

# **ADSORPTION OF METHYLENE BLUE DYE FROM INDUSTRIAL EFFLUENTS BY POLYMER POLYANILINE SYNTHESIZED ON JUTE FIBER**

Thesis submitted in partial fulfillment of the requirements for the degree of

**Master of Technology  
in  
Environmental Engineering**

*by*

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**CERTIFICATE**

This is to certify that the research work embodied in this dissertation entitled “**Adsorption of Methylene blue dye from Industrial Effluents by polymer polyaniline synthesized on jute fiber**” has been carried out in the Department of Environmental Engineering, Delhi Technological University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma to any university or institute. The work is approved for submission.

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## **DECLARATION**

I, hereby declare that the work being presented in the Project Report entitled **“Adsorption of methylene blue dye from industrial effluents by polymer polyaniline synthesized on jute fiber”** is my original work and an authentic report carried out during the period of 3<sup>rd</sup> Semester as a part of my major project.

The contents of this report has not been previously formed the basis or the award of any degree, diploma or other similar title or recognition and is being utilized by me for the submission of my Major Project Report to complete the requirements of Master’s Degree of Examination in Environmental Engineering, as per Delhi Technological University curriculum.

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## SYNOPSIS

During the last few decades, growth of industrialization and modernization at a rapid rate has created a negative impact on environment due to pollution of both the surface and subsurface waters. Anthropogenic activities which are of prime concern such as industrial activities majorly pollute the water through discharging toxic chemicals contaminated effluents. Toxic chemicals include heavy metals, such as chromium, copper, cadmium, mercury, zinc etc and also dyes. The presence of dye even at trace quantity is easily visible and physiologically can't accept for further use besides its toxic effects. Conventional treatment for dyes such as membrane technique, reverse osmosis, adsorption etc are widely practiced. Out of these methods, adsorption is the most commonly applied due to its ease in operation, cost effective, easy maintenance and effective dye removal. Activated carbon based adsorbents again are the most conventionally and effectively used adsorbents however production of dyes contaminated sludge etc is the main drawbacks. Employment of functionalized polymers containing several functional groups such as amines, carboxylate, ether, hydroxyl, sulphate, etc., as adsorbent for removal of dye ions has become a recent trend. However many of the reported functionalized polymers have complex synthesis procedure and cost ineffective. Therefore development of low cost functional polymer with easy synthesis procedure, moderate to high metal removal, rapid adsorption kinetics and reusability is necessary.

One of the most effective metal binding functional group is amine ( $-NH_2$ ) due to presence of lone pair of electron in  $sp^3$  hybridized atom of nitrogen. In the present study, an amine based polymers namely polyaniline (PANI) is synthesized to use as an adsorbent for dye removal from aqueous solution. Since polyaniline are very fine particles and segregation after adsorption is difficult, it's synthesized over the surface of jute fiber. Methylene blue (MB) was selected as model dye and study was carried out in batch mode operation. Optimum pH of MB adsorption by PANI-jute was observed at the range of pH 7- 10 due to formation of coordinate bond between the cationic MB dye & amines of the PANI-jute. Adsorption equilibrium time was observed to be highly rapid with almost 90% uptake within 5 minutes for higher concentration till 100 mg/L methylene blue. Chemical adsorption behavior is further well confirmed through fixing of kinetic data in Lagergren's Pseudo second order kinetic model. Insignificant adsorption through physical adsorption was confirmed through diffusion model and concluding the predominantly adsorption of MB by PANI-jute through chemical bond formation. Adsorption of MB by PANI-jute was able to be explained by both Langmuir and Freundlich isotherm with comparative value 31 & 29 error square respectively. Maximum amount of MB uptake capacity of PANI-jute was observed to be 111.11 mg/g from Langmuir's isotherm. Freundlich's isotherm 'n' value of 1.75 which is less than 10 and greater than 0 suggest the favorable adsorption of MB

by PANI-jute. The adsorbed methylene blue in PANI-jute were still able to recovered back almost 90% by mineral acids desorption. Further, the polymer adsorbent PANI-jute was reuse for more than 10 cycles, without any decreasing its MB uptake capability. Thus, the maximum uptake capacity of PANI-jute is higher than 1100 mg/g. The performance of PANI-jute when subjected to sactual industrial wastewater decrease by 10-15% due to the presence of other co-ions. PANI-jute showed stability during storage for as long as 12 months time period and provide a platform for its commercial purposes.

**Keywords: Dyes; Methylene Blue; amine; polymer; adsorption; desorption; polyaniline.**

## Table of Contents

| <b>Titles</b>                       |  |  | <b>Page No</b> |
|-------------------------------------|--|--|----------------|
| Certificate                         |  |  | i              |
| Acknowledgement                     |  |  | iii            |
| Declaration                         |  |  | iv             |
| <b>Synopsis</b>                     |  |  | v-vi           |
| List of Figures                     |  |  | ix-x           |
| List of Tables                      |  |  | xi             |
| <b>Chapter 1. Introduction</b>      |  |  | 1-4            |
| 1.1                                 | Dyes   |  | 2              |
| 1.2                                 | Removal of dyes                                      |  | 3              |
| 1.3                                 | Adsorption   |  | 3              |
| 1.4                                 | Objective of the present study                       |  | 4              |
| <b>Chapter 2. Literature Review</b> |  |  | 5-13           |
| 2.1                                 | Introduction   |  | 6              |
| 2.2                                 | Classification of dyes                               |  | 6              |
|                                     | 2.2.1 Classification based on the source of material |  | 7              |
|                                     | 2.2.1.1 Natural dyes                                 |  | 7              |
|                                     | 2.2.1.2 Synthetic dyes                               |  | 7              |
|                                     | 2.2.2 Chemical classification of dyes                |  | 7              |
|                                     | 2.2.3 Dyes according to the nuclear structure        |  | 8              |
|                                     | 2.2.4 Industrial classification of the dyes          |  | 8              |
| 2.3                                 | Methylene blue                                       |  | 8-9            |
| 2.4                                 | Effects of dyes                                      |  | 9              |
|                                     | 2.4.1 Effect of dyes in river                        |  | 10             |



|   |     |                                       |       |
|---|-----|---------------------------------------|-------|
|   | 2.5 | Removal techniques                    | 11    |
|   |     | 2.5.1 Ion exchange                    | 12    |
|   |     | 2.5.2 Membrane Process                | 12    |
| <b>Chapter 3 Materials and methods</b>  |     |                                       | 15-22 |
|   | 3.1 | Materials and reagents                | 16    |
|   | 3.2 | Synthesis of adsorbents               | 16-17 |
|   | 3.3 | Batch Mode adsorption experiments     | 18-19 |
|   | 3.4 | Desorption Experiments                | 19-20 |
|   | 3.5 | Analytical Techniques                 | 20-22 |
| <b>Chapter 4 Results and discussion</b> |     |                                       | 23-53 |
|   | 4.1 | Effect of Reaction pH                 | 24    |
|   | 4.2 | Effect of adsorption time             | 27    |
|   | 4.3 | Adsorption Kinetics                   | 28    |
|   |     | 4.3.1 First Order Adsorption Model    | 29    |
|   |     | 4.3.2 Second Order Adsorption Model   | 31    |
|   |     | 4.3.3 Elovich Kinetic Model           | 36    |
|   |     | 4.3.4 Diffusion Kinetic Model         | 38    |
|   | 4.4 | Effect of adsorbent dose              | 40    |
|   | 4.5 | Adsorption Isotherm                   | 42    |
|   |     | 4.5.1 Langmuir Isotherm               | 42    |
|   |     | 4.5.2 Freundlich Isotherm             | 43    |
|   | 4.6 | Desorption                            | 48    |
|   | 4.7 | Reuse                                 | 50    |
|   | 4.8 | Adsorption with industrial wastewater | 52-53 |
| <b>Chapter 5 Conclusion</b>             |     |                                       | 54-57 |

|                   |     |                        |       |
|-------------------|-----|------------------------|-------|
|                   | 5.1 | Conclusions            | 55    |
|                   | 5.2 | Recommendation         | 56    |
|                   | 5.3 | Scope of further study | 57    |
| <b>References</b> |     |                        | 58-61 |

## List of Figures

| Sl no. | Figure no. | Captions   | Page no |
|--------|------------|--|---------|
| 1      | 2.1        | : Chemical Structure of Methylene Blue   | 9       |
| 2      | 2.2        | : Schematic diagram of reverse osmosis and electro dialysis process  | 13      |
| 3      | 3.1        | : Synthesis scheme of polyaniline polymer  | 17      |
| 4      | 3.2        | : Synthesis process of polyaniline on jute fiber   | 17      |
| 5      | 3.3        | : SEM images of PANI-jute before & after MB adsorption   | 18      |
| 6      | 3.4        | : Adsorption batch experiments set up  | 19      |
| 7      | 3.5        | : Methylene Blue Desorption experimental set up.   | 20      |
| 8      | 3.6        | : Calibration curve of methylene blue at wavelength of 664 nm  | 22      |
| 9      | 4.1        | : Effect of solution pH on solubility of Methylene blue  | 25      |
| 10     | 4.2        | : Effect of reaction pH on adsorption of Methylene blue by PANI-jute at various reaction pH                          | 26      |
| 11     | 4.3        | : Mechanism of MB binding by PANI-jute at basic pH   | 26      |
| 12     | 4.4        | : Effect of reaction time on adsorption (%) of Methylene blue by PANI-jute at various initial concentration of MB    | 27      |
| 13     | 4.5        | : Effect of reaction time on adsorption of Methylene blue (mg/g) by PANI-jute at various initial concentration of MB | 28      |
| 14     | 4.6        | : Plot of time vs $\text{Log}(q_e - q_t)$ for First Order kinetic model  | 30      |
| 15     | 4.7(a)     | : Plot of time Vs $t/q_t$ for Second order kinetic model   | 32      |
| 16     | 4.7(b)     | : Plot of time Vs $t/q_t$ for Second order kinetic model   | 33      |
| 17     | 4.8(a-e)   | : Plot of $q_t$ value between Predicted and Experimental value for second order kinetic model                        | 34-36   |
| 18     | 4.9        | : Plot of $\text{Ln}(\text{time})$ Vs $q_t$ for Elovich Model kinetic model  | 37      |
| 19     | 4.10       | : Plot of Square root(time) Vs $q_t$ for diffusion kinetic model   | 39      |

|               |                   |   |   |                |
|---------------|-------------------|---|---|----------------|
| 20            | 4.11              | : | Plot of Removal(%) for MB Vs dose of PANI-jute  | 41             |
| 21            | 4.12              | : | Plot of Removal ( $q_e$ ) for MB Vs dose of PANI-jute   | 41             |
| 22            | 4.13              | : | Plot of Langmuir's isotherm for MB adsorption by PANI-jute  | 46             |
| 23            | 4.14              | : | Plot of Freundlich's isotherm for MB adsorption by PANI-jute  | 46             |
| <b>Sl no.</b> | <b>Figure no.</b> |   | <b>Captions</b>   | <b>Page no</b> |
| 24            | 4.15              | : | Comparison between experimental $q_e$ and predicted $q_e$ value of Langmuir & Freundlich's isotherm | 47             |
| 25            | 4.16              | : | Mechanism of methylene Blue desorption from PANI-jute   | 48             |
| 26            | 4.17              | : | Desorption of methylene blue  | 49             |
| 27            | 4.18              | : | Kinetics of MB desorption from PANI-jute  | 50             |
| 28            | 4.19              | : | Mixing of Dye industrial effluents and sewage   | 52             |
| 29            | 4.20              | : | Collection of Dye industrial effluents at (a) Badli & (b) Shahbad                                   | 53             |

## List of Tables

| Sl no. | Table no. | Captions   | Page no |
|--------|-----------|--|---------|
| 1      | 3.1       | : Experimental design for batch studies with Methylene blue and PANI-jute              | 21      |
| 2      | 3.2       | : Details of analytical instruments used in the present work                           | 22      |
| 3      | 4.1       | : Coefficients of first order model for MB adsorption by PANI-jute                     | 31      |
| 4      | 4.2       | : Coefficients of first order model for MB adsorption by PANI-jute                     | 33      |
| 5      | 4.3       | : Coefficients of Elovich's kinetic equation   | 38      |
| 6      | 4.4       | : Coefficients of Diffusion kinetic equation   | 40      |
| 7      | 4.5       | : Coefficients of Langmuir and Freundlich's isotherm                                   | 45      |
| 8      | 4.6       | : Comparison of MB maximum adsorption capacities of different adsorbent with PANI-jute | 47      |
| 9      | 4.7       | : Desorption of MB from PANI-jute  | 49      |
| 10     | 4.8       | : Recycling and reuse of PANI-jute for MB adsorption                                   | 51      |
| 11     | 4.9       | : Characteristics of Industrial effluents containing Methylene Blue                    | 53      |

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# **CHAPTER 1**

## **INTRODUCTION**

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# CHAPTER 1

## INTRODUCTION

The presence of several dyes in the environment is of major concern due to their toxicity to many life forms. A trace of dye in water is highly visible. Even discharging a small amount of dye can affect food webs and aquatic life due to the mutagenic and carcinogenic effects of the synthetic dyes. Therefore, the removal of dyes from waste effluents is always widely focused.

### 1.1 DYES

A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and requires a mordant to improve the fastness of the dye on the fiber. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments. The discharge of colored wastewater from these industries into natural streams has caused many significant problems such as increasing the toxicity and chemical oxygen demand (COD) of the effluent; it reduces the light penetration, which has a derogatory effect on photosynthetic phenomenon. Methylene Blue is widely used, having its various usage, temporary hair colorant, auto-oxidizing agent. Though it is not strongly hazardous, but it can cause some harmful effects. Acute exposure to Methylene blue causes increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans. Due to carcinogenic and mutagenic effects of synthetic dyes it affects the aquatic life and their food web.

## 1.2 REMOVAL OF DYES

These days mainly three procedures are used to removal of dyes:

- I. Conventional Treatment Process- It includes Coagulation, Flocculation, Biodegradation. Though this processes is simple and economically feasible but, sludge production is very high and it consist handling and disposal problems too. One more techniques is used Adsorption of activated carbon, this is most widely used adsorbent as it produce high quality effluent. The disadvantage of this process is Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process.
- II. Established Recovery Process: It includes Membrane separations, ion –exchange, oxidation. The disadvantage of this high pressure required, expensive, incapable of treating large volumes, and in oxidation process it requires high energy cost and chemicals.
- III. Emerging Removal Process: It includes advanced oxidation process, bioadsorbent biomass. But the first one is economically unfeasible, having technical constraints while second one is slow process and dependent on some constants (pH and salts).

## 1.3 ADSORPTION

Adsorption, the binding of molecules or particles to a surface, must be distinguished from *absorption*, the filling of pores in a solid. The binding to the surface is usually weak and reversible.

The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they present enormous surface areas per unit weight. Activated carbon is produced by



roasting organic material to decompose it to granules of carbon - coconut shell, wood, and bone are common sources. Silica gel is a matrix of hydrated silicon dioxide. Alumina is mined or precipitated aluminum oxide and hydroxide. Although activated carbon is a magnificent material for adsorption, its black color persists and adds a grey tinge if even trace amounts are left after treatment; however filter materials with fine pores remove carbon quite well.

