhoea. Methylene blue also causes irritation to the skin when in contact with it, methylene blue also turns urine and other body fluids blue temporarily, so those receiving the drug need to be warned to avoid unnecessary alarm.

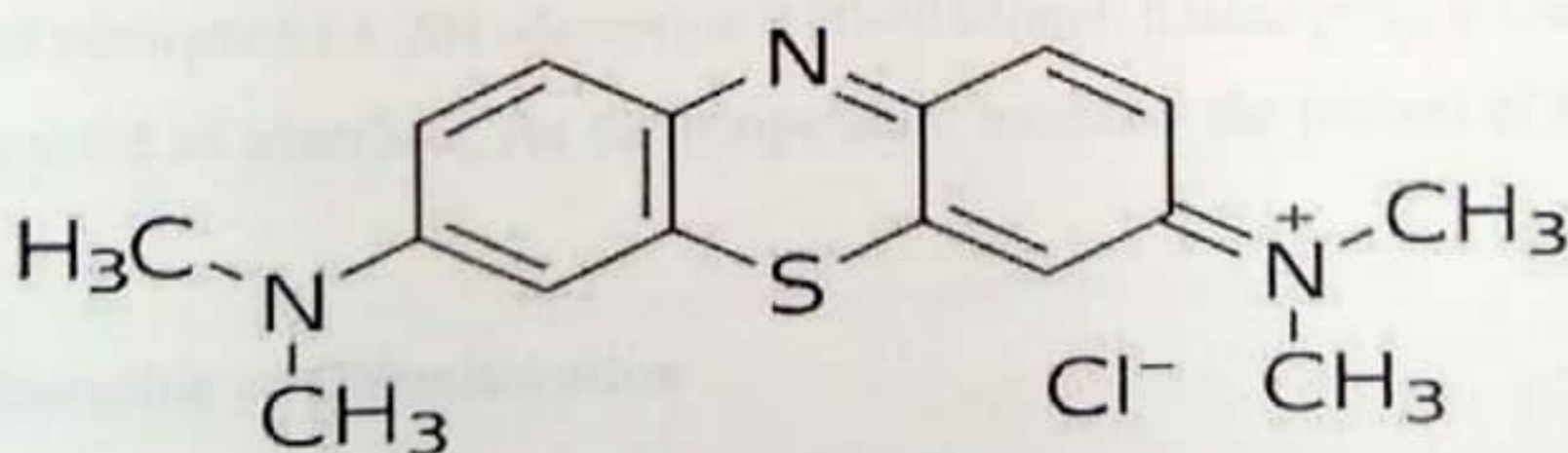


Figure 1.1: Chemical structure of Methylene Blue Dye

There are various ways to remove dyes from wastewater discharges like coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation. However, most of the methods for the

removal of dyes from dye containing wastewater have serious restrictions such as high cost, formation of hazardous by-products or intensive energy requirements. Therefore, the development of efficient, low-cost and environmentally friendly technologies to reduce dye content in wastewater is extremely necessary. Coagulations, chemical and electrochemical oxidations have low feasibility on large scale plants. Adsorption is rapidly gaining prominence among the treatment technologies and has noted that adsorption can produce high-quality water. Adsorption is preferred over these processes and is widely used due to low cost and high performance. Common adsorbents are activated carbon, alumina silica, wood, Fuller's earth, fired clay, and metal hydroxides. Economic advantages, performance efficiencies and environment are the main concerns when selecting an adsorbent, thus researchers generally goes for using low-cost adsorbents like activated carbon produced from banana peel.

1.6. Adsorption:

A mass transfer process which involves the accumulation of substance at the interface of the two phases, such as, gas-solid or liquid-solid is known as Adsorption. In this process adsorbate (which gets adhered) forms a layer on the surface of the adsorbent (the surface on which the adsorbate gets adhered). It is a surface phenomenon. The reverse of adsorption is termed as Desorption.

Physical Adsorption or Physisorption

When the force of attraction existing between adsorbate and adsorbent are weak Van der Waals forces of attraction, the process is called Physical Adsorption or Physisorption. Physical adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. ΔH adsorption is 20-40 kJ/mol. It takes place at low temperature below boiling point of adsorbate. As the temperature increases the process of Physisorption decreases.

Chemical Adsorption or Chemisorption

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bonds, the process is called Chemical adsorption or Chemisorption. Chemisorption takes place with formation of unit-layer of adsorbate on adsorbent. It has high enthalpy of adsorption i.e. ΔH adsorption is 200-400 kJ/mol. It can take

place at all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

1.6.1. Advantages of Adsorption:

Adsorption process possess more advantages when compared with other separation process because of its

High removal efficiency

Low maintenance costs

Ease of operation

Generation of no toxic slurries

Heterogeneous catalysis

Separation

1.7. Aim and Scope of the Present Study:

The main aim of the present study is to enhance the possibilities of developing an emphatic method for the removal of dyes from an aqueous solution by using the adsorbent namely *banana peel*. Many literatures have been reported that for the adsorption of dyes, factors like cost factor, slow pace of the process, residual toxicity and the rational losses makes them unfit to be used as agreed adsorbents. Hence the study mainly focuses on the identification of natural adsorbent which are capable of meeting the above criteria.

This investigation is focused on the adsorption of methylene blue on banana peel powder.

1.8. OBJECTIVES:

The following are the objectives of the work:

- Preparation of activated carbon from banana peel and dye solutions.
- Plotting of calibration chart.
- Calculation of various parameters(contact time, adsorbent dosage, initial dye concentration) on % removal of MB dye.
- Plotting of Adsorption Isotherms(both theoretical and simulated)
- Modelling of Adsorption Rate Kinetics.
- Estimation of kinetic parameters.

1.9. SCOPE OF THE FUTURE WORK;

The adsorbent used for the removal of methylene blue dye from aqueous solution, have no significant reports in literature. But in this study, the banana peel derived activated carbon has been utilized as suitable and effective adsorbent for the removal of MB dye from aqueous solution.

Several methods are available to modify the adsorbent surfaces chemically, and many plant matters are available as cost-free adsorbents, which may be utilized and modified, by any of the established surface modification methods. The prepared adsorbents may definitely be a better alternative to the commercially available adsorbents.

Therefore, a detailed adsorption study in the removal of dyes from wastewater could be carried out. Both industrially and commercially, adsorption is carried out in a packed column using activated carbon.

There are a lot of unexplored plant matters, and agricultural wastes available in India, which can be utilized to treat different kinds of industrial waste water. These materials can be chemically treated and surface modified, using physical or chemical methods, to prepare more efficient adsorbents, which serve as better alternatives to the commercial adsorbents.

There are several topics that can be addressed in continuation to this work. A brief discussion of these issues is presented below.

1. The prepared activated carbon can be used for the removal of other toxic metals and dyes from industrial wastewater.
2. The prepared activated carbon can be used for the removal of detergents, herbicides, pesticides and poly-aromatic hydrocarbons.
3. The prepared activated carbon can be used in air pollution control, solvent recovery, food processing, chemical and pharmaceutical industries, metal recovery and in catalysis.
4. The prepared activated carbon can be used in column adsorption study which can be used in industries.
5. This method for the preparation of activated carbon can be used for other low-cost biomass materials and by-product of agriculture and agricultural industries.

6. Cost analysis for the adsorption of dyes onto the low-cost adsorbent used in this study prepared from the agricultural solid waste material can be taken out and compared with the cost of commercially activated carbon.

7. The efficiency of the prepared low-cost activated carbon in the removal of other pollutants like phenols and toxic metals can be considered.

CHAPTER 2

LITERATURE REVIEW

Mubarak *et al.*, 2014 focused on the adsorption of the blue methylene on banana peels powder. The studies led to determine contacting time (40 minutes for 90% elimination of substrate methylene blue). However, this contacting time can vary with dye concentration. The optimization of parameter such as the temperature, agitation and initial concentration of dye has showed a sensitive improvement of the capacity and rate adsorption. Moreover, the adsorption of this compound is well described by both Langmuir and Freundlich isotherm models.

Ma *et al.*, 2015 prepared and investigated banana peel-activated carbon (BPAC) with a very high surface area of $1,950 \text{ m}^2 \text{ g}^{-1}$ for the removal of methylene blue (MB) or Orange II dye molecules from aqueous solutions. Results of adsorption experiments showed that the BPAC exhibited high adsorption capacity with cationic dyes. The maximal Orange II and MB uptakes were determined to be more than 333 and $1,263 \text{ mg g}^{-1}$, respectively. The zeta-potential analysis revealed that surface charge of BPAC is negative and hence the present activated carbon is excellent for adsorption of MB cationic dye from water. The adsorption equilibrium, kinetics, and thermodynamics of MB dye were investigated and the results indicated a monolayer chemical adsorption involving electrostatic attraction. BPAC was found to be a highly promising material for the effective removal of cationic contaminants such as MB dye from water.

Amela *et al.*, 2012 studied the removal of a basic dye, methylene blue, from an aqueous solution by biosorption on banana and orange Peels waste. The bio sorbent was chemically modified. To mentioned functional groups in order to determine their contribution to the adsorption of dyes. Fourier transform infrared (FTIR) was investigated. Kinetic study was also carried out to observe the effects of various process parameters. The maximum values of adsorption capacities for activated banana peel (ABP) was $19,671 \text{ mg/g}$ and $18,647 \text{ mg/g}$ for natural banana peel (NBP) at pH 4–8, 20°C . The results followed kinetic of pseudo second-order rate equation. The suitability of the adsorbent was tested by fitting the adsorption data with four isotherms, namely Freundlich, Langmuir and Temkin. The characteristic parameters for each isotherm had been determined.

Mane et al., 2012 used natural adsorbent banana and orange peel for removal of colour from waste effluent of textile industry. The materials were obtained and treated for the removal of colour at different doses. These materials also evaluated for the removal of colour at different pH and time. The materials were capable of removing colour from waste water, their colour removal capacity for banana peel was 87% and orange peel was 68 % respectively at normal pH and temperature conditions. The equilibrium time was found 55min for orange peel and 45min for banana peel. The experimental adsorption data fitted with Langmuir and Freundlich adsorption isotherms. The experimental result showed that the materials have good potential to remove colour from effluent and good potential as an alternate low-cost adsorbent.

Rafatullah et al., 2010 reviewed low-cost adsorbents for the removal of methylene blue (MB) from solution. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those which are not easily biodegradable. The removal of MB, as a pollutant, from waste waters of textile, paper, printing and other industries has been addressed by the researchers. Currently, a combination of biological treatment and adsorption on activated carbon is becoming more common for removal of dyes from wastewater. Although commercial activated carbon is a preferred adsorbent for colour removal, its widespread use is restricted due to its relatively high cost which led to the researches on alternative non-conventional and low-cost adsorbents. The purpose of this review article is to organize the scattered available information on various aspects on a wide range of potentially low-cost adsorbents for MB removal. These include agricultural wastes, industrial solid wastes, biomass, clays minerals and zeolites. Agricultural waste materials being highly efficient, low cost and renewable source of biomass can be exploited for MB remediation. It is evident from a literature survey of about 185 recently published papers that low-cost adsorbents have demonstrated outstanding removal capabilities for MB.

Jawad et al., 2018 developed Acid-treated banana peel (ATBP) by H_2SO_4 activation to be a potential adsorbent for methylene blue (MB) from aqueous solution. Batch mode adsorption studies were conducted by varying adsorbent dosage (0.02–0.30 g), solution pH (3–12), initial MB concentrations (10–300 mg/L) and contact time (0–1440 min). The adsorption data of MB by ATBP were in agreement with Langmuir isotherm, with maximum adsorption capacities of 250 mg/g at 303 K. The pseudo-first-order kinetic model best described the kinetic data. The adsorption of MB onto ATBP surface was endothermic in nature and spontaneous under the experimented conditions. Results supported the potential use of the ATBP as an effective adsorbent for the treatment of cationic dyes such as MB from aqueous solution.

Enniya et al., (2017) investigated the removal of the methylene blue by adsorption using dried apple peels. For this purpose, various experimental parameters were studied: pH adsorbent dose solution temperature and initial concentration of methylene blue. Adsorption data were modelled using Langmuir, Freundlich and Temkin adsorption isotherms.

Hashem et al., (2016) activated carbon (AC) derived from orange, mandarin, and banana peels has been utilized as an adsorbent for the removal of a cationic dye, methylene blue, from aqueous solutions. The batch adsorption technique was used with these materials under different conditions of contact time, initial dye concentration (10–100 mg/L), solution pH (4–12), and AC dosage (0.05–0.5 g). The characteristics of the prepared ACs were studied via FTIR, mercury porosimeter, and iodine number determination. Banana peels showed the highest removal efficiency compared with the other fruit peels. Adsorption isotherms were modelled with the Langmuir and Freundlich isotherms, and good fitting to the Freundlich isotherm was obtained. The kinetic data were analysed using pseudo-first-order, second-order, and intra particles diffusion models, with good fitting to the pseudo-second-order model. The obtained results indicate that AC represents an efficient low-cost adsorbent for the removal of MB from aqueous solutions.

Shalini Gautam et al., (2016) had investigated and focused on Removal of methylene blue from waste water using banana peel as adsorbent. The potential feasibility of activated and inactivated Banana peel powder for the removal of Methylene Blue from aqueous solution was investigated. The adsorption studies were carried out under varying conditions of pH, adsorbent dose and contact time. For both the adsorbents, the removal efficiency decreased as the adsorption increased, the percentage removal in activated adsorbent increased from 65% to 90% when the dose of the adsorbent was increased from 0.02 grams to 0.1 grams, and in case of inactivated adsorbent it increased from 55% to 84%. When the contact time was increased from 20 minutes to 120 minutes, maximum percentage removal was obtained at 120 minutes with 94% adsorption in case of activated adsorbent and 90% adsorption in case of inactivated adsorbent.

Flávio André Pavan et al., (2008) had investigated and focused on Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. The removal of colour from aquatic systems caused by presence of synthetic dyes is extremely important from the environmental view-point because most of these dyes are toxic, mutagenic and carcinogenic. In this present study, the yellow passion fruit (*Passiflora edulis* Sims. f.

flavicarpa DeGeneres) peel a powdered solid waste, was tested as an alternative low-cost adsorbent for the removal of a basic dye, methylene blue (MB), from aqueous solutions. Adsorption of MB onto this natural adsorbent was studied by batch adsorption isotherms at room temperature. The effects of shaking time and pH on adsorption capacity were studied. An alkaline pH was favourable for the adsorption of MB. The contact time required to obtain the maximum adsorption was 56 h at 25°C. Yellow passion fruit peel may be used as an alternative adsorbent to remove MB from aqueous solutions.

B.H. Hameed *et al.*, (2008) had investigated and focused on Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. The potential of garlic peel (GP), agricultural waste, to remove methylene blue (MB) from aqueous solution was evaluated in a batch process. Experiments were carried out as function of contact time, initial concentration (25–200 mg/L), pH (4–12) and temperature (303, 313 and 323 K). Adsorption isotherms were modelled with the Langmuir, Freundlich, and Temkin isotherms. The data fitted well with the Freundlich isotherm. The maximum monolayer adsorption capacities were found to be 82.64, 123.45, and 142.86 mg/g at 303, 313, and 323 K, respectively. The kinetic data were analysed using pseudo-first-order and pseudo-second-order models. The results indicated that the garlic peel could be an alternative for more costly adsorbents used for dye removal.

Taha M. Elmorsi *et al.*, (2011) had investigated and focused on Equilibrium Isotherms and Kinetic Studies of Removal of Methylene Blue Dye by Adsorption onto Miswak Leaves as a Natural Adsorbent. The effects of [MB]₀, pH, contact time and adsorbent dose were evaluated. An alkaline pH (10.6) was favourable to the adsorption of MB dye. Adsorption isotherm models, Langmuir, Freundlich and Temkin were used to simulate the equilibrium data. Langmuir equation was found to have the highest value of R² compared with other models. Furthermore, it was found that miswak leaves have a high adsorptive capacity towards MB dye (200 mg/g) and show favourable adsorption of MB dye with separation factor ($RL < 1$). In addition, pseudo-first-order, pseudo-second order and intra-particle diffusion were used to study the kinetics of MB adsorption onto miswak leaves. Adsorption process undergoes pseudo-second order kinetic as proved by the high value of R² and the low value of sum of squared error (SSE percentage). Results indicated that intra-particle diffusion is not the limiting step, and the adsorption process is spontaneous as indicated by the negative value of the Gibb's energy.

Helder Pereira de Carvalho *et al.*, (2015) had investigated and focused on the improvement of Methylene Blue (MB) from aqueous solutions by an electrocoagulation (EC)/banana peel (BP) adsorption coupling process. The kinetics of this coupling process was studied using different amounts of adsorbent material in order to identify the most appropriate dosage, for enhancing wastewater treatment. The influence of current density on the removal efficiency and energy consumption of the EC/BP coupling process was also determined. The coupling between electrocoagulation and BP showed that the addition of an appropriate BP dosage resulted in the enhancement of the removal rate of dyes especially at lower current densities, and in a considerable reduction in the contact time compared to the conventional simple EC process and simple adsorption process, having achieved efficiency removal of approximately 99%. Based on the high removal efficiency, short contact time and low energy consumption, the EC/BP coupling method could be recommended instead of the conventional simple EC.

D. Kavitha *et al.*, (2005) had investigated on Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Kinetic study showed that the adsorption of dye on coir pith carbon was a gradual process. Lager Gren first-order, second-order, intra particle diffusion model and Bingham were used to fit the experimental data. Equilibrium isotherms were analysed by Langmuir, Freundlich, Dubnin–Radushkevich, and Temkin isotherm. The adsorption capacity was found to be 5.87 mg/g by Langmuir isotherm for the particle size 250–500 μm . The equilibrium time was found to be 30 and 60 min for 10 and 20 mg/L and 100 min for 30, 40 mg/L dye concentrations, respectively. A maximum removal of 97% was obtained at natural pH 6.9 for an adsorbent dose of 100 mg/50 mL and 100% removal was obtained for an adsorbent dose of 600 mg/50 mL of 10 mg/L dye concentration. The pH effect and desorption studies suggest that chemisorption might be the major mode of the adsorption process. The change in entropy (ΔS^0) and heat of adsorption (ΔH^0) of coir pith carbon was estimated as 117.20 J/mol/K and 30.88 kJ/mol, respectively. The high negative value of change in Gibbs free energy indicates the feasible and spontaneous adsorption of methylene blue on coir pith carbon.

Noor A. Abdl-Hussein *et al.*, (2017) had studied the removing of Methylene blue dye (MB) using some plant's material (citrus utrantiforlial) by using batch system. The effect of dye concentrations, contact time, and adsorbent dosages on adsorption process were studied. The obtained results show that, MB dye removal was significantly enhanced with the use of adsorbent weight 0.7 mg which showed removal efficiency up to 94%. While the best contact

time was 90 min with removal efficiency 94.02%, and there was a reverse correlation between the initial dye and the removal efficiency.

Mahammedi Fatiha *et al.*, (2015) had studied the adsorption process using natural clay as an adsorbent for the removal of methylene blue from an aqueous solution. The influence of the initial dye concentration, contact time, pH, temperature, and dosage of bio-sorbent was investigated in batch experiments. This clay was characterized according to the following technique: scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

Shiv Pratap Raghuvanshi *et al.*, (2007) had studied the removal of basic dye (methylene blue) from aqueous solution, is investigated using it in two different forms: in raw form and in chemically treated (with sulphuric acid) form. The effect of contact time, dye concentration, adsorbent dose and the kinetics of adsorption were studied in batch experiments. At neutral pH and 4 gm/L of chemically activated and raw sawdust adsorbents, removal of 98.12% and 97.18% of methylene blue dye (at 100 mg/L concentration) from the aqueous solution, was the best result obtain during study. An average percentages removal difference of less than 5%, between two adsorbents was achieved under different conditions in the experiments. The data fit well in Freundlich isotherm.

Senthil kumar Ponnu Swamy *et al.*, (2010) had studied the methylene blue dye was adsorbed on an adsorbent prepared from cashew nut shell. A batch adsorption study was carried out with variable adsorbent amount, initial dye concentration, contact time and pH. Studies showed that the pH of aqueous solution affected by removal as a result of removal efficiency increased with increasing solution pH. The experimental data were analysed by Langmuir, Freundlich.

R. Karthik *et al.*, (2015) had studied the adsorption of methylene blue dye from water. The maximum adsorption was observed in 250 mg/L, and the same concentration followed for further optimization. For optimization, one parameter at a time method was followed at different pH (3.0, 5.0, 7.0, 9.0, 11), temperature (25, 30, 35, 40, and 45 °C), adsorbent dosage (1, 3, 5, 7, and 10%) and contact time (30, 60, 90, 120, 150, 180, and 210 min). The pH 7 and temperature 40 °C and contact time 120 min were found to be optimum.

Safae Benatar *et al.*, (2017) had studied the removal of methylene blue (MB) dye from aqueous solution by natural clay is used as an adsorbent. The parameters influencing the adsorption of MB such as contact time (20-120 min), adsorbent dose (0.4–4 gm/L), initial dye concentration (100-900 mg/L) temperature (22-60 °C) and pH of the solution (3-10) were studied. The

obtained results showed that the adsorption of MB onto clay is strongly dependent on the temperature, the initial dye concentration and pH of the solution. The kinetic study indicated that the adsorption of MB on the clay was well adapted to the pseudo-second order kinetic with a correlation coefficient $R^2 = 1$.

Himanshu Patel *et al.*, (2013) had studied the removal of Methylene Blue Dye from neem leaf powder. The process parameters like adsorbent dosage, pH, temperature and contact duration have been studied. The experimental data were analysed using Langmuir, Freundlich isotherm, in which adsorption capacities and intensities were evaluated. Three kinetic models, pseudo first-order, second-order and Eolic equations were applied to describe the adsorption process, in which correlation coefficient for each kinetic equation were calculated and evaluated.

Ezerie Henry Ezechi *et al.*, (2015) had studied the methylene blue dye was removed from synthetic effluents, using ageratum conyzoides leaf powder as an adsorbent. Effects of operating parameters such as pH, initial Methylene blue concentration, adsorbent weight and contact time were on methylene blue removal whereas stirring speed was constant at 100 rpm. Methylene blue removal decreased when initial concentration was increased but increased when adsorbent weight was increased. Removal of methylene blue by Ageratum conyzoides leaf powder was rapid and significantly above 80% in all initial concentrations examined. At optimum conditions of pH 3, 20 minutes of contact time and adsorbent weight of 60 mg for Methylene blue initial concentrations of 20 mg/L, 40 mg/L and 60 mg/L were studied.

Enenebeaku K. Conrad *et al.*, (2015) had studied the effectiveness of adsorption for dye removal from waste water has made it an ideal alternative to other expensive treatment methods. The potential of using raw cassava peel (RCP) as an adsorbent for the removal of methylene blue (MB) dye from aqueous solution. The adsorbent was characterized by Fourier transformer infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. The effect of experimental parameters such as pH, contact time, initial concentration of adsorbate and amount of adsorbent dosage was evaluated. The maximum adsorption capacity of RCP for MB was found to be 32.26 mg/g at 343 K and pH 8.0 and 90 mins contact time for 100 mg/L initial MB dye concentration. Adsorption isotherms were developed and equilibrium data fitted well to Langmuir, Freundlich, and Temkin isotherm models. Kinetic studies showed the adsorption process followed pseudo second-order kinetic model.

Sara. Dawood *et al.*, (2016) had studied the adsorption potential of bio-char for the removal of cationic dye Methylene Blue (MB) from aqueous solution. The effects of various temperature profiles on the production of EB bio-char were studied and the most efficient temperature profile was identified at 500 °C. Batch adsorption kinetic study showed that the amount of dye adsorbed q_t (mg/g) depends on various physiochemical process parameters such as initial solution pH, dye concentration, temperature, adsorbent dose. The optimum adsorption conditions were found at the initial dye concentration of 100 mg/l, initial solution pH of 11.3, adsorbent dose of 10 mg and solution temperature 55 °C. Furthermore, pseudo-first-order, pseudo-second-order and intraparticle diffusion models were fitted to examine the adsorption kinetics and mechanisms of adsorption. Equilibrium data were best represented by Langmuir isotherm model and gives a monolayer effective adsorption capacity of bio-char which is comparative to other adsorbents including commercial activated carbon.

Rakesh Kumar Ghosh *et al.*, (2016) had studied the removal of methylene blue from water by cotton stem ash as an adsorbent. The effect of process variables, namely, contact time, solution pH and adsorbent dose on adsorption of MB onto CSA were investigated. The adsorption kinetics and mechanism were tested with pseudo-first-order and pseudo-second-order model respectively. The maximum adsorption capacity of CSA was 20.42 mg/g. The feasibility parameter and free energy change were also calculated.

3. EXPERIMENTAL WORK

3.1. MATERIALS:

3.1.1. Adsorbent Preparation :

The adsorbent used in this work, banana peels powder was first washed with distilled water to remove impurities and then dried in air for 12 days, then ground in mortar and analyzed by size in order to obtain a fraction of powder which passes through 72 mesh and retains on pan.



Figure 3.1: Banana Plant



Figure 3.2: (a) Peel powder

(b) Fiber powder

3.1.2. ADSORBATE:

MB dye is used as adsorbate, discovered by Caro in 1876, its colour is blue, it gives blue coloured solution in aqueous solution, it is a basic cationic dye, heterocyclic aromatic chemical compound. It is a member of thi-azine class of dyes and has ox-red properties. Its chemical formula is $C_{16}H_{18}ClN_3S$, molecular weight is 39.85 g/mol.

3.2. CHEMICALS AND EQUIPMENTS USED:

Methylene Blue Dye, NaOH, UV- Spectroscopy.

In the present study we have been using the equipment's namely:

1. Electronic weighing balance
2. Orbital shaker (RIS-24)
3. pH Meter
4. UV Spectrophotometer

The working principle, mechanism and applications involved in the equipment's are described below.

3.3. ELECTRONIC WEIGHING BALANCE:

3.3.1. WORKING PRINCIPLE :

The basis of the rapid and exact working method of our weigh cells is the principle of Electro Magnetic Force Restoration (EMFR). The basic principle is comparable to a simple beam balance. The weight is laid on one side of the beam (coil arm).

3.3.2. MECHANISM:

The accuracy of weighing required depends on the scale of the reaction; if the reaction is being carried out on the spills of chemicals may seriously damage the mechanism.



Figure 3.3: Weighing Balance

3.4. ULTRA VIOLET-SPECTROSCOPY:

Light may be absorbed by a molecule or compound and this adsorption can readily be monitored. The adsorption of light in the ultra violet visible region of the electromagnetic radiation spectrum is due to electronic transition.

3.4.1. WORKING PRINCIPLE:

Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.

3.4.2. MECHANISM:

Ultraviolet-visible spectroscopy can predict the colour of the sample by using the visible and adjacent (near-UV and near-infrared [NIR]) ranges. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transactions.

3.4.3. APPLICATIONS:

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules.

Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.



Figure 3.4: UV- Spectrophotometer

3.5. METHODS:

3.5.1. Plotting Calibration Curve:

MB blue dye was measured by using electronic weighing balance and mixed with double distilled water to make sample solutions with different dye concentrations of 0 mg/l, 10 mg/l, 20 mg/l, 50mg/l, 100mg/l and their % absorbance were found out by using UV spectrophotometer at maximum wavelength (λ_{max}) of 650 nm. With these values a standard calibration curve was plotted. The equation of the curve was used to calculate the concentrations at various % absorbance values.



Figure 3.5: Collected samples for calibration chart.

3.6. EFFECTS OF VARIOUS PARAMETERS ON % REMOVAL OF METHYLENE BLUE:

3.6.1. EFFECT OF CONTACT TIME:

The effect of contact time on dye removal efficiency was studied by repetitive recycling of dye extract for 7 cycles after equilibrium, with the adsorbent dosage 1 g, initial dye concentration 10 mg/l at a room temperature.

3.6.2. EFFECT OF ADSORBENT DOSAGE:

The effect of adsorbent dosage on dye removal efficiency was conducted by varying it from 0.5 g and 1 g while keeping the initial dye concentration 10 mg/L at room temperature.

3.6.3. EFFECT OF INITIAL DYE CONCENTRATION:

The effect of initial dye concentration on removal of dye, test mixtures containing adsorbent dosage of 1 g was adjusted to various initial dye concentration range. And analysed for residual dye concentration by using spectrophotometer. The observations were carried out at 10 mg/l, 15 mg/l, 20mg/l of initial dye concentration.

3.7. ADSORPTION ISOTHERMS:

Dye solutions were prepared for three different initial dye concentrations were varied such as 10 mg/l, 15 mg/l, 20 mg/l keeping the adsorbent as 1 g. All these solutions were kept for adsorption studies. Their % absorbance were determined using UV spectrophotometer ($\lambda_{max} = 650\text{nm}$). These values were used to calculate C_e and q_e values. With these values we plot curves for Freundlich and Langmuir Isotherms and we determine the best fitting model.

3.7.1. LANGMUIR ISOTHERM MODEL:

$$1/q_e = 1/bq_0 C_e + 1/q_0$$

A curve $1/q_e$ vs $1/C_e$ is plotted, the intercept gives the q_0 value and slope gives the k_L value. The Langmuir equation or Langmuir isotherm relates the coverage or adsorption of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. The constant k_L is the Langmuir adsorption constant and increases with an increase in the strength of adsorption and with a decrease in temperature. Langmuir isotherms were plotted with $1/q_e$ against $1/C_e$.

3.7.2. FREUNDLICH ISOTHERM MODEL:

$$\ln(q_e) = \ln(k_F) + \ln(\ln(C_e))$$

A curve $\ln(q_e)$ vs $\ln(C_e)$ is plotted, the slope gives 'n' value and intercept gives k_F value.

3.8. EXPERIMENTAL PROCEDURE:

In this case, the experimental procedure is simple and done in semi-batch contactor which involves 10 mg/l, 10 mg/l, 15 mg/l, 20 mg/l of methylene blue with 0.5 g, 1 g, 1 g, 1 g respectively, of powdered banana peels as bed (wrapped inside a Whatman filter paper).

Initially, methylene blue solution of 500 ml was prepared. The process was performed at a constant flowrate of 10 ml/min. Then, the samples were collected for each cycle until the equilibrium. The collected samples were measured for absorbance by using UV-Visible Spectrophotometer at a wavelength of 650 nm.

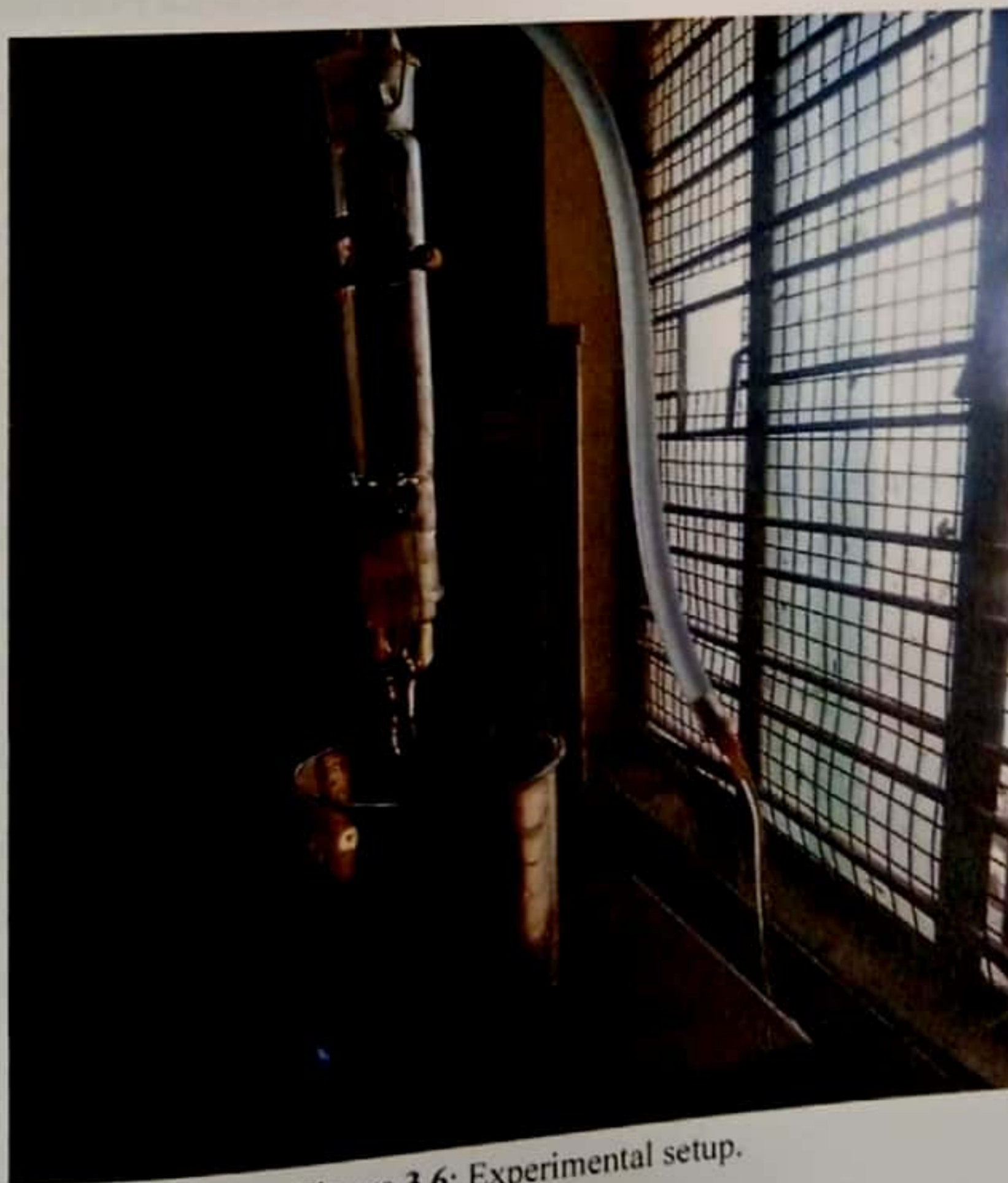


Figure 3.6: Experimental setup.



Figure 3.7: Collected samples.

3.9. ADSORPTION KINETICS:

In order to investigate the mechanism of adsorption and its potential rate controlling steps, kinetic models have been used. The adsorption kinetics of dye removal was analyzed by the pseudo first order, pseudo second order kinetic models.

3.9.1. PSEUDO FIRST ORDER:

$$\ln (q_e - q_t) = \ln q_e - K t$$

The kinetics of adsorption are modelled using the first order rate equation of Lager Gren. The straight-line plots of $\text{Log} (q_e - q_t)$ vs time at ambient temperature indicated the validity of Lange Gren equation and consequently the first order nature of the process involved in present study. The value of K at ambient temperature was calculated from the plot.

3.9.2. PSEUDO SECOND ORDER MODEL:

The Pseudo Second order model considers that the rate of adsorption metal ions is based on the square of number of vacant sites on the adsorbent. The pseudo second order rate equation is represented as,

$$t/q_t = 1/(K q_e^2) + t/q_e$$

A plot of t/q_t versus t should give a linear relationship for the applicability of the second order kinetic.

4.RESULTS AND DISCUSSIONS

4.1.1. CALIBRATION PLOT FOR METHYLENE BLUE

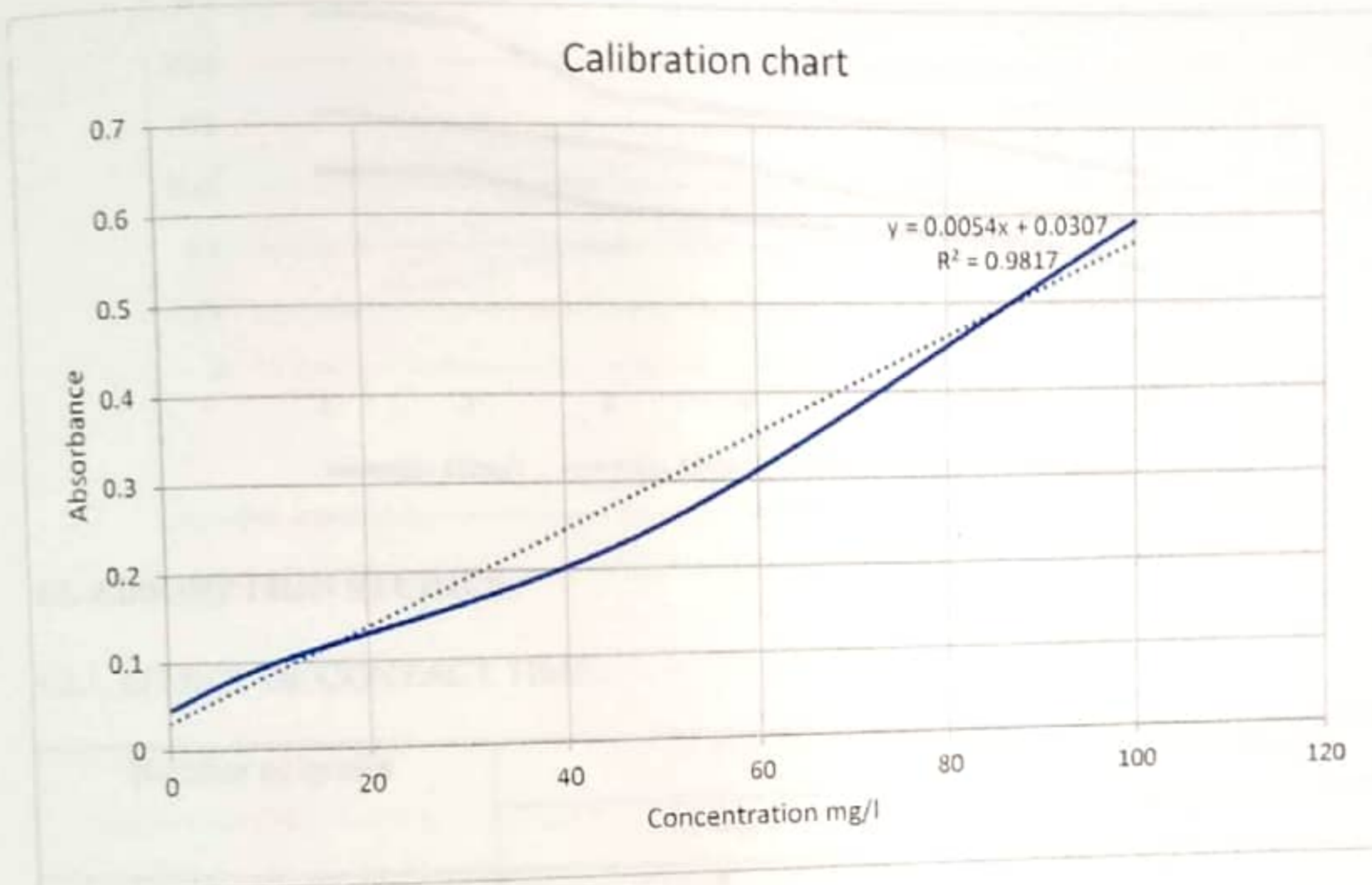


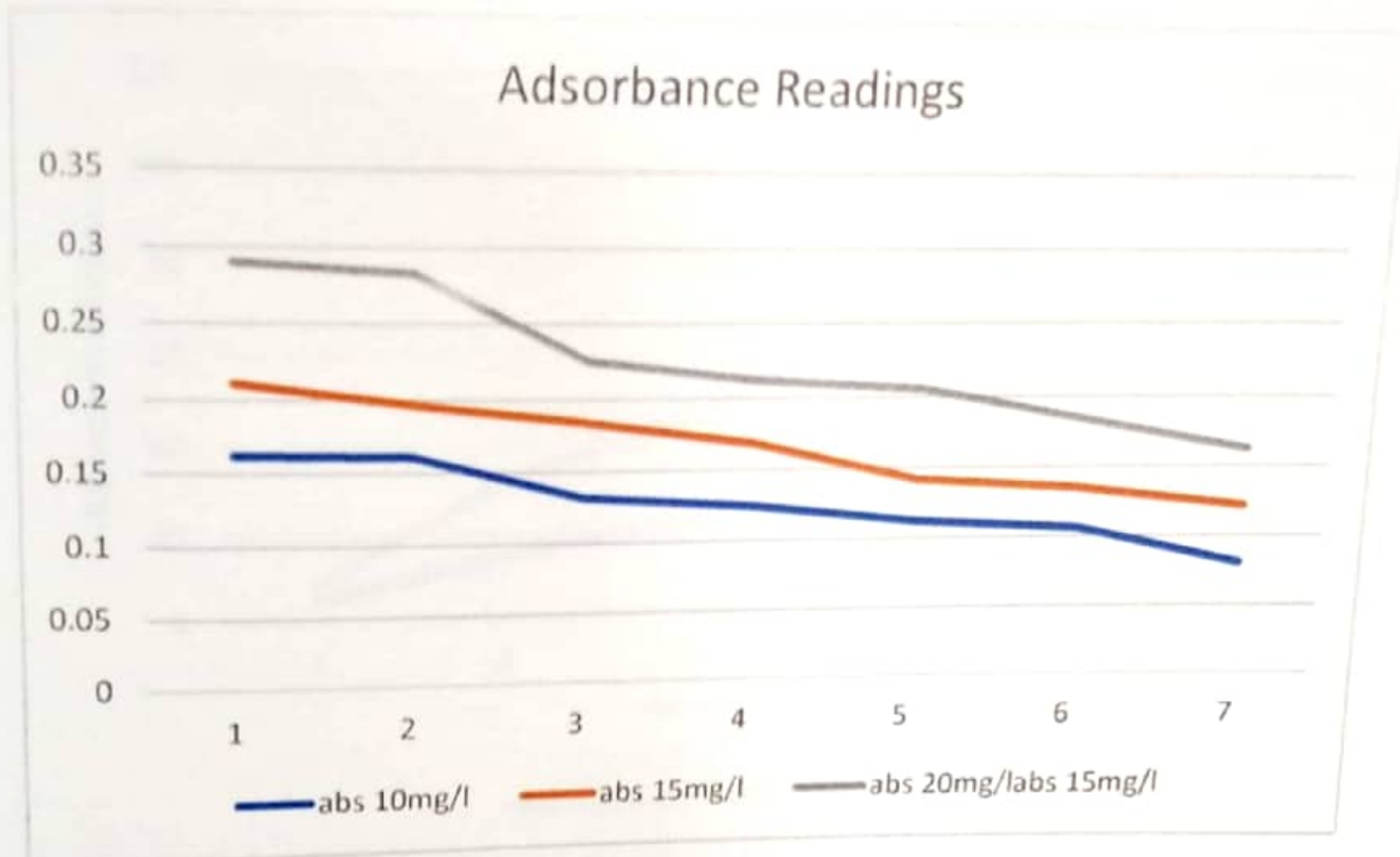
Figure 4.1: Calibration plot for MB

The removal percentage of dye from synthetic solution was calculated using the following reaction

$$\text{Removal of MB (\%)} = \frac{[(\text{Initial dye concentration} - \text{Final dye concentration})/\text{Initial dye concentration}] * 100}$$

4.1.2. ADSORPTION VALUES:

Cycle	abs 10mg/l	abs 15mg/l	abs 20mg/l
1	0.162	0.21	0.29
2	0.161	0.196	0.283
3	0.131	0.183	0.225
4	0.124	0.168	0.212
5	0.112	0.141	0.205
6	0.106	0.134	0.183
7	0.08	0.121	0.162



4.2. ADSORPTION STUDIES:

4.2.1. EFFECT OF CONTACT TIME:

Number of cycles	Adsorption Efficiency %	
	15 mg/l	20 mg/l
1	5	3.6
2	15	18.2
3	22.5	23.6
4	45	27
5	55	36
6	62.5	45.45

Table 4.1: Effect of contact time on % removal of MB

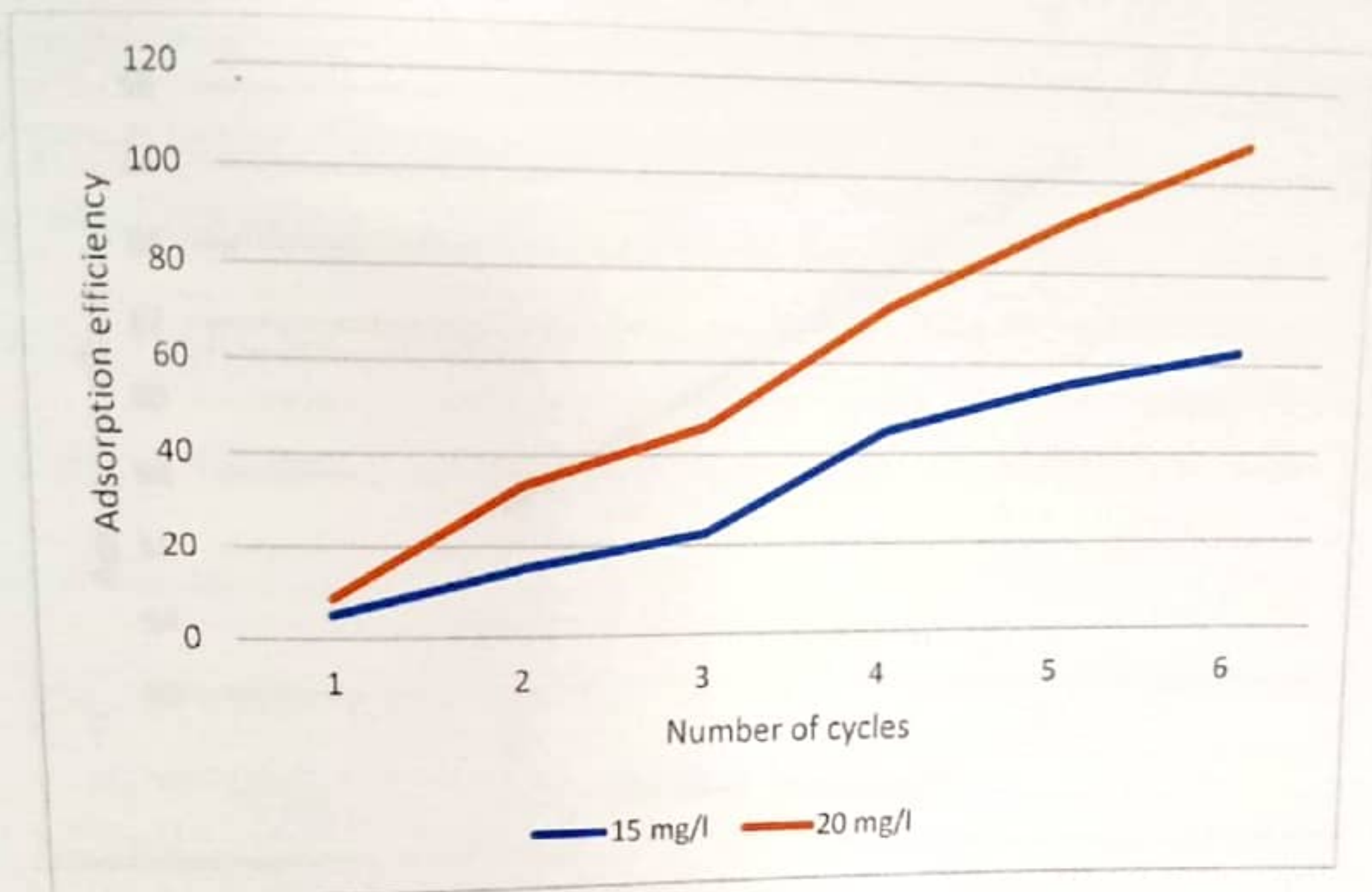


Figure 4.2: Effect of contact time on %removal of MB

The curves in the figure shows that at large contact times the maximum achievable dye removal efficiency is about 67.5% for 15 mg/l and 72.72% for 20 mg/l concentrated solutions. It is also observed that the removal of the dye increases with increase in contact time, but after some time, it gradually approaches a constant value, denoting attainment of equilibrium. The dye removal efficiency increases from 12.5% to 67.5% in case of 15 mg/l and 9.1% to 72.72% for banana peel powder by varying contact time from 50 min to 300 min, respectively.

4.2.2. EFFECT OF ADSORBENT DOSAGE:

Adsorbent Dosage(mg/l)	Adsorption efficiency%
1	57.14
2	66.6

Table 4.2: Effect of adsorbent dosage on % removal of MB

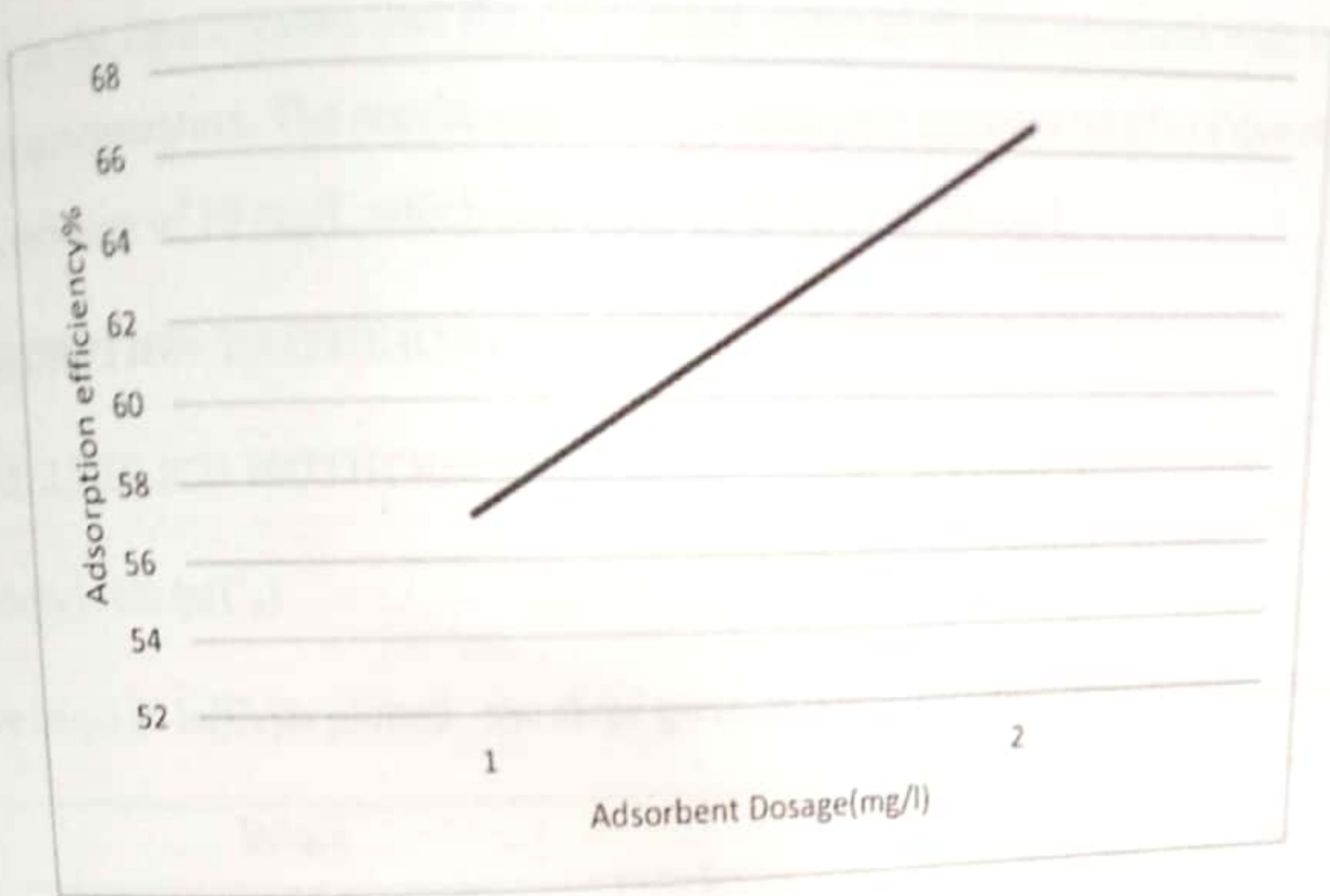


Figure 4.3: Effect of adsorbent dosage on % removal of MB

The curve in the figure shows that the percentage removal of dye increases with increase of adsorbent dosage. The results show that banana peel removes 57.14% of dye at a dosage of 1 g/L which increases to 66.6 at 2 g/L.

4.2.3. EFFECT OF INITIAL DYE CONCENTRATION:

Initial Dye Concentration (mg/lit)	Adsorption efficiency%
10	66.6
15	62.5
20	45.45

Table 4.3: Effect of Initial dye concentration on % removal of MB

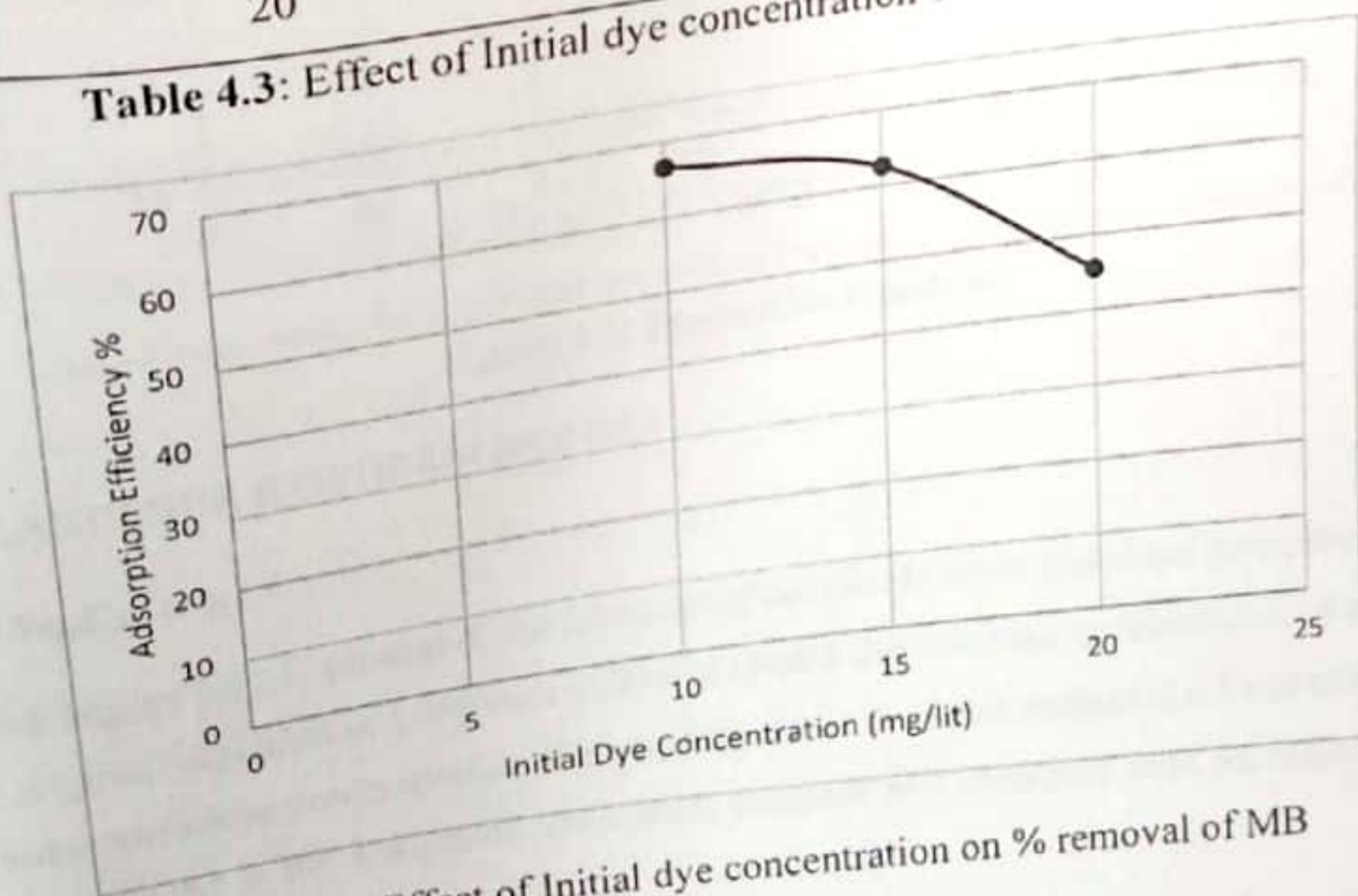


Figure 4.4: Effect of Initial dye concentration on % removal of MB

The curve in the figure shows that the percentage removal of dye decreases with increase of initial dye concentration. The results show that banana peel removes 66.6% of dye at an initial dye concentration of 10 mg/L which decreases to 45.45% at 20 mg/L.

4.3. ADSORPTION ISOTHERMS:

4.3.1. FREUNDLICH ISOTHERM MODEL:

$$\ln(q_e) = \ln(k_F) + \frac{1}{n} \ln(C_e)$$

A curve $\ln(q_e)$ vs $\ln(C_e)$ is plotted, the slope gives 'n' value and intercept gives k_F value.

$\ln(q_e)$	$\ln(C_e)$
2.72	2.211
2.80	2.81
3.166	3.19

Table 4.4: Freundlich isotherm values

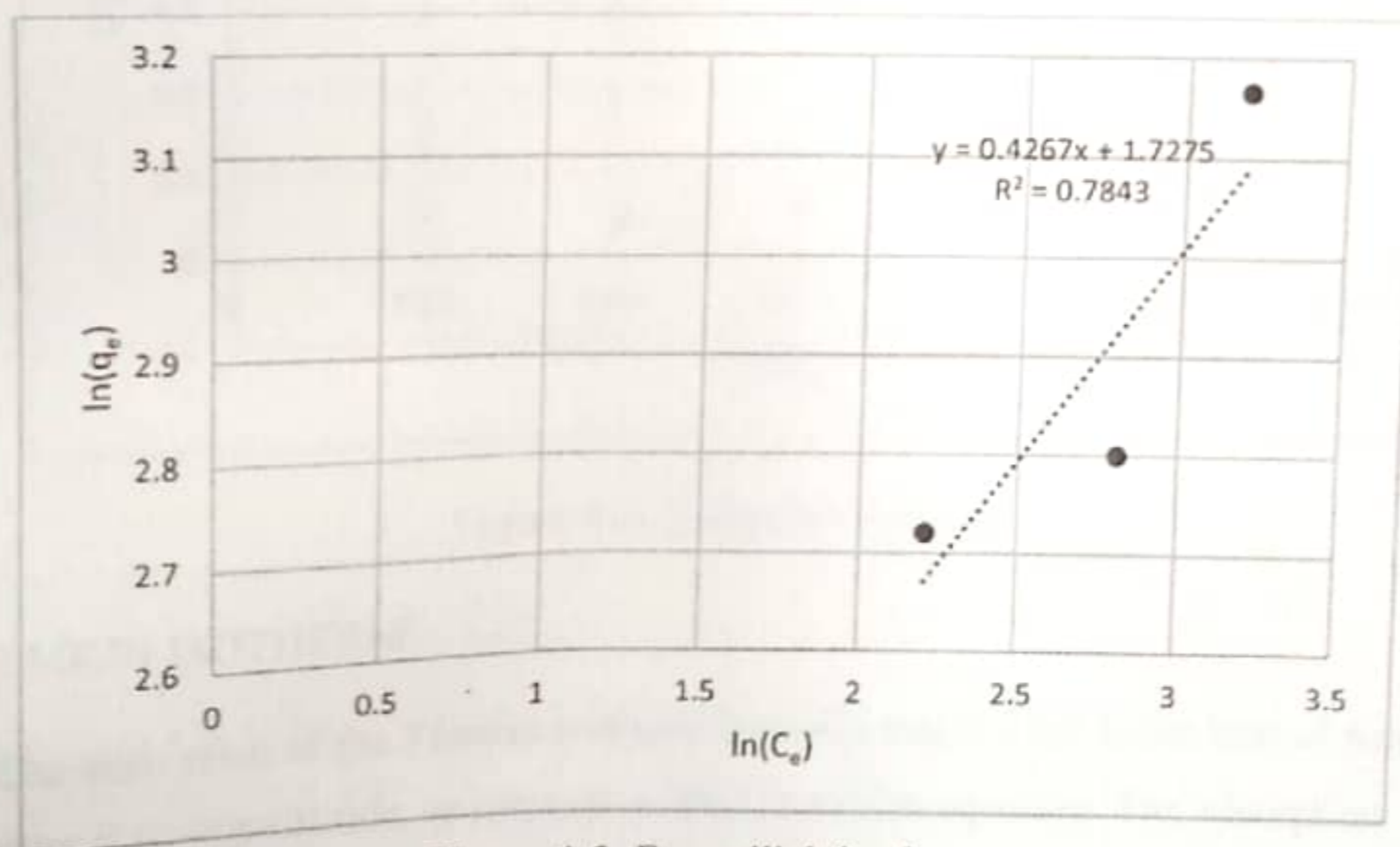


Figure 4.5: Freundlich isotherm

4.3.2. LANGMUIR ISOTHERM MODEL:

$$1/q_e = 1/bq_0C_e + 1/q_0$$

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

The Langmuir equation or Langmuir isotherm relates the coverage or adsorption of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature.

The constant K_f is the Langmuir adsorption constant and increases with an increase in the

strength of adsorption and with a decrease in temperature, Langmuir isotherms were plotted with $1/q_e$ against $1/C_e$.

$1/q_e$	$1/C_e$
0.658	0.109
0.0606	0.0598
0.042	0.0411

Table 4.5: Langmuir isotherm values

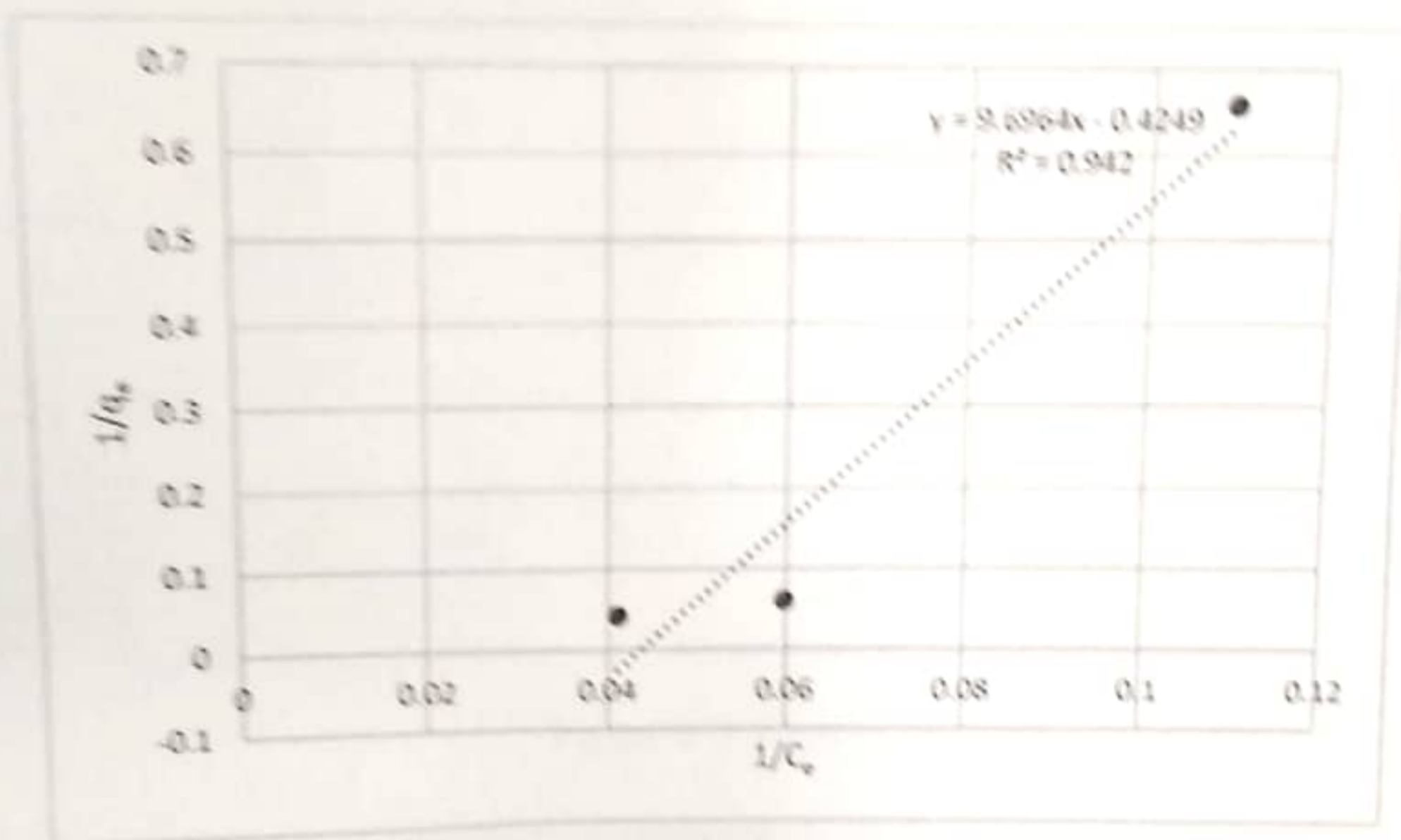


Figure 4.6: Langmuir isotherm

4.3.3. TEMKIN ISOTHERM:

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The adsorption experiment data were analysed by Temkin isotherm model in the linearized form,

$$q_e = B \ln C_e + B \ln A$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol), A is the equilibrium binding constant corresponding to the maximum binding energy (L/g), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K). The plot of q_e against $\ln C_e$ is given below.

q_e	$\ln(C_e)$
15.181	2.211
16.481	2.81
23.71	3.19

Table 4.6: Temkin isotherm values

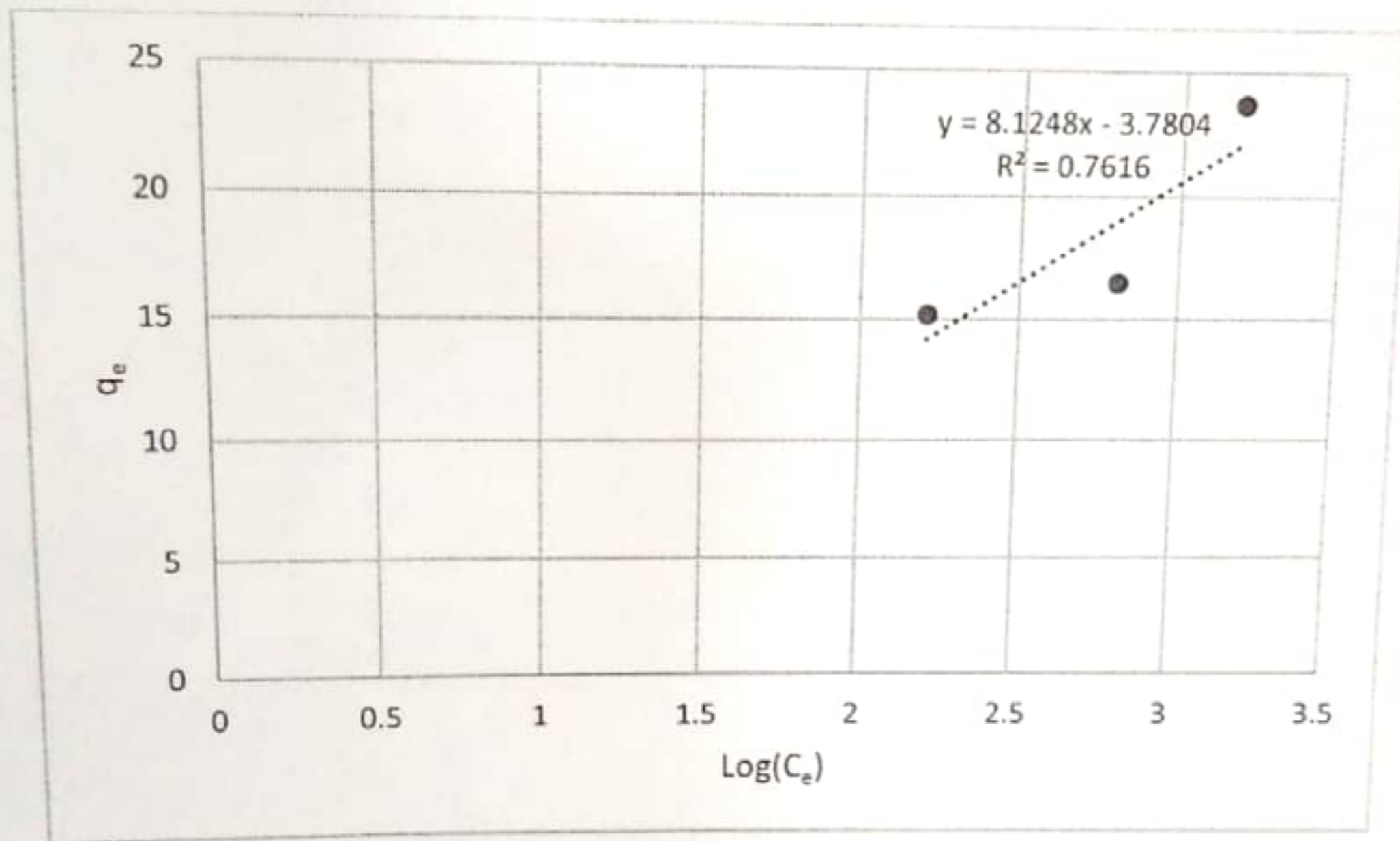


Figure 4.7: Temkin isotherm

4.3.4. Estimated Values of Constants of Isotherms from the Data:

The estimated values of the constants of the Isotherm models for the adsorption of methylene blue dye by using banana peel powder are given below

Freundlich isotherm		Langmuir Isotherm		Temkin Isotherm	
k_F	$1/n$	q_0	b	B	A
5.626	2.3435	-2.342	-0.044	8.1248	0.6279

Table 4.7: Kinetic constants for bio-sorbent

The recursion value of Langmuir Isotherm is more than that of the Freundlich and Temkin Isotherms ($0.942 > 0.7843 > 0.7616$). So, the adsorption of methylene blue dye is more likely to follow Langmuir Isotherm.