Temperature effects on adsorption are profound, and measurements are usually at a constant temperature. Graphs of the data are called *isotherms*. Most steps using adsorbents have little variation in temperature.

## **1.4 OBJECTIVE OF THE PRESENT STUDY**

After a through survey of the literatures, it can be observed that, there is an essential to study Methylene blue adsorption on functionalized based polymers to remove maximum amount using Bath process mode operation. The list of objectives for the complete study is thereby listed.

1. To study adsorption of Methylene Blue by poly-aniline jute through batch process and analyzing the effect on the following parameters:
  - Dose of adsorbent.
  - Concentration of MB ions in solution.
  - Presence of other ions in the solution.
2. To identify the appropriate kinetic model for removal of MB ions.
3. To identify appropriate adsorption isotherm for MB ion removal.
4. To Recover MB ions from the polymer adsorbent.
5. Reuse of adsorbent for further adsorption of MB.
6. Effectivity of polyaniline for removal of Methylene blue from actual industrial wastewater.

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# **CHAPTER 2**

# **LITERATURE REVIEW**

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## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1. INTRODUCTION**

Environmental pollution is one of the major and most urgent problems of the modern world. Many dyes and their breakdown products are carcinogenic, mutagenic and/or toxic to life. Industries are the greatest polluters, with the textile industry generating high liquid effluent pollutants due to the large quantities of water used in fabric processing. It is estimated that globally 280,000 tons of textile dyes are discharged in textile industrial effluent every year. Apart from the aesthetic point of view, dyes are undesirable because they can affect living creatures in the water discharged as effluent into the environment. In general, the final textile waste effluent can be broadly categorized into three types- high, medium and low strength on the basis of their COD content. Worldwide,  $10^6$  tons of synthetic dyes are produced annually, of which  $1- 1.5 \times 10^5$  tons are released into the environment in wastewaters. This release is because not all dye binds to the fabric during the dyeing processes, depending on the class of the dye, the losses in wastewaters can vary from 2% for basic dyes to as high as 50% for reactive dyes, leading to severe contamination. Out of all the dyes, methylene blue (MB) is the most commonly used for dyeing cotton, wood and silk. Although the dye is not regarded as a very toxic dye, MB can have various harmful effects on human being and animals. Once inhaled, it can cause heart rate increasing, nausea and vomiting.

#### **2.2 CLASSIFICATION OF DYES**

There is variation in the manner in which different fibers respond to dyestuffs and even the same fibers do not produce a full range of colors with a particular type of dye.

## 2.2.1. CLASSIFICATION BASED ON THE SOURCE OF MATERIAL

- Natural Dyes
- Synthetic Dyes

### 2.2.1.1 NATURAL DYES

These dyes are thereby specifically identified as dyes of the stated colour, and which may still be derived from animals or plants. Note that this is a classification based on the dye's source and colour. It contains no chemical information; neither does it imply that dyes with similar names but unique numbers are in any way related. It gives no information about the mechanism by which staining occurs. Natural dyes are often negatively charged. Positively charged natural dyes do exist, but are not common. In other words, the coloured part of the molecule is usually the anion. Although the molecular charge is often shown on a specific atom in structural formulae, it is the whole molecule that is charged. Many, but by no means all, natural dyes require the use of a mordant..

### 2.2.1.2. SYNTHETIC DYES

Dyes derived from organic or inorganic compound are known as synthetic dyes. Examples of this class of dyes are Direct, Acid, Basic, Reactive, Mordant, Metal complex, Vat, Sulphure , Disperse dye etc.

## 2.2.2. CHEMICAL CLASSIFICATION OF THE DYES

According to a system of chemical classification, dyes can be divided according to the nature of their Chromophore, a substance which gives color to the dye. Acridine dyes, derivatives of acridine  $>C=N$ -and  $>C=C$ , Anthraquinone dyes, derivatives of anthraquinone  $>C=O$  and  $>C=C$ , Phthalocyanine dyes, derivatives of phthalocyanine  $>C=N$ , Indophenol dyes,

derivatives of indophenol  $>C=N$ -and  $>C=O$  used in color photography, Quinone-imine dyes, derivatives of quinine used in paper.

### 2.2.3. DYES ACCORDING TO THE NUCLEAR STRUCTURE

Though not very popular but dyes can be categorized into types by using this method of classification:

- Cationic Dyes
- Anionic Dyes

### 2.2.4 INDUSTRIAL CLASSIFICATION OF THE DYES

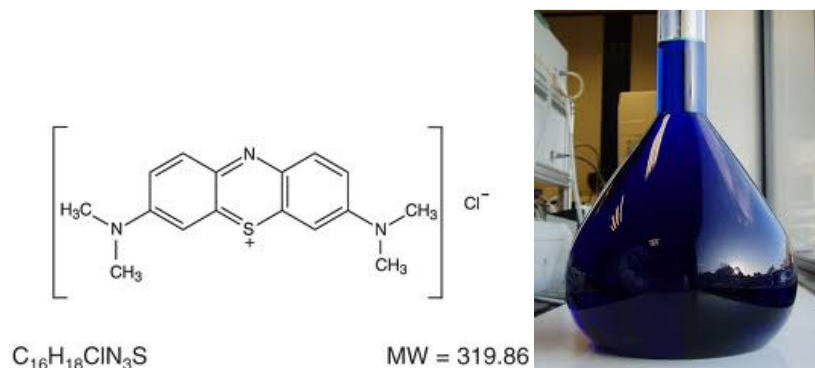
As globally majority of the dyestuff is primarily consumed by the textile industry. So, at this level a classification can be done according to their performances in the dyeing processes. Worldwide around 60% of the dyestuffs are based on azo dyes that gets consumed by in the textile finishing process. Major classes of dyes in textile finishing are given here. Major Dye classes and the substrates:

- Protein Textile Dyes
- Cellulose Textile Dyes
- Synthetic Textile Dyes

## 2.3 METHYLENE BLUE

Methylene blue was discovered in 1876 and is manufactured by a process, introduced about 1886, using dimethylaniline as the principal starting material. **Methylene blue** (CI 52015) is a heterocyclic aromatic chemical compound with the molecular formula  $C_{16}H_{18}N_3SCl$ . At room temperature it appears as a solid, odorless, dark green powder, that yields a blue solution when dissolved in water. It is mainly used on bast (soft vegetable fibres such as jute, flax, and hemp) and to a lesser extent on paper, leather, and mordanted cotton. It dyes silk and wool but has very poor light fastness on these fibres. It is also employed as a biological stain, in testing

milk for tubercular infection, and as a chemical oxidation–reduction indicator. Methylene Blue is used in the treatment of cyanide poisoning and methemoglobinemia (a blood disorder). It is also used as a diagnostic agent because of its blue staining properties. It administered orally and parentally. It is not available in any combination preparations. Its chemically identified as 3, 7-bis (dimethylamino) phenothiazine-5-ium chloride trihydrate and its structure is shown in Figure 2.1.



**Figure 2.1: Chemical structure of Methylene blue**

### 2.3 EFFECTS OF DYE

The presence of very small quantities of dyes in water (less than 1 ppm) is highly visible due to their brilliance. Depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms. The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously influence on the food chain. Dyes can remain in the environment for an extended period of time, because of high thermal and photo stability. For instance, the half-life of hydrolysed Reactive Blue 19 is about 46 years at pH 7 and 25 °C. Triple primary cancers involving kidney, urinary bladder and liver of dye workers are some of the reported effects. Most of the dyes, used in the textile industry are known only by their trade

name, while their chemical nature and biological hazards are not known. The mutagenicity of textile dyes (known only by their trade name, used in Pali, identified as one of the most polluted cities in India) and the effluents containing these dyes influence on the health of textile dyeing workers and the environment. The dyes were used in their crude form and no following purification was attempted, because they wanted to test the potential danger that dyes represent in actual use. The results clearly indicated that most of the used dyes are highly mutagenic. The formation of Decoloration of Textile Wastewaters 177 carcinogenic aromatic amine o-tolidine from the dye Direct Blue 14 by skin bacteria has been established. Textile dyes can cause allergies such as contact dermatitis and respiratory diseases, allergic reaction in eyes, skin irritation, and irritation to mucous membrane and the upper respiratory tract. Reactive dyes form covalent bonds with cellulose, woollen and PA fibres. It is assumed that in the same way reactive dyes can bond with  $-NH_2$  and  $-SH$  group of proteins in living organisms. A lot of investigations of respiratory diseases in workers dealing with reactive dyes have been made. Certain reactive dyes have caused respiratory sensitisation of workers occupationally exposed to them. Public perception of water quality is greatly influenced by the colour.

## **2.4 EFFECTS OF DYES IN RIVERS**

Industrial effluents containing synthetic dyes reduce light penetration in rivers and thus affect the photosynthetic activities of aquatic flora, thereby severely affecting the food source of aquatic organisms. The thin layer of discharged dyes that can form over the surfaces of the receiving waters also decreases the amount of dissolved oxygen, thereby affecting the aquatic fauna. Furthermore, dye-containing effluents increase biochemical oxygen demand. Dyes are in general stable organic pollutants that persist in the environment, and concern has been raised that such artificial compounds are xenobiotic. Therefore, methods for their degradation have been increasingly explored and development.

## **2.5 REMOVAL TECHNIQUE**

The removal of colour from wastewater is often more important than the removal of the soluble colourless organic substances. Removal of the dyes from the textile wastewater is often very costly, but a stringent environmental legislation has stimulated the textile sector in developing wastewater treatment plants.

### **2.5.1 ION EXCHANGE**

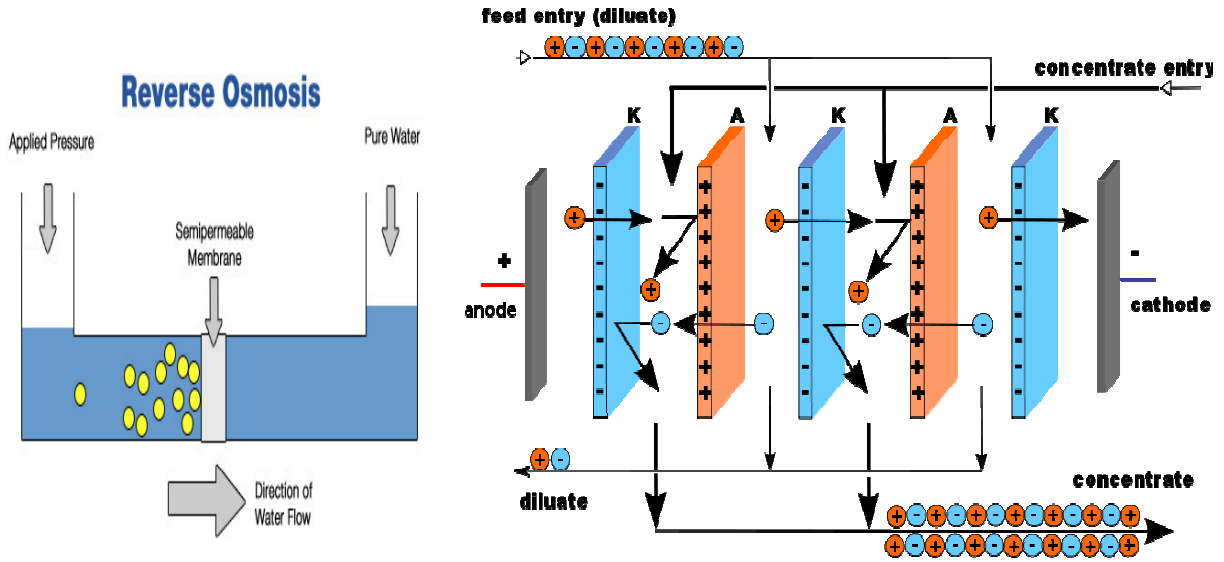
Ion exchange is a unit process in which ions are exchanged between a solution and an ion exchanger, an insoluble solid or gel. Chelating resins, such as amino-phosphonic and iminodiacetic resins have been manufactured with high selectivity for specific cationic ions. To date, ion exchange has had limited application because of the extensive pretreatment requirement, less life span of the ion exchange resins and requirement of complex regeneration system. Besides, most of the ion exchange resins are expensive and released other cations such as  $H^+$  or  $Na^+$  in aqueous solution. Process efficiency is strongly pH dependent as most metals bind with the resin at higher pH. Besides, high concentrations of influent total suspended solids can plug the ion exchange beds, and cause high head loss and inefficient operation. Ion exchange waste is highly concentrated and requires careful disposal. Excessive osmotic swelling and shrinking, chemical degradation and structural changes in the resin due to presence of oxidants, solvents and polymers in wastewater are also important factors that limit the useful life and performance of ion exchange resin.

### **2.5.2 MEMBRANE PROCESS**

Various membrane separation processes like reverse osmosis (RO), nanofiltration and electrodialysis are used for removal of dyes ions. RO involves an ionic exclusion process where small particles are rejected by the water layer adsorbed on the surface of the membrane, which is known as dense membrane. Nanofiltration is also a form of filtration that uses membranes to preferentially separate different ions. The membrane use is partially permeable to perform the



separation but pores are much larger than that of reverse osmosis. In case of electro dialysis (ED), ions are transported through semi permeable membrane under the influence of an electric potential. These membrane processes are expensive compared to conventional treatment, as high capital and operating costs are required by the higher energy input to develop pressure needed to operate. Other recognizable limitations include membrane fouling and deterioration with time resulting from deposition of soluble materials, organic materials, suspended and colloidal particles and other contaminants thus requiring high level of pretreatments to prevent it.



**Figure 2.2 : Schematic diagram of Reverse osmosis and Electro dialysis process**

Although modern dye removal technologies such as ion exchange, reverse osmosis and membrane systems are now becoming components in integrated systems that produce effluents of better quality while allowing for the recovery and reuse of dye, their use is limited because of the high capital and operational costs associated with them. Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of dye at trace quantities; however, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. Recently biosorption is evolved as an alternative treatment for removal of dyes. But still it has some limitations like, less effectiveness, slow reaction rate, difficulty in preparation, and

presence of some other constituents in the wastewater like COD may decrease dyes removal efficiency. Therefore there exists the need to develop low cost, effective, stable, ease at preparation and regenerable adsorbent materials, which are capable of removing dyes ions from aqueous solution.