4.3.5. PYTHON SIMULATION OF ADSORPTION ISOTHERMS:

PYTHON CODE:

```
import numpy as np
from scipy.interpolate import interp1d
import math
import matplotlib.pyplot as plt
#x=c0 and y=ce
x = np.array([24.31, 33.203, 48.02])
y = np.array([9.129, 16.722, 24.31])
#fitting curve for equilibrium values
m, b = np.polyfit(x, y, 1)
M=[m]*3
B=[b]*3
plt.subplot(221)
plt.plot(x,M*x+B)
#interpolating some values in between extreme values to get the curve more accurately
f = interp1d(x, y)
xnew = np.linspace(24.31, 48.02, num=48, endpoint=True)

#calculation part
temp_qe= xnew- m*xnew+b
ln_qe=[]
receprocal_qe=[]
for row in temp_qe:
    ln_qe.append(math.log(row))
    receprocal_qe.append(1/row)
ln_ce=[]
receprocal_ce=[]
for row in f(xnew):
    ln_ce.append(math.log(row))
    receprocal_ce.append(1/row)
#Fitting isotherms
plt.subplot(222)
r, s=np.polyfit(ln_ce,ln_qe,1)
R=[r]*48
S=[s]*48
plt.plot(ln_ce,np.array(ln_ce)*np.array(R)+np.array(S), 'o')
plt.xlabel('ln_ce')
plt.ylabel('ln_qe')
print("Freundlich eq=",r,'x',s)
plt.subplot(223)
p, q= np.polyfit(receprocal_ce, receprocal_qe,1)
P=[p]*48
Q=[q]*48
```



```

plt.plot( reeiprocal_ce, np.array(reeiprocal_ce)*np.array(P)+ np.array(Q), 'o'
)
plt.xlabel('reeiprocal_ce')
plt.ylabel('reeiprocal_qe')
print("Langmuir eq=",p,'x',q)
plt.subplot(224)
a,b=np.polyfit(ln_ce,temp_qe,1)
A=[a]*48
B=[b]*48
plt.plot(ln_ce,np.array(ln_ce)*np.array(A)+np.array(B), 'o')
plt.xlabel('ln_ce')
plt.ylabel('qe')
print("Temkin eq=",a,'x',b)
plt.show()

```

COMMAND PART:

PS C:\Users\sunil\Desktop\Sample_Project> python .\pro.py

Freundlich eq= 1.265946995953888 x -1.5502235172741508

Langmuir eq= 2.809313940059472 x -0.03298742541743023

Temkin eq= 9.248961286307303 x -18.09007133587966

PYTHON PLOT:

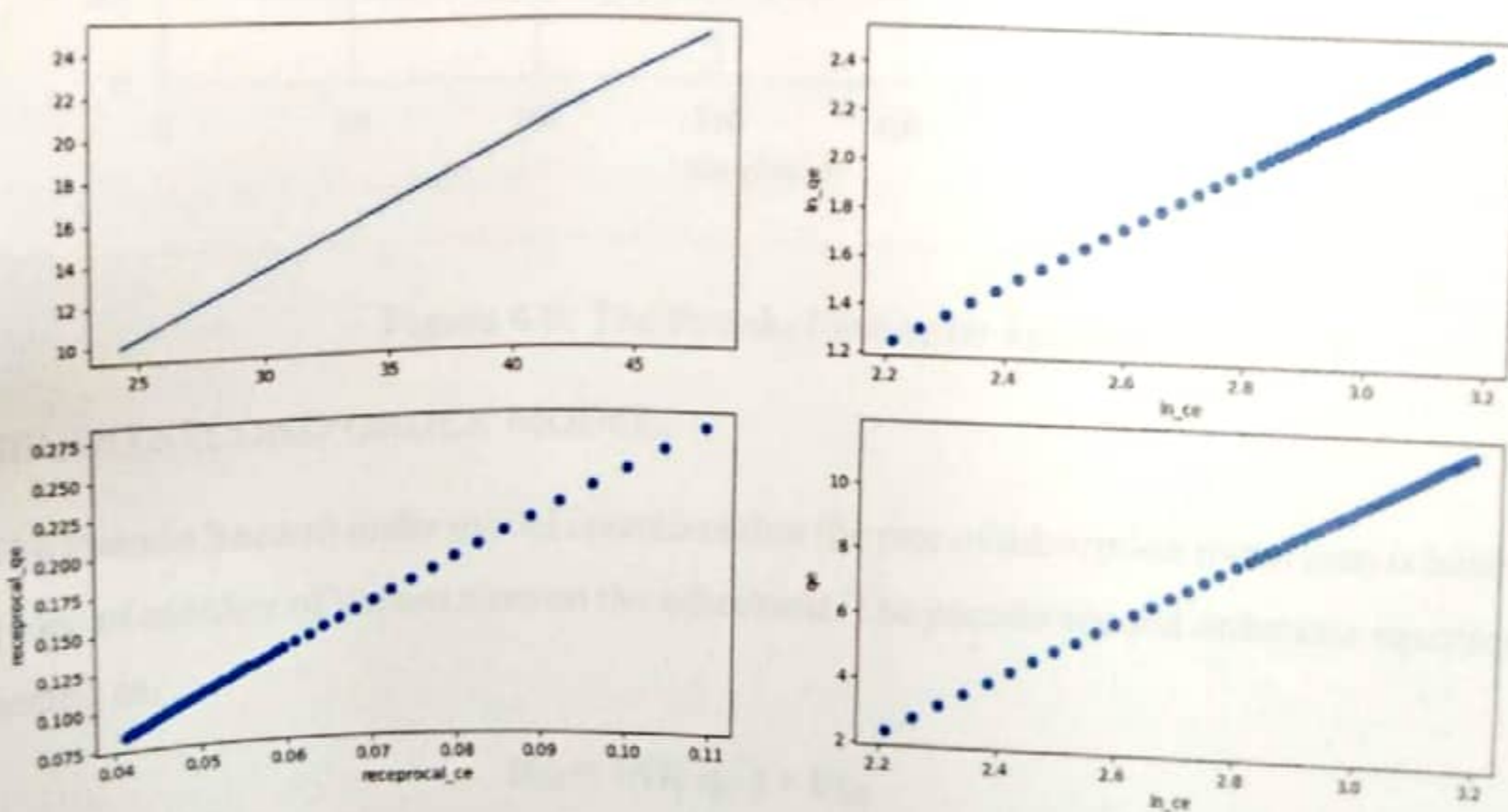


Figure 4.8: Python plots for adsorption isotherms

4.4. ADSORPTION KINETICS:

In order to investigate the mechanism of adsorption and its potential rate controlling steps, kinetic models have been used. The adsorption kinetics of methylene blue dye are analysed by the pseudo first order and pseudo second order.

4.4.1. PSEUDO FIRST ORDER:

$$\ln (q_e - q_t) = \ln q_e - K t$$

The kinetics of adsorption are modelled using the first order rate equation of Lager Gren. The straight-line plots of $\text{Log}(q_e - q_t)$ vs time at ambient temperature indicated the validity of Lange Gren equation and consequently the first order nature of the process involved in present study. The value of K at ambient temperature was calculated from the plot and shown in fig

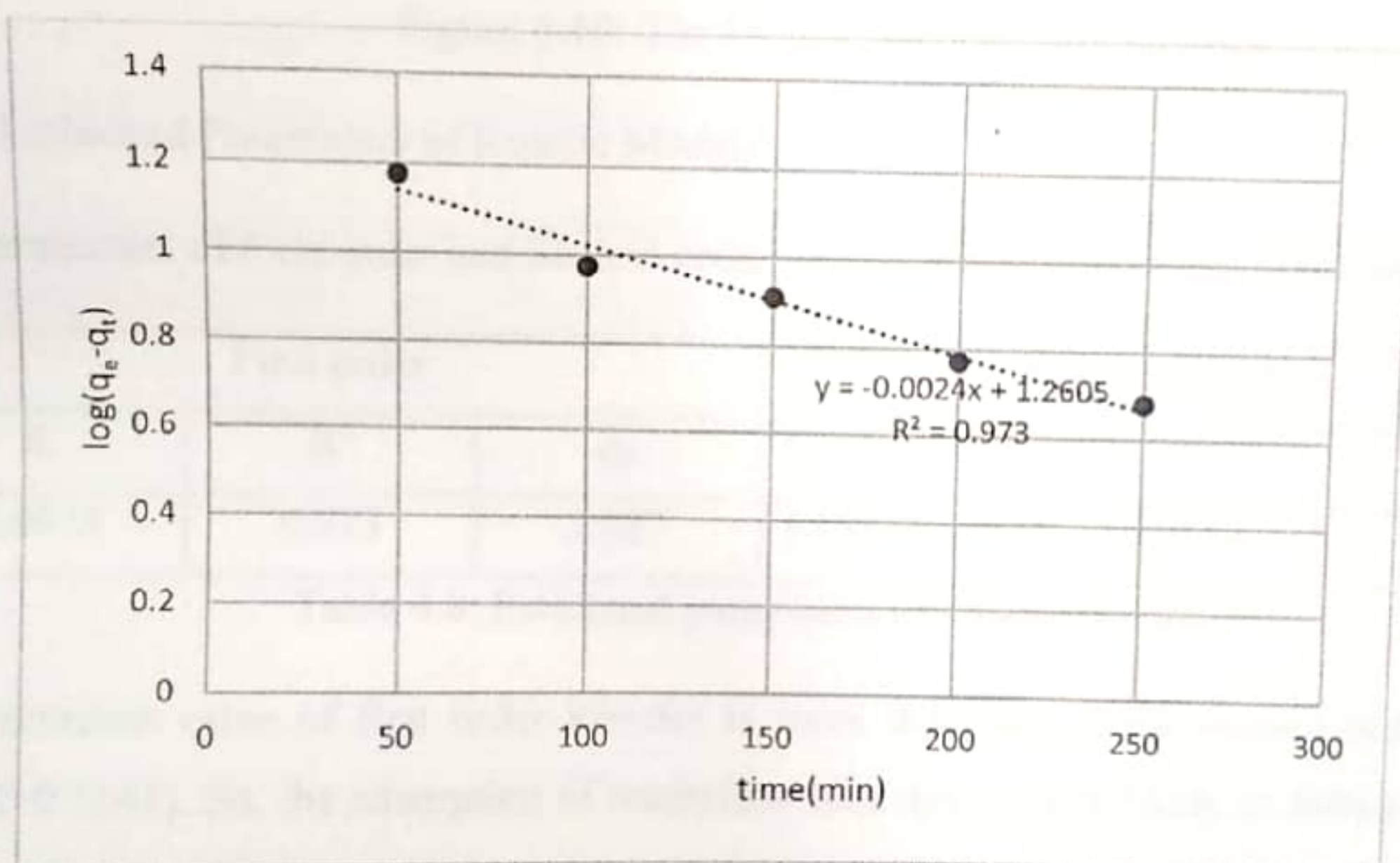


Figure 4.9: The Pseudo First order kinetics

4.4.2. PSEUDO SECOND ORDER MODEL:

The Pseudo Second order model considers that the rate of adsorption metal ions is based on the square of number of vacant sites on the adsorbent. The pseudo second order rate equation is represented as,

$$t/q_t = 1/(K q_e^2) + t/q_e$$

A plot of t/q_t versus t should give a linear relationship for the applicability of the second order kinetic. The following figure represents the Pseudo Second order sorption kinetics

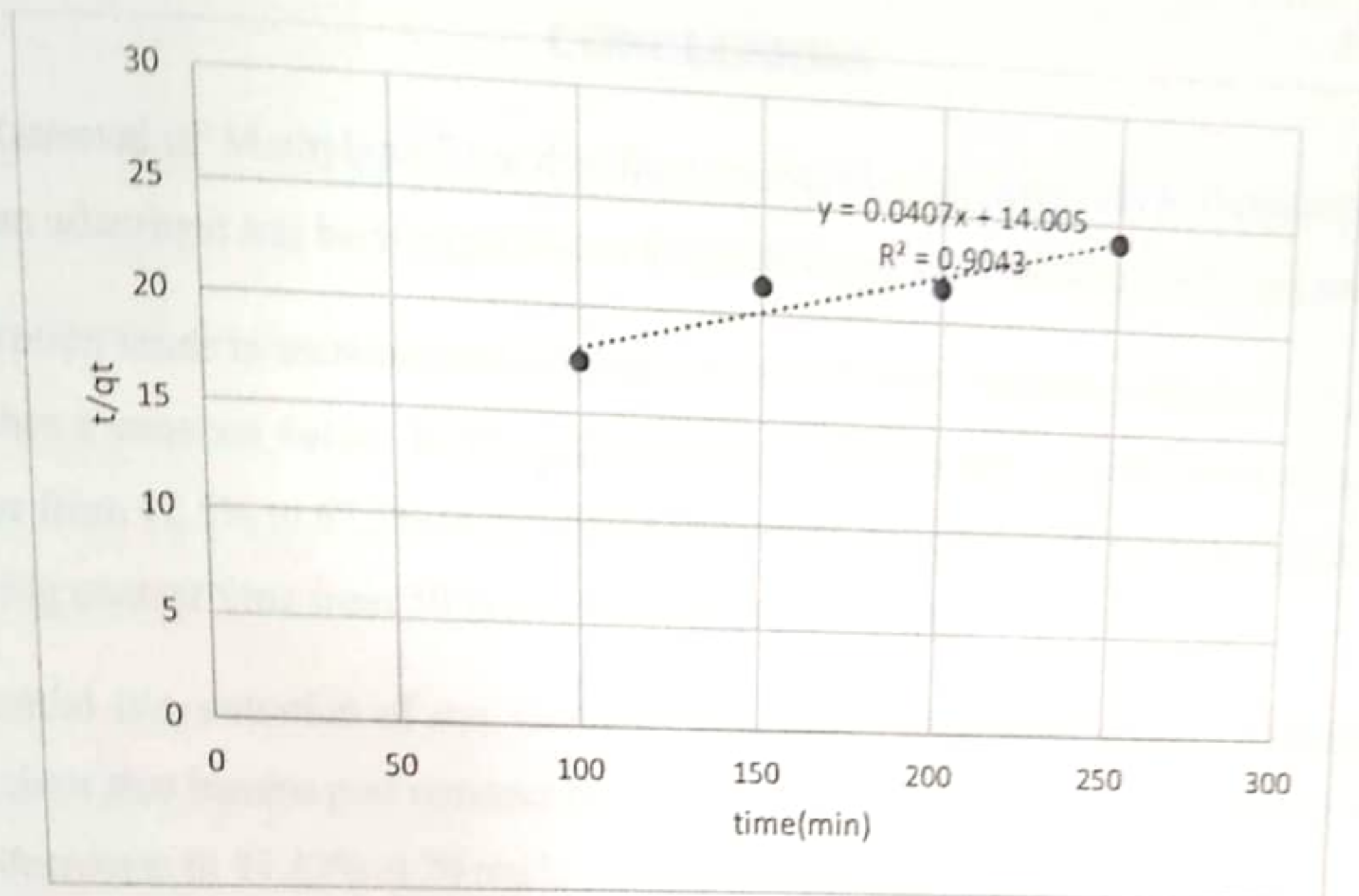


Figure 4.10: The Pseudo Second order kinetics

4.4.3. Estimated Parameters of Kinetic Models:

The parameters of First order and Second order models are estimated and given below.

First order			Second order		
K	R ²	q _e	K	R ²	q _e
0.0024	0.973	3.527	1.1827*10 ⁻⁴	0.9043	24.57

Table 4.8: Estimated parameters of Kinetic models

The recursion value of first order kinetics is more than that of the second order kinetics (0.973 > 0.9043). So, the adsorption of methylene blue dye is more likely to follow first order kinetics.

CHAPTER-5

CONCLUSIONS

Removal of Methylene Blue dye from an aqueous solution where banana peels were used as an adsorbent has been experimentally studied and the following observations made:

1. Adsorption tends to increase with increase in contact time, but after some time, it gradually approaches a constant value, denoting attainment of equilibrium. The dye removal efficiency increases from 12.5% to 67.5% in case of 15 mg/l and 9.1% to 72.72% for banana peel powder by varying contact time from 50 min to 300 min, respectively.
2. As initial concentration of dye increases, percentage removal of the dye decreases. The results show that banana peel removes 66.6% of dye at an initial dye concentration of 10 mg/L which decreases to 45.45% at 20 mg/L.
3. As adsorbent dosage increases, percentage removal of the dye increases. The results show that banana peel removes 57.14% of dye at a dosage of 1 g/L which increases to 66.6 at 2 g/L.
4. The process of adsorption with treated bio-sorbent follows Langmuir isotherm more strongly than Freundlich isotherm and Temkin Isotherm.
5. The process of adsorption with treated bio-sorbent follows Pseudo First order kinetics than Pseudo Second order kinetics.

CHAPTER-6

REFERENCES

- Moubarak, F., Atmani, R., Maghri, I., Elkouali, M. H., Talbi, M., Bouamrani, M. L., ... & Kenz, A. (2014). Elimination of methylene blue dye with natural adsorbent "banana peels powder". *Global Journal of Science Frontier Research: B Chemistry*, 14(1), 39-44.
- Ma, J., Huang, D., Zou, J., Li, L., Kong, Y., & Komarneni, S. (2015). Adsorption of methylene blue and Orange II pollutants on activated carbon prepared from banana peel. *Journal of Porous Materials*, 22(2), 301-311.
- Amela, K., Hassen, M. A., & Kerroum, D. (2012). Isotherm and kinetics study of biosorption of cationic dye onto banana peel. *Energy Procedia*, 19, 286-295.
- Gautam, S., & Khan, S. H. (2016). Removal of methylene blue from waste water using banana peel as adsorbent. *International journal of Science, Environment and Technology*, 5(5), 3230-3236.
- Mane, R. S., & Bhusari, V. N. (2012). Removal of colour (dyes) from textile effluent by adsorption using orange and banana peel. *International Journal of Engineering Research and Applications*, 2(3), 1997-2004.
- Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of hazardous materials*, 177(1-3), 70-80.
- Jawad, A. H., Rashid, R. A., Ishak, M. A. M., & Ismail, K. (2018). Adsorptive removal of methylene blue by chemically treated cellulosic waste banana (*Musa sapientum*) peels. *Journal of Taibah University for Science*, 12(6), 809-819.
- Enniya, I., & Jourani, A. (2017). Study of methylene blue removal by a biosorbent prepared with apple peels. *J. Mater. Environ. Sci.*, 8(12), 4573-4581.
- Hashem, F. S., & Amin, M. S. (2016). Adsorption of methylene blue by activated carbon derived from various fruit peels. *Desalination and Water Treatment*, 57(47), 22573-22584.
- Abd Al-Hussein, N.A Adsorption of Methylene Blue Dye from Aqueous Solutions by Using Some Plants Material Mesop. *Environ. J.* 2017, Vol. 3, No.3, pp. 74-78.
- Mahammedi Fatihaa , Benguella Belkaem Laboratory of Inorganic Chemistry and Environment, Abu Bakr Belkaid University 13000 Tlemcen, Algeria.

Ezerie Henry Ezchi, Shamsul Rahman bin Mohamed Kutty, Amirhossein Malakian, Mohamed Hasnain Isa, Nasiru aminu, and Ibrahim Umar Salihi.

Shiv Prathap Raghuvanshi, Renu Singh and C.P.Kaushik "Adsorption of Congo Red dye from aqueous solutions using Neem Leaves as adsorbent", *Asian Journal of Chemistry* Vol.20, No.7 (2008),4994-5000.

M.C Somasekhar Reddy, A.Varada Reddy "The use of Agricultural waste material, Jujuba Seeds for the removal of anionic dye from aqueous medium". *Journal of Hazardous materials* 203-204(2012),118-127

D. A. Nimkar S.K. Chavan " Removal of Methylene Blue Dye (Basic Dye) from Aqueous solution using Saw Dust as an Adsorbent.

Mohammed M.A., Shitu A. and Ibrahim A. " Removal of Methylene Blue Using Low Cost Adsorbent.

Enenebeaku K. Conrad, Okarocho J. Nnaemeka, Akalezi O. Chris " Adsorptive Removal of Methylene Blue from Aqueous Solution Using Agricultural Waste: Equilibrium, Kinetic and Thermodynamic studies.

Deepak Pathania, Pardeep Singh " Removal of Methylene Blue by adsorption onto activated carbon developed from Ficus carica bast.

Million Mulugeta and Belisti Lelisa " Removal of Methylene Blue(MB) Dye from Aqueous Solution by Bioadsorption onto Untreated Parthenium hysterophorus Weed.

Senthil Kumar Ponnusamy, Subramaniam Ramalingam, Kannaiyan Sathishkumar " Removal of Methylene Blue Dye from Aqueous solution by Activated Carbon prepared from Cashew Nut Shell as a new low – cost adsorbent.

Kaustuha Mohanty " Removal of Methylene Blue Dye from Aqueous Solution by Activated Carbon prepared from Pea Shells. 29

Rezvan Zeynolabedin, Azam Marjani, Aref Shokri, Majid Saghi and Mohammad Hossein Bigtan " Removal of methylene blue dye from aqueous solutions by elaeagnus gasterifolia as an adsorbent".

R. Karthik, R. Muthazhilan, A. jaffar Hussain, K. Ramalingam & V.Rekha "Effective removal of Methylene Blue dye from water using three different low-cost adsorbents.

Gang Sun and Xiangjing Xu "sun flower stalks as adsorbents for color removal from textile waste water". *Ind.eng.chem.Res.*(1997),36,808-812.

Gopal C.panda and sujoy k.das, "jute stick powder as a potential Bio-mass for the removal of Methylene Blue and rhodamine B from their aqueous solution". *Journal of hazardous materials.* (2008).

JNTUA COLLEGE OF ENGINEERING, ANANTAPUR
DEPARTMENT OF CHEMICAL ENGINEERING
Final PROJECT Work-EVALUATION SHEET

S. No.	Admission number	Clear Hypothesis (10 M)	Objectives (10 M)	Methodology of execution (10 M)	Interpretation of the results (10 M)	Total Marks (40 M)
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						
13.						
14.						
15.						
16.						
17.						
18.						
19.						
20.						
21.						
22.						
23.						
24.						
25.						
26.						
27.						
28.						
29.						
30.						

* Maximum (10 M) and Minimum (5 M)

Signature of Evaluator's

(1)

(2)

(3)

Head, Chemical Engineering

A project report on
**STEADY STATE SIMULATION OF AN ISOTHERMAL PFR BY
USING DWSIM**

A dissertation submitted in partial fulfillment of the requirements

For the award of the Degree of

BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

BY

A D GUNASEKAR	(17001A0848)
VADDE JAYALAKSHMI	(17001A0810)
KURUBA LAKSHMI HARSHA VARDHAN	(17001A0806)
BOBBILI NIKHILA	(17001A0840)

Under the esteemed guidance of

Dr.DILIP KUMAR BEHARA

Associate Professor

Department of Chemical Engineering
JNTUACEA



**DEPARTMENT OF CHEMICAL ENGINEERING
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR
COLLEGE OF ENGINEERING (AUTONOMOUS)
ANANTAPURAMU-515002**

2021

A project report on
**STEADY STATE SIMULATION OF AN ISOTHERMAL PFR BY
USING DWSIM**

A dissertation submitted in partial fulfillment of the requirements

**For the award of the Degree of
BACHELOR OF TECHNOLOGY**

IN

CHEMICAL ENGINEERING

BY

A D GUNASEKAR	(17001A0848)
VADDE JAYALAKSHMI	(17001A0810)
KURUBA LAKSHMI HARSHA VARDHAN	(17001A0806)
BOBBILI NIKHILA	(17001A0840)

**Under the esteemed guidance of
Dr.DILIP KUMAR BEHARA**

Associate Professor

Department of Chemical Engineering

JNTUACEA



DEPARTMENT OF CHEMICAL ENGINEERING

JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR

COLLEGE OF ENGINEERING(AUTONOMOUS)

ANANTAPURAMU-515002

2021

DEPARTMENT OF CHEMICAL ENGINEERING
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR
COLLEGE OF ENGINEERING(AUTONOMOUS)
ANANTAPURAMU - 515002



CERTIFICATE

This is to certify that the dissertation entitled **“STEADY STATE SIMULATION OF AN ISOTHERMAL PFR BY USING DWSIM”** is the bonafide work done and submitted to Jawaharlal Nehru Technological University Anantapur College of Engineering(Autonomous), Anantapuramu during the academic year 2020-2021 in partial fulfillment of the requirements for the award of the degree of Bachelor of Technology in Chemical Engineering by

A D GUNASEKAR	(17001A0848)
VADDE JAYALAKSHMI	(17001A0810)
KURUBA LAKSHMI HARSHA VARDHAN	(17001A0806)
BOBBILI NIKHILA	(17001A0840)

The contents of this report have not been either partially or fully submitted to any other institute for the award of either any other degree or diploma.

PROJECT GUIDE

Dr.DILIP KUMAR BEHARA,
Associate Professor

HEAD OF THE DEPARTMENT

Dr.L.G.S.SHARADA,
Associate Professor

DECLARATION

I declare that this project report titled “**Steady state simulation of an isothermal PFR by using DWSIM**” submitted in partial fulfilment of the degree of B.Tech in **Chemical engineering** is a record of original work carried out by us under the supervision of **Dr. Dilip Kumar Behara**, and has not formed the basis for the award of any other degree or diploma, in this or any other institution or university. In keeping with the ethical practice in reporting scientific information, due acknowledgements have been made wherever the findings of others have been cited.

A.D.Gunasekar	(17001A0848)
Vadde Jayalakshmi	(17001A0810)
Kuruba Lakshmi Harsha Vardhan	(17001A0806)
Bobbili Nikhila	(17001A0840)

ACKNOWLEDGEMENTS

This satisfaction and euphoria that accompanies the successful completion of any task would be incomplete without the mention of the people who made it possible, whose constant guidance and encouragement crown all efforts with success.

First of all, we take this opportunity to express our deepest gratitude to our project guide **Dr.DILIP KUMAR BEHARA**, Associate Professor, Department of Chemical Engineering, JNTUA College of Engineering, Ananthapuramu, for giving us this opportunity to work under his esteemed guidance. We are greatly indebted to him for his kindness, generosity, consistent involvement and encouragement throughout our project work.

Our sincere thanks to **Dr. Lt. S. SHARADA**, Head of the department for providing with the facilities for the completion of the project.

We also express our sincere thanks to **Dr. S. V. Satyanarayana, M. Kalyan kumar** and other teaching faculty for their valuable teaching throughout the course and necessary encouragement.

We convey our thanks to all the Non-Teaching Staff of the department who have helped us in several ways in completion of this project successfully.

With gratitude

A.D.Gunasekar	(17001A0848)
Vadde Jayalakshmi	(17001A0810)
Kuruba Lakshmi Harsha Vardhan	(17001A0806)
Bobbili Nikhila	(17001A0840)

ABSTRACT

This project work reports steady state simulation results of a plug flow reactor (PFR) system using DWSIM. The reaction investigated in this work was production of ethyl benzene using ethylene and benzene as the reactants. Ethyl benzene being one of the important raw materials in production of several industrially important chemicals and is often produced alongside with diethylbenzene as an undesired side product. In our simulation this particular aspect has been examined to maximize the conversion of ethyl benzene from its reactants. Here we have studied the effects of feed flow rate on steady state behaviour of PFR and also obtain the optimum feed flow rate in order to maximize the conversion and yield with special consideration of consecutive reactions where one product was desired and another one was undesired. Also we have studied the effect of reactor volume on the yield. It seems to be that increase in reactor volume decreases the formation of undesired product.

Keywords: Ethylbenzene, DWSIM, property packages, yield

CONTENTS

List of contents	Page no
Acknowledgement	I
Abstract	II
List of Figures	V
List of Tables	VI
Nomenclature	VII
Chapter 1-Introduction	1-5
1.1 Prelude	1
1.2 Chemical reactors	1
1.3 Dwsim	1
1.4 Ethyl benzene	2
1.5 Organization of chemical reactions	3
1.6 General description and Reaction types	4
1.7 Background of present research work	5
1.8 Research objectives	5
Chapter 2-Literature survey	6-7
Chapter 3- Plug flow reactor	8-11
3.1 Different types of chemical reactors	8-11
3.1.1 Batch reactor	8
3.1.2 Continuous stirred tank reactor	8
3.1.3 Plug flow reactor	9-11
Chapter 4-Ethyl benzene	12-15
4.1 Introduction	12
4.2 Properties of ethylbenzene	12
4.3 Production of ethylbenzene	12-15

List of contents**Page no**

Chapter 5- Simulation work	16-31
5.1 DWSIM software	16
5.2 Property method	16
5.3 Property package descriptions	16-20
5.4 Steady state simulation	21
5.5 Simulation step	21-30
5.5.1 Effect of feed flow rate	30
5.5.2 Effect of reactor volume	31
Chapter 6-Results and discussion	32-40
6.1 Effect of feed flow rate	32-34
6.2 Effect of reactor volume	35-40
Chapter 7-Conclusion	41
Future work	42
References	43-45

LIST OF FIGURES

Fig .No.	Title	Page No.
6.1	Benene feed flow rate vs % Yield of ethyl benzene by using different thermodynamic packages	34
6.2	Volume of reactor vs % Yield of Diethyl benzene by using Chao-Seader model	37
6.3	Volume of reactor vs %Yield of Diethyl benzene By using NRTL model	37
6.4	Volume of reactor vs %Yield of Diethyl benzene By using Peng-Robinson model	38
6.5	Volume of reactor vs %Yield of Diethyl benzene By using Grayson-Streed model	38
6.6	Volume of reactor vs %Yield of Diethyl benzene By using Lee-Kesler-Plocker model	39

LIST OF TABLES

Table.No.	Title	Page.No.
6.1	Comparison between benzene feed flow rate and Product feed flow rate by using different thermodynamic Packages	32
6.2	Comparison between benzene feed flow rate and %yield of Diethyl benzene by using different thermodynamic Packages	33
6.3	Comparison between volume of a reactor and diethyl Benzene flow rate by using different thermodynamic Packages	35
6.4	Comparison between volume of a reactor and %yield of Diethyl benzene by using different thermodynamic Packages	36

NOMENCLATURE

- E - Ethylene
- B- Benzene
- EB- Ethylbenzene
- DEB- Diethyl benzene
- CSTR- Continuous stirred tank reactor
- PFR- Plug flow reactor
- CS- Chao Seader
- PR- Peng Robinson

This chapter highlights the importance of chemical reactors and also application of DWSIM in reactor design. It focuses on the uses of ethyl benzene which plays a main role in the petrochemical industry as halfway in the production of styrene, the raw material for the production of polystyrene and a common plastic material. The background of the present thesis work is summarized along with the objectives.

1.1 PRELUDE

Reactions are usually the core of chemical processes in which comparatively low-cost raw materials are transferred into important products, useful to mankind in various forms. Understanding the basics of chemical kinetics and thermodynamics are key before designing chemical reactors. Basically, kinetics and thermodynamics help in understanding how fast or slow the reaction is progressing and to what extent the reaction will progress. Designing chemical reactors is a tedious process and it requires plenty of expertise starting from conceptualization to validation of data. Dwsim provides a platform in executing methods and predicts the effect of various parameters and variables reminiscent of a real-time system.

1.2 CHEMICAL REACTORS

The application of chemical reactors is very large and it is not only confined within the ambit of chemical industries but also petrochemical industries and any other process plants. Chemical kinetics and reactor design is the core to the understanding of the production of almost all chemicals. As mentioned in the a foresaid paragraph that designing chemical reactors is a tedious process and it requires plenty of expertise, starting from conceptualization to validation of data. Optimization of the best possible combination in designing is the key. One particular route may yield a low reactor price but the handling of chemicals,post production might be very expensive. The economics of the whole plant must be studied in a great deal.

1.3 DWSIM

It is a process demonstrating instrument for steady state simulation, design, performance, optimization and planning for chemicals, speciality chemicals,petrochemicals and metallurgy industries.

The challenges

The chemical process industries are best with cases over fluctuating market conditions government guidelines w.r.t environmental issues etc. however there is no scope for any sluggishness and there has always been an effort to increase productivity with efficient mechanisms in place with improved economics of the plant and the country. When confronted with complicated situations like this, process engineers have little choice but to resort to strong and powerful software tools to answer them.

The opportunity

Steady state simulation is a prevailing process engineering tool that empowers engineers to simulate plant performance and examine their results quickly -exploiting the modern software and engineering technology to optimize plant performance and effectiveness.

The solution

Modelling and simulation involves deep understanding of the process starting from conceptualization to model development to its solution. It basically gives an idea to figure out what actually makes the process tick. Understanding the process and troubleshooting it as and when required makes process simulation such an attractive area to venture into. Dwsim is a strong software and free software paving the way for giving ready made solution to many challenging issues related to any process industry in a quick and legible way. Using Dwsim engineers can design , simulate and troubleshoot the process as and when the need arises.

1.4 ETHYL BENZENE

Ethylbenzene is a colorless liquid with a syrupy, gasoline odor. It is a small aromatic hydrocarbon. Ethylbenzene is manufactured through an alkylation of benzene. The alkylation can happen in vapor or in liquid phase and both alkylation use a zeolite or an aluminium chloride catalyst.

Uses of ethyl benzene:

As dissolvable: In inks, elastic cements, varnishes and paints.

As an anti-knock agent: Ethylbenzene is supplementary to gas as an against thump specialists significance it reduces motor thumping and acceleration the octane rating.

As recuperation of regular gas: Ethylbenzene may be infused into the ground.

Ethylbenzene : Assumes a critical part in the petrochemical business as a most of the way in the creation of styrene, the precursor to polystyrene, a typical plastic material. In 2012, more than 99% of ethylbenzene created was devoured in the generation of styrene.

Ethylbenzene is much of the time found in other made items, including pesticides, cellulose , acetic acid derivation and manufactured elastic.

1.5 ORGANIZATION OF CHEMICAL REACTIONS

Mostly chemical reactions are classified into two types; they are homogeneous reaction and heterogeneous reaction. Heterogeneous reactions are further classified into four different types; they are fluid-fluid reactions, non-catalytic gas-solid reactions, catalytic gas-solid reactions and catalytic gas-liquid-solid reactions.

The reactions occur between two immiscible phases i.e., gas-liquid or liquid-liquid is called as fluid-fluid reactions. These types of reactions generally take place at the interface. The overall reaction rate depends on the miscibility of the reactant available interface area and mass transfer rates.

The reactions like combustion, gasification of coal and roasting of pyrites; which generally take place on the solid surface are called non-catalytic gas solid reactions. The reaction occurs when the gaseous reactants are transported to the interface where it reacts with the solid reactant. The reaction rate depends on surface area and the mass transfer rate of the gaseous reactants.

The reactions in which both reactant and products are gaseous are called catalytic gas-solid surface. Porous particles are generally used to provide large surface area to facilitate the reaction . The reaction rate depends on diffusion rate of reactant into the interior of the catalyst pore and diffusion of product out the catalyst pore.

The reactions in which three states are involved i.e (solid,liquid and gas) are called catalytic gas-liquid-solid reactions. Here the solid surface acts as a catalyst and has a special reacting

sites. Solid surface normally covered with liquid reactants and gaseous reactants are diffusion onto the catalytic site.

1.6 GENERAL DESCRIPTION AND REACTION TYPES

Chemical reactions relating to the chemical, petrochemical and oil industries are executed in distinct apparatus so-called reactors. There are distinct types of reactors projected to face exceptionally diverse operating circumstances., both in relationships of the nature of the chemical species involved(reactants and products of the reaction) and of the physical circumstances under which they operate .

In general, a chemical reactor needs to be able to carry out at least three functions:

- Offer the essential residence time for the reactants to complete the chemical reaction;
- Permit the needed heat exchange;
- To enable the chemical reaction , it brings all the phases into near contact.

Consequently, reactor categories range from huge measurement ceaseless reactors, similar to those embraced for synergist breaking responses , particularly for oil refineries, gadgets of unobtrusive measurements, as spasmodic mixed reactors for advanced microelectronic applications and reactors of minuscule measurements(small scale reactors), intended for biomedical establishments or for in situ generation of greatly dangerous or perilous mixes. Converters and burners, reactant or generally, embraced for vitality generation can likewise be recorded among reactors.