The most widely used are biodegradation (El-Sheekh et al 2009), flocculation–coagulation (Canizares 2006), chemical oxidation (Salem and El-maazami 2001), decolorisation of synthetic dyes by agricultural waste (Neetu et al, 2012), treatment of Methylene blue with solar photo catalyst (Janhavi and S.K.Singh 2012) and adsorption. Among these methods, adsorption technique has been proven to be effective and attractive for the treatment of dye-bearing wastewaters (Yao et al., 2010). Adsorption is also a comparatively cheap and effective method in the removal of MB dyes. The adsorption characteristics of MB dyes on various adsorbents, such as activated carbon (AC), agriculture waste, silica, clay, industrial solid wastes, sewage sludge (Rafatullah et al., 2010) etc. have been extensively investigated. Among these adsorbents, perhaps AC is the most widely used adsorbent for the MB's removal based on its high adsorption capacity and fast removal rate because of their huge specific surface area and specific surface reactivity (Park and Kim, 1999), but it is prohibitively expensive. The waste materials and by-products from the agriculture assume to be low-cost adsorbents due to their abundance in nature and surface functional groups. The raw agricultural solid wastes such as leaves (Han et al., 2009; Weng et al., 2009), fibers (Kavitha and Namasivayam, 2007), fruits peels (Hameed and Ahmad, 2009), seeds (Hameed 2009) and waste materials from forest industries such as sawdust (Hamdaoui, 2006), bark (Rafatullah et al., 2010) etc. have been used as adsorbents for the removal of dyes. Despite the number of successful systems employing various physicochemical and biological processes, economical removal of colour from effluents remains a major problem. It is obvious that each process has its own constraints in terms of cost, feasibility, practicability, reliability, stability, environmental impact, sludge production, operational difficulty, pre-treatment requirements, the extent of the organic removal and potential toxic by-products. Also, the use of a single process may not completely decolourise the wastewater and degrade the dye molecules. Even when some processes are reported to be successful in decolourising a particular wastewater, the same may not be applicable to other types of coloured wastewaters. Certainly, the effective removal of dye from industrial coloured wastewater is a challenge to the manufactures and researchers, as some of the processes are

neither economical nor effective. The amount of water consumed in textile industries must also be considered because the traditional textile finishing industry consumes around 100 L of water in the processing of a kg of textile material. Since these concerns about the environment are gaining momentum, it is necessary to develop better economically and environmentally friendly treatment technologies.

Various functionalized polymers have affinity towards metal ions and dyes. Jute fiber being low cost and easily available can be used in many chemical processes aiming several scientific and technical applications because of its low weight, high surface area during the reaction process. In the present work a functionalized polymer namely polyaniline is synthesized over surface of jute fiber. Main objective of the study is to determine the dyes removal capacity of this functionalized polymer through lab-scale investigation. Studies were conducted in batch with Methylene Blue (MB) as the model metal. Effects of pH, dose of adsorbent and initial MB ion concentration on MB removal efficiency were investigated. Desorption of MB ion and reuse of polyaniline was also studied. Finally, efficiency of the adsorbent was also checked with actual industrial waste water and its difference from synthetic results is investigated.

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**CHAPTER 3**

**MATERIALS AND METHODS**

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## **CHAPTER 3**

### **MATERIALS AND METHODS**

This study was conducted with synthetic wastewater prepared from distilled water containing the desired concentration of Methylene Blue. All chemicals used were of analytical grade and distilled water was used for preparation of solutions. This chapter is divided into four sections – materials, synthesis of Polymer adsorbent, set-up of experimental batch process, Desorption experiment and analytical techniques.

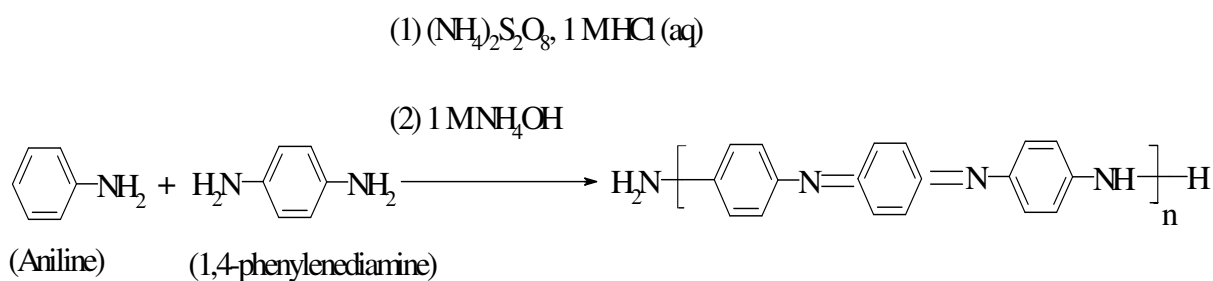
#### **3.1 MATERIALS AND REAGENTS**

Commercial grade aniline [ $C_6H_5NH_2$ ] purchased from CDH chem. was purified by distilling over KOH pellets in presence of small amount of zinc dust to prevent aerial oxidation. Methanol ( $CH_3OH$ ), para-phenylenediamine, ammonium peroxydisulphate and Methylene blue were purchased from Titan biotech and Qualigens chem and were used as received. Single distilled water prepared in the laboratory was used for all experiments.

#### **3.2 SYNTHESIS OF ADSORBENT**

Polyaniline was synthesized by oxidation of aniline ( $C_6H_5NH_2$ ) in presence of 1,4-phenylenediamine, a chain terminator in acidic aqueous medium in presence of an oxidant, ammonium peroxydisulfate [ $(NH_4)_2S_2O_8$ ]. The synthesis scheme of PANI is shown in Figure 3.1 (Yang et al., 2004). Aniline (2.00 ml, 21.5 mmol) and 1,4-phenylenediamine (0.330 g, 3.05 mmol) were dissolved in 66 mL of 1 M HCl (aq.). The mixture was cooled in iced bath to 0- 5 °C followed by addition of 5 g jute fibers and stirred for 5 min. The polymerization reaction started after introduction of pre-cooled (5 °C) solution containing ammonium peroxydisulfate (1.62 g, 7.10 mmol) and 16 mL of 1 M HCl (aq.). The reaction mixture was maintained at 5 °C for 65 min and then kept for overnight at room temperature (25°C). Then the liquid was decanted

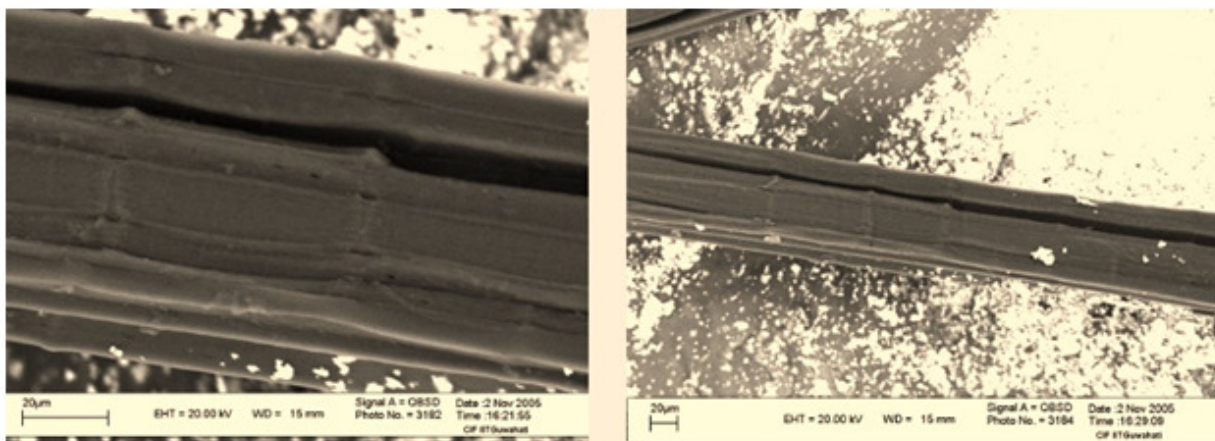
from PANI-jute fiber. To ensure complete deprotonation of PANI-jute, alkali treatment was given by soaking PANI-jute in 1 M  $\text{NH}_4\text{OH}$  for 5 min. The products were then washed with distilled water to adjust the solution to neutral pH. Finally, the blue black colored PANI-jute fiber was dried at 40 °C in the oven. The photographs of synthesis of PANI-jute are shown in Figures 3.2. The SEM images of PANI-jute before and after MB adsorption is also shown in Fig. 3.3



**Figure 3.1: Synthesis scheme of polyaniline polymer**



**Figure 3.2: Synthesis process of polyaniline on jute fiber**



**Figure 3.3: SEM images of PANI-jute before & after MB adsorption**

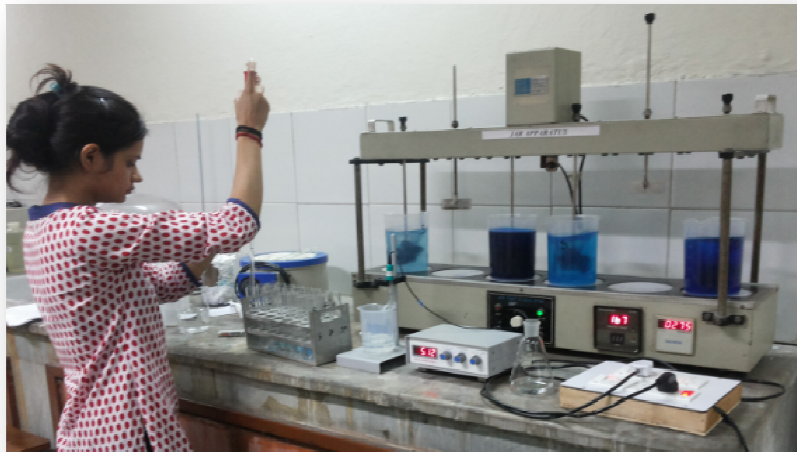
### **3.3 BATCH MODE ADSORPTION EXPERIMENTS**

Batch mode adsorption experiments were conducted at room temperature (23- 25 °C) except where mentioned. All batch studies were carried out with 1000 mL of metal solution in 2 L (two-liter) beaker to prevent the spill off of the solution during experiment. Predetermined quantities of adsorbent were added in the beaker and to achieve the degree of mixing and adsorption equilibrium, a magnetic stirrer was employed with speed adjusted at 100 rpm. A paddle stirrer was also employed with speed adjusted at 1000 rpm to check the difference in metal removal due to different mode of physical mixing of Methylene blue solution ranging from pH 3- 11 were well adjusted by using 0.1 N of HCl and NaOH whereas extreme pH were adjusted using 1 N acid/base solution. Acid/base were preferred than buffer as it was observed more economical when adsorption experiments were conducted in large scale. However for experiment with higher dose of adsorbent exhibiting high fluctuation in pHs, buffer prepared from potassium hydrogen orthophosphate was used to minimize the fluctuation. Addition of acid/base solution to adjust the pH never exceeded 1% of the total volume of the reactor. The adsorption batch experiment is shown in Fig. 3.4. The amount of Methylene blue adsorbed by

adsorbent was calculated based on the difference of metal ion concentration in aqueous solution before and after adsorption according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3.1)$$

where,  $q_t$  is the amount of MB ions adsorbed per unit weight of adsorbent (mg/g) at time  $t$ ,  $C_0$  and  $C_t$  are the concentrations of MB ions (mg/L) at initial time and at time  $t$  respectively,  $V$  is the initial volume of metal ions sample (L) and  $m$  is mass of adsorbent (g). When  $t$  is equal to the equilibrium contact time,  $C_t = C_e$ ,  $q_t = q_e$ , then the amount of MB ions adsorbed at equilibrium,  $q_e$  was calculated using equation (3.1).



**Figure 3.4: Adsorption batch experiments set up using Jar Apparatus**

### **3.4 DESORPTION EXPERIMENTS**

For desorption experiment, 250 mL desorbent was added in a 1 L beaker and mixing was done by magnetic stirrer along with adsorbent containing Methylene blue. The picture of



desorption experiments conducted is shown in Figure 3.5. This was subjected to end over jar apparatus as a shaker at (20-30 rpm) for 20- 30 min. Then it was again filtered and desorbed concentrations of sample were determined in the spectrophotometer. Amount of desorption (%) was calculated using Equation 3.2.

$$Desorption(\%) = \frac{C_{des}V_{des}}{(C_o - C_e)V_{ads}} \times 100 \quad (3.2)$$

where  $C_o$  is the initial concentration of MB ions for adsorption,  $C_e$  the final MB ions concentration after adsorption,  $V_{ads}$  the volume of sample for adsorption experiment,  $C_{des}$  the final concentration after desorption and  $V_{des}$  the volume of desorbent employed.



**Figure 3.5: Methylene Blue Desorption experimental set up using Magnetic Stirrer**

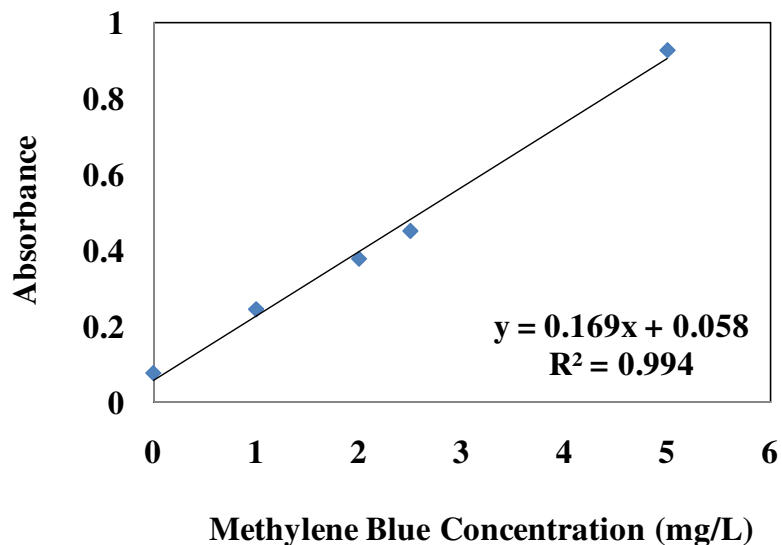
### **3.5 ANALYTICAL TECHNIQUES**

All analyses were carried out according to APHA (1998). Measurement of MB was carried out in spectrophotometer at 664 nm wavelength. The calibration curve obtained and used for estimating the MB concentration is shown in Fig. 3.6. Drying and ignition of polymer was

done using a drying oven and a muffle furnace respectively. During adsorption experiment, degree of mixing was provided by employing magnetic stirrer or Jar test apparatus (Paddle Stirrer). Solution pH was measured by a digital pH meter. All weighing of reagents and adsorbents was carried out in an analytical weighing balance.

**Table 3.1: Experimental design for batch studies with Methylene blue and PANI-jute**

| Experimental Set | Variable parameters                  | Control parameters   | Purpose   |
|------------------|--------------------------------------|--|---|
| 1                | pH                                   | Concentration and Dose   | Effect on absorption of Methylene blue due to variation in Ph                                   |
| 2                | Time                                 | Concentration and Dose   | Optimization of time for removal of methylene blue  |
| 3                | Dose (0.1, 0.2, 0.5, 1, 2, 4, 6 & 8) | Initial Concentration of MB: 20, 50 & 100 mg/L   | Adsorbent dose test   |
| 4                | Desorbent strength (M): 0.01, 0.1, 1 | Initial MB: 50 mg/L;<br>PANI-jute dose: 1 g/L<br>Desorbent: HCl, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> | Desorption  |
| 5                | Adsorption-desorption cycles         | MB Conc :50 mg/L, Vol:250 ml,<br>Desorbent acid strength: 0.01; dose 2 g/L.  | Total adsorption capacity of the polymer adsorbent PANI-jute through several recycle and reuse. |
| 6                | Different Dye industrial effluents   | Initial MB concentration and dose  | To evaluate the effectiveness of PANI-jute  |



**Figure 3.6: Calibration curve of methylene blue at wavelength of 664 nm.**

**Table 3.2: Details of analytical instruments used in the present work**

| <b>Instrument /Equipment</b> | <b>Manufacturer</b>  |
|------------------------------|--|
| Electronic balance           | Type: BL-220H NO: D455005045                                       |
| Digital pH meter             | Model: $\mu$ pH System 361, M/S Systronics India Ltd., India       |
| Spectrophotometer            | Systronics 169   |
| Magnetic Stirrer             | Model: LS04B, Eltek motors, electrocarfts, Goregaon (east) Mumbai. |
| Jar test flaculator          | Serial no-094,OPT voltage: 230V 50HZ                               |
| Hot Air Oven                 | DKM 4000, Yamato   |

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# **CHAPTER 4**

## **RESULT AND DISCUSSION**

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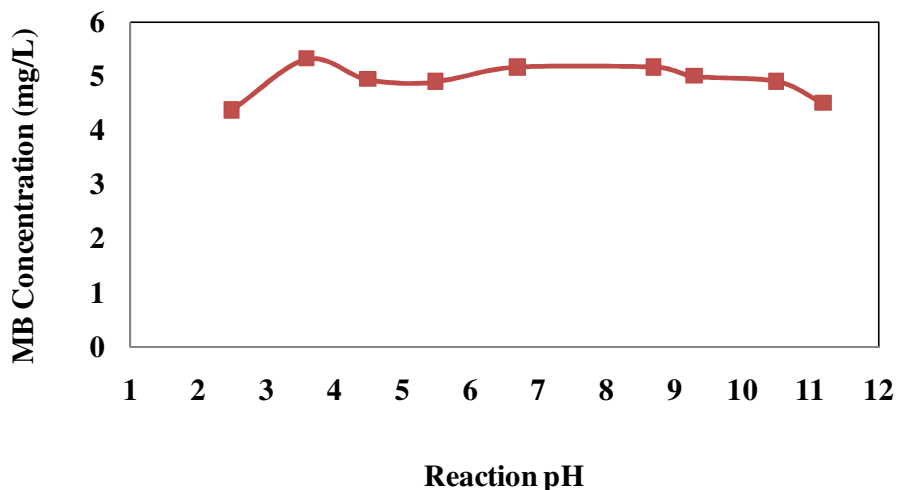
## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

In the present work removal of Methylene Blue was studied by polymer polyaniline synthesized on surface of jute fiber. MB adsorption studies were conducted in batch mode. The experimental studies were conducted in five sets and are shown in Table 4.1. Set 1 was carried out for investigation of effects of reaction pH towards adsorption and identification of the binding mechanism of MB over PANI-jute. Set 2. was carried out to evaluate the effects of initial MB concentration on adsorption. From the data obtained, adsorption kinetics study was also carried out. Effect of PANI-jute dose on MB adsorption was studied by conducting Set 3 experiments. In order to study the reversible process of adsorption, Set 4 experiments was conducted and desorption process was studied. Finally reuse of the adsorbent was studied through Set 5 experiments and evaluates the total adsorption capacity of the polymer adsorbent PANI-jute through several recycle and reuse.

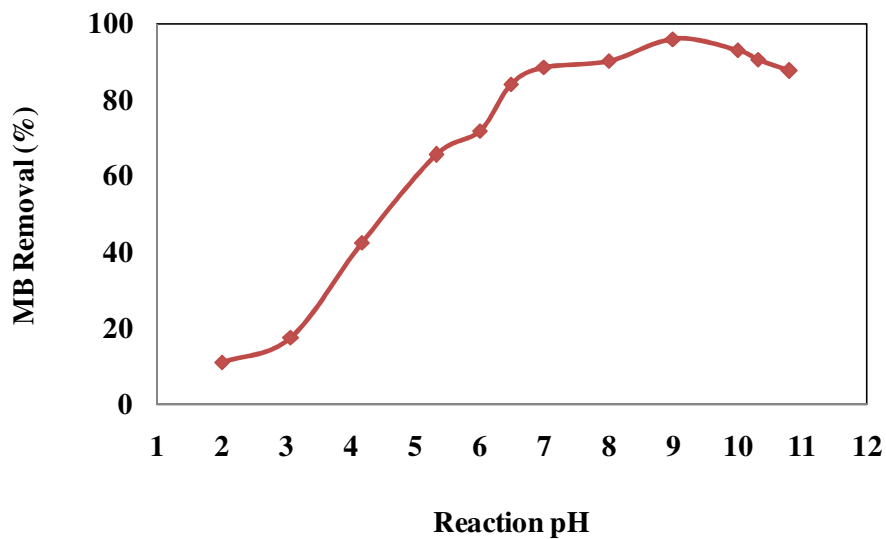
#### **4.1 EFFECT OF REACTION pH**

Solution pH is one of the most important parameter to reveal the mechanism of adsorption. The effect of solution pH effect is firstly studied by conducting control experiment without any adsorbents. From Fig. 4.1, it's clear that the solubility of MB is consistent from pH range of 2- 12. Secondly, various pH range of MB solution was contacted with PANI-jute and the result is shown in Fig. 4.2.

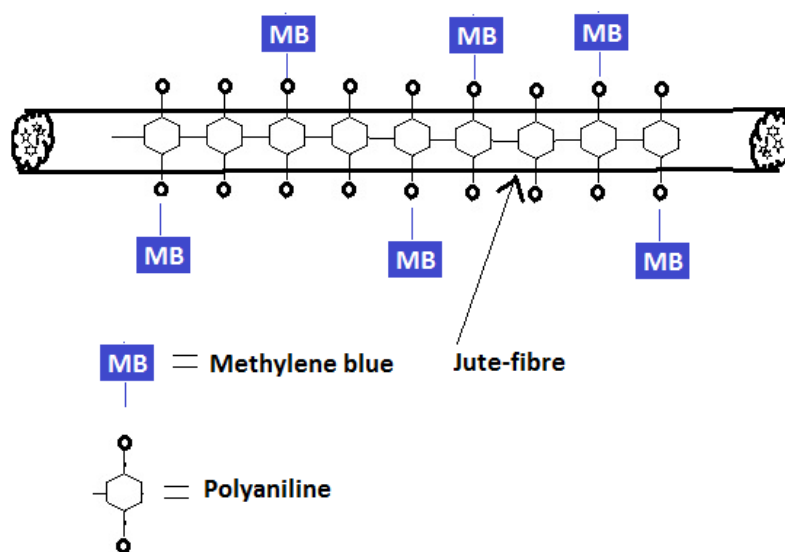


**Figure 4.1: Effect of solution pH on solubility of Methylene blue (Initial MB: 5 mg/L)**

The pH of dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity (Yasemin, 2006). The effect of pH on the adsorption of MB at equilibrium ( $q_e$ ) by MB is shown in Fig. 4.2. The removal(%) at acidic pH is lesser with 15% to 40% with increased in pH from 2 to pH 5. Lower adsorption at acid pH was probably due to the presence of excess of protons ( $H^+$ ) ions competing with the dye cations for adsorption sites. At higher pH values (6–11) the dye adsorption increased to almost 85% and attain almost constant. The surface of MB contains a large number of active sites, and the solute (dye) uptake can be related to the active sites and also to the chemistry of the solute in the solution. At higher pH, the surface of MB particles become negatively charged, which enhances the positively charged MB cations through electrostatic forces of attraction (Yasemin, 2006). Similar trend was observed for adsorption of methylene blue onto *Posidonia oceanica* (L.) fibres (Ncibi et al., 2007), yellow passion fruit peel (Pavan et al., 2008) and methyl violet onto sunflower seed hull (Hameed 2008).



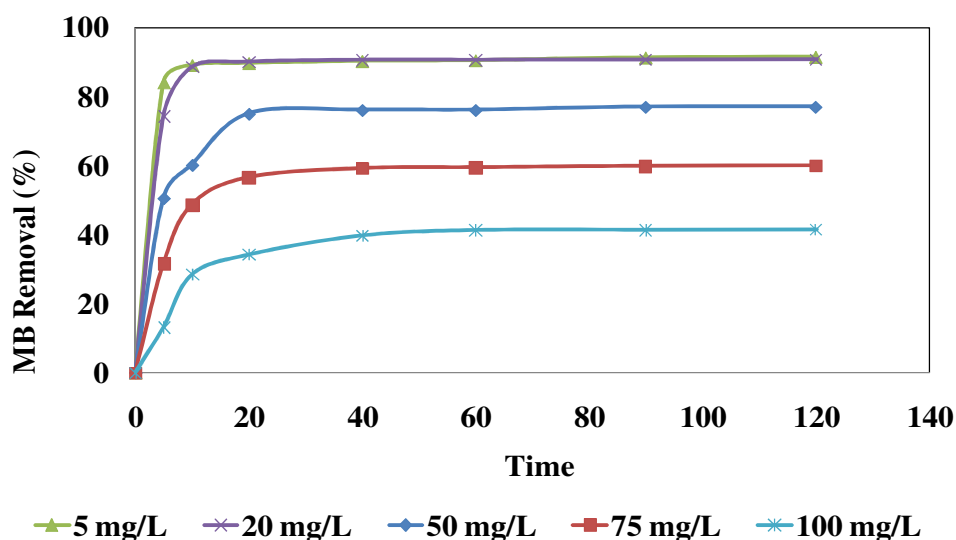
**Figure 4.2: Effect of reaction pH on adsorption of Methylene blue by PANI-jute at various reaction pH (Initial MB: 50 mg/L; dose: 1 g/L)**



**Figure 4.3: Mechanism of MB binding by PANI-jute at basic pH**

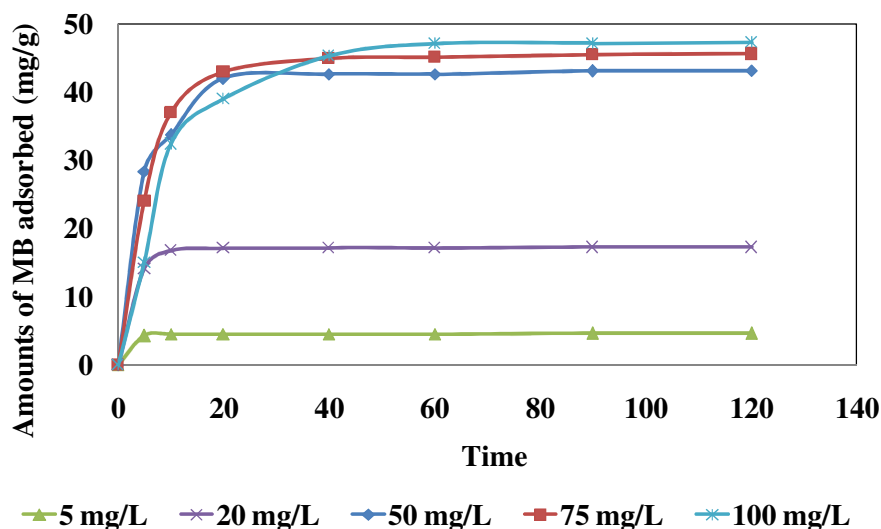
## 4.2 EFFECT OF ADSORPTION TIME

The effect of initial MB concentration on the adsorption was investigated varying initial MB concentration in the range of 5–100 mg/L. Batch experiments were performed at solution pH of 8.0 with 1 g/L PANI-jute adsorbent. Removals of MB ions (%) with time at varying initial MB concentrations and amounts of MB adsorbed are shown in Fig. 4.4 and 4.5 respectively. The equilibrium between MB and PANI-jute was attained within 5 minutes at initial MB concentration of 5 mg/L and 20 minutes for all higher MB concentrations. Equilibrium time increased to 90 minutes for almost all MB concentration to 100 mg/L and was constant beyond that. The MB adsorption yield decreased with increase in initial concentration of MB. At MB concentration of 5 mg/L, 88% removal was achieved. When initial lead concentration was increased to 100 mg/L, MB removal decreased to 40%. However, MB uptake increased with increase in initial MB ion concentration (Fig. 4.5). At initial MB concentrations of 5 mg/L, MB uptake was 4.1 mg/g and increased to 40 mg/g at initial MB concentration of 100 mg/L. The reason was probably with increase in concentration, the number of MB ions increased and so chances of contact between MB ions and adsorption sites also increased. This was responsible for higher MB uptake by unit amount of adsorbent.



**Figure 4.4: Effect of reaction time on adsorption (%) of Methylene blue by PANI-jute at various initial concentration of MB (Reaction pH: 8; dose: 1 g/L)**





**Figure 4.5: Effect of reaction time on adsorption of Methylene blue (mg/g) by PANI-jute at various initial concentration of MB (Reaction pH: 8; dose: 1 g/L)**

### 4.3 ADSORPTION KINETICS

Adsorption kinetics is the rate of adsorption of adsorbate towards adsorbent. Slow kinetics will require more time to remove adsorbate effectively. Therefore to achieve large amount of adsorbate removal in short time, reactor volume needs to be increased. Chemical adsorption however displayed rapid kinetics due to formation of chemical bond. The adsorption kinetics of metal can be well treated and explained by Lagergren's first and second order kinetic models (Ho 2006). In order to examine the kinetics of Methylene Blue ion removal, the first order and second order kinetic models were tested with experimental data obtained from batch MB removal experiments.

### 4.3.1 FIRST ORDER ADSORPTION MODEL

The first order kinetic model was suggested by Lagergren for the sorption of solid/liquid systems. First order kinetic model for removal of metal ion was observed by various researchers during removal of methylene blue by (Periasamy and Namasivayam, 1996), activated carbon from coconut coir pith (Kadirvelu and Namasivayam, 2003) and waste Fe<sup>2+</sup>/Cr<sup>3+</sup> hydroxide (Namasivayam and Ranganathan, 1995). The first order adsorption kinetic rate equation is given as

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (4.1)$$

where,  $q_e$  and  $q_t$  are the amounts of MB ions adsorbed on adsorbent (mg/g) at equilibrium and at time  $t$ , respectively, and  $k_1$  is the rate constant of first order adsorption (min)<sup>-1</sup>.