To classify a reactor, the quantity of stages in the reactor itself, whether there are unsettling frameworks and the method of operation(constant reactor, semi-nonstop or intermittent) crucial to be complicated. It ought to additionally be noticed the most synthetic reactors are furnished with warmth trade mechanically assembly as outer coats or inwards curls with a liquid coursing through them to go about as a warm vector to permit both warmth supply and evacuations.

sites. Solid surface normally covered with liquid reactants and gaseous reactants are diffusion onto the catalytic site.

1.6 GENERAL DESCRIPTION AND REACTION TYPES

Chemical reactions relating to the chemical, petrochemical and oil industries are executed in distinct apparatus so-called reactors. There are distinct types of reactors projected to face exceptionally diverse operating circumstances., both in relationships of the nature of the chemical species involved(reactants and products of the reaction) and of the physical circumstances under which they operate .

In general , a chemical reactor needs to be able to carry out at least three functions:

- Offer the essential residence time for the reactants to complete the chemical reaction;
- Permit the needed heat exchange;
- To enable the chemical reaction , it brings all the phases into near contact.

Consequently, reactor categories range from huge measurement ceaseless reactors, similar to those embraced for synergist breaking responses , particularly for oil refineries, gadgets of unobtrusive measurements, as spasmodic mixed reactors for advanced microelectronic applications and reactors of minuscule measurements(small scale reactors), intended for biomedical establishments or for in situ generation of greatly dangerous or perilous mixes. Converters and burners, reactant or generally, embraced for vitality generation can likewise be recorded among reactors.

To classify a reactor, the quantity of stages in the reactor itself, whether there are unsettling frameworks and the method of operation(constant reactor, semi-nonstop or intermittent) crucial to be complicated. It ought to additionally be noticed the most synthetic reactors are furnished with warmth trade mechanically assembly as outer coats or inwards curls with a liquid coursing through them to go about as a warm vector to permit both warmth supply and evacuations.

1.7 BACKGROUND OF PRESENT RESEARCH WORK

Ethylbenzene is an important raw material for the production of various other industrially important chemicals. Its industrial importance has attracted various researchers across the globe to study their chemical synthesis using PFR configuration. During synthesis it is almost imperative that some by products will get produced from the stoichiometry. In production of ethylbenzene, diethyl benzene is produced as a byproduct which is undesirable. The reactions involved are basically consecutive reactions. Presence of small amount of diethyl benzene generally leads to cross polymerization and requires to be avoided. In cases like this, reactor design becomes challenging simply because both yield and conversion need to be considered.

1.8 RESEARCH OBJECTIVES

- To study the effects of feed flow rate on steady state behaviour of PFR by using alkylation of benzene reaction and also to obtain optimum conditions in order to maximize the yield of ethylbenzene where one product is desired and another one is undesired.
- To study the effect of volume on steady state behaviour of PFR by using alkylation of benzene reaction and to obtain the optimum conditions in order to maximize the yield of ethylbenzene..
- To study the simulation results by using different thermodynamic packages and compare them with the results.

Coming to the research and studies on ethylbenzene and its yield, various research had been studied on ethylbenzene.

Elene khelebnikova (2016), her paper and research considers the benzene alkylation with ethylene model development with the use of zeolite catalyst. A list of reactions occurring in the alkylation reactor was made and the thermodynamic possibility of determination of these reactions by the change of gibbs energy was defined. The paper presents the hydrocarbons transformation scheme, which includes the grouping of components on the basis of their reactivity and the degrees of compensation values of the corresponding reactions.

Prasanna kumar sahuo(2011), studied about the optimization of the production of ethylbenzene by liquid-phase benzene alkylation. This process involves the reaction of benzene with ethylene to form ethylbenzene. Ethylene reacts with ethylbenzene to form undesired product diethyl benzene, if the temperature of reactor or concentration of ethylene are high. Diethyl benzene is the highest-boiling component in the system;it comes out the bottom of the distillation columns. The economic optimum steady-state design is developed that minimizes total annual cost. Thus it provides a classic example of an engineering design and optimization of a process.

John D. carson (1967), studied about the analog simulation of a plug flow reactor. He presents the importance of analog and digital computers in the field of reaction kinetics. The analog computer is used to simulate a chemical reaction, the hydrolysis of acetic anhydride. The hydrolysis reaction takes place in a tubular reactor. The reactor system is used to obtain experimental data for the hydrolysis reaction. The data is obtained at reactor temperatures between 75 and 100°F.

3.1 DIFFERENT TYPE OF CHEMICAL REACTORS**3.1.1 BATCH REACTOR**

The established batch reactor is a splendidly blended vessel in which reactants are changed over to items throughout a clump cycle. All variables change rapidly with time. The reactants are charged into the vessel. Heat and/or impetus is added to launch response. Reactant fixations lessening and item focuses increment with time. Temperature or weight is controlled by coveted time direction. Batch time is likewise an outline and working variable, which has a solid effect on profitability.

Temperature profiles are made so that change and yield targets are accomplished while not surpassing warmth exchange limit impediments. These ideal temperature profiles rely upon science. For instance, if the response is reversible and exothermic, the temperature profile may increase to a high temperature to get the responses going and afterward drop off with time to keep away from the decline in the compound balance consistent at high temperature. On the off chance that the response is reversible and endothermic, the temperature profile would ascend to the most elevated conceivable temperature as fast as could be allowed on the grounds that the synthetic harmony steady increments with temperature .

On the off chance that all the reactants are charged to the reactor, the reactant focuses are at first expansive, which implies that the response rate is high and the warmth exchange burden is high toward the start of the batch cycle unless the temperature is kept low. The beginning high reactant fixation issue can be evaded by utilizing a "bolstered batch reactor." Some material is at first charged to the reactor, yet the majority of the reactant is sustained over the span of the cluster cycle. This causes the volume of the fluid in the reactor to increment with time, so volume and in addition arrangements and temperatures are untouched fluctuating.

3.1.2 CONTINUOUS STIRRED-TANK REACTOR

The fluid in the reactor is thought to be flawlessly blended, that is with no spiral, hub or precise slopes in properties (temperature and arrangement). The item stream has a piece and a

temperature that are precisely the same as the substance of the fluid all through the vessel. This is constantly genuine both under consistent state conditions and progressively anytime .

This normal for a CSTR instantly creates a characteristic shortcoming of the CSTR kind of reactor, that is, the convergence of reactant in the vessel is the same as the amassing of reactant in the item. The amassing of reactant is contrarily identified with transformation

3.1.3 TUBULAR PLUG FLOW REACTOR

Plug flow reactor consists of a long straight pipe in which the reactive fluid transits at steady state. A PFR is similar to CSTR in being a flow reactor, but is different in its mixing characteristics. PFR is different from batch reactor in being a flow reactor, but is similar in the progressive change of properties with position replacing time. These features are explored further in this section, but first elaborate the characteristics of a PFR as follows:

1. The flow through the vessel both input and output streams are continuous, but not necessarily at constant rate; the flow in the vessel is plug flow.
2. The system mass inside the vessel is not necessarily fixed.
3. There is no axial mixing of fluid inside the vessel.
4. There is complete radial mixing of fluid inside the vessel (i.e., in the plane perpendicular to the direction of flow); thus, the properties of fluid including its velocity are uniform in this plane.
5. The density of the flowing system may vary in the direction of flow.
6. The system is operating at steady state conditions.
7. The reactor is assumed to be isothermal.

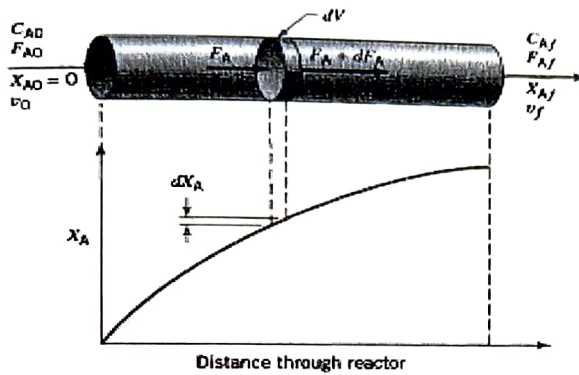
MATERIAL BALANCE

- In a plug flow reactor the composition of the fluid varies from point to point along a flow path; consequently, the material balance for the reaction component must be made for a different element of volume dV . Thus, for reactant A, the balance equation becomes

$$\text{Input} = \text{output} + \text{disappearance by reaction} + \text{accumulation}$$

- If the system is at steady state, then accumulation tends to be zero.

PERFORMANCE EQUATION OF PFR



From the figure

Input of A, moles/time = F_A

Output of A, moles/time = $F_A + dF_A$

Disappearance of A by reaction, moles/time = $(-r_A)dV$

Therefore the overall balance equation is as follows:

$$F_A = (F_A + dF_A) + (-r_A)dV$$

It may be simplify into

$$F_{A0}dX_A = (-r_A)dV$$

- This, then, is the equation which accounts for A in the differential section of the reactor of volume dV . For the reactor as a whole the expression must be integrated. Now F_A , the feed rate is constant, but r is certainly dependent on the concentration or conversion of materials. Grouping the terms accordingly, we obtain

4.1 INTRODUCTION

Ethylbenzene is an organic compound with the formula $C_6H_5CH_2CH_3$. The aromatic hydrocarbon is important in the petrochemical industry and as an intermediate in the production of styrene, which is used for making polystyrene, it is a common plastic material. Also present in small amounts in crude oil, ethylbenzene is produced by combining benzene and ethylene in an acid-catalysed chemical reaction. It is used as a solvent for aluminium bromide in anhydrous electro deposition of aluminium. Ethylbenzene is an ingredient in some paints and solvent grade xylene is nearly always contaminated with a few per cent of ethylbenzene.

4.2 PROPERTIES OF ETHYL BENZENE

Appearance : Clear, colourless liquid

Molecular formula : C_8H_{10}

Molar mass : $106.17 \text{ g mol}^{-1}$

Density : 0.8665 g/mL

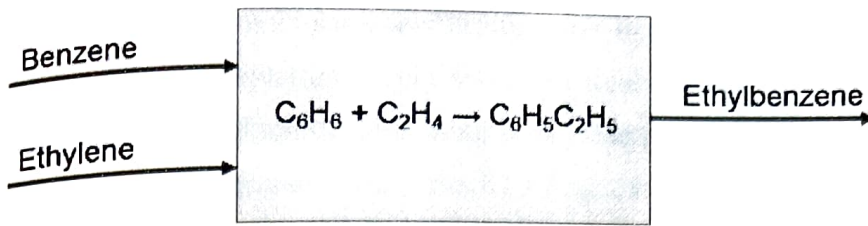
Melting point : $-95 \text{ }^\circ\text{C}$, 178 K , $-139 \text{ }^\circ\text{F}$

Boiling point : $136 \text{ }^\circ\text{C}$, 409 K , $277 \text{ }^\circ\text{F}$

Solubility in water : 0.015 g/100 mL ($20 \text{ }^\circ\text{C}$).

4.3 PRODUCTION OF ETHYL BENZENE

We continue to investigate the feasibility of constructing a new, grass-roots, 80,000 tonne/y, ethylbenzene (EB) facility (99.8 mol%), using benzene and ethylene as raw materials. As the final part of the feasibility study, we would like you to study the details of the reactor and separation section of proposed plant and then optimize the complete process. Your final design should be an optimized process and should include all unit operations necessary to produce the desired amount and purity of ethyl benzene.



4.3.1 Mixed Liquid-Vapor Phase Zeolite Catalyst Process

Process Description

This process involves the use of a Y zeolite catalyst, capable of converting benzene and dilute ethylene to ethylbenzene. The catalyst itself has excellent resistances to sulfur and water and also has good regeneration qualities, all the while ensuring great ethylene conversion, good ethylbenzene selectivity and longer operational period. The alkylation reactions take place in an alkylation reactor which primarily consists of two sections: the catalytic distillation section and the standard distillation section. The catalytic bed is found at the top of the column. Benzene is fed as a liquid from the top of the column while the ethylene is fed as a vapor from the bottom of catalytic section. This counter-current action causes the ethylene to rapidly dissolve in the benzene liquid phase and react to form ethylbenzene on the catalyst sites. Since, the reaction is extremely exothermic, the energy is used to cause distillation of the products, namely, ethylbenzene & poly-ethylbenzene (PEB). The alkylation reaction is carried out at a temperature of 140-185 °C and a pressure of 1.6-2.1 MPa. After separation of the PEB, the transalkylation reactions take place in another reactor.

Safety & Environmental Issues

There are no significant environmental and safety issues with this process as it operates at a relatively low temperature and pressure. However, it is important to note that this process still produces residual oil as one of its final by-products which can cause significant pollution and therefore, should be dealt properly by recycling or reusing it for other chemical processes. Additionally, the catalyst, albeit it has a long lifetime, still needs to be properly disposed off, as it can cause damage to the environment.

Economic Issues

1) The major cost in this process comes from the use of expensive catalysts that are crucial to the process.

2) Another important economic issue to consider would be the design and manufacture of the alkylation reactor. The alkylation would serve the dual purpose of housing the catalytic reaction and standard distillation. Combining both these processes together means that the reactor column has to be designed from scratch leading to increased capital costs.

4.3.2 Vapor-Phase Zeolite Catalyst Process

Process Description

The Mobil-Badger ethylbenzene process is considered to be the most successful vapor phase technology. In this process, fresh benzene stream is vaporized and pre-heated to a certain temperature; after which it is fed to multistage of fixed-bed reactor containing the zeolite catalyst. Moreover, the ethylene stream is introduced to the reactor through multiple stages to enhance contact between the reactants. The alkylation occurs in the vapor phase at a temperature range from 400 °C to 450°C and the pressure for each plant is usually between 2-3, MPa. The poly ethyl-benzene (PEB) recovered from the distillation column is mixed with benzene. After heating and vaporizing the mixture, it is fed into a transalkylator where the PEB reacts with the benzene to form additional ethylbenzene. The effluent from the reactor, consisting of unreacted benzene, PEBs, trace impurities and ethylbenzene, is fed into a “benzene column” for distillation. Benzene is removed from the top of the column, along with light hydrocarbons. These are stripped in an overhead stripper with the benzene being recycled to the reactors again, while the light hydrocarbons are vented to be used as a fuel. The presence of light hydrocarbons can be attributed mostly to the ethane in the ethylene feed and non-aromatic components that decompose in the fresh benzene feed. The bottoms product from the benzene column is fed in the ethylbenzene column to recover ethylbenzene from the top, while the bottoms product consisting of PEB is fed into a PEB column for further distillation. This column generates PEB as an overhead product which is recycled to the transalkylation for the production of ethylbenzene. The bottoms product is known as “residue” and is usually found in very small quantities and is also used as a fuel. The catalyst in this process is zeolite based and “is less sensitive to water, sulfur and other poisons than the Lewis acid catalysts”. Due to coke formation overtime as a result of high temperature, the catalyst becomes deactivated. Hence, it is important to regenerate the catalyst from time to time. This regeneration takes up-to 36 hours and is important after every 6-8 weeks of operation. Therefore, it is important that the process

has two parallel reactors, where one reactor is used when the other is taken out of production because catalyst regeneration.

Safety & Environmental Issues

- 1) The alkylation reaction takes place at high temperature (400-450°C) and high pressure (2-3 MPa). This means that the column would need to be constructed out of special materials of construction in order to safely accommodate such high pressures and temperatures.
- 2) Formation of coke on the catalyst means that it needs to be regenerated from time to time. This regeneration is done by the burning the catalyst to form CO₂. CO₂ is a greenhouse gas and causes significant environmental damage by destroying the ozone layer.
- 3) High temperatures also result in side-reactions of byproducts, such as aromatics, are known to be carcinogenic and also mutagenic.

Economic Issues

- 1) In order to regenerate the catalyst, specific regeneration equipment would be required which increases the capital cost of the plant [6].
- 2) Since the reactors are taken off for catalyst regeneration, a substitute reactor needs to be present to continue production. This also causes the capital cost to be increased.
- 3) High temperatures and pressures mean that the equipment needs to be made out of special materials of constructions which can be expensive, leading to increased costs.
- 4) Lastly, high temperatures and pressures also cause an increase in energy costs which lead to an increase in operating costs.

In this chapter the simulation methodology is discussed.

5.1 DWSIM SOFTWARE

Dwsim version 6.4.8 was used for the simulation work.

5.2 PROPERTY METHOD

Chao-Seader, NRTL, Peng-Robinson, Grayson-Streed, Lee-Kesler-Plocker thermodynamic models were used as the property method.

5.3 PROPERTY PACKAGE DESCRIPTIONS

Equations of State (EOS)

Equation of State models have proven to be very reliable in predicting the properties of most hydrocarbon based fluids over a wide range of operating conditions. Their application focuses on primarily non-polar or slightly polar components.

GCEOS

The GCEOS model allows you to define and implement your own generalized cubic equation of state including mixing rules and volume translation.

Chao Seader & Grayson Streed Models

The Chao Seader and Grayson Streed methods are older, semi-empirical methods. The Grayson Streed correlation is an extension of the Chao Seader method with special emphasis on hydrogen. Only the equilibrium data produced by these correlations is used by HYSYS. The Lee-Kesler method is used for liquid and vapour enthalpies and entropies.

Chao Seader

Use the Chao Seader (CS) method for heavy hydrocarbons, where the pressure is less than 10342 kPa (1500 psia), and temperatures range between -17.78 and 260°C (0-500°F). The CS property package is used for the steam systems. The CS property package can also be used for three-phase flashes, but is restricted to the use of pure H₂O for the second liquid phase.

The CS method, though limited in scope, may be preferred in some instances. For example, CS is recommended for problems containing mainly liquid or vapour H₂O because the property package includes special correlations that accurately represent the steam tables. The following tables give an approximate range of applicability for CS method and under what conditions CS is applicable.

Method	Temp (°F)	Temp (°C)	Pressure (psia)	Pressure (kPa)
CS	0 to 500	-18 to 260	<1,500	<10,000

Conditions of Applicability:

For all hydrocarbons (except CH₄): $0.5 < Tr < 1.3$ and $P_{mixture} < 0.8$
 If CH₄ or H₂ is present: molal average $Tr < 0.93$
 CH₄ mole fraction < 0.3
 mole fraction dissolved gases < 0.2

When predicting K values for:

Paraffinic or Olefinic Mixtures liquid phase aromatic mole fraction < 0.5
 Aromatic Mixtures liquid phase aromatic mole fraction > 0.5

Chao-Seader (CS) uses the CS-RK method for calculating VLE and the Lee Kesler method for calculating Enthalpy and Entropy. The vapour phase fugacity coefficients are calculated with the Redlich Kwong equation of state. The pure liquid fugacity coefficients are calculated using the principle of corresponding states. Special functions are incorporated for the calculation of liquid phase fugacities for N₂, CO₂ and H₂S. These functions are restricted to hydrocarbon mixtures with less than five percent of each of the above components.

As with the Vapour Pressure models, H₂O is treated using a combination of the steam tables and the kerosene solubility charts from the API Data Book. This method of handling H₂O is not very accurate for gas systems. Although three phase calculations are performed for all systems, it is important to note that the aqueous phase is always treated as pure H₂O with these correlations.

Grayson Streed

The GS correlation is an extension of the Chao-Seader method with special emphasis on H₂. Only the equilibrium results produced by these correlations are used by HYSYS. The Grayson-Streed correlation is recommended for use with systems having a high concentration of H₂ because of the special treatment given H₂ in the development of the model. The GS correlation can also be used for simulating topping units and heavy ends vacuum applications. This correlation may also be slightly more accurate in the simulation of vacuum towers. The Grayson-Streed (GS) property package can be used for three-phase flashes, but is restricted to the use of pure H₂O for the second liquid phase.

The following tables gives an approximate range of applicability for the GS method and under what conditions the method is applicable:

Method	Temp (°F)	Temp (°C)	Pressure (psia)	Pressure (kPa)
GS	0 to 800	-18 to 425	<3,000	<20,000

Conditions of Applicability:

For all hydrocarbons (except CH₄):

$$0.5 < Tr < 1.3 \text{ and } Pr_{\text{mixture}} < 0.8$$

If CH₄ or H₂ is present:

$$\text{molal average } Tr < 0.93$$

$$\text{CH}_4 \text{ mole fraction } < 0.3$$

$$\text{mole fraction dissolved gases } < 0.2$$

When predicting K values for:

Paraffinic or Olefinic Mixtures

$$\text{liquid phase aromatic mole fraction } < 0.5$$

Aromatic Mixtures

$$\text{liquid phase aromatic mole fraction } > 0.5$$

Grayson-Streed (GS) uses the GS-RK to calculate VLE and Lee-Kesler to calculate Enthalpy and Entropy.

The vapour phase fugacity coefficients are calculated with the Redlich Kwong equation of state. The pure liquid fugacity coefficients are calculated using the principle of corresponding states. Modified acentric factors are included in HYSYS' GS library for most components. Special functions are incorporated for the calculation of liquid phase fugacities for N₂, CO₂, and H₂S. These functions are restricted to hydrocarbon mixtures with less than five percent of each of the above components.

As with the Vapour Pressure models, H₂O is treated using a combination of the steam tables and the kerosene solubility charts from the API Data Book. This method of handling H₂O is

not very accurate for gas systems. Although three phase calculations are performed for all systems, it is important to note that the aqueous phase is always treated as pure H₂O with these correlations.

NRTL

The Non-Random-Two-Liquid (NRTL) equation is an extension of the Wilson equation. It uses statistical mechanics and the liquid cell theory to represent the liquid structure. It is capable of representing VLE, LLE, and VLLE phase behaviour. The NRTL property package is used for chemical systems and HF Alkylation with highly non-ideal chemicals.

NRTL uses the following calculation methods:

For liquid:

- NRTL method for VLE
- Cavett method for Enthalpy and Entropy

For vapour:

- Ideal Gas, RK, Virial, Peng Robinson, and SRK methods for VLE
- Ideal Gas, RK, Virial, Peng Robinson, and SRK methods for Enthalpy and Entropy

Like the Wilson equation, the NRTL is thermodynamically consistent and can be applied to ternary and higher order systems using parameters regressed from binary equilibrium data. It has an accuracy comparable to the Wilson equation for VLE systems. The NRTL equation in HYSYS contains five adjustable parameters (temperature dependent and independent) for fitting per binary pair. The NRTL combines the advantages of the Wilson and van Laar equations.

- Like the van Laar equation, NRTL is not extremely CPU intensive and can represent LLE quite well.
- Unlike the van Laar equation, NRTL can be used for dilute systems and hydrocarbon-alcohol mixtures, although it may not be as good for alcohol-hydrocarbon systems as the Wilson equation.
- The five adjustable parameters for the NRTL equation in HYSYS are the a_{ij} , a_{ji} , b_{ij} , b_{ji} , and α_{ij} terms.

Note: Due to the mathematical structure of the NRTL equation, it can produce erroneous multiple miscibility gaps. The equation uses parameter values stored in HYSYS or any user supplied value for further fitting the equation to a given set of data.

Peng-Robinson

The Peng-Robinson (PR) model is ideal for VLE calculations as well as calculating liquid densities for hydrocarbon systems. Several enhancements to the original PR model were made to extend its range of applicability and to improve its predictions for some non-ideal systems. However, in situations where highly non-ideal systems are encountered, the use of Activity Models is recommended.

The PR property package rigorously solves any single-, two-, or three-phase system with a high degree of efficiency and reliability and is applicable over a wide range of conditions:

- Temperature Range $> -271^{\circ}\text{C}$ or -456°F
- Pressure Range $< 100,000$ kPa or 15,000 psia

The PR property package also contains enhanced binary interaction parameters for all library hydrocarbon-hydrocarbon pairs (a combination of fitted and generated interaction parameters), as well as for most hydrocarbon-non-hydrocarbon binaries. For non-library or hydrocarbon hypo components, HC-HC interaction parameters are generated automatically by HYSYS for improved VLE property predictions.

Lee-Kessler Plocker

The Lee-Kesler Plocker model is the most accurate general method for non-polar substances and mixtures and is recommended for Ethylene Towers. LKP uses the Lee-Kesler-Plocker method to calculate VLE and uses the Lee Kesler method to calculate Enthalpy and Entropy. Plocker applied the Lee Kesler equation to mixtures, which itself was modified from the BWR equation.

5.4 STEADY STATE SIMULATION

5.4.1. Chemical Kinetics

The specific chemistry used to understand the steady state behavior of CSTR and demonstrate the use of DWSIM is the reaction of ethylene (E) with benzene (B) to form the favored product ethylbenzene (EB). There is a repeated reaction that produces an unwanted product di-ethylbenzene (DEB). A third reaction associates benzene and diethyl benzene to form ethylbenzene .



The reactions follow in the liquid phase and are assumed to be irreversible. The reaction rates of the three reactions are assumed to be those given here:

$$R_1 = (C_E)(C_B)(1.528 \times 10^6) e^{(-71130000)/RT} \quad \rightarrow (3.4)$$

$$R_2 = (C_E)(C_{EB})(2.778 \times 10^3) e^{(-83680000)/RT} \quad \rightarrow (3.5)$$

$$R_3 = (C_{DEB})(C_B)(0.4167) e^{(-62760000)/RT} \quad \rightarrow (3.6)$$

The units of R are $\text{kmol s}^{-1} \text{m}^{-3}$. Concentrations have units of kmol/m^3 . Activation energies have units of J/kmol. Temperature is in degrees Kelvin . C_E is the concentration of ethylene; C_B is the concentration of benzene.

C_{EB} is the concentration of ethyl benzene; C_{DEB} is the concentration of diethylbenzene.

5.5 SIMULATION SETUP

The step by step procedure to make the desired arrangement is as follows.

- 1) First, after opening the Dwsim software , we should enter the required compounds used in simulation work.

File Edit Insert Tools Dynamics Utilities Optimization Results Plugins Spreadsheet Windows View Help

Settings Solve Flowsheet (F5) Abort Solver (Pause/Break) Dynamics

Settings

Compounds Thermodynamics Reactions Mass and Energy Balances System of Units Floating Tables and Property Lists Miscellaneous

Components / Compounds

Search

Added	Name	Tag	CAS Number	Formula	Database	CP
<input checked="" type="checkbox"/>	Ethylene		74-85-1	CH ₂ CH ₂	ChemSep	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/>	Benzene		71-43-2	C ₆ H ₆	ChemSep	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/>	Ethylbenzene		100-41-4	C ₆ H ₅ CH ₂ CH ₃	ChemSep	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/>	O-diethylbenzene		135-01-3	C ₆ H ₄ (CH ₂ CH ₃) ₂	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Air		132259-10-0	(N ₂ O.781102)O.209(Ar)	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Argon		7440-37-1	Ar	ChemSep	<input checked="" type="checkbox"/>
<input type="checkbox"/>	Bromine		7726-95-6	Br ₂	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Carbon tetrachloride		56-23-5	CCl ₄	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Carbon monoxide		630-08-0	CO	ChemSep	<input checked="" type="checkbox"/>
<input type="checkbox"/>	Carbon dioxide		124-38-9	CO ₂	ChemSep	<input checked="" type="checkbox"/>
<input type="checkbox"/>	Carbon disulfide		75-15-0	CS ₂	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Phosgene		75-44-5	COCl ₂	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Trichloroacetyl chloride		75-02-8	CCl ₃ COCl	ChemSep	<input type="checkbox"/>
<input type="checkbox"/>	Hydrogen chloride		7647-01-0	HCl	ChemSep	<input checked="" type="checkbox"/>

View Selected Compound
 Import from Online Sources
 Import from JSON File
 Order Compounds By: Default (As Added)

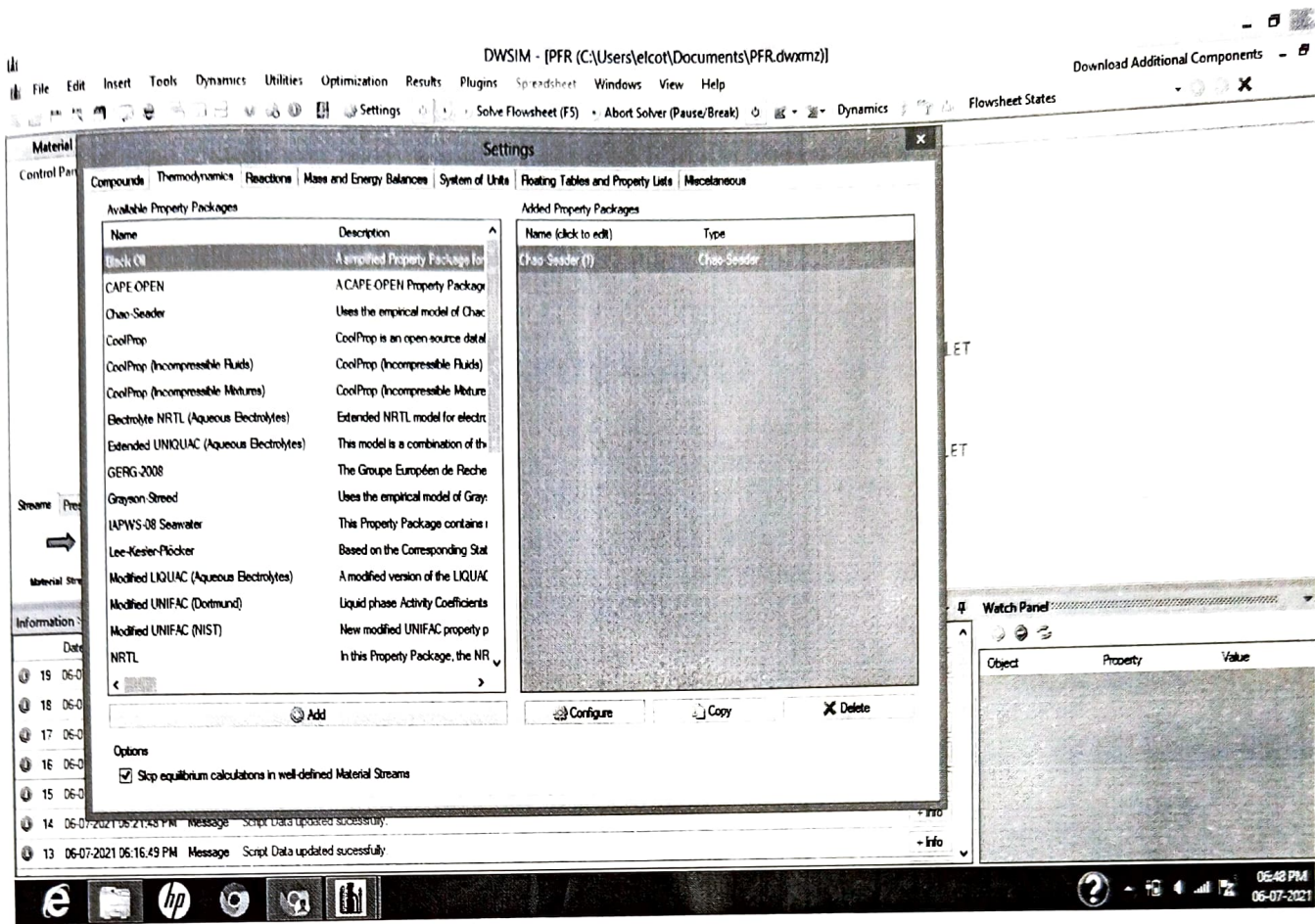
Petroleum Fractions

Start Bulk C7+ Petroleum Characterization Utility

Start Distillation Curves Petroleum Characterization Utility

Open Assay Manager

2) After selecting the compounds, we should select the suitable thermodynamic package from the options.



Most thermodynamic models have binary interaction parameters which are fitted to experimental data. Always check if the selected thermodynamic package has interaction parameters for the compounds in the simulation, if required. In our case, we selected CHAO-SEADER as the thermodynamic package.

3.) After selected the thermodynamic package, simulation page opens. Select two material streams namely ethylene and benzene. Enter the properties like pressure, temperature of those streams.

ETHYLENE (Material Stream)

Information Connections

General Info

Object: ETHYLENE
 Status: Calculated (06-05-2021 03:08:53 PM)
 Linked to:

Property Package Settings

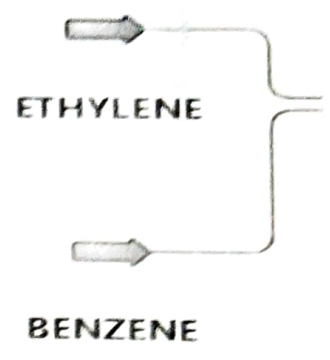
Property Package: Chao-Seader (1)

Input Data Results Annotations Dynamics Floating Tables

Stream Conditions Compound Amounts

Rash Spec	Temperature and Pressure (TP)	
Temperature	25	C
Pressure	1.01325	bar
Mass Flow	20198.3	kg/h
Molar Flow	720	kmol/h
Volumetric Flow	17513	m3/h
Specific Enthalpy	-1.63395	kJ/kg
Specific Entropy	-0.00378236	kJ/[kg.K]
Vapor Phase Mole Fraction	1	

Material Streams Spread
 Control Panel Mode Search



Streams Pressure Changers Separators



Information

	Date	Type
23	06-07-2021 07:07:46 PM	Messa
22	06-07-2021 07:02:46 PM	Messa
21	06-07-2021 06:56:48 PM	Messa
20	06-07-2021 06:51:48 PM	Messa
19	06-07-2021 06:46:48 PM	Messa

BENZENE (Material Stream) Material Streams Spreadsheet

Control Panel Mode Search

Information Connections

General Info

Object: BENZENE

Status: Calculated (06-05-2021 03:34:58 PM)

Linked to:

Property Package Settings

Property Package: Chao-Seader (1)

Input Data Results Annotations Dynamics Floating Tables

Stream Conditions Compound Amounts

Flash Spec: Temperature and Pressure (TP)

Temperature: 25 C

Pressure: 1.01325 bar

Mass Flow: 196842 kg/h

Molar Flow: 2520 kmol/h

Volumetric Flow: 225.487 m³/h

Specific Enthalpy: -427.284 kJ/kg

Specific Entropy: -1.21458 kJ/[kg.K]

Vapor Phase Mole Fraction: 0

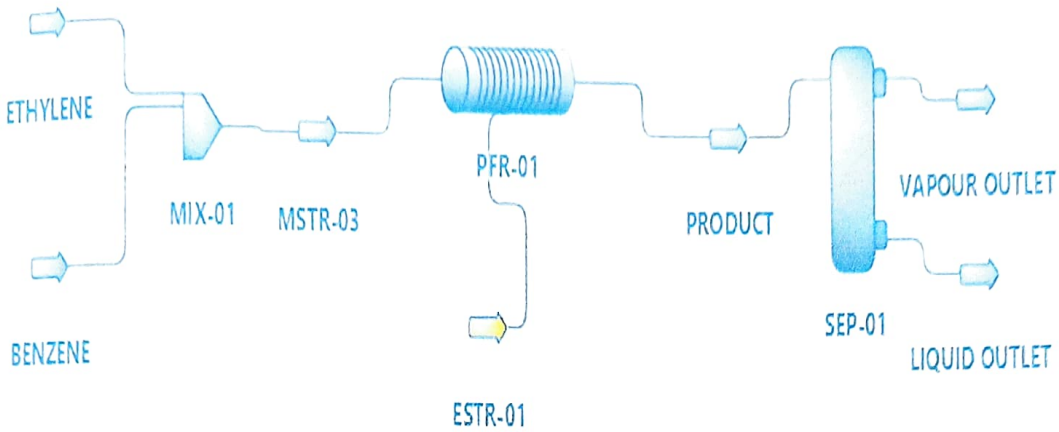
Streams Pressure Changers Separators/Tan

Material Stream Energy Stream

Information

Date	Type
24 06-07-2021 07:12:46 PM	Message
23 06-07-2021 07:07:46 PM	Message
22 06-07-2021 07:02:46 PM	Message
21 06-07-2021 06:56:48 PM	Message
20 06-07-2021 06:51:48 PM	Message

4.) Then, connect those two material streams to a plug flow reactor. Also connect a energy stream to the reactor. Since, we are operating the reactor at isothermal conditions, enter the operating conditions of the reactor. The schematic arrangement of our simulation is as follows.



The operating conditions of the reactor are shown below.

The screenshot shows the DWSIM software interface for a Plug-Flow Reactor (PFR-01). The left sidebar displays the reactor's configuration and results. The main window shows the process flow diagram from the previous image.

Configuration:

- Object: PFR-01
- Status: Calculated (06-05-2021 03:35:00 PM)
- Connections:
 - Inlet Stream: MSTR-03
 - Outlet Stream: PRODUCT
 - Energy Stream: ESTR-01
- Calculation Parameters:
 - Reaction Set: Default Set
 - Calculation Mode: Isothermic
 - Outlet Temperature: 10.5122 °C
 - Reactor Volume: 100 m³
 - Reactor Length: 1 m
 - Catalyst Loading: 0 kg/m³
 - Catalyst Particle Diameter: 0 mm
 - Catalyst Void Fraction: 0

Results:

Property	Value	Units
Heat Loss	982.655	kW
Liquid residence time	0.0056117	h
Pressure drop	0.0255728	bar

Information Log:

Date	Type	Message
06-07-2021 07:27:46 PM	Message	Script Data updated successfully
06-07-2021 07:22:46 PM	Message	Script Data updated successfully
06-07-2021 07:17:46 PM	Message	Script Data updated successfully
06-07-2021 07:12:46 PM	Message	Script Data updated successfully
06-07-2021 07:07:46 PM	Message	Script Data updated successfully
06-07-2021 07:02:46 PM	Message	Script Data updated successfully
06-07-2021 06:55:48 PM	Message	Script Data updated successfully

5.) After the simulation setup, enter the reactions which takes place inside the reactor. Since, we already seen that there are three reactions takes place inside the reactor.

DWSIM - [PFR (C:\Users\elcor\Documents\PFR.dwxmz)]

File Edit Insert Tools Dynamics Utilities Optimization Results Physics Feedstocks Utilities Help

Material Streams Spreadsheet

Control Panel Mode Search

ETHYLENE

BENZENE

MIX-01

Compounds

Reaction Set

Name

Default Set

Identification

Name ETHYL BENZENE

Description

Components, Stoichiometry and Reaction Orders

Name	Molar Weight	ΔH_f (kJ/kg)	Include	BC	Stoich. Coeff.	DO	PO
Ethylene	28.0532	1871.8	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	-1	1	0
Benzene	78.1118	1061.04	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	-1	1	0
Ethylbenzene	106.165	281.825	<input checked="" type="checkbox"/>	<input type="checkbox"/>	1	0	0
O-diethylbenzene	134.218	-141.214	<input type="checkbox"/>	<input type="checkbox"/>	0	0	0

Stoichiometry OK Balance Heat of Reaction (kJ/kmol_BC) -105470

Equation CH2CH2 + CHCHCHCHCHCH -> [C]H5CH2CH3

Kinetic Reaction Parameters

Base Component Ethylene Basis Molar Concentrations T_{min} (K) 0

Phase Liquid T_{max} (K) 2000

Kinetics Specification Simple Advanced Pyromat Solver Help

Velocity Constants for Direct and Reverse Reactions (k and k')

Direct Reaction Arrhenius A 1528000 E 71130000 J/mol

User-Defined: f(T), T in K

Reverse Reaction Arrhenius A' 0 E' 0 J/mol

User-Defined: f(T), T in K

Amount Units kmol/m3 Velocity Units

Cancel OK

Download Additional Components

States

CHCHCH -> CHCHCH

CHCH3 -> CHCHCH

CHCHCH2C6

Pressure Changes Separators/Tanks

Material Stream Energy Stream

Information

Date	Type	Message
15-07-2021 03:56:55 PM	Tip	If ac
15-07-2021 03:56:55 PM	Tip	To lo li
15-07-2021 03:56:55 PM	Tip	Use obj
15-07-2021 03:56:55 PM	Tip	Pre
15-07-2021 03:56:55 PM	Tip	Ho
15-07-2021 03:56:55 PM	Message	File C:\Users\elcor\Do

File Edit Invert Tools Dynamics Utilities Optimization Results Diagnostics Compendium Windows View Help

Material Streams Spreadsheet Control Panel Mode Search

ETHYLENE BENZENE MIX-01

Streams Pressure Changes Separators/Tanks

Information

Date	Type	Message
15-07-2021 04:01:42 PM	Message	Scn
15-07-2021 03:56:55 PM	Tip	If ac
15-07-2021 03:56:55 PM	Tip	To cha
15-07-2021 03:56:55 PM	Tip	Use sec
15-07-2021 03:56:55 PM	Tip	Pre
15-07-2021 03:56:55 PM	Tip	Hold SHIFT during DWS
15-07-2021 03:56:55 PM	Message	File C:\Users\elcot\Documents\PFR.dwxmz loaded successfully.

Edit Kinetic Reaction

Identification
Name: DIETHYLBENZENE
Description:

Components, Stoichiometry and Reaction Orders

Name	Molar Weight	ΔHf (kJ/kg)	Include	BC	Stoch. Coeff.	DO	RO
Ethylene	28.0532	1871.8	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	-1	1	0
Benzene	78.1118	1061.04	<input type="checkbox"/>	<input type="checkbox"/>	0	0	0
Ethylbenzene	106.165	281.825	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	-1	1	0
O-diethylbenzene	134.218	-141.214	<input checked="" type="checkbox"/>	<input type="checkbox"/>	1	0	0

Stoichiometry: OK Balance Heat of Reaction (kJ/mol_BC): -101384

Equation: CH2CH2 + [C6H5]CH2CH3 <=> CH3CH2[C6H4]CH2CH3

Kinetic Reaction Parameters

Base Component: Ethylene Basis: Molar Concentrations T_{min} (K): 0
Phase: Liquid T_{max} (K): 2000

Kinetics Specification: Simple Advanced Python Script Help

Velocity Constants for Direct and Reverse Reactors (k and k')

Direct Reaction: Arrhenius A: 2778 E: 83680000 J/mol
 User-Defined: f(T), T in K

Reverse Reaction: Arrhenius A': 0 E': 0 J/mol
 User-Defined: f(T), T in K

Amount Units: kmol/m³ Velocity Units:

Cancel OK

CH3CH2 <-> CH3CH2
CH3 <-> CH3
CH3CH2C6H6

State

aty Value

DWSIM - [PFR (C:\Users\elcot\Documents\PFR.dwxmz)]

Download Additional Components

File Edit Insert Tools Dynamics Utilities Optimization Results Plugins Spreadsheet Windows View Help

Edit Kinetic Reaction

Material Streams Spreadsheet

Control Panel Mode Search

ETHYLENE

BENZENE

MIX-01

Streams Pressure Changers Separators/Tanks

Material Stream Energy Stream

Information

Date	Type	Message
15-07-2021 04:01:42 PM	Message	Scr
15-07-2021 03:56:55 PM	Tip	If sc
15-07-2021 03:56:55 PM	Tip	To cha
15-07-2021 03:56:55 PM	Tip	Use sec
15-07-2021 03:56:55 PM	Tip	Pre:
15-07-2021 03:56:55 PM	Tip	Hold SHIFT during DWS
15-07-2021 03:56:55 PM	Message	File C:\Users\elcot\Doc

Compounds The

Reaction Sets

Name

Default Set

Identification

Name: (1)ETHYL BENZENE

Descripto

Components, Stoichiometry and Reaction Orders

Name	Molar Weight	AHf (kJ/kg)	Include	BC	Stoich. Coeff	DO	PO
Ethylene	28.0532	1871.8	<input type="checkbox"/>	<input type="checkbox"/>	0	0	0
Benzene	78.1118	1061.04	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	-1	1	0
Ethylbenzene	106.165	281.825	<input checked="" type="checkbox"/>	<input type="checkbox"/>	2	0	0
O-diethylbenzene	134.218	-141.214	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	-1	1	0

Stoichiometry OK Balance Heat of Reaction (kJ/kmol_BC) -4085.5

Equation: C1=CC=CC=C1 + CH3CH2C6H4CH2CH3 <=> 2C6H5CH2CH3

Kinetic Reaction Parameters

Base Component: Benzene Basis: Molar Concentrations Tmin (K): 0

Phase: Liquid Tmax (K): 2000

Kinetics Specification: Simple Advanced Python Script Help

Velocity Constants for Direct and Reverse Reactions (k and k')

Direct Reaction: Arrhenius A: 0.4167 E: 62760000 J/mol

User-Defined: f(T), T in K

Reverse Reaction: Arrhenius A': 0 E': 0 J/mol

User-Defined: f(T), T in K

Amount Units: kmol/m3 Velocity Units:

Cancel OK

DWSIM - [PFR (C:\Users\elcot\Documents\PFR.dwxmz)]

Download Additional Components

File Edit Insert Tools Dynamics Utilities Optimization Results Plugins Spreadsheet Windows View Help

Solve Flowsheet (F5) Abort Solver (Pause/Break) Dynamics Flowsheet States

Material Streams Spreadsheet Charts Flowsheet Dynamics Manager Script Manager

PFR-01 (Plug-Flow Reactor (PFR))

Settings

Compounds Thermodynamics Reactions Mass and Energy Balances System of Units Floating Tables and Property Lists Miscellaneous

Reaction Sets

Name	Description
Default Set	Default Reaction Set

Chemical Reactions

Name	Type	Equation
ETHYL BENZENE	Kinetic	$\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \leftrightarrow$
DIETHYLBENZENE	Kinetic	$\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \leftrightarrow \text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_3$
(1)ETHYL BENZENE	Kinetic	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \leftrightarrow \text{C}_6\text{H}_4\text{CH}_2\text{CH}_3$

OUTLET
OUTLET

Indicators Controllers Other

Property Value

Property	Value
Delta-T	
Heat Load	-982.6
Liquid residence time	0.00961
Pressure drop	0.02557

23 06-07-2021 07:07:46 PM Message Script Data updated successfully

ETHYLENE (M... BENZENE (Mat... PFR-01 (Plug... ESTR-01 (Ener...

07:41 PM 06-07-2021

By carefully analyzing the above chemical reactions and rate kinetics we would have the following conclusion about feed flow rate and reactor volume.

Here we showed the pictures only for chao-seader thermodynamic package. Run the simulation for different thermodynamic packages like NRTL, PENG-ROBINSON, GRAYSON-STREED and LEE-KESLER PLOCKER and note down the results.

5.5.1 Effect of feed flow rate

The feed flow rate of benzene must be greater than the feed flow rate of ethylene in order to lower formation of undesired product i.e. diethyl benzene. Increasing the feed flow rate of benzene also has negative impacts such as increasing separation cost which is added to the production cost i.e. minimizing the profit margin.

The solution for above problem is optimizing the feed flow rate by using the Dwsim by keeping the one of the feed flowrate constant and varying the other one.

2.2 Effect of reactor volume

Reactor provides sufficient residence time to the reactants where the reactants are converted to products. In case of exothermic reaction heat removal is necessary in that case reactor provides sufficient reactor area for jacketed cooling. Increasing the reactor volume provides better cooling but aggregate the residence time and capital cost. Decreasing the reactor volume may lead to the process become uncontrollable and it lead to the formation of undesired product.

6.1 EFFECT OF FEED FLOW RATE

First, we do the optimization of feed flow rate, for this we need to fix other quantities like reactor volume and temperature. From the literature review we have a good idea about reactor temperature and reactor volume which may or maynot be optimum values.

Let's take the feed flow rate of ethylene is $F(E)=0.2$ kmol/s and the reactor volume be $V=100\text{m}^3$.

By varying the benzene flow rate $F(B) = 0.3, 0.4, 0.5, 0.6, 0.7(\text{kmol/s})$ and run the simulation as follows.

As we know, DWSIM has various inbuilt thermodynamic packages so finding best one is little bit difficult. So, we simulate the process using different thermodynamic packages and atleast we should select the best thermodynamic package which gives better yield than other thermodynamic packages.

TABLE 6.1 Comparison of benzene flow rate with ethyl benzene flow rate for different thermodynamic packages

Ethylene (Feed) (kmol/s)	Benzene (feed) (kmol/s)	Ethyl benzene(kmol/s)				
		Chao-seader	NRTL	Peng-Robinson	Grayson-Streed	Lee-kesle r-plocker
0.2	0.3	0.008088	4.08×10^{-6}	0.00378	0.0083	0.00306
0.2	0.4	0.01045	4.93×10^{-6}	0.00493	0.01076	0.0144
0.2	0.5	0.012757	5.66×10^{-6}	0.00605	0.0262	0.00493
0.2	0.6	0.0301407	8.90×10^{-6}	0.00715	0.01553	0.0209
0.2	0.7	0.0172509	8.20×10^{-6}	0.00824	0.0146	0.00676

Then, calculate the yield of ethylbenzene according to the formula,

$$\text{yield of ethylbenzene} = \frac{\text{Moles of ethylbenzene formed}}{\text{Moles of benzene fed}}$$

TABLE 6.2 Comparison of benzene flow rate and Yield of ethylbenzene for different thermodynamic packages

Ethylene (feed) (kmol/s)	Benzene (feed) (kmol/s)	% Yield of Ethylbenzene				
		Chao-Seeder	NRTL	Peng-Robinson	Grayson-Stred	Lee-Kesler-Plöcker
0.2	0.3	2.696	0.00132	1.26	2.76	1.2
0.2	0.4	2.892	0.001198	1.23	2.69	3.6
0.2	0.5	3.625	0.001132	1.21	3.49	0.986
0.2	0.6	5.023	0.001483	1.191	2.588	4.18
0.2	0.7	2.4644	0.001171	1.117	2.08	0.9657

The plot of benzene flow rate versus % yield of ethylbenzene using different thermodynamic packages are shown below.

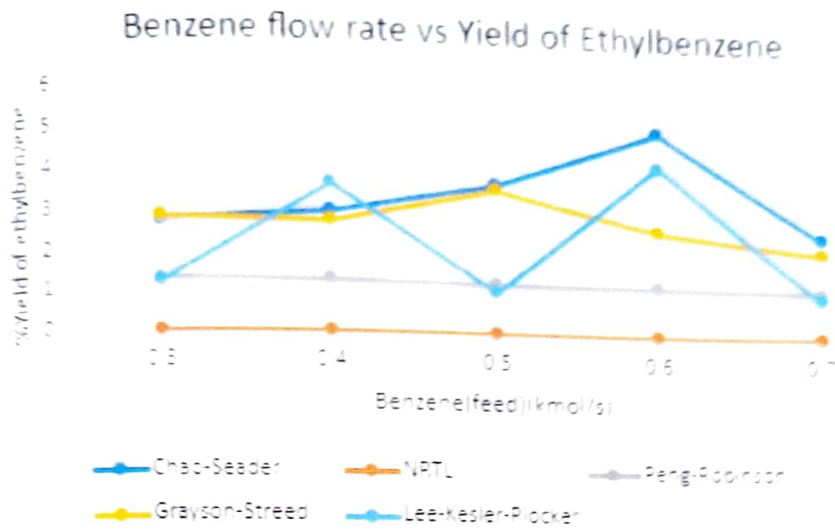


Figure 6.1 Benzene flow rate vs %yield of ethylbenzene using different thermodynamic packages

Inferences from table and graphs

The graph shown above shows the plot of benzene feed flow rate versus yield of ethylbenzene (desired product) using five different thermodynamic packages. Since, our primary product is ethylbenzene and our motive is to increase the yield of ethylbenzene. By analyzing the plots shown above, CHAO-SEADER model yields maximum amount of ethylbenzene and it shows the favourable variations.

Since, we already discussed about the thermodynamic packages and their properties. The reason behind that Chao-Sedaer model shows favourable variation is, CS is recommended for problems containing mainly liquid or vapour H_2O because the property package includes special correlations that accurately represent the steam tables. Also, our operating conditions lies within the operating range of Chao-Seader model.

By analysing the CHAO-SEADER model, the yield of ethylbenzene increases with increases in benzene flow rate upto benzene flow rate becomes 0.6 kmol/s. After this flow rate, the yield starts to decrease. So, we can take $F(B)=0.6$ kmol/s as a optimum benzene feed flow rate which yields maximum amount of ethylbenzene.

6.2 EFFECT OF REACTOR VOLUME

Similarly like above here we fixing the feed flow rate of benzene $F(B)=0.4$ and ethylene $F(E)=0.2$ kmol/s.

By varying the reactor volume $V= 100, 200, 300, 400, 500, 600, 700, 800, 900$ and run the simulation and obtained stream results as follows. Run the simulation for different thermodynamic packages and note down the results.

TABLE 6.3 Comparison of Volume of reactor with Diethyl benzene flow rate by using different thermodynamic packages.

Volume of reactor(m ³)	Diethyl benzene(kmol/s)				
	Chao-Seader	NRTL	Peng-Robinson	Grayson-Streed	Lee-Kesler-Plockler
100	4.51×10^{-7}	1×10^{-13}	5.63×10^{-8}	2.831×10^{-7}	4.86×10^{-7}
200	3.92×10^{-7}	1×10^{-13}	5.63×10^{-8}	2.831×10^{-7}	4.99×10^{-7}
300	3.66×10^{-7}	1×10^{-13}	5.26×10^{-8}	2.828×10^{-7}	4.47×10^{-7}
400	3.40×10^{-7}	1×10^{-13}	4.41×10^{-8}	2.831×10^{-7}	4.92×10^{-7}
500	3.11×10^{-7}	2.797×10^{-13}	5.58×10^{-8}	2.37×10^{-7}	4.89×10^{-7}
600	2.97×10^{-7}	1×10^{-13}	5.260×10^{-8}	2.828×10^{-7}	4.87×10^{-7}
700	2.77×10^{-7}	1×10^{-13}	5.49×10^{-8}	2.83×10^{-7}	3.81×10^{-7}
800	2.57×10^{-7}	1×10^{-13}	4.41×10^{-8}	2.831×10^{-7}	3.66×10^{-7}
900	2.41×10^{-7}	1×10^{-13}	5.39×10^{-8}	2.802×10^{-7}	3.53×10^{-7}

Moles of diethyl benzene form

$$\text{Yield of diethyl benzene} = \frac{\text{Moles of diethyl benzene form}}{\text{Moles of diethyl benzene fed}}$$

TABLE 6.4 Comparison of Volume of reactor with the %Yield of diethyl benzene by using different thermodynamic packages

Volume(m ³)	%Yield of diethyl benzene				
	Chao-Seader	NRTL	Peng-Robinson	Grayson-Streed	Lee-Keeler-Plucker
100	1.1275*10 ⁻⁵	2.5*10 ⁻¹¹	1.4075*10 ⁻⁵	7.075*10 ⁻⁵	1.215*10 ⁻⁴
200	9.8*10 ⁻⁵	2.5*10 ⁻¹¹	1.407*10 ⁻⁵	7.0775*10 ⁻⁵	1.2475*10 ⁻⁴
300	9.15*10 ⁻⁵	2.5*10 ⁻¹¹	1.315*10 ⁻⁵	7.07*10 ⁻⁵	1.1175*10 ⁻⁴
400	8.5*10 ⁻⁵	2.5*10 ⁻¹¹	1.1025*10 ⁻⁵	7.0775*10 ⁻⁵	1.23*10 ⁻⁴
500	7.775*10 ⁻⁵	6.9925*10 ⁻¹¹	1.395*10 ⁻⁵	5.925*10 ⁻⁵	1.225*10 ⁻⁴
600	7.425*10 ⁻⁵	2.5*10 ⁻¹¹	1.315*10 ⁻⁵	7.07*10 ⁻⁵	1.2175*10 ⁻⁴
700	6.925*10 ⁻⁵	2.5*10 ⁻¹¹	1.3725*10 ⁻⁵	7.075*10 ⁻⁵	9.525*10 ⁻⁴
800	6.425*10 ⁻⁵	2.5*10 ⁻¹¹	1.1025*10 ⁻⁵	7.075*10 ⁻⁵	9.15*10 ⁻⁴
900	6.025*10 ⁻⁵	2.5*10 ⁻¹¹	1.4825*10 ⁻⁵	7.005*10 ⁻⁵	8.825*10 ⁻⁴

The plots of volume of a reactor vs yield of diethyl benzene for different thermodynamic packages are shown below.

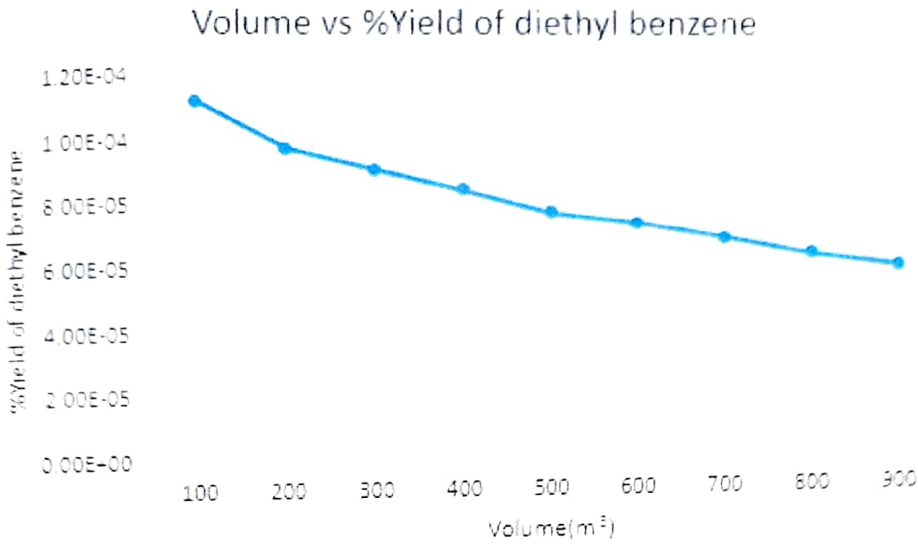


FIGURE 6.2 Volume of reactor vs % Yield of Diethyl benzene by using Chao-Seader model

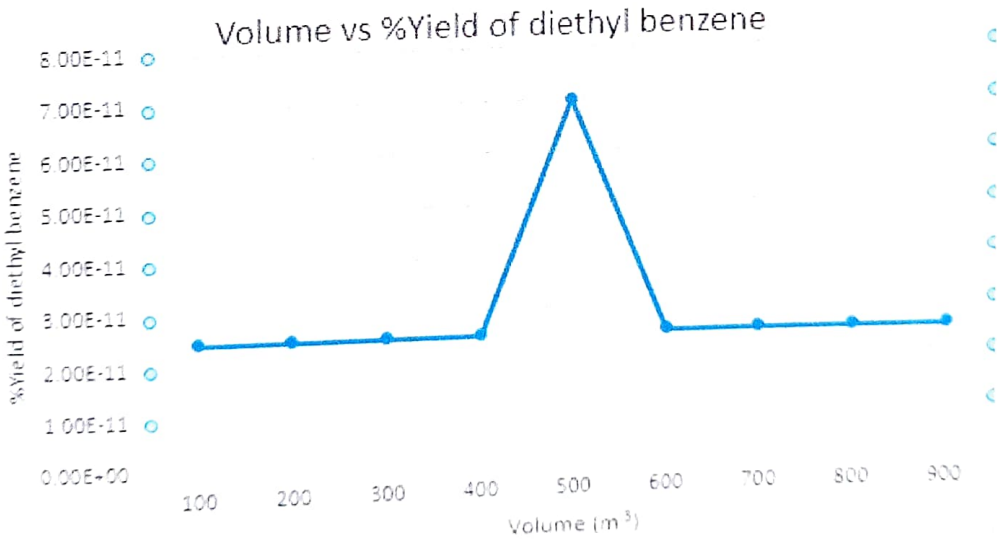


FIGURE 6.3 Volume vs % Yield of Diethyl benzene flow rate by using NRTL model

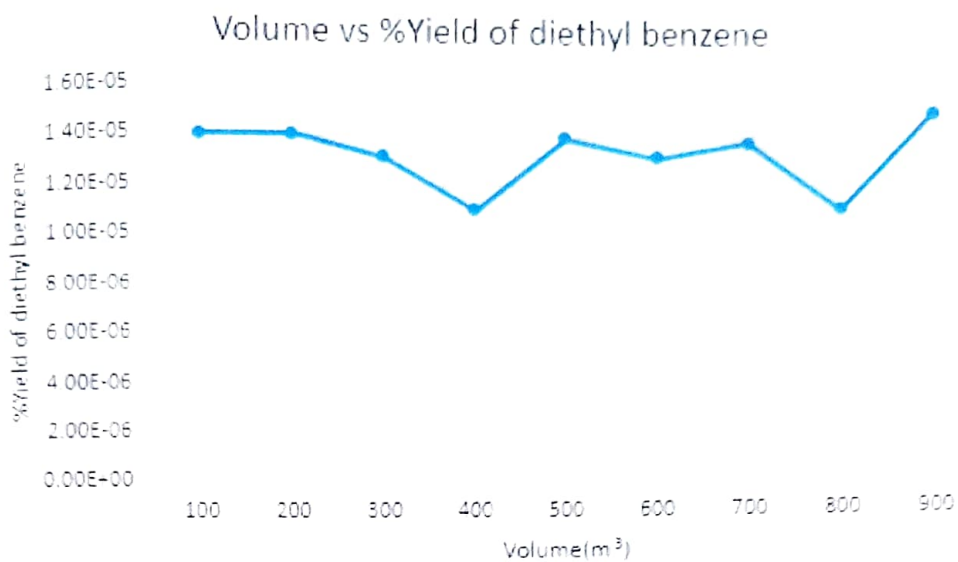


FIGURE 6.4 Volume vs %Yield of Diethyl benzene flow rate by using Peng-Robinson model

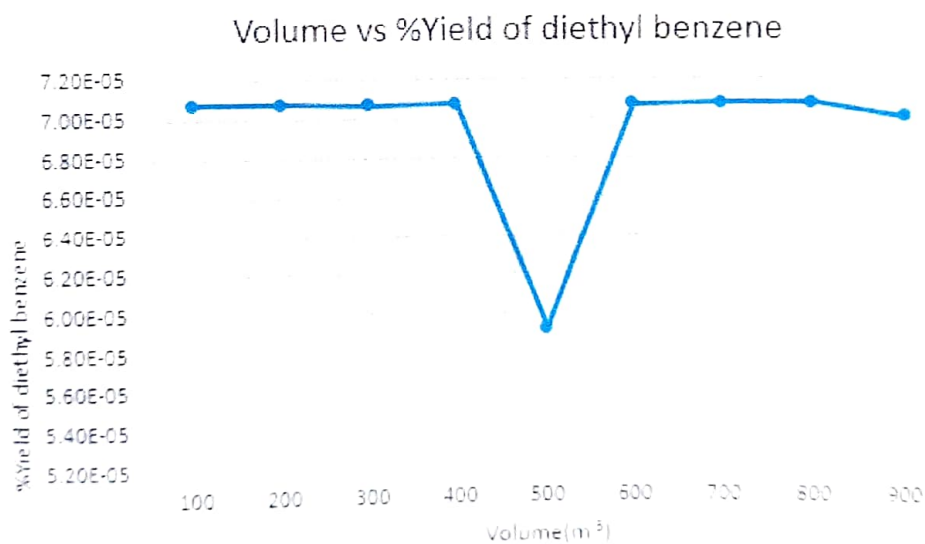


FIGURE 6.5 Volume vs %Yield of Diethylbenzene flow rate by using Grayson-Streed model

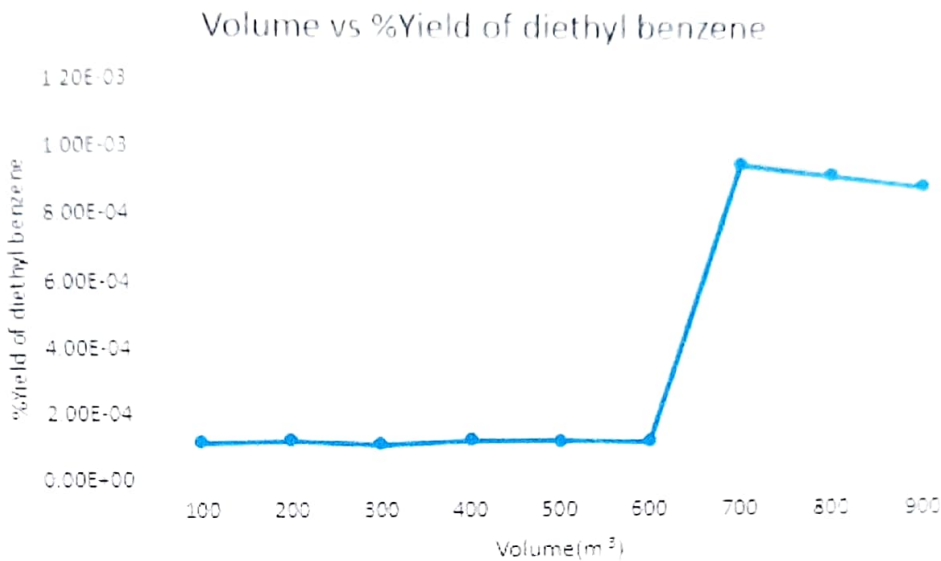


FIGURE 6.10 Volume vs %Yield of Diethyl benzene flow rate by using Lee-Kesler-plocker model

Inferences from tables and graphs

By carefully analyzing the tables and graphs we could have the following conclusions.

Since, diethyl benzene is our undesired product. So we want diethyl benzene to be in low amount at any cost. From the above plots, it is clear that all the thermodynamic packages except Chao-Seader shows irregular variations with increase in volume of reactor.

From the above discussion about property packages, we would conclude that NRTL can be applied to a systems with wide range of boiling points. But, in our systems the boiling points of the components doesn't vary much. After analysing the property packages, we can conclude that, the properties of the Chao-Seader model matches the operating conditions of our system and since Chao-Seader is specialised for hydrocarbon systems. These are the reason behind that Chao-Seader model shows favourable variations.

Chao-Seader model depicts that increases in volume of reactor leads to decrease in diethyl benzene yield which is a favourable variation to us. Thus, we can conclude that Chao-Seader model shows favourable variations between volume of reactor and diethyl benzene.

This project work reports steady state simulation of a plug flow reactor system using DWSIM. The reaction investigated in this work was production of ethylbenzene using ethylene and benzene as the reactants. Ethylbenzene being one of the important raw materials in production of several industrially important chemicals is often produced alongside with diethyl benzene as an undesired side product.

In our simulation, this particular aspect has been examined to maximize the conversion of ethyl benzene from its reactants. Here we have studied the effect of feed flow rate on steady state behaviour of PFR and also obtained the optimum feed flow rate in order to maximize the yield with special consideration of consecutive reactions where one product was desired and another one was undesired.

Here, we have simulated the system with five different thermodynamic packages namely Chao-Seader, Peng-Robinson, NRTL, Grayson-Streed and Lee-Kesler-Plocker. Among the thermodynamic packages, Chao-Seader model shows favourable variations for both the plots.

According to Chao-Seader model, yield of ethylbenzene increases with increases in benzene feed flow rate upto benzene flow rate becomes 0.6 kmol/s. At benzene flow rate of 0.6 kmol/s, the yield reaches maximum and then decreases. Similarly, yield of diethyl benzene decreases with increases in volume of reactor. Thus, Chao-Seader model produces better yield of ethyl benzene than other thermodynamic packages.

FUTURE SCOPE

As a continuation of this work, it can be extended in studying the dynamic simulation aspects with various controlling mechanisms in place and to figure out controller parameters and settings. Similarly, different reactor volumes (variable hold-ups) may also be used in series to study their effect in overall conversion of this reaction and optimize the variables.

Here we simulate only for an isothermal PFR. But, in future we can simulate for a non-isothermal PFR and can also study about the temperature effects.

Here we simulate the system by using five thermodynamic packages. In future studies, we can simulate with some other thermodynamic packages and compare them.

JNTUA COLLEGE OF ENGINEERING, ANANTAPUR
DEPARTMENT OF CHEMICAL ENGINEERING
Final PROJECT Work-EVALUATION SHEET

S. No.	Admission number	Clear Hypothesis (10 M)	Objectives (10 M)	Methodology of execution (10 M)	Interpretation of the results (10 M)	Total Marks (40 M)
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						
13.						
14.						
15.						
16.						
17.						
18.						
19.						
20.						
21.						
22.						
23.						
24.						
25.						
26.						
27.						
28.						
29.						
30.						

* Maximum (10 M) and Minimum (5 M)

Signature of Evaluator's

(1)

(2)

(3)

Head, Chemical Engineering

A Project Report on

CORROSION INHIBITION STUDIES OF SENNA AURICULATA LEAVES
EXTRACT ON MILD STEEL IN H₂SO₄ AND HNO₃ SOLUTIONS

Submitted in partial fulfillment of the requirements for the award of the Degree of

BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

Under the esteemed guidance of

Dr. DILIP KUMAR BEHARA

Ph.D (IITK)

Associate Professor of Chemical Engineering

& Head of The Department

Department of Chemical Engineering

JNTUA College of Engineering

Ananthapuramu

By

A.DEVI	(18001A0840)
M.NAGA GANESH	(18001A0809)
B.VIJAY KUMAR	(18001A0822)
N.NAVEEN KUMAR	(19005A0807)



DEPARTMENT OF CHEMICAL ENGINEERING
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR
COLLEGE OF ENGINEERING (AUTONOMOUS)
ANANTHAPURAMU-515002 (A.P)

2018 - 2022

A Project Report on

**CORROSION INHIBITION STUDIES OF SENNA AURICULATA LEAVES
EXTRACT ON MILD STEEL IN H₂SO₄ AND HNO₃ SOLUTIONS**

Submitted in partial fulfillment of the requirements for the award of the Degree of

BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

Under the esteemed guidance of

Dr. DILIP KUMAR BEHARA

Ph.D (IITK)

Associate Professor of Chemical Engineering

& Head of The Department

Department of Chemical Engineering

JNTUA College of Engineering

Ananthapuramu

By

A.DEVI	(18001A0840)
M.NAGA GANESH	(18001A0809)
B.VIJAY KUMAR	(18001A0822)
N.NAVEEN KUMAR	(19005A0807)



DEPARTMENT OF CHEMICAL ENGINEERING
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR
COLLEGE OF ENGINEERING (AUTONOMOUS)
ANANTHAPURAMU-515002 (A.P)

2018 - 2022

JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANANTAPUR
COLLEGE OF ENGINEERING (AUTONOMOUS)
ANANTHAPURAMU-515002 (A.P)
DEPARTMENT OF CHEMICAL ENGINEERING



CERTIFICATE

This is to certify that the project work on “CORROSION INHIBITION STUDIES OF SENNA AURICULATA LEAVES EXTRACT ON MILD STEEL IN H₂SO₄ AND HNO₃ SOLUTIONS” is the bonafide work done and submitted to Jawaharlal Nehru Technological University Anantapur College of Engineering (Autonomous), Ananthapuramu, during the academic year 2021-2022 in partial fulfillment of the requirements for the award of the Degree of Bachelor of Technology in Chemical Engineering by

A. DEVI	(18001A0840)
M. NAGA GANESH	(18001A0809)
B. VIJAY KUMAR	(18001A0822)
N. NAVEEN KUMAR	(19005A0807)

The results embodied in this project report are not submitted to any other university or institution for the award of any degree or diploma.