After integrating eq. (4.1) for the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_e$ ,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4.2)$$

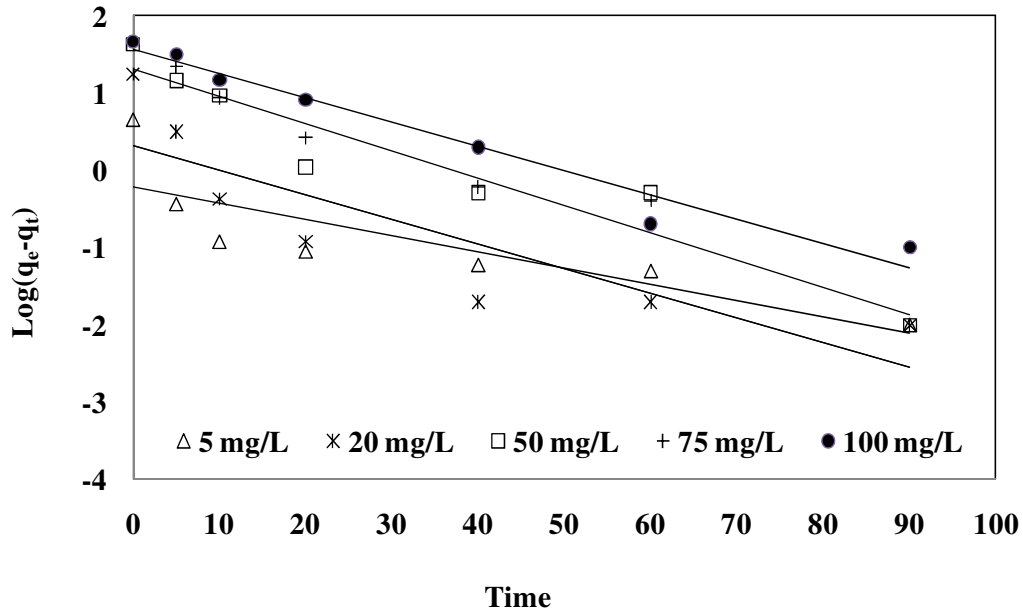
Thus, MB uptake can be expressed as a function of time, for first order model by eq. (4.3) derived from eq. (4.2).

$$q_t = q_e (1 - e^{-k_1 t}) \quad (4.3)$$

Sum of errors squared calculated from kinetic models are also analyzed using eq. (4.4)

$$SSE = \sum \frac{(\text{exp } q_e - \text{cal } q_e)^2}{\text{exp } q_e} \quad (4.4)$$

where,  $exp\ q_e$  is the experimental MB uptake value and  $cal\ q_e$  is the MB uptake value calculated from the theoretical adsorption kinetic models. The straight line plots of  $\log(q_e - q_t)$  against time (t) using eq. (4.2) are shown in Figure 4.6 (using experimental data from Figure 4.4). First order rate constant,  $k_1$  and theoretical MB uptake,  $q_e$ , and correlation coefficient ( $R^2$ ) values are presented in Table 4.1. The correlation coefficients increased from 0.695 to 0.964 with initial MB concentration increased from 5 mg/L to 100 mg/L. However, correlation coefficients alone should not be considered for judging the fitness of the model (Chiron et al., 2003). Hence, an attempt was made to compare experimental data (from Figure 4.4) with theoretical data (calculated using eq. 4.3), which are shown in Table 4.1. It can be observed that experimental data did not fit properly into the first order model. It underestimated the MB uptake for all the concentrations, except for that of 100 mg/L concentration where it underestimated the MB uptake. Chi square of more than 25 for all initial MB concentration also rules out the fixing of first order model. Since first order kinetic model was unable to predict MB removal by PANI-jute properly, attempt was made to find 2<sup>nd</sup> order model.



**Figure 4.6: Plot of time vs  $\text{Log}(q_e - q_t)$  for First Order kinetic model**

**Table 4.1: Coefficients of first order model for MB adsorption by PANI-jute**

| Initial MB concentration (mg/L) | $k_1$ | $q_e$ (Exp) | $q_e$ (Predicted) | Correlation Coefficient ( $R^2$ ) | SSE |
|---------------------------------|-------|-------------|-------------------|-----------------------------------|-----|
| 5                               | 0.020 | 4.56        | 0.80              | 0.695                             | 25  |
| 20                              | 0.031 | 17.46       | 1.36              | 0.742                             | 105 |
| 50                              | 0.035 | 44.63       | 3.71              | 0.917                             | 243 |
| 75                              | 0.028 | 46.45       | 3.65              | 0.916                             | 255 |
| 100                             | 0.031 | 49.15       | 4.76              | 0.964                             | 232 |

#### 4.3.2 SECOND ORDER ADSORPTION MODEL

The second order adsorption kinetic rate equation was used by various authors (Chiron et al., 2003) and given as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4.5)$$

where,  $q_e$  and  $q_t$  are the amounts of MB ions adsorbed on adsorbent (mg/g) at equilibrium and at time  $t$ , and  $k_2$  (g/mg.min) is the rate constant of the second order adsorption.

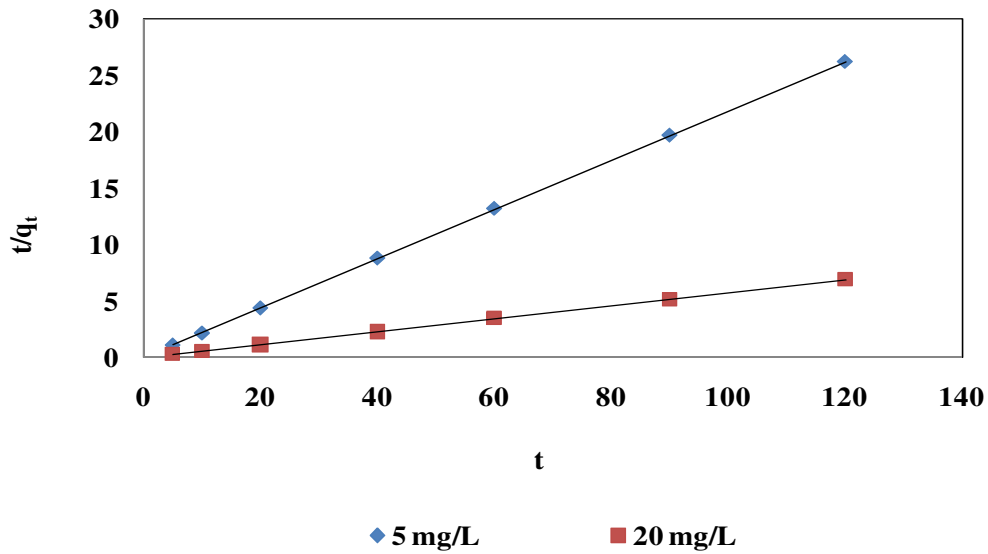
Integrating (eq. 4.5) for the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_e$ , leads to

$$\frac{1}{q_e - q_t} - \frac{1}{q_e} = k_2 t \quad (4.6)$$

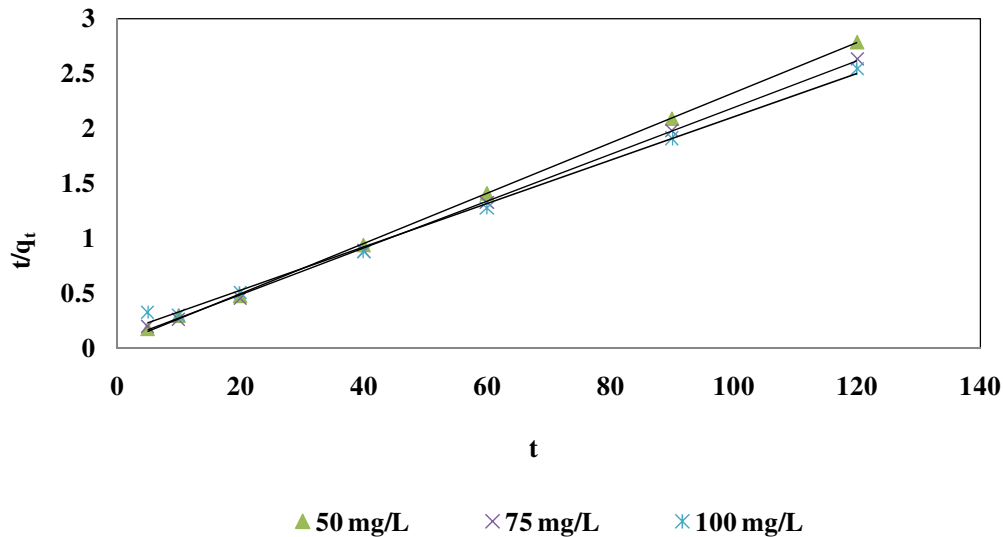
$$\text{or, } q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (4.7)$$

$$\text{or, } \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4.8)$$

The straight line plots of  $t/q_t$  against  $t$  (eq. 4.8) for various MB concentrations are shown in Figure 4.6. The rate constant,  $k_2$  and theoretical MB uptake,  $q_e$  was determined from the intercept, and the slope of the plot respectively and are presented in the Tables 4.2. The correlation coefficient ( $R^2$ ) values from the Table 4.2 and the Figure 4.6 shows that the experimental data fits into a second order kinetic adsorption model. In Figure 4.7, experimental data (from Figure 4.4) and theoretical data (using eq. 4.8) are shown against time. Figure 4.7 shows that it underestimated the MB uptake initially up to 10-20 min especially for higher concentrations, after that it correlated the experimental data well up to equilibrium time of 120 min.



**Figure 4.7(a): Plot of time Vs  $t/q_t$  for Second order kinetic model**



**Figure 4.7(b): Plot of time Vs  $t/q_t$  for Second order kinetic model**

**Table 4.2: Coefficients of first order model for MB adsorption by PANI-jute**

| Initial MB concentration (mg/L) | $k_2$ | $q_e$ (Exp) | $q_e$ (Predicted) | Correlation Coefficient ( $R^2$ ) | SSE  |
|---------------------------------|-------|-------------|-------------------|-----------------------------------|------|
| 5                               | 0.440 | 4.56        | 4.58              | 1                                 | 0.00 |
| 20                              | 0.112 | 17.46       | 17.54             | 0.99                              | 0.24 |
| 50                              | 0.010 | 44.63       | 45.45             | 0.99                              | 0.91 |
| 75                              | 0.007 | 46.45       | 47.61             | 0.99                              | 1.47 |
| 100                             | 0.002 | 49.15       | 52.63             | 0.99                              | 4.68 |

Further, SSE values were calculated from experimental and calculated MB uptakes with time. Table 4.2 shows that SSE value of 0.00 to 4.00, suggesting MB removal kinetics at varying initial MB concentrations followed second order model. Figure 4.8(a-e) showed experimental data matched perfectly with theoretical values.

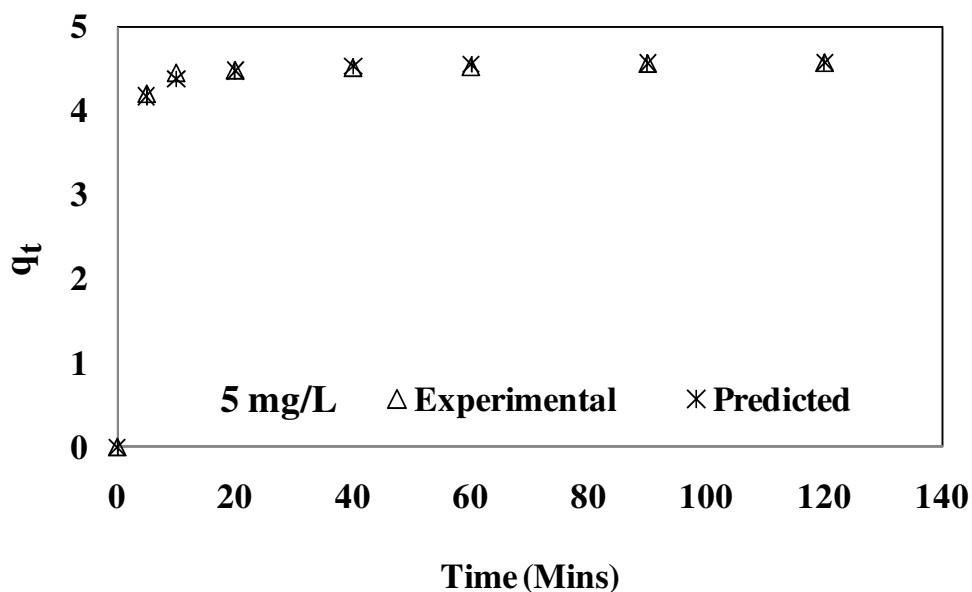


Figure 4.8(a): Plot of  $q_t$  value between Predicted and Experimental value for second order kinetic model

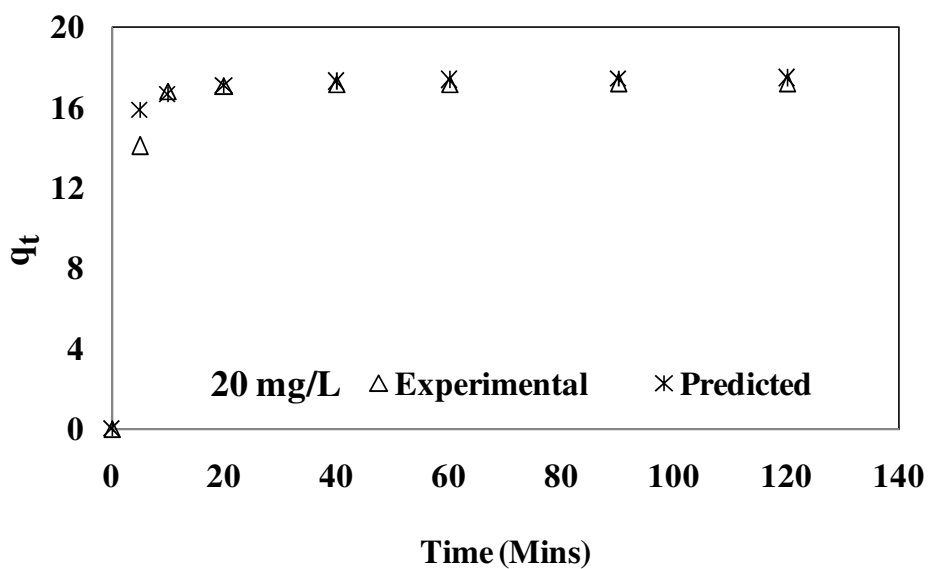


Figure 4.8(b): Plot of  $q_t$  value between Predicted and Experimental value for second order kinetic model

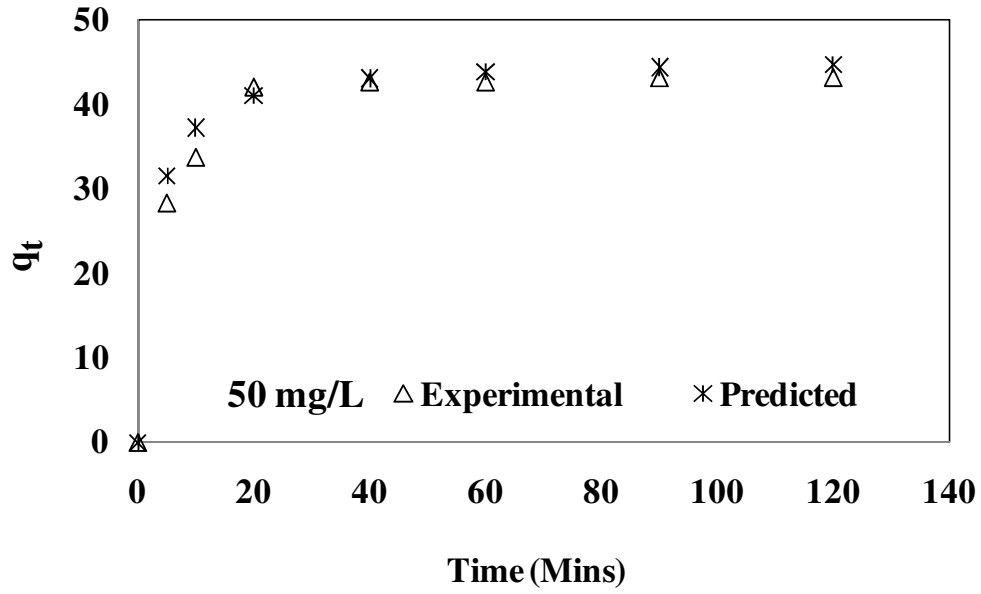


Figure 4.8(c): Plot of  $q_t$  value between Predicted and Experimental value for second order kinetic model