SUPERVISOR & HEAD OF THE DEPARTMENT

Dr. B. DILIP KUMAR Ph.D (IITK)

Associate Professor &

Head Of the Department,

Department of Chemical Engineering,

JNTUA College of Engineering Ananthapuramu.

DECLARATION

I declare that the project work described in this dissertation entitled "Corrosion Inhibition studies of Senna Auriculata Leaves extract on Mild steel in H₂SO₄ and HNO₃ Solutions" has been originally carried out by us under the supervision of Dr. Dilip Kumar Behara, Associate professor & Head of the Chemical Engineering Department, JNTU College of Engineering, Anantapur. The results embodied in this project report have not been submitted to any other University or Institute for the award of any other Degree.

S.NO	Name of the Student	Signature
1	A. DEVI (18001A0840)	A. Devi
2	M. NAGA GANESH (18001A0809)	M.N. Ganesh
3	B. VIJAY KUMAR (18001A0822)	B. Vijay Kumar
4	N. NAVEEN KUMAR (19005A0807)	N. Naveen Kumar

Place: Anantapuramu

Date:

ACKNOWLEDGEMENT

This satisfaction and euphoria that accompanies the successful completion of any task would be incomplete without the mention of the people who made it possible, whose constant guidance and encouragement crown all efforts with success.

First of all, we take this opportunity to express our deepest gratitude to our project guide **Dr. DILIP KUMAR BEHARA**, Associate Professor & Head Of the Department, Department of Chemical Engineering, JNTUA College of Engineering, Ananthapuramu, for giving us this opportunity to work under his esteemed guidance. We are greatly indebted to him for his kindness, generosity, consistent involvement and encouragement throughout our project work.

We sincerely thank **Dr. DILIP KUMAR BEHARA**, Head of the Chemical Engineering Department, for the valuable help provided. We would like to thank our faculty, technical staff, B.Sheeba Jeswitha(M.Tech) for their help during this project work.

We express our sincere thanks to **Prof. S. V. Satyanarayana, Sri M. Kalyan Kumar, Lt. Dr. S. Sharada**, and other teaching faculty for their valuable teaching and encouragement throughout the course.

We also convey our thanks to all the Non-Teaching Staff of the department who have helped us in several ways in completing our project successfully.

With gratitude

A.DEVI (18001A0840)

M.NAGA GANESH (18001A0809)

B.VIJAY KUMAR (18001A0822)

N.NAVEEN KUMAR (19005A0807)

LIST OF CONTENTS

CHAPTER	CONTENT	PAGE NO.
	ABSTRACT	1
1	INTRODUCTION	2-11
	1.1 CORROSION	3
	1.1.1 DEFINITION OF CORROSION	
	1.1.2 PROBLEMS WITH CORROSION	
	1.2 MECHANISM OF CORROSION	3
	1.3 GREEN INHIBITORS	6
	1.4 TYPES OF GREEN CORROSION INHIBITORS	7
	1.4.1 ANODIC CORROSION INHIBITORS	
	1.4.2 CATHODIC CORROSION INHIBITORS	
	1.4.3 MIXED CORROSION INHIBITORS	
	1.5 ADSORPTION OF CORROSION INHIBITORS	8
	1.5.1 ADSORPTION ISOTHERMS	
	1.6 CORROSION INHIBITION OF MILD STEEL AND ITS MONITORING TECHNIQUES	9
	1.6.1 WEIGHT LOSS METHOD	
	1.7 OBJECTIVES	11
2	LITERATURE SURVEY	12-22
3	MATERIALS AND METHODS	23-29
	3.1 MATERIALS	23
	3.1.1 PREPARATION OF REAGENTS	
	3.1.2 GLASSWARE AND EQUIPMENT USED	
	3.2 ELECTRODES	23
	3.3 COMPOSITION OF MILD STEEL	23
	3.4 METHODS	24
	3.4.1 PREPARATION OF ELECTRODES	
	3.4.2 ELECTROLYTE PREPARATION	
	3.5 PREPARATION OF INHIBITOR	24

	3.5.1 PREPARATION OF INHIBITOR FROM SENNA AURICULATA LEAVES	
	3.6 EVALUATION OF INHIBITION EFFICIENCY	26
	3.6.1 WEIGHT LOSS METHOD	
	3.6.1.1 METHODOLOGY	
	3.6.2 ELECTROCHEMICAL POLARIZATION STUDIES	
	3.6.2.1 TAFEL CURVES METHODOLOGY	
	RESULTS AND DISCUSSIONS	30-40
4	4.1 WEIGHT LOSS MEASUREMENTS	30
	4.2 ELECTROCHEMICAL POLARIZATION STUDIES	33
	4.2.1 TAFEL CURVES	
	4.3 LANGMUIR ADSORPTION ISOTHERMS	36
	4.4 STANDARD FREE ENERGY ADSORPTION	38
	CONCLUSIONS AND FUTURE SCOPE	40
	REFERENCES	41-45

LIST OF FIGURES

Figure name	Page no
Fig 1.1 Aqueous corrosion of iron	4
Fig 1.2 Atmospheric corrosion	5
Fig 1.3 Formation of surface protecting layer on metal surface	6
Fig 1.4 Adsorption process of corrosion inhibitors on metal surface	8
Fig 3.1 Preparation of Senna Auriculata(Avaram) leaf Inhibitor	25
Fig 3.2 Methodology of weight loss process	27
Fig 3.3 Potentiometer set up along with the electrodes	28
Fig 4.1 Inhibition efficiency of SCL in 1M H ₂ SO ₄ acid medium	30
Fig 4.2 Inhibition efficiency of SCL in 1M HNO ₃ acid medium	31
Fig 4.3 Corrosion rate of SCL in 1M H ₂ SO ₄ acid medium	32
Fig 4.4 Corrosion rate of SCL in 1M HNO ₃ acid medium	35
Fig 4.5 Polarization curves in the presence of Senna Auriculata Leaves extract in 1M HNO ₃	35
Fig 4.6 Polarization curves in the presence of Senna Auriculata Leaves extract in 1M H ₂ SO ₄	35
Fig 4.7 Langmuir adsorption isotherm plot for the adsorption of various concentrations of SCL extract on the surface of mild steel in H ₂ SO ₄ medium	36
Fig 4.8 Langmuir adsorption isotherm plot for the adsorption of various concentration of SCL extract on the surface of mild steel in HNO ₃ medium	

LIST OF TABLES

Table name	Page No.
Table 3.1: Composition of Low Carbon Steel	23
Table 4.1: Corrosion parameters obtained from weight loss measurements for mild steel in 1M H ₂ SO ₄ containing various concentrations of SCL extract	32
Table 4.2: Corrosion parameters obtained from weight loss measurements for mild steel in 1M HNO ₃ containing various concentrations of SCL extract	33
Table 4.3: Electrochemical polarization parameters of mild steel in 1 M H ₂ SO ₄ in the absence and presence of the best concentration of SCL extract	34
Table 4.4: Electrochemical polarization parameters of mild steel in 1 M HNO ₃ in the absence and presence of the best concentration of SCL extract	34
Table 4.5: The data of Langmuir adsorption isotherm fitting for mild steel in 1M H ₂ SO ₄ containing Senna Auriculata Leaves extract	38
Table 4.6: The data of Langmuir adsorption isotherm fitting for mild steel in 1M HNO ₃ containing Senna Auriculata Leaves extract	38
Table 4.7: K _{ads} and ΔG _{ads} for Senna Auriculata Leaves extract in 1M H ₂ SO ₄	39
Table 4.8: K _{ads} and ΔG _{ads} for Senna Auriculata Leaves extract in 1M HNO ₃	39

ABSTRACT

INTRODUCTION

The extract of *Senna Auriculata* (SCL) is studied for corrosion inhibition of mild steel in 1M H_2SO_4 and 1M HNO_3 acid media at room temperature. As mild steel does not have a high resistance to corrosion in its untreated form, the resistance to corrosion is provided by applying a surface protection film of corrosion inhibitors to its exposed parts. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are Biodegradable and also several inhibitor species, which are abundantly available in plants, leaves and flowers will act as good corrosion inhibitors. This research is to investigate the ability of phytochemicals such as flavonoids, alkaloids, tannins and phenol compounds in the Leaf extract of *Senna Auriculata* to reduce corrosion rates on mild steel. Corrosion inhibition rate is examined by the weight loss method. The polarization curves obtained indicate that the inhibitor in the present study will act as a mixed type. The adsorption of SCL on the surface of the mild steel was found to obey the Langmuir adsorption isotherm.

Keywords: *Senna Auriculata*, Corrosion inhibitors, Phytochemicals, Polarization curves.

CHAPTER-1

INTRODUCTION

Mild steel is the most widely used engineering material throughout the world due to its vast applications in different fields such as ships, oil, nuclear powerplants, chemical, gas, metallurgical and petroleum industries. However, stringent climatic conditions will hinder its usage in both alkaline and acidic mediums. For example, the hydrogen had the possibility of degrading the protective film in acidic climatic conditions (low pH) and leading to severe corrosion. Similarly, in alkaline climatic conditions (high pH), a thin film of water is deposited continuously on the surface due to the cathodic reaction resulting in the reduction of oxygen. To overcome this problem we need to find some remedial solutions. As we know that many research groups are testing by using organic and inorganic inhibitors to overcome the problem of corrosion[9]. However, due to their toxicity, the environment is degraded so restrictions are made to protect the marine and as well as atmospheric pollution. Because of this, we need to find inhibitors that are eco-friendly those are green inhibitors such as plant extracts, fruit peel extracts, root extracts, etc. which is available at low cost and not toxic in nature. Further, the use of green inhibitors is adopted in preventing or controlling the corrosion because of its high adsorptive properties which can form a film and stop the flow of foreign species from to come on the surface. Generally, the green inhibitors consist of compounds like O, N, S, and P that make strong bonds with Fe atoms and form the film to resist corrosion. It is known from the literature that on average the green inhibitors are adsorbed up to 75% to 98% giving a high yield of inhibition efficiency. Because of the presence of phytochemical species such as flavonoids and tannins, alkaloids, saponins, terpenoids will increase the inhibition efficiency[30]. As we know that the nitrogen and sulphur containing species have a greater affinity towards mild steel. It is known from the literature that Senna Auriculata leaves extract has nitrogen, oxygen, sulphur containing compounds. These inhibitors are easily grown under tropical climatic conditions throughout the year with less cost and the past studies reveal that these inhibitors have shown better results in inhibiting corrosion of mild steel in acidic medium (HCl)[25].

1.1 Corrosion:

1.1.1 Definition of Corrosion:

Corrosion is a natural process, in which the destruction of metal takes place by chemical or electrochemical reactions with the environment. Corrosion is a Latin word that means gnawed away or eroded. It converts the unstable metal to a chemically more stable state in the form of oxides and hydroxides, not only in metals corrosion can occur in the Ceramics polymers. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases[11].

1.1.2 Effects of Corrosion:

The harmful effects of the corrosion are more serious than the loss of metal[4]. Such as

1. The thickness of metal leads to a breakdown in its structure.
2. Damage to the bridge supports that could cause a bridge failure.
3. The products which are stored in metal containers will be contaminated.
4. The main problem in many industries is leakage of water in pipes and damage to underground pipes.
5. The efficiency and durability of the product decreased because of corrosion.

1.2 Mechanism of Corrosion:

Corrosion mechanism in aqueous solution has been amply demonstrated. In atmospheric corrosion which also exemplifies uniform corrosion, a very thin layer of electrolyte is present. It is probably demonstrated by putting a small drop of seawater on a piece of steel. On comparing atmospheric corrosion with aqueous corrosion, the following differences are observed.

On a metal surface exposed to the atmosphere, only a limited quantity of water and dissolved ions are present, whereas the access to oxygen present in the air is unlimited. Corrosion products are formed close to the metal surface, unlike the case of aqueous corrosion, and they may prevent further corrosion by acting as a physical barrier between the metal surface and

environment, particularly if they are insoluble as in the case of copper or lead. The following fig(1.1) shows a simplified mechanism of aqueous corrosion of iron.

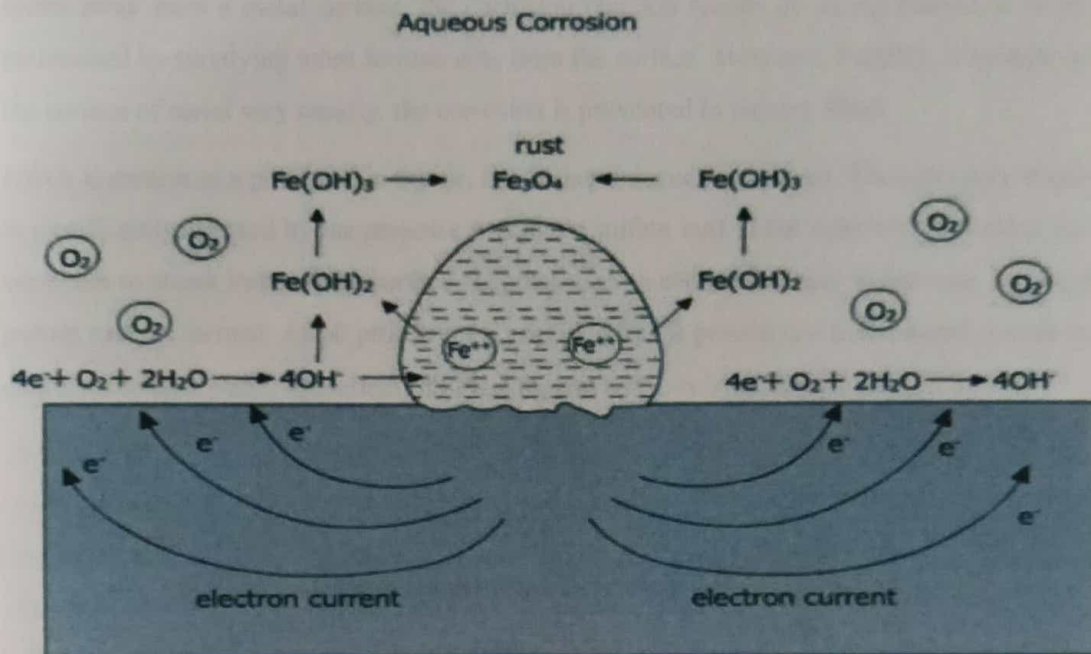
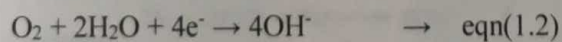


Fig 1.1 Aqueous corrosion of iron

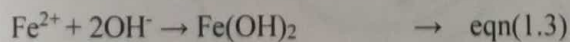
At the anodic areas, anodic reaction takes place:



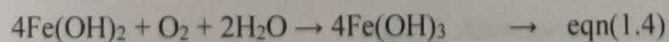
At the cathodic areas, reduction of oxygen takes place:



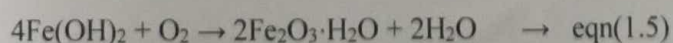
The OH⁻ ions react with the Fe²⁺ ions produced at the anode:



With more access to oxygen in the air, Fe(OH)₂ oxidizes to Fe(OH)₃ and later it loses its water:



Ferrous hydroxide is converted to hydrated ferric oxide or rust by oxygen.



Rust (Fe₂O₃·H₂O) is formed halfway between the drop center and the periphery which is alkaline. The electrons flow from the anode (drop center) to the cathode (periphery) in the

1.3. Green inhibitors:

Green inhibitors are used increasing day by day due to the restrictions and regulations that regular corrosion inhibitors and their toxicity. Here we are reporting that naturally occurring products are a good source of green corrosion inhibitors because the extract is mostly containing the necessary elements such as oxygen, carbon, nitrogen and sulphur, these are active organic compounds. The adsorption of these compounds on the mild steel forms a film that protects the surface and resists corrosion. There are many applications in textile and food processing industries. The adsorption depends on physical and chemical adsorption. The development of green chemistry is novel for new corrosion green inhibitors and the mechanism of adsorption, How these inhibitors act in different media and their role in different metals. The inhibitors which cause toxicity now are replaced with green corrosion inhibitors[27]. We are using these green inhibitors in solid form or liquid form with a small amount of concentration to stop the corrosion process. The inhibitor's efficiency depends on the phytochemicals that are present in the extract such as flavonoids, saponins, tannins, alkaloids etc. The effect of corrosion rate by adsorption of effective species on metal surfaces when added to many industrial systems through changing the rate of anodic and cathodic reactions. The ions aggressively interact with metallic structures because of diffusion rate. Increasing electrical resistance of the metal surface by forming a film on it.

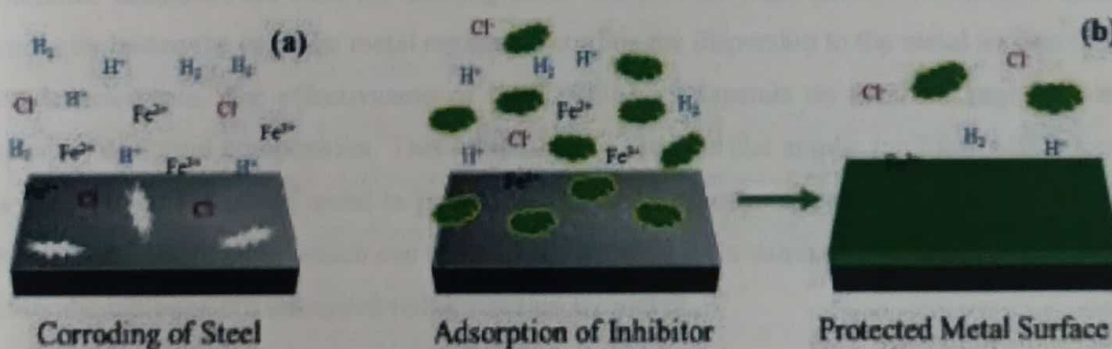


Fig 1.3 Formation of surface protecting layer on metal surface

There are many plants in our surroundings that will work as inhibitors[17]. In the figure(1.3), it is clearly shown that the adsorption of inhibitor molecules on the surface of the metal by forming a film type layer across the metal surface.

1.4 Types of green inhibitors:

There are three types of inhibitors related to this mechanism[18]. They are

- 1) Anodic corrosion inhibitors
- 2) Cathodic corrosion inhibitors
- 3) Mixed corrosion inhibitors

1.4.1 Anodic corrosion inhibitors:

Anodic inhibitors are chemical substances that form a protective layer of oxide film on the surface of the metal, causing resistance to corrosion. These inhibitors change the anodic reactions in the chemical cell, forcing the metallic surface into the passivation region. These are also known as passivators. These inhibitors work on anodic potential so that a passive film is formed on a metal surface, which then inhibits the anodic metal dissolution reaction. The most common anodic inhibitors are chromate, molybdate, Nitrite, Orthophosphate etc. Due to the chemical characteristics of anodic inhibitors, they are unsafe.

1.4.2 Cathodic corrosion inhibitors:

Cathodic inhibitors are used for slowing down the cathodic reaction. This can also work to correctly hasten the cathodic metal regions to confine the dispersion to the metal surface of the eroded elements. The effectiveness of these inhibitors depends on the flow regime, water quantity and fluid composition. This inhibitor also same as like anodic inhibitor which forms a layer on the surface of metal to prevent corrosion. Examples of cathodic inhibitors include sulfite and bisulfite ions which can react with oxygen to form sulphates. Another example of a cathodic inhibitor is a catalyzed redox reaction by nickel.

1.4.3 Mixed corrosion inhibitors:

Mixed inhibitors are organic compounds that account for 80% of all inhibitors which do not fall under the anodic and cathodic type. These inhibitors affect both anodic and cathodic reactions and most of them are organic compounds. They protect the metal by adsorption on the metal surface.

1.5 Adsorption of corrosion inhibitors:

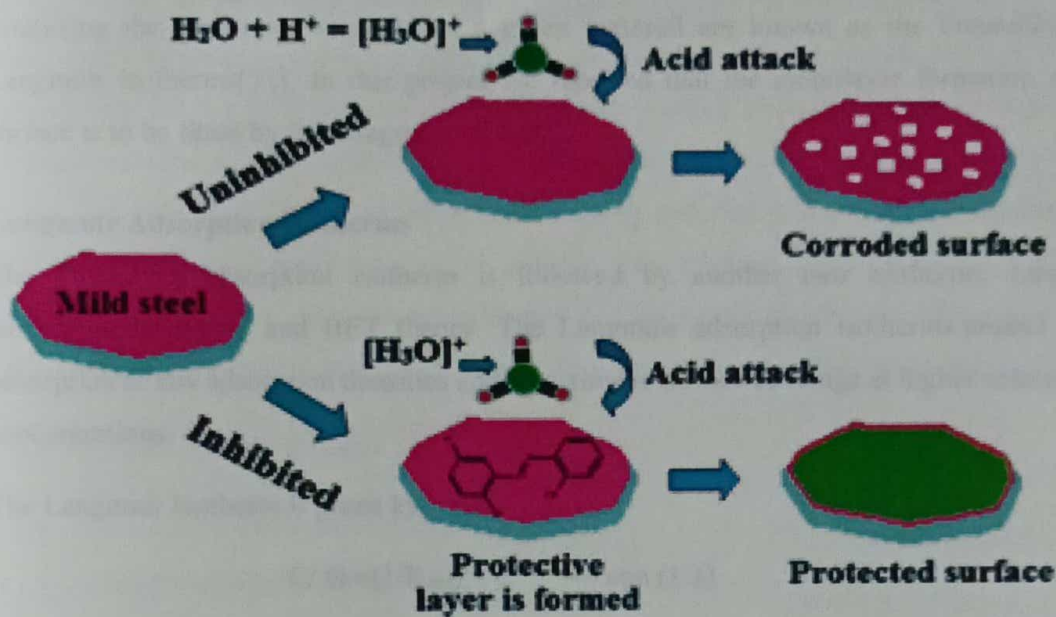


Fig 1.4 Adsorption process of corrosion inhibitors on metal surface

The effect of inhibitors adsorbed on metallic surfaces in acid solutions is to slow down the cathodic reaction as well as the anodic process of dissolution of the metal. Such effect is obtained by forming a barrier of diffusion or by means of the blockage of the reaction sites. Organic amines are examples of adsorption-type inhibitors[49].

1.5.1 Adsorption isotherms:

Adsorption of organic inhibitors onto metal surface is usually described by adsorption isotherms. It is widely acknowledged that adsorption isotherms provide useful insights into the mechanism of corrosion inhibition and provide important clues on the nature of metal-inhibitor interactions. Adsorption-bond strength can be deduced from the adsorption isotherm, which shows the equilibrium relationship between concentration of inhibitors on the surface and that one in the bulk solution. It should be noted that these isotherms represent the case of adsorption when only upto a mono layer of adsorbate formed on the surface, thus excluding multilayered adsorbate films.

Adsorption isotherms have been of immense importance to researches dealing with environmental protection and adsorption techniques. The two primary methods used for predicting the adsorption capacity of a given material are known as the Freundlich and Langmuir isotherms[31]. In this project we reported that the monolayer formation on the surface is to be fitted by the Langmuir isotherm.

Langmuir Adsorption Isotherms

The Freundlich adsorption isotherm is followed by another two isotherms, Langmuir adsorption isotherms and BET theory. The Langmuir adsorption isotherms predict linear adsorption at low adsorption densities and a maximum surface coverage at higher solute metal concentrations.

The Langmuir Isotherm is given by

$$C/\Theta = (1/K_{ads}) + C \quad \rightarrow \text{eqn (1.1)}$$

Where C is the inhibitor concentration, Θ is the degree of surface covered by the inhibitor and K_{ads} is the adsorption equilibrium constant

Freundlich Adsorption Isotherm

Freundlich adsorption gives the variation in the quantity of gas adsorbed by a unit mass of solid adsorbent with the change in pressure of the system for a given temperature. The expression for the Freundlich isotherm can be represented by the following equation:

$$x/m = kP^{1/n} \quad \rightarrow \text{eqn (1.2)} \quad \text{where } n > 1$$

Where x is the mass of the gas adsorbed, m is the mass of the adsorbent, P is the pressure and n is a constant which depends upon the nature of adsorbent and the gas at a given temperature.

Taking the logarithm on both the sides of the equation, we get,

$$\text{Log}(x/m) = \text{log}(k) + (1/n)\text{log}(P) \quad \rightarrow \text{eqn (1.3)}$$

1.6 Corrosion Inhibition of Mild steel and its Monitoring Techniques:

In this project we are using a leaf extract of *Senna Auriculata* for inhibition of mild steel. We using this leaf extract because it contains phytochemicals like flavonoids and tannins and saponins etc. Now a days many industries facing this problem corrosion because of equipment damage and serviceability of equipments are reduced and it causes huge losses. It is necessary to prevent corrosion. There are various monitoring techniques for corrosion inhibition of mildsteel. Corrosion monitoring is a process that evaluates and monitors equipment components, structures, process units, and facilities for signs of corrosion. To extend the life and serviceability of assets while increasing safety and reducing replacements costs.

1.6.1 Weight loss methods:

- Non- electrochemical methods
- Electrochemical methods

Non-electrochemical methods:

There are number of non- electrochemical methods used to study the efficiency of inhibitors on metal corrosion. Among these weight loss methods and gasometric methods are frequently used.

Weight loss method:

The difference in weight of the metal due to corrosion is measured by exposing the metal specimen of known area to the corrosive environment for a known period of time . Then the corrosion rate is calculated. Weight loss method has been used for corrosion study and inhibitive action of compounds in various media. Here in reported that using the coupons we inserted in different media for some time and calculate the weight loss. Weight loss method were carried out to calculate corrosion rate ($\text{gm}/\text{cm}^2\text{h}$), percentage inhibition efficiency (%IE) and the metal surface coverage(Θ) using the following[25].

Corrosion rate:

Corrosion rate is determined by

$$\text{Corrosion rate (mmpy)} = kW/ATD \quad \rightarrow \text{eqn(1.4)}$$

Where $k = 8.76 \times 10^4$ (constant)

W= weight loss in g

(weight loss is the difference between weights of mild steel before and after immersion of mild steel in acid medium.)

A = Area of the specimen (cm²)

D = Density of medium g/cm³

T = time exposed in hours

Calculation of Surface Coverage

The surface coverage is calculated by

$$\text{Surface coverage}(\Theta) = (W_0 - W_i) / W_0 \quad \rightarrow \text{eqn(1.5)}$$

Inhibition Efficiency

The inhibition efficiency is calculated for the effective inhibitor by using the formula

$$\text{Inhibition Efficiency } \eta (\%) = ((W_0 - W_i) / W_0) * 100 \quad \rightarrow \text{eqn(1.6)}$$

Where W_0 and W_i are weight loss per unit time in the absence and presence of the extract in aci solution.

1.7 Objectives:

- Synthesis of effective and low cost green inhibitors from Senna Auriculata leaves.
- Determination of corrosion rate and inhibition efficiency by weight loss method in both H₂SO₄ and HNO₃ acid solutions.
- Determination of type of inhibitor from polarization curves.
- Determination of type of adsorption on mild steel surface and fitting to Langmuir Isotherms.

CHAPTER-2

LITERATURE REVIEW

POPOOLA, LEKAN TAOFEEK. et al (2013) reported that the principles of corrosion must be understood in order to effectively select materials and to design, fabricate, and utilize metal structures for the optimum economic life of facilities and safety in oil and gas operations. Also, oil and gas materials last longer when both inhibitors and protective coatings are used together than when only batch inhibition was used. However, it is recommended that consultations with the process, operations, materials, and corrosion engineers are necessary for the fitness of things to save billions of dollars wasted on corrosion in the oil and gas industries. [1]

BALDEV, AND U. KAMACHI MUDALI (2006) reported that the development of materials for applications in spent nuclear fuel reprocessing plants. International efforts have resulted in the development of advanced materials like nitric acid grade (NAG) special austenitic stainless steels, Ti-5% Ta, Ti-5% Ta-1.8% Nb, Cr-W-Si, Nb-W, zirconium based alloys etc. for highly corrosive nitric acid environments. A critical review of performance of current and promising materials and their associated fabrication technologies for manufacturing is attempted. [2]

SA UMOREN, IB OBOT, EE EBENSO, NO OBI-EGBEDI (1998-2006) reported that the corrosion inhibition of aluminium in HCl solution in the presence of exudate gum from *Raphia hooker* at a temperature range of 30⁰C-60⁰C was studied using weight loss and thermometric techniques. The exudate gum acts as an inhibitor in the acid environment. The inhibition efficiency increases with an increase in inhibitor concentration but decreases with an increase in temperature. The inhibitive effect of the *Raphia hookeri* exudate could be attributed to the presence of some phytochemical constituents in the exudate which is adsorbed on the surface of the aluminium metal. [3]

TEDMON, CRAIG S., ED. (1974) reported that the enormous effect and impact of corrosion processes in the energy conversion and power generation segments of the economy can be seen, at least in part, in the diverse range of topics covered in this volume. In many of the technologies discussed in these papers, corrosion problems are the limiting factors to advancing the state-of-the-art. [4]

KINLEN, PATRICK J., VINOD MENON, AND YIWEI DING (1999) reported that the application of the scanning reference electrode technique (SRET) to the study of PANI coatings on carbon steel. SRET results demonstrate that conductive PANI "passivates" pinhole defects

in coatings on carbon steel. In addition, it is shown that phosphonic acid salts of PANI are more effective for corrosion protection than sulfonic acid salts. A model is proposed which entails passivation of the metal surface through anodization of the metal by PANI and formation of an insoluble iron-dopant salt at the metal surface. © 1999 The Electrochemical Society. All rights reserved. [5]

TWITE, R. L., AND GORDON P. BIERWAGEN (1998) reported that the newer alternatives include low temperature cationic plasma deposition, sol-gel and ceramic coatings, various inorganic and organic inhibitors and conducting polymers including some based on double helical structures. Although ultimate protection has not been achieved by one single technique, it is believed that a combination of the most promising alternatives will provide the desired protection. [6]

GRUNDMEIER, GUIDO. W. SCHMIDT, AND M. STRATMANN (2000) reported that the application of electrochemical techniques for corrosion studies of organic coatings on reactive metals is considered from an analytical and mechanistic standpoint. Techniques such as electrochemical impedance spectroscopy (EIS), scanning vibrating electrodes and scanning Kelvinprobe (SKP) are powerful tools to better understand the fundamental processes of corrosion at defects and underneath coatings. [7]

KINLEN, P. J., D. C. SILVERMAN, AND C. R. JEFFREYS (1997) reported that a key potential advantage that the ICP coating technology offers is toleration of pinholes and minor scratches. The basis for this argument is that, since the (Inherently Conducting Polymers) ICP coating is conductive, the entire coating acts to passivate any areas of exposed metal. This paper describes a model for polyaniline (PANI) corrosion protection and presents data that clearly demonstrate significant corrosion protection in a salt fog environment. ESCA and electrochemical data are presented which show that an Fe-PANI complex is formed in the process of coating steel with PANI. The Fe-PANI complex is shown to catalytically reduce oxygen. [8]

CHOU, T. P., et al (2001) reported that The corrosion resistance of sol-gel derived, organic-inorganic, silica-based hybrid coatings with various amounts of organic content was studied. Hybrid sols were prepared by copolymerizing tetraethyl orthosilicate (TEOS) and 3-methacryloxypropyltrimethoxysilane (MPS) with a two-step acid-catalyst process. Hybrid coatings were dip-coated on 304 stainless steel substrates and annealed at 300 °C for 30 min. Such prepared hybrid coatings were found to be relatively dense, uniform and defect-free. The

adhesion and flexibility of the coatings were characterized. The influences of the amount of organic component incorporated into the coatings and the aging of sols on corrosion protection were studied. [9]

EMEKA E OGUZIE (2007) reported that the inhibitive action of leaf extracts of *Sansevieria trifasciata* on aluminium corrosion in 2M HCl and 2M KOH solutions was studied using the gasometric technique. The results indicate that the extract functioned as a good inhibitor in both environments and inhibition efficiency increased with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives. Temperature studies revealed a decrease in efficiency with the rise in temperature and corrosion activation energies increased in the presence of the extract. A mechanism of physical adsorption is proposed for the inhibition behavior. The adsorption characteristics of the inhibitor were approximated by the Freundlich isotherm. [10]

ZHU, DANQING, AND WIM J. VAN OOIJ (2003) reported that a highly cross linked or dense interfacial layer that developed between the silane film and the aluminium oxide is the major contributor to the corrosion protection of AA 2024-T3. The formation of this interfacial layer heavily restricts pit growth underneath via retarding the transport of corrosion products, as well as effectively blocks a number of cathodic sites available for cathodic reactions. [11]

KHALED, K. F (2009) reported that methionine derivatives have a very good inhibitive effect on the corrosion of mild steel in 0.5 M sulphuric acid solution. Tafel polarization studies have shown that methionine derivatives act as mixed-type inhibitors, and their inhibition mechanism is adsorption assisted by hydrogen bond formation. Impedance results indicate that the values of the constant phase element tend to decrease with increasing methionine derivatives concentrations due to the increase in the thickness of the electrical double layer. In addition, both polarisation resistance and inhibition efficiency E_i (%) tend to increase with increasing inhibitors concentrations due to the increase of the surface coverage, i.e., the decrease of the electrochemically active surface area. The quantum mechanical approach may well be able to foretell molecular structures that are better for corrosion inhibition. [12]

DE SOUZA, FERNANDO SILVIO, AND ALMIR SPINELLI (2009) reported that the adsorption of caffeic acid onto the mild steel surface consequently the inhibition of the corrosion process. Caffeic acid acts by decreasing the available cathodic reaction area and modifying the activation energy of the anodic reaction. A mechanism is proposed to explain the inhibitory action of the corrosion inhibitor. [13]

KHAMIS, E., AND N. ALANDIS (2002) reported that the environmentally friendly investigated compounds are namely: thyme, coriander, hibiscus, anis, black cumin and Garden cress. Electrochemical impedance spectroscopy has been successfully used to evaluate the performance of these compounds. Potentiodynamic polarization curves indicate that the studied compounds are mixed-type inhibitors. The order of increasing inhibition efficiency was correlated with the change of the constituent active materials of the compounds. Thyme, which contains the powerful antiseptic thymol as the active ingredient, offers excellent protection for steel surfaces. [14]

LAHHIT, N., et al (2011) reported that essential oil from fennel (*Foeniculum vulgare*) (FM) was tested as a corrosion inhibitor of carbon steel in 1 M HCl using electrochemical impedance spectroscopy (EIS), Tafel polarisation methods and weight loss measurements. The results show that the increase of the charge-transfer resistance (R_{ct}) with the oil concentration supports the molecules of oil adsorption on the metallic surface. The polarization plots reveal that the addition of natural oil shifts the cathodic and anodic branches towards lower currents. Such shifts indicate that FM oil acts as a mixed-type inhibitor. The global rate of corrosion estimated by weight loss measurements confirms the above results. [15]

KHALED, K. F (2008) reported that a new safe corrosion inhibitor namely N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-yl)-guanidine (NTG) has been synthesized and its inhibitive performance towards the corrosion of mild steel in 1M hydrochloric acid and 0.5 M sulphuric acid has been investigated. Corrosion inhibition was studied by chemical method (weight loss) and electrochemical techniques including the Tafel extrapolation method and electrochemical impedance spectroscopy (EIS). These studies have shown that NTG was a very good inhibitor in acid media and the inhibition efficiency was up to 99% and 96% in 1M HCl and 0.5M H₂SO₄, respectively. Polarization measurements reveal that the investigated inhibitor is cathodic in 1M HCl and mixed-type in 0.5M H₂SO₄. Activation energies of the corrosion process in absence and presence of NTG were obtained by measuring the temperature dependence of the corrosion current density. [16]

RAJA. PANDIAN BOTHI, et al (2013) reported the inhibition effect of *Neolamarckia cadamba* crude extract (bark, leaves) and pure alkaloid (3 β -isodihydrocadambine) were investigated for mild steel corrosion in a 1M HCl medium. Potentiodynamic polarization, electrochemical impedance, scanning electron microscopy, FTIR spectroscopy and molecular modeling were employed for this study. Results showed that crude extracts and 3 β -

isodihydrocadambine reduced the corrosion rate significantly at all concentrations. Polarization measurements indicated that these green inhibitors acted through mixed-type inhibition. [17]

QIANG, YUJIE, ET al (2017) reported that four allyl imidazolium-based ionic liquids (ILs) with various lengths of alkyl chains were developed for the corrosion inhibition of copper in 0.5 M sulphuric acid. Electrochemical techniques, morphological characterization, theoretical calculations were combined to investigate the inhibition performance and mechanism. The results show that the corrosion circumstance of copper in sulphuric aqueous solution is efficiently inhibited by these ILs. Their favourable performance is ascribed to the formation of ILs-adsorption films, which follow the Langmuir adsorption isotherm. [18]

BENDAHOU, M., M. BENABDELLAH, AND B. HAMMOUTI (2006) reported that the inhibition efficiency increased with the concentration of the natural oil to attain 73% at 10 g/l. Good agreement between the various methods explored was observed. Polarisation measurements showed that rosemary oil acted essentially as a cathodic inhibitor. [19]

E KHAMIS F BELLUCCI et al (1991) The corrosion inhibition of nickel in acid solutions by 2-(triphenyl phosphoranylidene) succinic anhydride (2TPSA) has been investigated using DC and AC techniques. The percentage inhibition was up to 85 percent at a concentration of 400 μ M of 2TPSA. The inhibitor used was found to shift the corrosion potential to less negative values and to decrease the anodic dissolution of nickel and hydrogen evolution reaction. [20]

RAJA PANDIAN BHOTI & GOPALAKRISHNAN SETHURAMAN et al (2008) reported that the corrosion inhibitive effect of the extract of black pepper on mild steel (MS) in 1 M H_2SO_4 media was evaluated by conventional weight loss studies (303–323 K), electrochemical studies viz., Tafel polarization, ac impedance and scanning electron microscope (SEM) studies. The inhibition is through adsorption which is found to follow the Temkin adsorption isotherm. Tafel polarization method revealed the mixed mode inhibition of black pepper extract. SEM studies provide the confirmatory evidence for the protection of MS by the green inhibitor. [21]

G N MU et al (1996) reported that the effect of metallic cations on corrosion inhibition of the anionic surfactant of cold-rolled mild steel in HCl by sodium dodecyl sulfonate (SDS) was investigated using the weight-loss method. A marked inhibition synergism was found. Accelerated corrosion occurred in a lower concentration range of La^{3+} , but a powerful inhibition synergism appeared at a special concentration range for the mixture of La^{3+} and SDS. Results were evaluated in light of the adsorption theory. [22]

N A ODEWUMNI, S A UMOREN & G M ZASEM et al(2015) reported that the Three agro-waste products were investigated for their corrosion inhibition potentials for mild steel in HCl. Inhibitive action of the extracts could be attributed to the adsorption of the extracts' components on mild steel surface by physisorption mechanism according to Langmuir adsorption isotherm model and functions as mixed-typed inhibitors as revealed by potentiodynamic polarization studies. [23]

MIRGHASEM HOSSEINI & STIJIN F L MERTENS et al (2003) reported that the two newly synthesized bases were studied as inhibitors for the corrosion of mild steel in 0.5M Sulphuric acid. Results of weight loss, electrochemical impedance and tafel polarisation measurements consistently identify both compounds as inhibitors with efficiency of 95% at concentration of 400 ppm. [24]

K.HEMA, BR. VENKATRAMAN, A. SUBRAMANIA (2015) reported that Senna auriculata leaves (SCL) extract as a corrosion inhibitor for carbon steel in 1 N HCl was thoroughly investigated by chemical and electrochemical methods. The inhibition efficiency obtained by both these methods has good agreement with each other. The effects of temperature and immersion time on carbon steel in 1 N HCl were also studied. The maximum inhibition efficiency of 75.65% was obtained at the best concentration of 800 ppm of SCL extract. The polarization studies revealed that the inhibition action of SCL extract was under mixed control. The free energy of adsorption and the influence of temperature on the adsorption of SCL extract on carbon steel have also been reported. The adsorption of SCL extract on the surface of carbon steel was found to obey the Langmuir adsorption isotherm. [25]

HEINZ-HELMUT PERKAMPUS et al (2013) reported that the formulation of the Bouger-Lambert beer law in 1852 is created on basis of quantitative evaluation of absorption measurements at an early date. With the development and structure of matter which paved way for many discussions of the theory of electronic spectroscopy have been published. [26]

J ROSALINE VIMALA, A LEEMA ROSE & S RAJA et.al (2011) reported that the flowers of cassia auriculata can be used as an effective inhibitor of mild steel in HCl medium. Inhibitor is found to increase with increasing concentration of plant extract. The inhibitive action of plant extract is discussed basis of adsorption of stable complex at mild steel surface. Potentiodynamic polarisation curves reveal that the inhibition efficiency of up to 74.7% can be obtained from the plant extract. [27]

A RAJENDRAN & C KARTHIKEYAN et.al (2012) reported that air dried flowers of cassia auriculata is used as corrosive inhibitor on aluminium and mild steel in HCl. It is ascertained

that the inhibition increases with increase in concentration of extracts but decreases with an increase in temperature. The inhibitive effect could be attributed to the presence of phytochemical constituents in the extract which is adsorbed on the surface of the aluminium and mild steel surface. [28]

M ABDALLAH, HATEM M ATLASS, BA AL JAHDALY et.al (2018) reported that aqueous extracts of curcumin parsley and cassia bark exhibit inhibition effect on carbon steel in H_2SO_4 medium which are inspected utilizing some techniques such as galvanostatic and potentiodynamic anodic polarization and weight loss measurements. The outcome indicated that the percentage inhibition efficiency increases with increase in the concentration of the extract due to its horizontal adsorption on the carbon steel surface. These extracts act as pitting corrosion inhibitors by shifting the pitting potential to more noble values. [29]

R KARTHIK, P MUTHUKRISHNAN, A ELANGO VAN, B JEYAPRABHA et.al (2014) reported that anti corrosive activity of cassia senna leaf extract has been investigated using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, scanning electron microscopy and x-ray diffraction studies. Results show that the inhibition efficiency decreases with rise of temperature from 308k to 313k. Polarisation studies show that the leaf extract is mixed-type inhibitor. Scanning electron microscopy studies confirm the adsorption of extract on mild steel surfaces. [30]

EDDY N.O and EBENSO, E.E (2008) reported the kinetics and mathematical studies on corrosion inhibition of mild steel in 2.5M H_2SO_4 by MUSA SAPIENTUM PEELS extract. They reported that the inhibition efficiency of the extract is found to vary with concentrations, temperature, period of immersion and pH and it is a spontaneous process and occurred according to Langmuir and temkin adsorption isotherms. The Corrosion Rate, RN was decreases with increasing concentrations of inhibitor. Activation energy increases, inhibitor efficiency decreases with increasing temperature. [31]

GOPAL JI et.al (2014) on corrosion science reported the inhibitor of MUSA PARADISICA PEEL extract for mild steel in 1M HCl solution by weight loss measurement, electrochemical spectroscopy and TAFEL polarization techniques. They characterized the extract by FT-IR spectroscopy and HPLC. They studied from TAFEL polarization, banana peels extracts functioned as an anodic inhibitor in HC solution. Further analysis of HPLC revealed that the peel contains gels-catechin, dopamine and adsorbate which was responsible for inhibition AFM images, they were concluded that the banana peel is effectively inhibitor for steel in HCl. [32]

M. RAMANANDA SINGH et.al (2015) reported that the corrosion inhibition of LITCHI PEELS (LITCHI CHINENSIS) for mild steel in 0.5M H₂SO₄ by weight loss method, potentiodynamics polarization and electrochemical impedance spectroscopy (EIS). They reported that the LITCHI peels acts as a mixed-type inhibitor. The inhibition of corrosion is found to be due to adsorption of the extract on metal surface, which is in conformity with Langmuir's adsorption isotherm. They found from the studies of UV-Vis, Fourier transform infrared (FT-IR) spectroscopy and Scanning electron microscopy (SEM), the inhibition of corrosion of mild steel occurs through adsorption of the inhibition molecules. [33]

M.RAMANANDA SINGH (2012) corrosion sci reported that corrosion inhibition of mild steel by ADHATODA VASICA plant extracts in 0.5M H₂SO₄ and he studied the mechanism of inhibition by weight-loss method, EIS. He found that inhibitor acts as mixed type inhibitor and corrosion of mild steel in 0.5M H₂SO₄ solution increases on increasing its concentration and decreases with temperature. He found that it obeyed Langmuir isotherm and increases the activation energy of the corrosion process in the presence of extract. [34]

R. SARATHA et.al (2009) reported the kinetics and mathematical studies of corrosion inhibition of mild steel in 1M HCl by CITRUS AURANTIIFOLIA leaves extract by weight loss method and electrochemical studies. They found that inhibition efficiency increases with increasing extract concentration. They investigated the theoretical fitting of isotherm by Langmuir, Temkin, and Freundlich. They found that inhibitor efficiency was up to 97.15%. The main inhibitor constituents are linoleic acid, oleic acid, xanthylein. [35]

R. SARATHA et al. (2009) reported the kinetics and mathematical studies of corrosion inhibition of mild steel in 1N H₂SO₄ medium by acid extract of NYCATANTHES ARBORTRISTICS leaves by weight loss and polarization method. They found that inhibitor having efficiency 90% at 1% concentration. They observed that polarization studies indicate the inhibitor to be a mixed type both cathodic as well as anodic reactions. [36]

SAVIOUR A. UMOREN et al. (2013) reported inhibition of mild steel corrosion by data palm seed extract in 1M HCl and 0.5M H₂SO₄ solution. It was found that inhibitor efficiency increased with an increase in the extract concentration and decreased with an increase in temperature and immersion time. They observed it obeyed Langmuir adsorption isotherm. They found that palm seed extract is a better corrosion inhibitor for mild steel in HCl than in a H₂SO₄ solution. [37]

SAVIOUR A. UMOREN, MOSES M. SOLOMON, UBONG M EDUOK reported that the kinetics on inhibition of mild steel corrosion in 0.5M H₂SO₄ solution by ethanol and acetone extracts of coconut coir dust. They observed that inhibition efficiency increased with an increase in temperature. They found that a pronounced effect noted with ethanol extract in 0.5M H₂SO₄ and reported that mechanism followed by Freundlich isotherm and it is a spontaneous reaction. [38]

L.R.CHAUHAN et al. (2006) reported the kinetics of Corrosion inhibition of mild steel in 5% and 15% aqueous HCl solution by ZENTHOXYLUM ALATUM PLANT extract by weight loss and EIS method. They reported that corrosion inhibition efficiency increases with increasing plant extract concentration. They investigated on effect of temperature on the corrosion behavior of mild steel. They observed that the extract is more effective in 5%HCl than in 15%HCl. XPS and FT-IR show that the compounds present in plant extract form corrosion inhibitive layer by reacting with iron ions present on the mild steel surface. They found that the adsorption of inhibitive molecules obeys the Langmuir adsorption isotherm. [39]

M.A. QURAIISHI, AMRISH SINGH et al. (2010).They were reported the kinetics and mathematical studies on corrosion inhibition of mild steel in 1M HCl and 0.5M H₂SO₄ by MURRAYA KOENIGII leaves(curry leaves) extract by weight loss and EIS methods. They found that inhibitor efficiency increases with increase in extract concentration. They were studied about effect of temperature, immersion time and acid concentration on corrosion behaviour. Further it is spontaneous process and obeyed Langmuir adsorption isotherm. They further observed that efficiency slightly better in HCl solution than the H₂SO₄ solution. The main constituents of extract of MURRAYA KOENIGII are murrafoline-1, pyrayafoleline-D and mahabinine-A. Due to formation of amine group, the inhibitor molecules get adsorbed on mild steel surface. [40]

K.O. ORUBITE et al. (2003).They were reported that the corrosion inhibitor of mild steel in HCl acid solution by extract of leaves of NYPA FRUTICANS WURMB. They had studied by weight loss and hydrogen gas evolution techniques. They found that high inhibition efficiency of fruticans was 75.11% and 70.18% for DPC at 30 °C. From the results, they said that extract serve as a inhibitor in corrosion of mild steel in HCl solution. The efficiency of the extract showed lower at high temperatures. They found that leaves of N. fruticans serve as effective inhibitor of the corrosion of mild steel in Hydrochloric acid media. [41]

E. CHAIEB, A. BOUYANZER, B. HAMMOUTI et al. (2008) they reported the kinetics on corrosion inhibitor of steel in 1M HCl by eugenol (Eug) and its derivatives and studied by using weight loss and EIS methods. They found that maximum inhibitor efficiency attained was 91% at 0.1737 g/l. They investigated concentration and temperature variation according to inhibitor. They further observed the efficiency of the inhibitor increased with increase of temperature. It obeys Langmuir adsorption isotherm, mixed type inhibitor. [42]

UMOREN, S.A. et al. (2007) reported the corrosion inhibitor of SIDA ACUTA (SA) for mild steel in 1M H₂SO₄ solution by chemical (weight loss and hydrogen evolution) and spectroscopy (AAS, FI-AR and UV-V) techniques at 30⁰c-60⁰C. They were investigated that leaves (LV) and stem (ST) extracts from SIDA ACUTA inhibits the corrosion. The inhibition efficiency increases with increase in extract concentration but decreases in rise in temperature. They found that the leaves(LV) are better compared to stem(ST) due to the presence of higher concentrations of phyto-constituents in LV than in ST extracts of S.ACUTA by forming insoluble complexes (FE-SA) with iron ions. [43]

PATRICIA E. ALVEREZ et al. (2017) reported the corrosion inhibitor of ROLLINIA OCCIDENTALIS (RO) for carbon steel in HCl solution. They were investigated the influence of rolliniastain-1 and motrilin present in RO resist the corrosion of carbon steel. They reported that from PC studies the RC extract is act as a mixed type inhibitor from 1M, the carbon steel surface is having geometric blocking effect with the adsorbed inhibitor species. They found that inhibitor adsorption follows a Langmuir adsorption isotherm. Further analysis of spectroscopic, the complex formation between metal cations and compounds present in the ROLLINIA OCCIDENTALIS extract. [44]

A. RODRIGUEZ-TORRES et al. (2018) reported the corrosion inhibitor of PRUNUS PERSICA of AISI 1018 carbon steel in 0.5M H₂SO₄ at 25⁰C by weight loss method. They found that 600 ppm of PRUNUS PERSICA extract are good for CORROSION INHIBITION(CI) and PPC evidenced that extract is mixed-type inhibitor with cathodic predominance. Their investigation shows that a high abundance of Vitamin-e (α -tocopherol) and β -Bitopherol detected by GC-MS in phytochemicals which is a part of PRUNUS PERSICA extract leads to blockage of steel active sites by an inhibitor which causes less damage to the surface of the metal. [45]

M. MEHDIPOUR et al. (2014) were reported the environmentally friendly inhibitor for corrosion protection of Stainless Steel in 1M H₂SO₄ by electrochemical techniques and

Scanning Electron Microscope. They found that extract (Aloe) was a mixed-type inhibitor with anodic action. The major Aloe compounds including Aloin, Aloesin, Aloe-resin and Aloe Encodin (as a Bio-transformation of Aloin) are composed of many oxygen atoms in functional groups of O-H, C=O, C-O and O-heterocyclic ring, allowing aloe extract to protect Stainless Steel from corrosion. They reported the Langmuir adsorption isotherm is best to describe adsorption of aloe extract on surface (physical interaction). [46]

M.K.SHARMA et al. (2008) reported that corrosion inhibitor of *PROSOPIS CINERARIA* for mild steel in HCl, H₂SO₄ and in acid mixture (HCl and H₂SO₄) by weight loss method. They found that efficiency increases with increase in extract concentration and the fruit extract of *PROSOPIS CINERARIA* shows maximum Corrosion Inhibition Efficiency (CIE) compared to stem-bark and leaves extracts. Further analysis said that plant extract of *PROSOPIS CINERARIA* is also used to replace toxic chemicals. [47]

C.KAMAL et al. (2010) were reported that corrosion inhibition of *SPIRULINA PLATENSIS* for mild steel in 1M HCl and 1M H₂SO₄ by weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis. They found that the inhibition efficiency is better in H₂SO₄ medium than in HCl medium. They investigated that corrosion inhibition of *S. platensis* follows Temkin adsorption isotherm, and values of ΔG were indicative of physisorption. They found that light another facet of this microalga as it has so far been used only to produce antioxidant principles, finding extensive use in medicine especially as nutraceutical. [48]

KENNETH KANAYO ALANEME et al. (2015) were reported that the corrosion inhibition of *HUNTERIA UMBELLATA* seed husk extract for mild steel in 1M HCl and 1M H₂SO₄ by Mass loss method, Atomic Absorption spectroscopy (AAS), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). They investigated that the extract contain O-H, C-N and unsaturated C=C functional groups which were identified as contributing to the corrosion exhibited by the extracts. They found that the inhibition efficiency increases with increase in extract concentration and decreases with increase in temperature. The inhibition efficiency of the extracts was reported to be very high in 1M HCl compared to 1M H₂SO₄ solution. The Langmuir adsorption isotherm best fits the data suggesting physical adsorption between the extract and the metal surface. [49]

CHAPTER-3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 PREPARATION OF REAGENTS

1M Sulphuric Acid:

53.2 ml of conc. Sulphuric acid was diluted with distilled water and made it upto 1000ml.

1M Nitric Acid:

63 ml of conc. Nitric Acid with was diluted with distilled water and made it upto 1000ml.

3.1.2 Glassware and Equipment used:

Reflux Apparatus, Electronic Weighing Balance, 250ml Beakers, Measuring jars.

3.2 ELECTRODES

To perform the electrochemical polarization analysis three electrodes were used. The mild steel is used as the working electrode. The remaining two electrodes were platinum mesh as counter electrode and AgCl as a reference electrode.

3.3 COMPOSITION OF MILD STEEL

Table 3.1: Composition of Mild Steel

The elemental composition of CS grade were GRADE. DP780(GI) as follows

S.NO	COMPOSITION	WEIGHT (%)
1	Carbon	0.086
2	Silica	0.012
3	Manganese	1.35
4	Phosphorous	0.013
5	Aluminum	0.046
6	Sulphur	0.005
7	Molybdenum	0.001
8	Titanium	0.009
9	Chromium	0.02

3.4 METHODS

3.4.1 PREPARATION OF ELECTRODES

The Mild Steel of thickness 0.1 cm is cut into rectangular pieces of sizes. Prior to the testing, the samples were abraded with the emery papers for proper polishing of the metal surfaces without any dust particles or other layers on it. The specimen is again cleaned with distilled water and Acetone to remove dust particles.

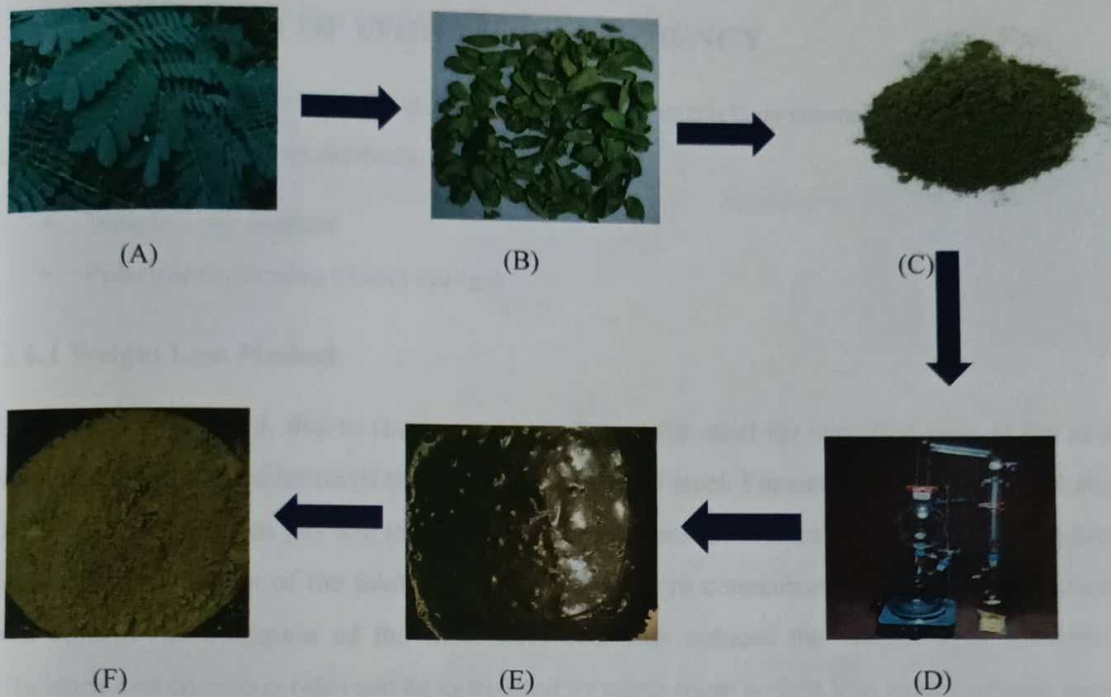
3.4.2 ELECTROLYTE PREPARATION

1M of H_2SO_4 and HNO_3 solutions are prepared by diluting the appropriate amount of concentrated chemical with distilled water. The different amounts of 2,4,6,8,10 ml of 800ppm SCL aqueous extract were added to the acids while performing the experiments [24].

3.5 PREPARATION OF INHIBITOR

3.5.1 Preparation of Inhibitor from Senna Auriculata Leaves

Leaves of Senna Auriculata (Avaram) were cleaned and dried in hot air. The dried leaves were pulverized and made it well into powder. 10g of the leaf powder was refluxed in 100 ml of distilled water for an hour. The refluxed solution was filtered through whatmann No.1 filter paper and then the filtrates were dried in a Vacuum drier to suck the moisture and air dried to get the dried compound [25] as shown in the below fig 3.1



(A) Collection of fresh Senna Auriculata leaves, (B) Drying leaves in shade, (C) Grinding dried leaves into powder form, (D) Refluxing the dried leaves powder with distilled water, (E) Residue obtained after the refluxing process and subjected to filtration (F) powder obtained after drying.

Fig 3.1 Preparation of Senna Auriculata (Avaram) leaf Extract

3.6 EVALUATION OF INHIBITOR EFFICIENCY

The performance of experimental details with the plant extracts as corrosion inhibitors of mild steel are calculated in two methods. They are

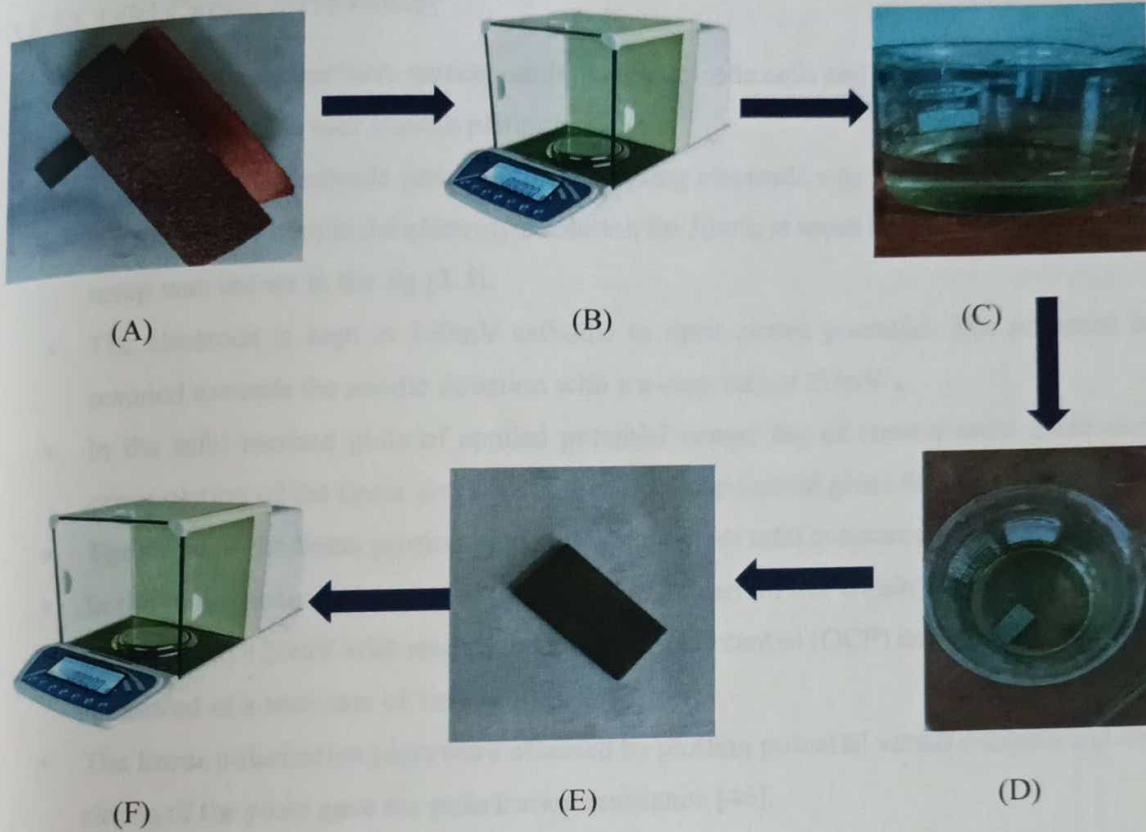
- Weight Loss method
- Polarization Studies (Tafel curves)

3.6.1 Weight Loss Method

In weight loss method, due to the immersion of the mild steel for specified time in the acid medium causes the oxidation of the iron present in mild steel. Formation of Fe^{2+} ions and also the release of hydrogen gas will take place, which causes the weight loss of mild steel to take place. By the addition of the inhibitor extract of different concentrations in the acid medium will control the oxidation of the mild steel and thus reduces the weight loss. Inhibition efficiency and corrosion rates can be calculated by using these weight loss values of mild steel.

3.6.1.1 Methodology

- A specimen of mild steel in 1cm x 2cm x 1cm dimensions were taken and noted its weight.
 - 1M solution of H_2SO_4 was prepared.
 - 100ml of H_2SO_4 was taken in a beaker and inhibitor was added into the beaker such that the solutions contain 200ppm of SCL extract in the acid medium.
 - Specimen was placed in the beaker containing inhibitor for 3 hours.
 - After 3 hours, the specimen was taken out from the beaker and cleaned with double-distilled water.
 - The specimen was dried and weighed on the weighing balance.
 - The corrosion rate and inhibition efficiency values are calculated with the obtained weight loss values.
 - Similarly the same process is repeated for 400,600,800ppm concentrations of inhibitor extract.
 - The entire process is repeated for 1M of HNO_3 solution as another acidic medium [25].
- The methodology is as shown in below fig 3.2



(A) Rubbing the mild steel with emery paper, (B) Weighing the mild steel after cleaning, (C) Adding the SCL inhibitor to acid solution, (D) Immersion of mild steel in extract solution, (E) Taking out the mild steel and cleaning it with distilled water, (F) Noting the final weight of mild steel.

Fig 3.2 Methodology of weight loss process

The Corrosion rates, Surface Coverage and Inhibition Efficiency values were calculated by using the equations (1.4),(1.5)&(1.6) respectively

3.6.2 ELECTROCHEMICAL POLARIZATION STUDIES

3.6.2.1 Tafel Curves Methodology

- Polarization studies were carried out in three electrode cells and in a potentiometer, the counter electrode was smooth platinum mesh.
- The reference electrode was AgCl. The working electrode was mild steel specimen.
- All these were kept in the electrolyte solution for 30min at room temperature. The entire setup was shown in the fig (3.3).
- The electrode is kept at 150mV cathodic to open circuit potential. The potential is scanned towards the anodic direction with a sweep rate of 20mV/s.
- In the tafel method plots of applied potential versus log of current were made and extrapolation of the linear portion of the corrosion potential gives the current density.
- The slope of the linear portion in the tafel plots gives tafel constants.
- In the linear polarization the measurements were carried out within the potential range of -20mV to +20mV with respect to Open Circuit Potential (OCP) and the response was measured at a scan rate of 1mV/s.
- The linear polarization plots were obtained by plotting potential versus currents and the slopes of the plots gave the polarization resistance [46].



Fig 3.3 Potentiometer setup along with the electrodes

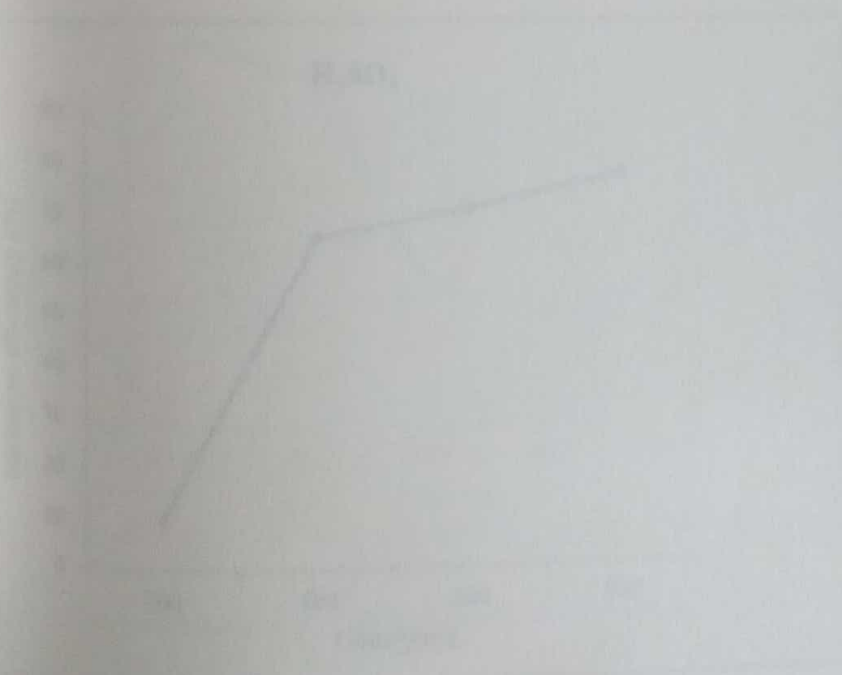
Calculation of Inhibition Efficiency

The Inhibition Efficiency(IE) is calculated by using the following formula [25]

$$IE (\%) = (I_{corr} - I_{corr}^*) / I_{corr} \times 100 \quad \rightarrow \text{eqn(3.4)}$$

Where I_{corr} and I_{corr}^* are corrosion current in the absence and presence of the SCL extract in 1 M H_2SO_4 and HNO_3 solutions.