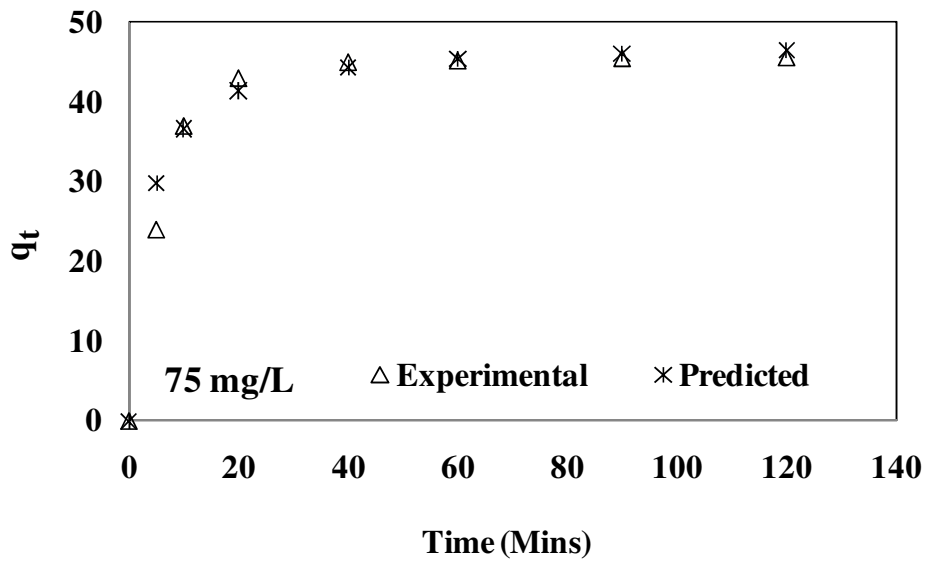
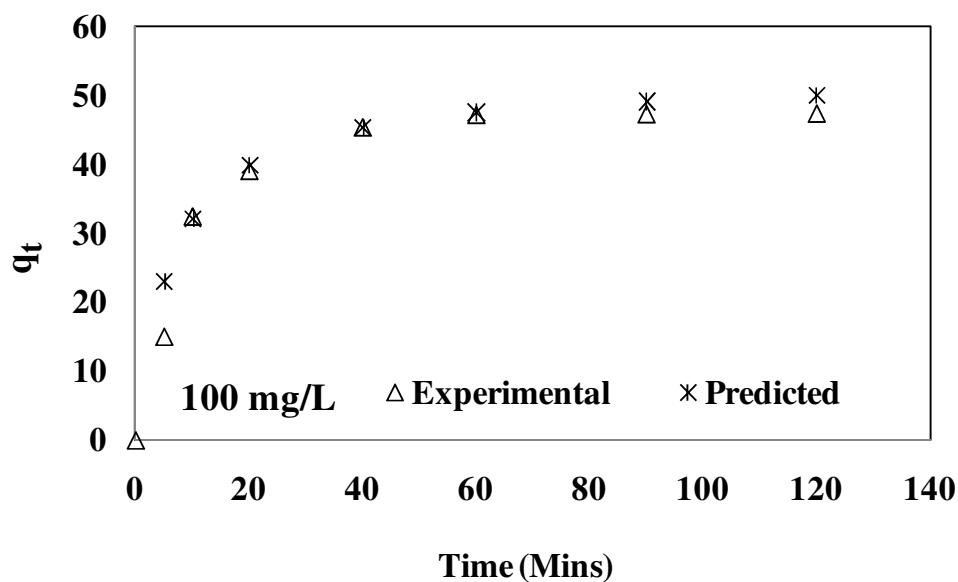


Figure 4.8(d): Plot of  $q_t$  value between Predicted and Experimental value for second order kinetic model





**Figure 4.8(e): Plot of  $q_t$  value between Predicted and Experimental value for second order kinetic model**

### 4.3.3 ELOVICH KINETIC MODEL

Since the adsorptions of MB ion were presumably chemisorption, the kinetic data were treated with Elovich equation. Elovich equation described adsorption on highly heterogeneous adsorbents (Ho et al., 2002) like AFC and confirms the chemisorptions even though do not predict any definite mechanism.

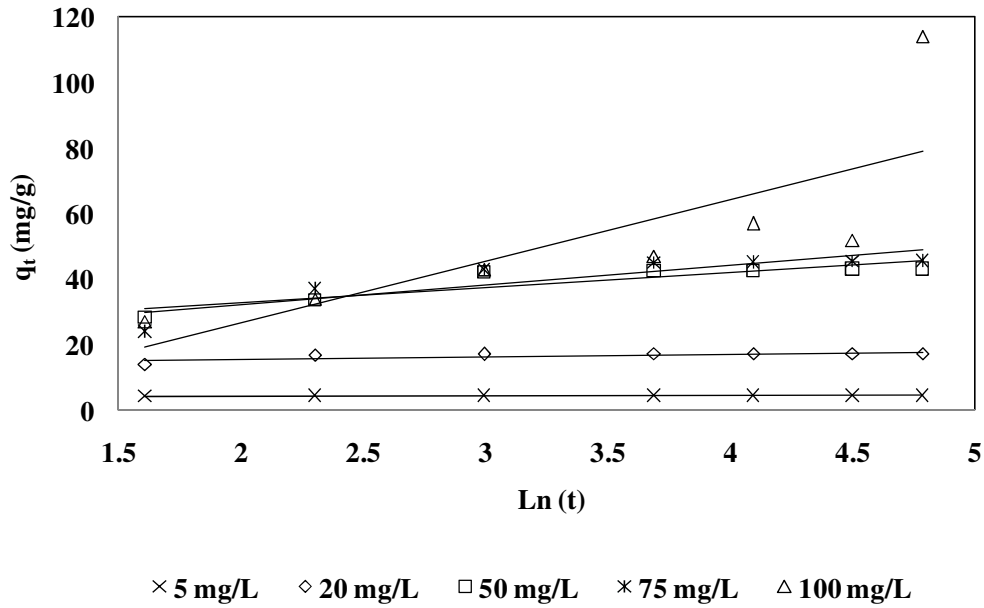
$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (4.9)$$

where,  $\alpha$  is the initial adsorption rate constant ( $\text{mmol L g}^{-1}\text{min}^{-1}$ ) and  $\beta$  ( $\text{g mmol}^{-1} \text{L}^{-1}$ ) is the desorption rate constant during any one experiment. When the adsorption is based on energetically heterogeneous surface, the parameter  $\beta$  is related to the distribution of activation energies. In the diffusion control model,  $\beta$  is a function of both the particle structural–chemical

characteristics and solute diffusion coefficient. By assuming that  $\alpha\beta t \gg 1$  and by applying the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$  (Ho and McKay, 1998), Elovich equation becomes

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \tag{4.10}$$

Plotting  $q_t$  Vs  $\ln(t)$  of MB (Fig. 4.9) yields straight lines and constants were evaluated from the slope and intercepts (Table 4.3). Correlation coefficients  $R^2$  of well below 0.80 for all varied initial MB concentration suggest the non applicability of Elovich equation.



**Figure 4.9: Plot of Ln(time) Vs  $q_t$  for Elovich Model kinetic model**

**Table 4.3: Coefficients of Elovich's kinetic equation**

| Initial MB Concentration (mg/L) | Slope | Intercept | R <sup>2</sup> |
|---------------------------------|-------|-----------|----------------|
| 5                               | 0.095 | 4.144     | 0.78           |
| 20                              | 0.744 | 14.13     | 0.576          |
| 50                              | 4.531 | 23.82     | 0.806          |
| 75                              | 5.981 | 20.26     | 0.771          |
| 100                             | 18.85 | -11.17    | 0.599          |

#### 4.3.4 DIFFUSION MODEL

Since Elovich equation does not explain a definite mechanism the intraparticle diffusion model was also tested. The initial rate of the intraparticle diffusion may be expressed by the following equation (Annadurai et al., 2002):

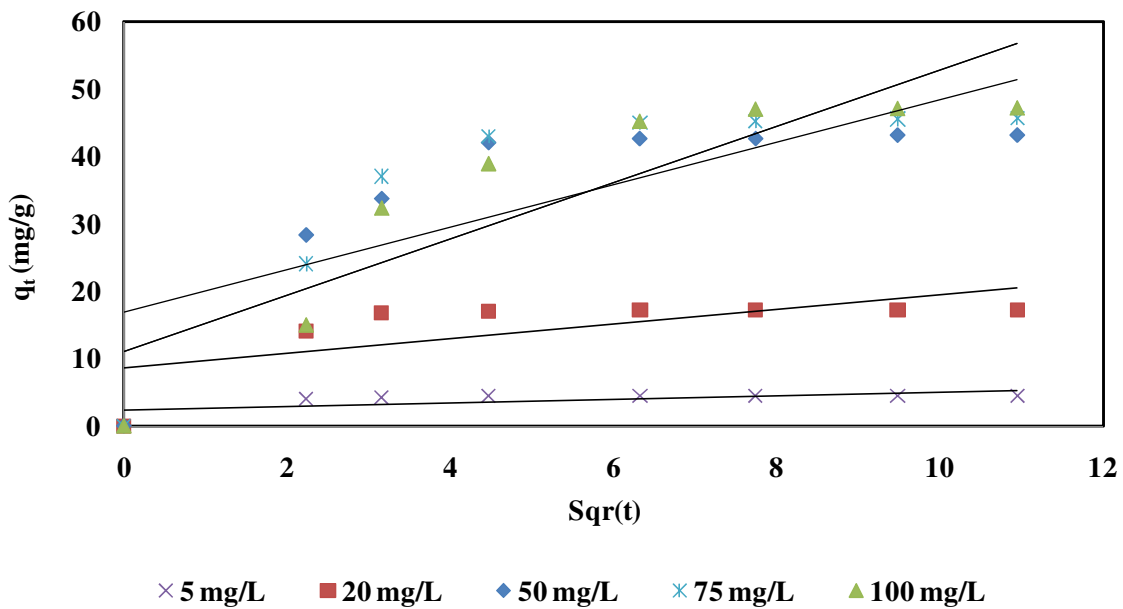
$$q_t = f(t)^{(1/2)} \quad (4.11)$$

The rate parameters for intraparticle diffusion ( $k_p$ ) at different initial concentrations may be obtained using the following equation, where  $q_t$  is the amount of MB ions adsorbed on PANI-jute at different instance of time  $t$  (h):

$$q_t = k_p \cdot t^{(1/2)} \quad (4.12)$$

According to this model, it can be assumed that the mechanism involves the diffusion of the species if a straight line is obtained passing through the origin from the plot of Eq. 4.15, and the slope of the linear curve is the rate constant of intraparticle transport ( $k_p$ ). As can be seen in Fig. 4.10 ( $q_t$  Vs  $t^{1/2}$ ) for MB, the first sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second portion is the gradual adsorption stage where

intraparticle diffusion is rate-controlled. The third portion is attributed to the final equilibrium stage, where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations in solution. In the intermediate stage where the adsorption is gradual, the process may be controlled by intraparticle diffusion. The rate of uptake might be limited by the size of the adsorbate molecule, the concentration of the adsorbate and its affinity to the adsorbent, the diffusion coefficient of the adsorbate in the bulk phase, the pore-size distribution of the adsorbent, and the degree of mixing (Ozcan and Ozcan, 2004). The coefficient of the diffusion model is shown in Table 4.4. With  $R^2$  value of lesser than 0.8 for almost all MB initial concentration, the adsorption of MB by PANI-jute is confirmed to be not diffusion. Thus its hereby suggest the non physical but predominantly chemical behavior of adsorption.



**Figure 4.10: Plot of Square root(time) Vs  $q_t$  for diffusion kinetic model**

**Table 4.4: Coefficients of Diffusion kinetic equation**

| Initial MB Concentration (mg/L) | Slope | Intercept | R <sup>2</sup> |
|---------------------------------|-------|-----------|----------------|
| 5                               | 0.271 | 2.407     | 0.412          |
| 20                              | 1.082 | 8.599     | 0.806          |
| 50                              | 3.142 | 16.99     | 0.623          |
| 75                              | 3.503 | 16.22     | 0.660          |
| 100                             | 4.165 | 11.05     | 0.78           |

#### **4.4 EFFECT OF ADSORBENT DOSE**

Effect of adsorbent dose on MB uptake was studied by varying the adsorbent dose from 0.5 g/L to 8 g/L for three varied initial MB concentration of 20, 50 and 100 mg/L. Initial pH was adjusted to 8. MB removal (%) and uptake with adsorbent dose for various MB concentrations are shown in Fig. 4.11 and Fig.4.12 respectively. It was observed that MB removal (%) for all the MB concentrations increased from 15% to 80% with increase in the adsorbent dose. The number of adsorption sites or surface area increases with the weight of the adsorbent and hence results in a higher percent of metal removal at a high dose. However, MB uptakes decreased with increase in the adsorbent dose from 84 mg/g to 4 mg/g. This is due to the fact that at higher adsorbent dose, the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of “q” indicating the adsorption sites remain unsaturated.

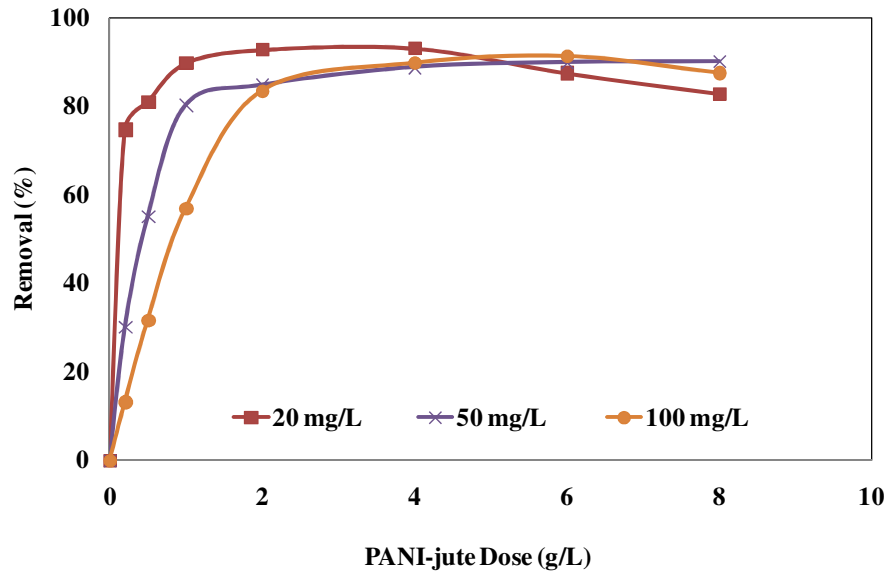


Figure 4.11: Removal(%) of MB with varied dose of PANI-jute

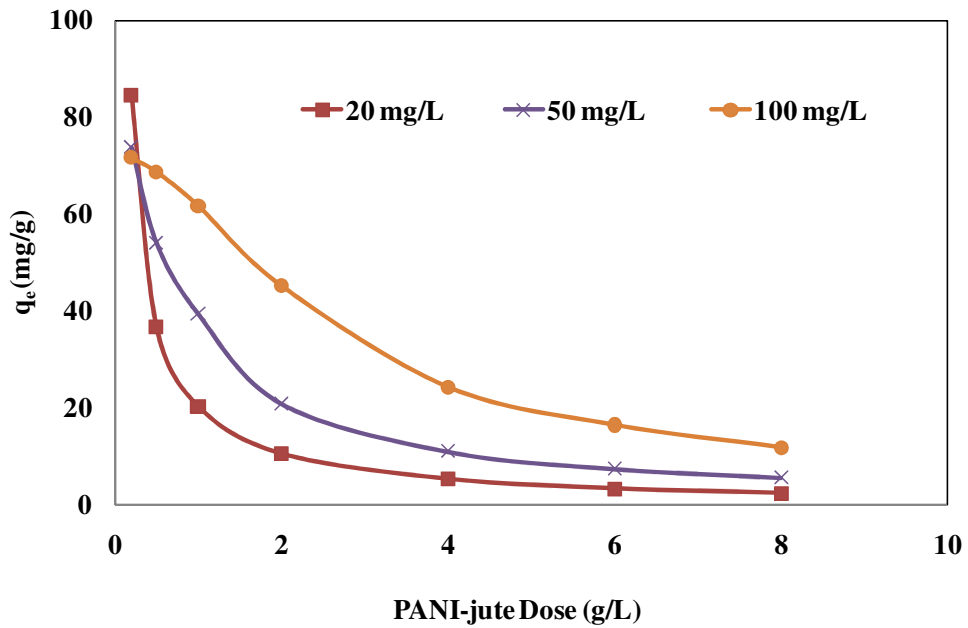


Figure 4.12: Plot of Removal ( $q_e$ ) for MB Vs dose of PANI-jute

## 4.5 ADSORPTION ISOTHERM

Adsorption isotherm is a mathematical model or functional expression to depict the distribution of solute between the solid and liquid phase at equilibrium at a constant fixed temperatures. The isotherm model relates the amount of solute adsorbed per weight of adsorbent ( $q_e$ ), with amount of solute retain in solvent ( $C_e$ ) at equilibrium. Commonly, the amount  $q_e$  increase with increase in  $C_e$  value, but not in direct proportion. Several mathematical model or isotherms were developed based on certain assumptions. Langmuir isotherm, Freundlich isotherm, Langmuir-Freundlich isotherm, BET isotherm, Temkin, Redlich–Peterson etc. are some of the well known models out of which Langmuir and Freundlich isotherm are the commonly and mostly applied models in MB adsorption from aqueous solution.

### 4.5.1 LANGMUIR ISOTHERM

Langmuir isotherm is based on the following assumptions: (a) each surface site can be singly occupied, (b) there are no lateral interactions between adsorbed species, (c) the enthalpy of adsorption is independent of surface coverage and (d) energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes). The first assumption implies the validity of Langmuir isotherm for monolayer adsorption. At a given time, the rate of adsorption  $K_a$ , is proportional to the solute concentration ( $C_e$ ) in liquid phase and fraction of free sites or vacant sites ( $1-\theta$ ), where ‘ $\theta$ ’ represents the fraction of complete monolayer coverage that exist (Langmuir 1918). Similarly, rate of desorption at the same time can be represented by  $K_d\theta$ . Equating the rate of adsorption and rate of desorption for equilibrium,

$$K_d\theta = K_a C_e (1 - \theta)$$

or,  $\theta = \frac{K_a C_e}{K_d + K_a C_e} = \frac{b C_e}{1 + b C_e}$  (4.13)

The adsorption coefficient  $b = \frac{K_a}{K_d}$ , is related to the enthalpy of adsorption ( $\Delta H$ ) by

$$b = b_0 \exp^{-\Delta H / RT}$$

where  $b_0$  is constant related to entropy,  $R$  is the universal gas constant,  $T$  is the temperature ( $^{\circ}\text{K}$ ) (Voice and Weber 1983).

As  $q_e$  is proportional to  $\theta$ , therefore, equation (4.13) can be written as,

$$q_e = \frac{bQ_m C_e}{1 + bC_e} \quad (4.14)$$

where  $q_m$  is the maximum adsorption for a complete monolayer coverage. Equation (4.14) can be rearranged in variety of linear forms.

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (4.15)$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (4.16)$$

$$q_e = Q_m - \frac{q_e}{bC_e} \quad (4.17)$$

#### 4.4.2 FREUNDLICH ISOTHERM

Freundlich model or van Bemmelen equation has been developed for adsorption system with emphasis on two factors, namely the lateral interaction between the adsorbed molecules and the energetic surface heterogeneity. The equation has the general form (Freundlich 1906)

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

but it is well cited in logarithmic form as



$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4.18)$$

where  $K_f$  and  $n$  are empirical constant. Here,  $K_f \propto RT \text{ nb } \exp(\Delta H/RT)$ . The Freundlich constant 'n' indicates the degree of favourability of adsorption and its value should be lying in the range of 1 to 10 for classification as favorable adsorption. A smaller value of (1/n) indicates a stronger bond between adsorbate and adsorbent, while a higher value for  $K_f$  indicates higher rate of adsorption. Equation (4.18) suggests that with increase in  $C_e$ , adsorption capacity ( $q_e$ ) would increase without restriction, which is practically impossible. The model may simulate concentrations far outside the range of the defining batch experiment. Extrapolating equation (4.18) into such concentration regions hence may give results of unknown, but potentially very large error. For example, it is likely that there is a limiting value to the partition coefficient at lower concentrations, possibly reflecting sorption on only the most active sites as concentrations approach zero. This limits the application of Freundlich model at higher  $C_e$  values. However in practical situation, adsorption process are sufficiently dilute and one never encounters the region where Freundlich equation breaks down for this region and Freundlich isotherm equation implies that the energy distribution of adsorption site is of exponential (Cooney 1999).

In order to identify the best fit isotherm model, Chi square test was done by the following equation 4.19. (Ho et al, 2005)

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad (4.19)$$

where,  $q_e$  is the experimental data of the equilibrium MB uptake (mg/g) and  $q_{em}$  is the equilibrium uptake calculated from isotherm models (mg/g).

The linear plots of Langmuir isotherm is shown in Fig. 4.13 with  $1/C_e$  Vs  $1/q_e$ . Also the linear plot of Freundlich isotherm with  $\text{Log}(C_e)$  Vs  $\text{Log}(q_e)$  is plotted in Fig. 4.14. The correlation coefficients and the coefficients are shown in Table 4.4. It shows that Langmuir isotherm fitted experimental data better than the Freundlich model as it showed larger  $R^2$  value as compared to the Freundlich model. The Langmuir curves had good linearity (Correlation

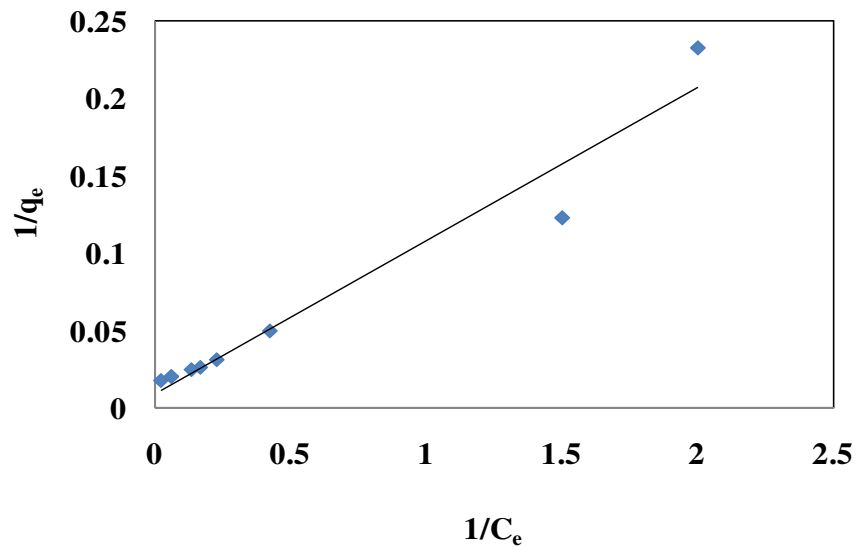
coefficient > 0.95) for PANI-jute doses indicating strong binding of MB ions to the surface of PANI-jute during adsorption. The Langmuir monolayer capacity (a) or maximum adsorption capacity is observed to be 111.11 mg/g. The adsorption equilibrium parameter b, which reflects quantitatively the affinity between the adsorbent and the adsorbate is 0.092 L/g. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ( $R_L$ ), which is defined by the following relation.

$$R_L = \frac{1}{1 + bC_0} \quad (4.20)$$

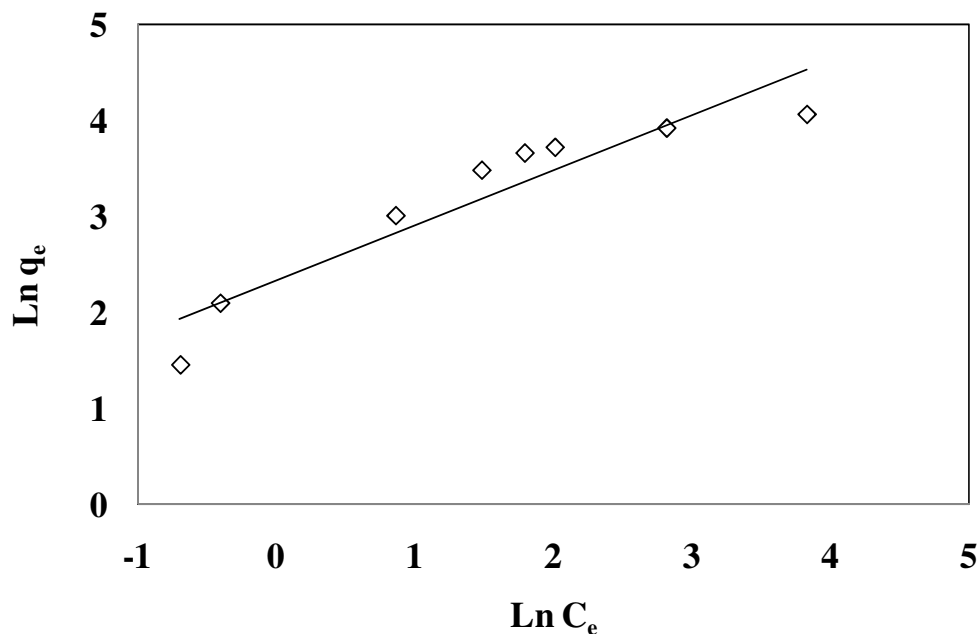
where b is the Langmuir constant  $C_0$  is the initial liquid phase MB ion concentration and for favorable adsorption  $0 < R_L < 1$ . The  $R_L$  values of 0.09 to 0.69 with initial MB of 5 mg/L to 100 mg/L showed favorable adsorption of MB by PANI-jute. A comparison of the maximum capacity 'a' of PANI-jute with other unconventional adsorbents reported in literature is given in Table 4.6. Differences of MB uptake are due to the properties of each adsorbent such as structure, functional groups and surface areas. The Freundlich coefficient,  $K_f$ , representing adsorption capacity is 10.37 L/g. Also the 'n' value of Freundlich is 1.75 which is between 1 to 10, suggesting favorable adsorption of MB by PANI-jute. Above,  $\lambda^2$  for Langmuir is higher with 31 than that of 28 for Freundlich. This observation further suggests the lesser error and better fit isotherm of Freundlich. Thus it can be conclude that only  $R^2$  cannot be the sole factor for suggesting the better fit isotherm. As such the adsorption of MB on PANI-jute can be relatively explained by both the isotherms. Further the plot of comparison of  $q_e$  value of experimental and predicted through both Langmuir and Freundlich isotherms is shown in Fig. 4.15.

**Table 4.5: Coefficients of Langmuir and Freundlich's isotherm**

| Langmuir       |             |          |                | Freundlich     |                |      |                |
|----------------|-------------|----------|----------------|----------------|----------------|------|----------------|
| R <sup>2</sup> | a<br>(mg/g) | b (L/mg) | λ <sup>2</sup> | R <sup>2</sup> | K <sub>f</sub> | N    | λ <sup>2</sup> |
| 0.952          | 111.11      | 0.092    | 31.05          | 0.883          | 10.37          | 1.75 | 28.66          |



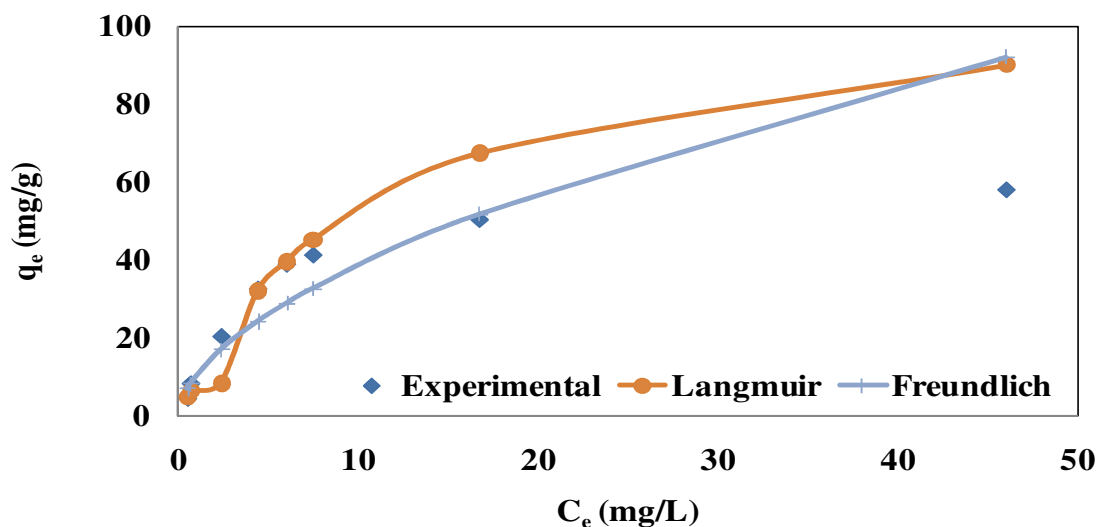
**Figure 4.13: Plot of Langmuir's isotherm for MB adsorption by PANI-jute**