The weight loss measurement is done in the absence and presence of SCL extract concentration ranging from 0.001 to 0.01 g/l. In this method, the corrosion rate and the inhibition efficiency is calculated using linear polarization technique extract on mild steel. The observed corrosion parameters are plotted in Figure (3.3 and 3.4). It is clear from the table that the percentage of inhibition efficiency is increased with the concentration of SCL extract. The decrease in corrosion rate with increasing concentration of SCL is due to the fact that the surface coverage of mild steel by the adsorbed molecules is increased. The molecular weight of SCL extract is 200. The molecular weight of HNO_3 is 63.03 g/mol and H_2SO_4 is 98.08 g/mol. From the recorded weight loss data, the corrosion rate (corr.) and the Inhibition Efficiency (IE) were calculated using the following eqn (3.4) (3.5)



CHAPTER-4

RESULTS AND DISCUSSIONS

4.1 WEIGHT LOSS MEASUREMENTS:

Weight loss of mild steel in 1 M H_2SO_4 and 1 M HNO_3 was determined at room temperature in the absence and presence of SCL extract concentrations ranging from 200ppm to 1000ppm. In this method, the corrosion rate and the inhibition efficiency is calculated using Senna Auriculata Leaves extract on mild steel. The obtained corrosion parameters are depicted in Tables (4.1 and 4.2). It is clear from the tables that the percentage of inhibition efficiency increases with the concentration of SCL extract. The decrease in corrosion rate with an increase in the concentration of SCL is due to the fact that the surface coverage of metal increases by the adsorption of inhibitor molecules. The maximum inhibition efficiency of 76.8% is obtained at the concentration of 800 ppm of extract in Sulphuric acid medium and 93.9% is obtained at the concentration of 1000 ppm of extract in Nitric acid medium. From the measured weight loss data, the corrosion rate (mmpy) and the Inhibition Efficiency (IE) were calculated using the equations (1.4)&(1.6)

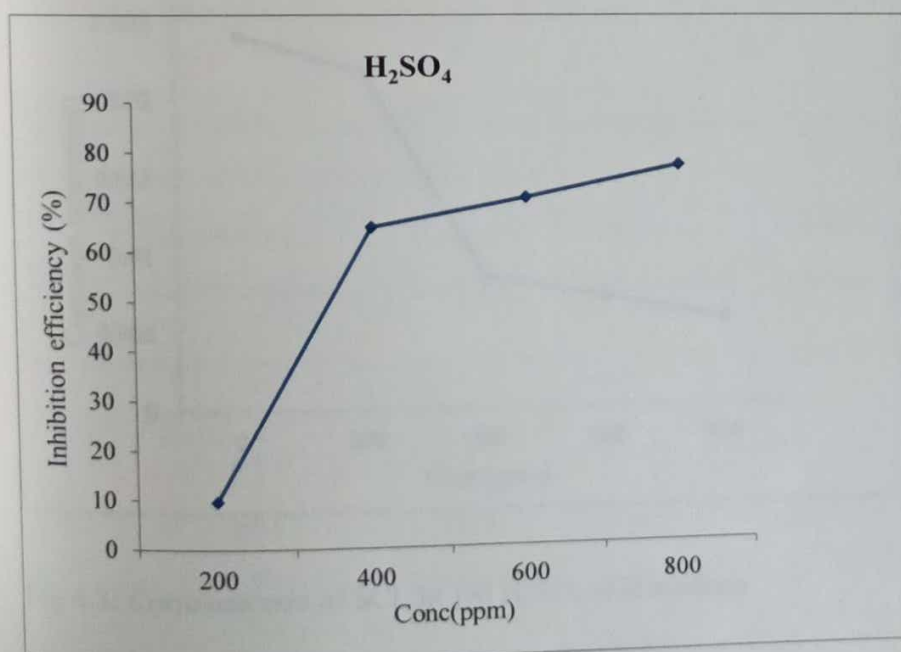


Fig 4.1: Inhibition efficiency of SCL in 1M H_2SO_4 acid medium

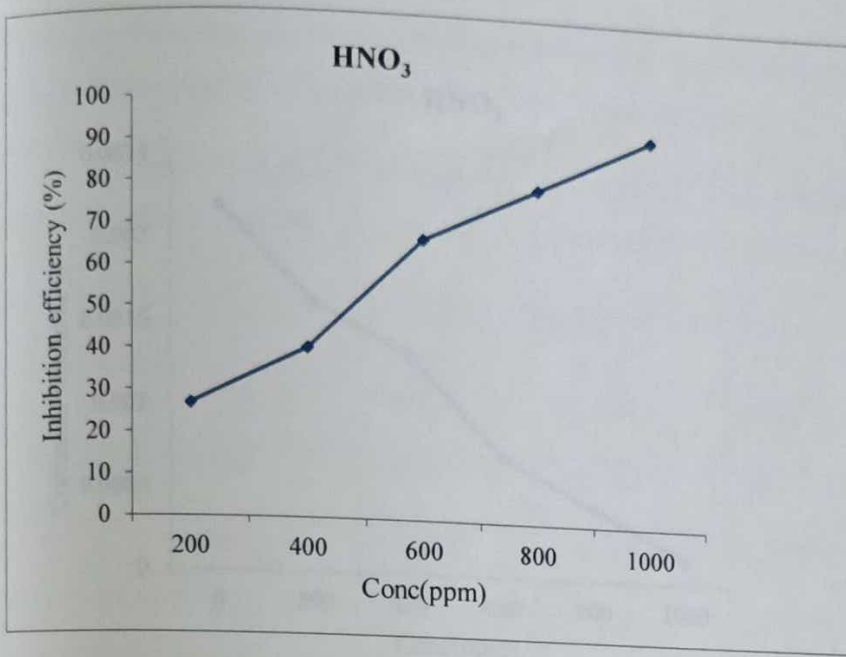


Fig 4.2: Inhibition efficiency of SCL in 1M HNO₃ acid medium

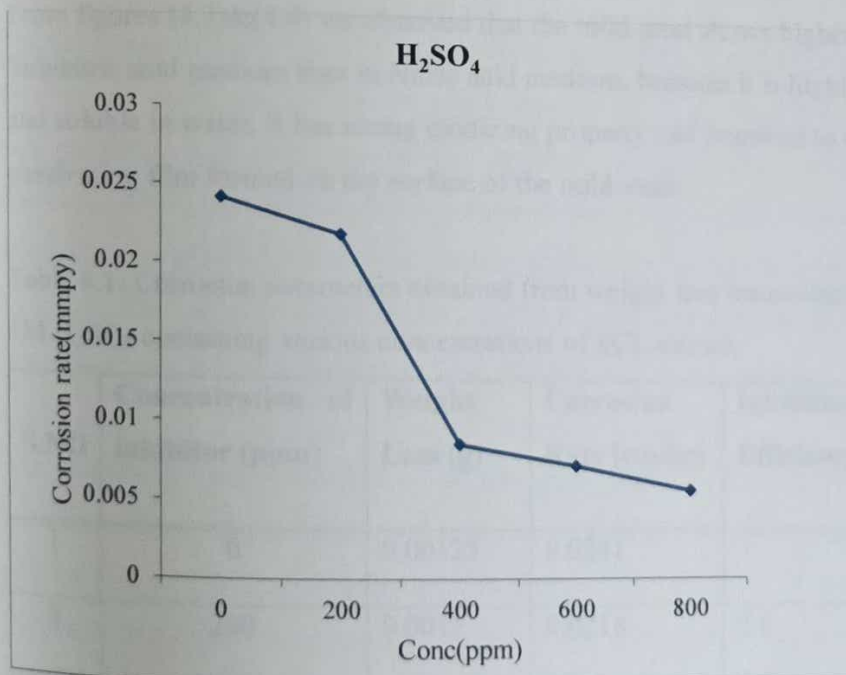


Fig 4.3: Corrosion rate of SCL in 1M H₂SO₄ acid medium

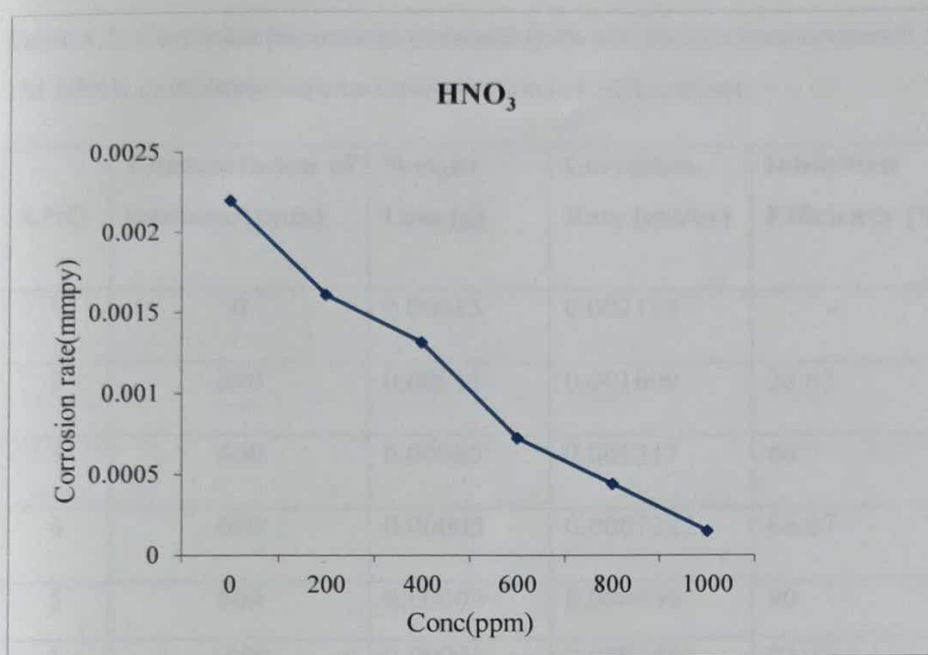


Fig 4.4: Corrosion rate of SCL in 1M HNO₃ acid medium

From figures (4.3)&(4.4) we observed that the mild steel shows higher corrosion rates in Sulphuric acid medium than in Nitric acid medium, because it is highly corrosive, reactive and soluble in water. It has strong oxidizing property and potential to break down the passivating film formed on the surface of the mild steel.

Table 4.1: Corrosion parameters obtained from weight loss measurements for mild steel in 1M H₂SO₄ containing various concentrations of SCL extract.

S.NO	Concentration of inhibitor (ppm)	Weight Loss (g)	Corrosion Rate (cm/hr)	Inhibition Efficiency (%)	Surface Coverage(Θ)
1	0	0.00125	0.0241	-	-
2	200	0.0011	0.0218	9.6	0.096
3	400	0.00044	0.00849	64.8	0.648
4	600	0.00037	0.00714	70.4	0.704
5	800	0.00029	0.0056	76.8	0.768

Table 4.2: Corrosion parameters obtained from weight loss measurements for mild steel in 1M HNO₃ containing various concentrations of SCL extract.

S.NO	Concentration of inhibitor(ppm)	Weight Loss (g)	Corrosion Rate (cm/hr)	Inhibition Efficiency (%)	Surface Coverage (Θ)
1	0	0.00015	0.002195	-	-
2	200	0.00011	0.001609	26.67	0.2667
3	400	0.00009	0.001317	40	0.40
4	600	0.00005	0.0007242	66.67	0.6667
5	800	0.00003	0.000439	80	0.80
6	1000	0.00001	0.0001463	93.33	0.9333

4.2 Electrochemical polarization studies:

The behaviour of Tafel curve of SCL inhibitor in 1M H₂SO₄ and 1M HNO₃ in the presence and absence of inhibitors of different amounts of 2, 4, 6, 8, 10 ml of 800ppm inhibitor concentration. It is clear that as the inhibitor concentration increases the corrosion rate decreases means that the anodic curve shifts to positive potentials and the cathodic curve shifts to negative potentials. As the concentration of inhibitor increases the shift in the cathodic curve increases. The inhibitor has an inhibitive effect on the rate of hydrogen evaluation reaction. On the other hand, the inhibitor has a slight effect on the anodic curves.

The calculated electrochemical polarization parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic Tafel slope (b_a and b_c) values and Corrosion rate and Inhibition Efficiency are depicted in Tables (4.3) and (4.4). It was obvious from Figures (4.5) and (4.6) that Tafel curves are not shifted markedly to the corrosion potential for the optimum concentration (800 ppm) of SCL extract. It indicates that the SCL extract works through the mixed mode of inhibition[25]. The I_{corr} value for the best concentration of SCL extract was decreased when compared to blank solution. This decrease in I_{corr} is an indication of a decrease in corrosion reaction since corrosion current is proportional to the magnitude of the corrosion reaction. The I_{corr} , b_a and b_c values were changed upon the addition of SCL

extract, which means the extract molecules are adsorbed both on the anodic and cathodic sites. This results in the inhibition of both anodic metal dissolution and cathodic hydrogen evolution reactions.

Table 4.3: Electrochemical polarization parameters of mild steel in 1M H₂SO₄ in the absence and presence of the best concentration of SCL extract.

Amount of SCL extract added (ml)	E _{corr} (V)	I _{corr} (A)	Tafel slope (mV/decade)		Corrosion rate(mmpy)	Inhibition Efficiency(%)
			Anodic slope(b _a)	Cathodic slope(b _c)		
0	-0.0934	0.006	83.33	92.28	46.418	-
2	-0.0935	0.0056	79.48	88.7	43.612	6.667
4	-0.093	0.0055	74.17	85.54	42.762	8.33
6	-0.0898	0.0049	61.15	84.13	38.55	18.33
8	-0.0976	0.0046	76.4	71.54	36.036	23.33
10	-0.0982	0.0035	78.4	70.6	34.021	41.66

Table 4.4: Electrochemical polarization parameters of mild steel in 1M HNO₃ in the absence and presence of the best concentration of SCL extract.

Amount of SCL extract added (ml)	E _{corr} (V)	I _{corr} (A)	Tafel slope (mV/decade)		Corrosion rate(mmpy)	Inhibition Efficiency(%)
			Anodic slope(b _a)	Cathodic slope(b _c)		
0	-0.0998	0.006	93.6	90.87	46.488	-
2	-0.0226	0.0049	129.49	60.75	38.647	18.33
4	-0.047	0.00282	90.416	80.013	21.8205	53
6	-0.038	0.00216	76.13	78.94	17.921	64
8	-0.0252	0.00142	53.36	53.151	10.984	76.33
10	-0.0256	0.00125	63.93	69.204	9.7277	79.16

4.2.1 Tafel Curves:

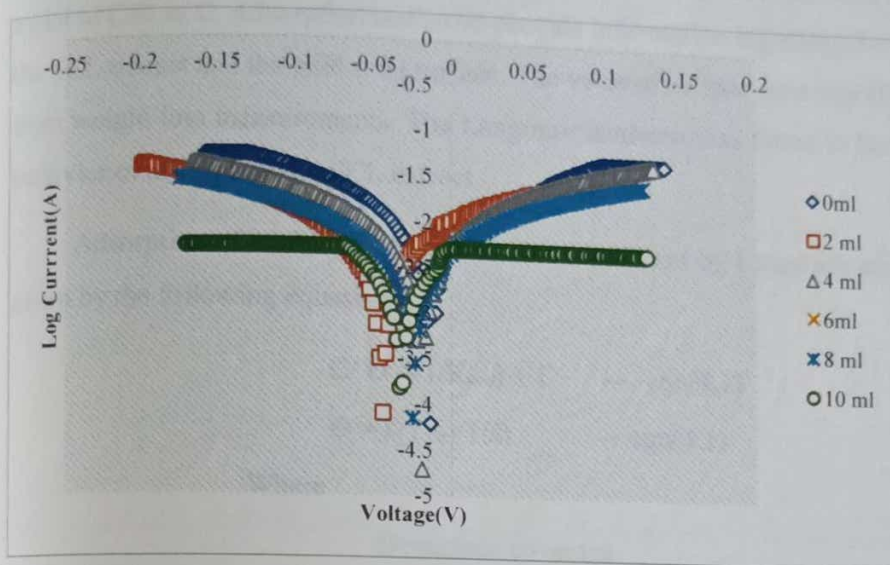


Fig 4.5 The polarization curves in the presence of Senna Auriculata Leaves extract in 1M HNO₃.

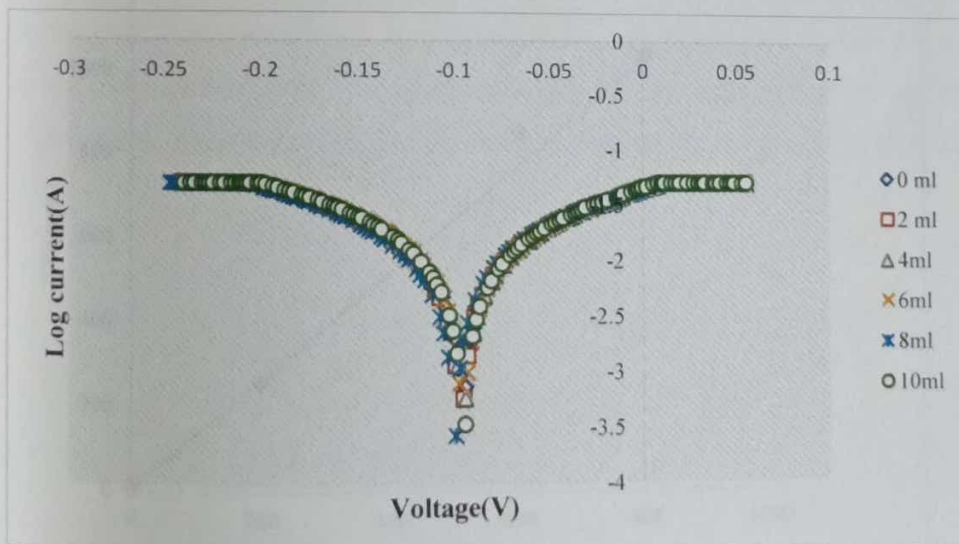


Fig 4.6 The polarization curves in the presence of Senna Auriculata Leaves extract in 1M H₂SO₄.

4.3 LANGMUIR ADSORPTION ISOTHERMS:

Langmuir adsorption isotherm was employed to fit the experimental data by weight loss. It is a plot of C/Θ vs C . Adsorption isotherms provide information regarding the interaction between the SCL extract and the mild steel surface. The value of surface coverage (Θ) has been obtained from weight loss measurements. The Langmuir isotherm was found to be the best description behavior of adsorption for SCL extract.

Adsorption of inhibition molecules on carbon steel by Langmuir adsorption isotherm is given by the following equations

$$C/\Theta = (1/K_{ads}) + C \rightarrow \text{eqn(4.1)}$$

$$\Theta = \eta (\%) / 100 \rightarrow \text{eqn(4.2)}$$

Where

Θ =surface coverage

C =concentration of inhibitor(mg/L)

K_{ads} =adsorption equilibrium constant.

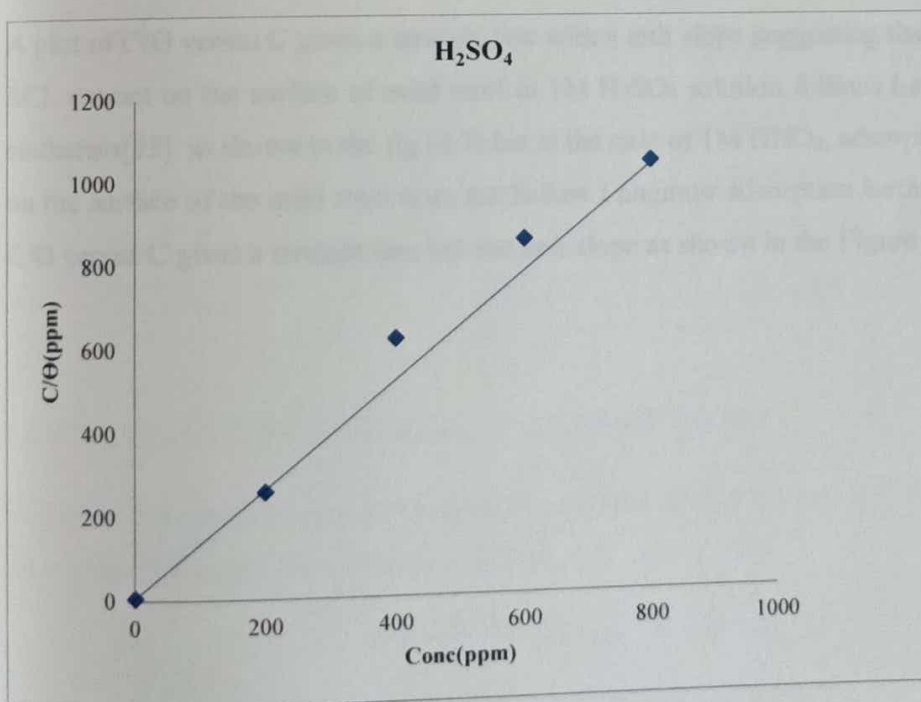


Figure 4.7 Langmuir adsorption isotherm plot for the adsorption of various concentrations of SCL extract on the surface of mild steel in H₂SO₄ medium.

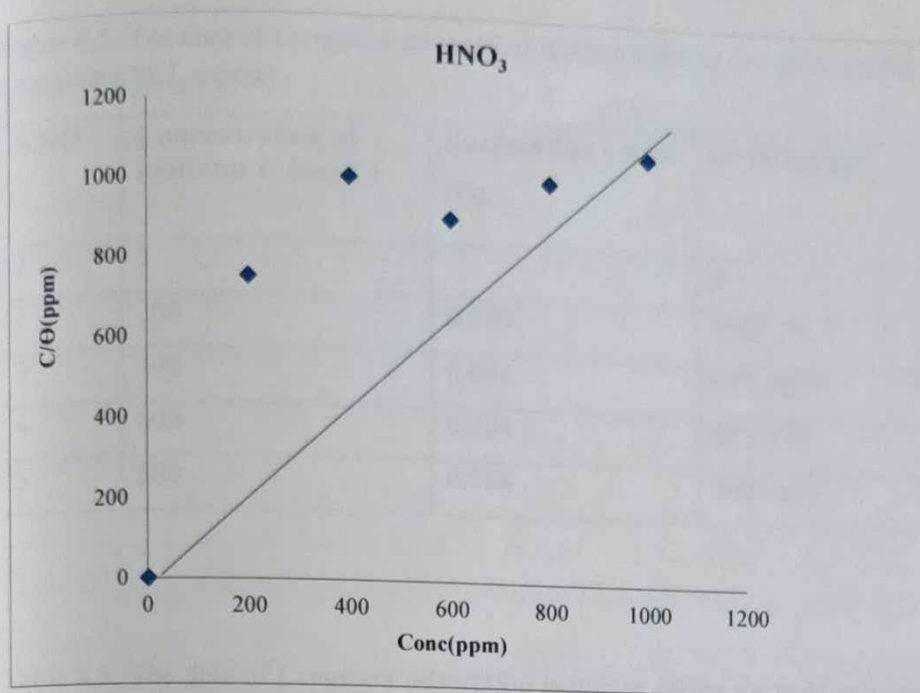


Figure 4.8 Langmuir adsorption isotherm plot for the adsorption of various concentrations of SCL extract on the surface of mild steel in HNO_3 medium.

A plot of C/θ versus C gives a straight line with a unit slope suggesting that the adsorption of SCL extract on the surface of mild steel in 1M H_2SO_4 solution follows Langmuir adsorption isotherms[25] as shown in the fig (4.7) but in the case of 1M HNO_3 , adsorption of SCL extract on the surface of the mild steel does not follow Langmuir adsorption isotherms as the plot of C/θ versus C gives a straight line but not unit slope as shown in the Figure (4.8).

Table 4.5: The data of Langmuir adsorption isotherm fitting for mild steel in 1M H₂SO₄ containing SCL extract.

S.NO	Concentration of inhibitor C (mg/L)	Surface Coverage (Θ)	C/ Θ(mg/L)
1	0	-	0
2	200	0.096	2083.33
3	400	0.648	617.2839
4	600	0.704	852.272
5	800	0.768	1041.667

Table 4.6: The data of Langmuir adsorption isotherm fitting for mild steel in 1M HNO₃ containing SCL extract.

S.NO	Concentration of inhibitor C (mg/L)	Surface Coverage (Θ)	C/ Θ (mg/L)
1	0	-	0
2	200	0.2667	749.9
3	400	0.4	1000
4	600	0.6667	899.955
5	800	0.8	1000
6	1000	0.9333	1071.4668

4.4 STANDARD FREE ENERGY ADSORPTION:

Adsorption equilibrium constant (K_{ads}) can be correlated with the standard free energy of adsorption (ΔG^0_{ads}) by the following equation

$$K_{ads} = (\exp -\Delta G/ RT)/ C_{water} \rightarrow \text{eqn(4.3)}$$

Where C_{water} is the density of water in the solution (1×10^6 mg/L)

R is Universal gas constant (8.314 J/mol K)

T is absolute temperature (K)

Adsorption process is caused by electrostatic attraction between the charged metal surface and charged organic molecules. As the values of free energy of adsorption are less than -20 kJ mol^{-1} , where the mode of inhibition is due to physisorption. The negative sign of free energy of adsorption indicates that the adsorption of SCL extract on the mild steel surface is a spontaneous process[25]. The major constituents present in SCL extract are alkaloids. These compounds adsorbed on the mild steel surface made a barrier for charge and mass transfers leading to a decrease in the interaction of mild steel with the corrosive environment. As a result, the corrosion rate of mild steel decreased. The formation of a film layer prevents the corrosion of mild steel.

Table 4.7: K_{ads} and ΔG_{ads} for Senna Auriculata Leaves extract in 1M H_2SO_4

S.NO	Concentration of inhibitor C (ppm)	$K_{ads} \times 10^{-6}$ (L/mg)	ΔG_{ads} (KJ/mol)
1	0	-	-
2	200	1621.7	-18.6195
3	400	1174.3	-17.806
4	600	960.7	-17.298
5	800	480	-15.5526

Table 4.8: : K_{ads} and ΔG_{ads} for Senna Auriculata Leaves extract in 1M HNO_3

S.NO	Concentration of inhibitor C (ppm)	$K_{ads} \times 10^{-6}$ L/mg)	ΔG_{ads} (KJ/mol)
1	0	-	-
2	200	1333.9	-18.127
3	400	1111.99	-17.669
4	600	1000	-17.401
5	800	986	-17.366
6	1000	934	-17.2296

CONCLUSIONS

- Green corrosion extracts are very good inhibitors under a variety of corrosive environments for most of metals. Corrosion inhibition studies of mild steel using Senna Auriculata Leaves extract in 1M H₂SO₄ and 1M HNO₃ mediums were reported.
- Weight loss studies confirm the prominent role of inhibitors in decreasing the corrosion rate as well as increasing the inhibition efficiency with increase in the concentration of the inhibitor.
- This extract is rich in saponins, tannins, alkaloids and flavonoids which facilitate forming bonds and therein fetch to form a film that combats corrosion.
- The electrochemical polarization studies showed that the aqueous extract of SCL acts as a mixed inhibitor for mild steel in 1M H₂SO₄ and 1M HNO₃ acid solutions.
- The adsorption of the SCL extract follows Langmuir adsorption isotherm in H₂SO₄ medium but not in HNO₃ medium.
- The obtained free energy adsorption values indicate that the adsorption of the SCL extract on mild steel is due to the physisorption process.

FUTURE SCOPE

- Several studies can also be pursued in the performance of the combination of inhibitors, effect of an alkaline environment on different metallic surfaces.
- These corrosion inhibition studies can also be conducted with many other acid mediums and also at different concentrations of the mediums.
- These inhibitors can be further investigated for corrosion inhibition of other metals and at different temperatures.
- Scanning Electron Microscopy (SEM) technique can used for the chemical characterization of the sample(metal) and to observe the formation of the protecting film of the inhibitor extract on the surface of the metals.
- Corrosion inhibition studies can be carried with many other plants which are available around the world.
- Fourier Transform Infrared Spectroscopy (FTIR) technique can be used to identify and to characterize the phytochemicals present in the plant extracts.

REFERENCES

1. Popoola, Lekan Taofeek, et al. "Corrosion problems during oil and gas production and its mitigation." *International Journal of Industrial Chemistry* 4.1 (2013): 35.
2. Baldev, and U. Kamachi Mudali. "Materials development and corrosion problems in nuclear fuel reprocessing plants." *Progress in Nuclear Energy* 48.4 (2006): 283-313.
3. SA Umoren, IB Obot, EE Ebenso, NO Obi-Egbedi. "The Inhibition of aluminium corrosion in hydrochloric acid solution by exudate gum from *Raphia hookeri*" *Desalination* 247 (1998-2006), 561-572.
4. Tedmon, Craig S., ed. *Corrosion problems in energy conversion and generation*. Corrosion Division, Electrochemical Society, 1974.
5. Kinlen, Patrick J., Vinod Menon, and Yiwei Ding. "A mechanistic investigation of polyaniline corrosion protection using the scanning reference electrode technique." *Journal of the Electrochemical Society* 146.10 (1999): 3690-3695.
6. Twite, R. L., and Gordon P. Bierwagen. "Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys." *Progress in organic coatings* 33.2 (1998): 91-100.
7. Grundmeier, Guido, W. Schmidt, and M. Stratmann. "Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation." *Electrochimica Acta* 45.15-16 (2000): 2515-2533.
8. Kinlen, P. J., D. C. Silverman, and C. R. Jeffreys. "Corrosion protection using polyaniline coating formulations." *Synthetic Metals* 85.1-3 (1997): 1327-1332.
9. Chou, T. P., et al. "Organic-inorganic hybrid coatings for corrosion protection." *Journal of Non-Crystalline Solids* 290.2-3 (2001): 153-162.
10. Oguzie, Emeka. "Corrosion Inhibition and Adsorption Behavior of Methionine on Mild Steel in Sulfuric Acid and Synergistic Effect of Iodide Ion." *Journal of Colloid and Interface Science*, 2007.
11. Zhu, Danqing, and Wim J. van Ooij. "Corrosion protection of AA 2024-13 by bis-[3-(triethoxysilyl) propyl] tetrasulfide in sodium chloride solution.: Part 2: a mechanism for corrosion protection." *Corrosion Science* 45.10 (2003): 2177-2197.
12. Khaled, K. F. "Monte Carlo simulations of corrosion inhibition of mild steel in 0.5 M sulphuric acid by some green corrosion inhibitors." *Journal of Solid State Electrochemistry* 13.11(2009): 1743-1756.

13. de Souza, Fernando Silvio, and Almir Spinelli. "Caffeic acid as a green corrosion inhibitor for mild steel." *Corrosion science* 51.3 (2009): 642-649.
14. Khamis, E., and N. Alandis. "Herbs as new type of green inhibitors for acidic corrosion of steel." *Materialwissenschaft und Werkstofftechnik: Entwicklung, Fertigung Prüfung Eigenschaften und Anwendungen technischer Werkstoffe* 33.9 (2002): 550-554.
15. Lahhit, N., et al. "Fennel (*Foeniculum vulgare*) essential oil as green corrosion inhibitor of carbon steel in hydrochloric acid solution." *Portugaliae Electrochimica Acta* 29.2 (2011): 127-138.
16. Khaled. K. F. "New synthesized guanidine derivative as a green corrosion inhibitor for mild steel in acidic solutions." *Int. J. Electrochem. Sci* 3.4 (2008): 462-475.
17. Raja. Pandian Bothi, et al. "Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media" *Corrosion Science* 69 (2013): 292-301.
18. Qiang, Yujie, et al. "Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid." *Corrosion Science* 119 (2017): 68-78.
19. Bendahou, M., M. Benabdellah, and B. Hammouti. "A study of rosemary oil as a green corrosion inhibitor for steel in 2 M H₃PO₄." *Pigment & resin technology* 35.2 (2006): 95-100.
20. Khamis, E., et al. "Acid corrosion inhibition of nickel by 2-(triphenosphoranylidene) succinic anhydride." *Corrosion* 47.9 (1991): 677-686.
21. Raja, Pandian Bothi, and Mathur Gopalakrishnan Sethuraman. "Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel." *Materials letters* 62.17-18 (2008): 2977-2979.
22. Mu, G. N., et al. "Effect of metallic cations on corrosion inhibition of an anionic surfactant for mild steel." *Corrosion* 52.11 (1996): 853-856.
23. Odewunmi, N. A., S. A. Umoren, and Z. M. Gasem. "Watermelon waste products as green corrosion inhibitors for mild steel in HCl solution." *Journal of Environmental Chemical Engineering* 3.1 (2015): 286-296.
24. Hosseini, Mirghasem, et al. "Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media." *Materials Chemistry and Physics* 78.3 (2003): 800-808.

25. K.HEMA, BR. Venkatraman, A. Subramania. "Corrosion Inhibition of Aqueous Extract of Senna Auriculata Leaves on Carbon Steel in Hydrochloric Acid Medium". *Chemical Science* 4(4), 927-939, 2015.
26. Perkampus, Heinz-Helmut. UV-VIS Spectroscopy and its Applications. Springer Science& Business Media, 2013.
27. J R Vimala , AL Rose, S Raja. "Cassia auriculata extract as corrosion inhibitor for mild steel in acid medium" *International Journal of ChemTech Research* 3(4), 1791-1801,2011.
28. A Rajendran, C Karthikeyan. "The inhibitive effect of extract of flowers of Cassia auriculata in 2M HCl on the corrosion of aluminium and mild steel" *International Journal of Plant Research* 2(2), 9-14,2012.
29. M Abdullah, Hatem M Atlass, BA Al Jahdaly, MM Salem. "Some natural aqueous extracts of plants as green inhibitor for carbon steel corrosion in 0.5 M Sulphuric acid" *Green Chemistry Letters and Reiewes*11(3), 189-196, 2018.
30. R Karthik, P Muthukrishnan, E Elangovan, B Jeyaprabha, P Prakash. "Extract of Cassia senna as green inhibitor for the corrosion of mild steel in 1M Hydrochloric acid solution" *Advances in Civil Engineering Materials* 3 (1), 413-433, 2014.
31. Ebenso, E. E., N. O. Eddy, and A. O. Odiongenyi. "Corrosion inhibitive properties and adsorption behaviour of ethanol extract of Piper guinensis as a green corrosion inhibitor for mild steel in H₂SO₄." *African Journal of Pure and Applied Chemistry* 2.11 (2008): 107-115.
32. Ji, Gopal, et al. "Musa paradisica peel extract as green corrosion inhibitor for mild steel in HCl solution." *Corrosion Science* 90 (2015): 107-117.
33. Singh, M. Ramananda, Prachi Gupta, and Kaushal Gupta. "The litchi (Litchi Chinensis) peels extract as a potential green inhibitor in the prevention of corrosion of mild steel in 0.5 M H₂SO₄ solution." *Arabian Journal of Chemistry* (2015).
34. Singh, M. Ramananda. "A green Approach: A corrosion inhibition of mild steel by adhatoda vasica plant extract in 0.5 M H₂SO₄." *environments* 10 (2013): 19.
35. Saratha, R., S. V. Priya, and P. Thilagavathy. "Investigation of Citrus aurantiifolia leaves extract as corrosion inhibitor for mild steel in 1 M HCl." *Journal of chemistry* 6.3 (2009): 785-795.
36. Saratha, R., and V. G. Vasudha. "Inhibition of mild steel corrosion in 1N H₂SO₄medium by acid extract of nycatanthes arbortristis leaves." *Journal of Chemistry* 6.4 (2009): 1003-1008.

37. Umoren, Saviour A., Zuhair M. Gasem, and Ime B. Obot. "Natural products for material protection: inhibition of mild steel corrosion by date palm seed extracts in acidic media." *Industrial & Engineering Chemistry Research* 52.42 (2013): 14855-14865.
38. Umoren, Saviour A., et al. "Inhibition of mild steel corrosion in H₂SO₄ solution by coconut coir dust extract obtained from different solvent systems and synergistic effect of iodide ions: Ethanol and acetone extracts." *Journal of Environmental Chemical Engineering* 2.2 (2014): 1048-1060.
39. Chauhan, L. R., and G. Gunasekaran. "Corrosion inhibition of mild steel by plant extract in dilute HCl medium." *Corrosion Science* 49.3 (2007): 1143-1161.
40. Quraishi, M. A., et al. "Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulfuric acid solutions by the extract of *Murraya koenigii* leaves." *Materials Chemistry and Physics* 122.1 (2010): 114-122.
41. Orubite, K. O., and N. C. Oforka. "Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of *Nypa fruticans* Wurmb." *Materials Letters* 58.11 (2004): 1768-1772.
42. Chaieb, E., et al. "Inhibition of the corrosion of steel in 1 M HCl by eugenol derivatives." *Applied Surface Science* 246.1-3 (2005): 199-206.
43. Eduok, U. M., S. A. Umoren, and A. P. Udoh. "Synergistic inhibition effects between leaves and stem extracts of *Sida acuta* and iodide ion for mild steel corrosion in 1 M H₂SO₄ solutions." *Arabian Journal of Chemistry* 5.3 (2012): 325-337.
44. Alvarez, Patricia E., et al. "Rollinia occidentalis extract as green corrosion inhibitor for carbon steel in HCl solution." *Journal of Industrial and Engineering Chemistry* 58 (2018): 92-99.
45. Rodríguez-Torres, A., et al. "Effect of green corrosion inhibition by *Prunus persica* on AISI 1018 carbon steel in 0.5 M H₂SO₄." *Int J Electrochem Sci* 13 (2018): 3023-3049.
46. Mehdipour, M., B. Ramezanzadeh, and S. Y. Arman. "Electrochemical noise investigation of Aloe plant extract as a green inhibitor on the corrosion of stainless steel in 1 M H₂SO₄." *Journal of Industrial and Engineering Chemistry* 21 (2015): 318-327.
47. Sharma, M. K., et al. "Inhibitive effect of *Prosopis cineraria* on mild steel in acidic media." *Corrosion engineering, science and technology* 43.3 (2008): 213-218.
48. Kamal, C., and M. G. Sethuraman. "Spirulina platensis—A novel green inhibitor for acid corrosion of mild steel." *Arabian Journal of Chemistry* 5.2 (2012): 155-161.
49. Alaneme, Kenneth Kanayo, Sunday Joseph Olusegun, and Oluwabunkunmi Tomi Adelowo. "Corrosion inhibition and adsorption mechanism studies of *Hunteria*

umbellata seed husk extract on mild steel immersed in acidic solutions." Alexandria Engineering Journal 55.1 (2016): 673-681.

JNTUA COLLEGE OF ENGINEERING, ANANTAPUR
DEPARTMENT OF CHEMICAL ENGINEERING
Final PROJECT Work-EVALUATION SHEET

S. No.	Admission number	Clear Hypothesis (10 M)	Objectives (10 M)	Methodology of execution (10 M)	Interpretation of the results (10 M)	Total Marks (40 M)
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						
13.						
14.						
15.						
16.						
17.						
18.						
19.						
20.						
21.						
22.						
23.						
24.						
25.						
26.						
27.						
28.						
29.						
30.						

* Maximum (10 M) and Minimum (5 M)

Signature of Evaluator's

(1)

(2)

(3)

Head, Chemical Engineering