**Figure 4.14: Plot of Freundlich's isotherm for MB adsorption by PANI-jute**

**Table 4.6: Comparison of MB maximum adsorption capacities of various adsorbent with PANI-jute**

| S. no | Adsorbent                            | Maximum MB adsorption capacity (mg/g) | References             |
|-------|--------------------------------------|---------------------------------------|------------------------|
| 1     | Activated carbon                     | 6.33                                  | Ghaedi et al, 2013     |
| 2     | Cotton stalk                         | 147.06                                | Deng et al, 2011       |
| 3     | Phosphoric Acid treated cotton stalk | 222.22                                | Deng et al, 2011       |
| 4     | Sulphuric acid treated cotton stalk  | 555.56                                | Deng et al, 2011       |
| 5     | Garlic peel                          | 142.86                                | Hameed and Ahmad, 2009 |
| 6     | Saw Dust                             | 111.97                                | Hamdaoui, 2006         |
| 7     | Crushed Bricks                       | 80.60                                 | Hamdaoui, 2006         |
| 8     | Vermiculite hydrogel composites      | 1685                                  | Liu, 2010              |
| 9     | Dehydrated peanut hull               | 161.3                                 | Ozer et al, 2007       |

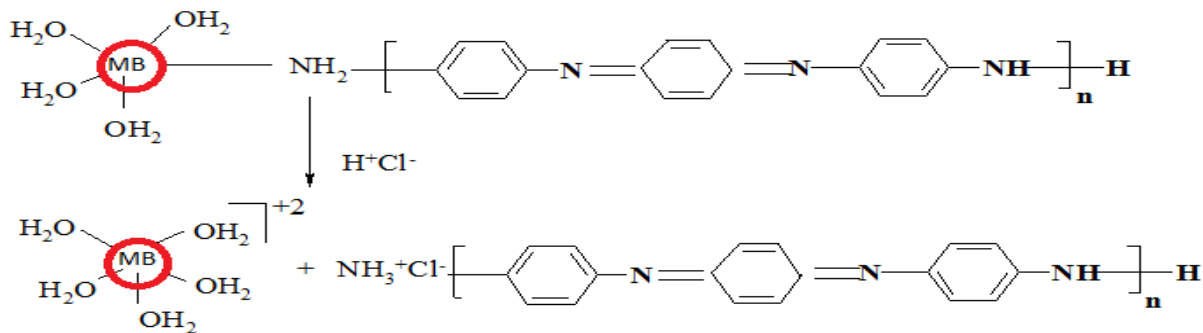


**Figure 4.15: Comparison between experimental  $q_e$  and predicted  $q_e$  value of Langmuir & Freundlich's isotherm**

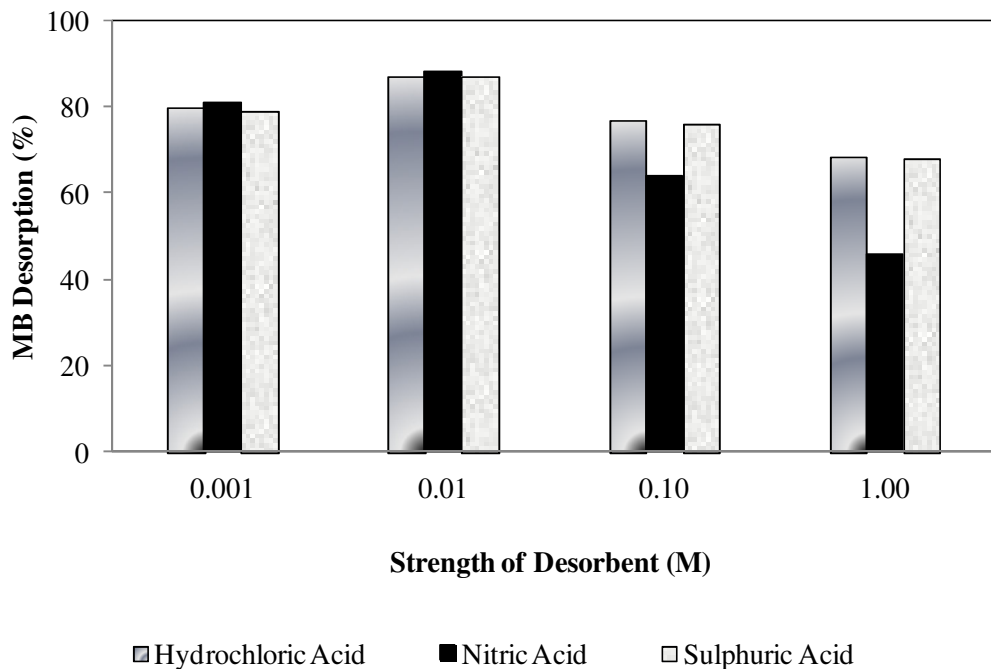
## 4.6 DESORPTION

Since the adsorption of MB by PANI-jute is due to chemical bond formation, there is higher chance of recovery of adsorbed MB ions from the PANI-jute through introduction of desorbents. The desorbents need to have higher affinity for MB than amines of PANI-jute. Mineral acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> are employed as a desorbent with varied strength & the results are shown in Table 4.7. The mechanism of MB desorption is also shown in Figure 4.16. It can be seen that, with the increase in strength of mineral acids from 0.001 M to 0.01 M, the desorption of MB increases from 80- 87%, 81- 88% and 79- 87% for HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> respectively. The introduction of more acids or protons (H<sup>+</sup>) replaces the MB ions from the amine surface of PANI-jute and thus recovers more MB ions. However, further increase of desorbent strength from 0.01 M to 1 M, yields decrease in desorption to 68%, 46%, & 68% for HCl, HNO<sub>3</sub> & H<sub>2</sub>SO<sub>4</sub> respectively. It can be explained by the fact that, at extreme pH i.e. pH less than 2.5, the absorbance of MB decreases probably due to formation of other complex ions.

Another observation during the desorption of MB from PANI-jute was that, the time required for complete desorption was observed to be around 5-10 minutes. Its shown in Fig. 4.17. For both the mineral; acids of 0.01 M and 0.001 M strength, complete desorption was over within 10 minutes. Such rapid desorption also suggest the chemical adsorption and desorption or rather the chemically binding mechanism of amines of PANI-jute and methylene blue.



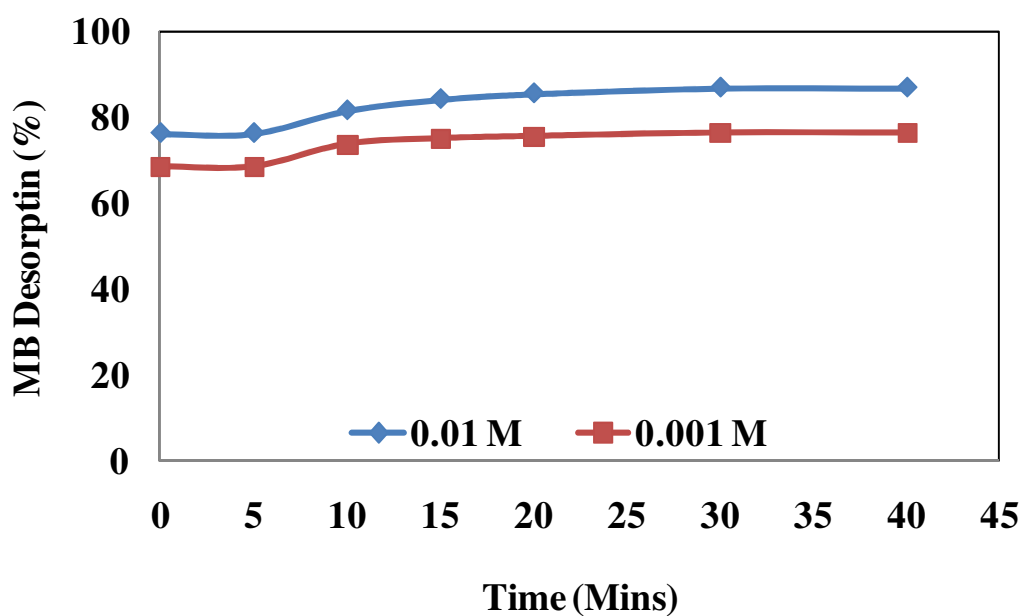
**Figure 4.16: Mechanism of methylene Blue desorption from PANI-jute**



**Figure 49: Desorption of MB from PANI-jute**

**Table 4.7: Desorption of MB from PANI-jute**

| <b>Desorbent</b>      | <b>HCl</b> |      |      |      | <b>HNO<sub>3</sub></b> |      |      |      | <b>H<sub>2</sub>SO<sub>4</sub></b> |      |      |      |
|-----------------------|------------|------|------|------|------------------------|------|------|------|------------------------------------|------|------|------|
| <b>Strength (M)</b>   | 0.001      | 0.01 | 0.10 | 1.00 | 0.001                  | 0.01 | 0.10 | 1.00 | 0.001                              | 0.01 | 0.10 | 1.00 |
| <b>Desorption (%)</b> | 80         | 87   | 76   | 68   | 81                     | 88   | 64   | 46   | 79                                 | 87   | 76   | 68   |



**Figure 4.17: Kinetics of MB desorption from PANI-jute**

## 4.7 REUSE

The investigation on desorption of methylene blue (MB) suggest recovery of more than 87% by the mineral acids. Therefore, capability of PANI-jute to reuse is explored to evaluate the number of adsorption–desorption cycles. The result of recycle is shown in Table 4.8 and can be seen that more than 10 cycles can be effectively conducted without decrease in adsorption as well as desorption of MB effectively. Hence altogether the uptake capacity by PANI-jute is increased by 10 folds i.e. 111mg/g to 1111mg/g and further chances of recycling can still be conducted.

**Table 4.8: Recycling and reuse of PANI-jute for MB adsorption**

| Adsorption-Desorption Cycles | MB Concentration (mg/L) |       | MB removal (%) | Desorption MB        |       |
|------------------------------|-------------------------|-------|----------------|----------------------|-------|
|                              | Initial                 | Final |                | Concentration (mg/L) | (%)   |
| 1                            | 55                      | 6.04  | 89.04          | 40.06                | 81.66 |
| 2                            | 55                      | 6.09  | 88.94          | 40.95                | 83.57 |
| 3                            | 55                      | 5.21  | 90.55          | 38.99                | 78.17 |
| 4                            | 55                      | 5.62  | 89.80          | 39.70                | 80.26 |
| 5                            | 55                      | 5.21  | 90.55          | 51.24                | 81.23 |
| 6                            | 55                      | 4.56  | 91.73          | 39.47                | 78.10 |
| 7                            | 55                      | 5.68  | 89.69          | 38.11                | 77.13 |
| 8                            | 55                      | 4.67  | 91.51          | 44.20                | 87.68 |
| 9                            | 55                      | 6.27  | 88.61          | 40.95                | 83.88 |
| 10                           | 55                      | 6.15  | 88.83          | 41.78                | 85.37 |



## 4.8 ADSORPTION WITH INDUSTRIAL WASTEWATER

Adsorption with actual industrial waste water was conducted with sample collected from dye industries of Delhi. The collection of samples are shown in Figure 4.18 & 4.19. The characteristics of industrial dye are shown in Table 4.9.



**Figure 4.18: Mixing of Dye industrial effluents and sewage in Badli's drain**



**Figure 4.19: Collection of Dye industrial effluents at (a) Badli & (b) Shahbad**

**Table 4.9: Characteristics of Industrial effluents containing Methylene Blue**

| Sl No | Industrial Sites | pH   | Concentration of Methylene Blue (mg/L) after dilution with domestic sewage | Removal (%) by PANI- jute | TSS (mg/L) |
|-------|------------------|------|--|---------------------------|------------|
| 1     | Badli            | 6.87 | 3  | 40                        | 150        |
| 2     | Shahbad          | 6.52 | 4.5  | 42                        | 160        |
| 3     | Bawana           | 6.34 | 5.2  | 38                        | 140        |

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**CHAPTER 5**

**CONCLUSION AND**

**RECOMMENDATIONS**

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## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

This lab-scale study was conducted in batch mode with synthetic wastewater containing methylene blue dye. An amine based functionalized polymers polyaniline synthesized on jute fiber (PANI-jute) was prepared and employed for the removal of MB ions. After studying the synthetic sample of methylene blue, the adsorbent was further subjected to MB contaminated actual industrial wastewater and the effectivity of the polymer adsorbent is evaluated.

#### 5.1 CONCLUSIONS

From the present study, major conclusions were drawn and are listed below.

1. From the calibration curve of Methylene Blue (MB) at 664 nm wavelength, estimation of max MB concentration is observed to be 5 mg/L with 0.94 absorbance. Higher concentrations of MB are estimated by diluting well below 5 mg/L.
2. Polymer adsorbent was prepared by oxidation of aniline with para-phenylenediamine in the presence of ammonium peroxydisulphate and synthesized on the surface of jute fiber.
3. MB was observed to be soluble till concentration of 100 mg/L at wide pH ranges of pH 2- 11 .Optimum pH of MB adsorption by PANI-jute was observed at the range of pH 7- 10, with 80- 85% removal for initial MB concentration of 5- 100 mg/L.
4. Binding of MB by PANI-jute was observed to be through formation of coordinate bond between the cationic MB dye & amines of the PANI-jute
5. Adsorption equilibrium time for MB was observed to be 20 min for lower MB concentration of 5-20 mg/L and 120 min for higher concentration upto 100 mg/L. However 85% of adsorption of all varied initial MB concentration was observed to be 5- 10 minutes, suggesting rapid chemical adsorption behavior of MB on PANI-jute.
6. Adsorption of MB by PANI-jute obeyed Lagergren's pseudo second order kinetic model indicating the chemical adsorption behavior.

7. Diffusion kinetic model was not able to explain the adsorption kinetics suggesting the insignificant physical adsorption behavior.
8. With increase in PANI-jute dose from 0.1 to 8 g/L, removal percentage of MB increases from 15-80%. This is due to increase in adsorption site with weight of adsorbent. However amount of MB uptake decrease from 84 mg/L to 4mg/L with increase in dose. Higher the adsorbent dose, the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of 'q' indicating the adsorption site remains unsaturated.
9. Adsorption of PANI-jute was able to explain by both Langmuir and Freundlich isotherm with comparative value 31& 29 error square respectively. Maximum amount of MB uptake capacity of PANI-jute was observed to be 111.11 mg/g from Langmuir's isotherm. Freundlich's isotherm 'n' value of 1.75 which is less than 10 and greater than 0 suggest the favorable adsorption of MB by PANI-jute.
10. Desorption of MB by mineral acids yields almost 80-90 % of MB.
11. PANI-jute after desorption was able to reuse for more than 10 cycles, without any decreasing its MB uptake capability. Thus, the maximum uptake capacity of PANI-jute is higher than 1100 mg/g.
12. The performance of PANI-jute when subjected to actual industrial wastewater decrease by 10-15% due to the presence of other co-ions.

## **5.2. RECOMMENDATIONS**

After the complete experimentation and observation, following recommendation are made:

1. Poly-Aniline jute fiber may be used as adsorbent for removal of Methylene Blue dye in industries.
2. Batch process can be used in small scale industries e.g. khadi industries.
3. Adsorbent can be successfully desorbed and reused for removal of dyes for more than one cycle.

### **5.3. SCOPE OF FURTHER STUDIES**

Following are the scope of my present study:

- 1.** Further study can be conducted by using proper set-up for batch process having more effluent and high adsorbent dose.
- 2.** Performance evaluation of the batch process with actual industrial wastewater needs to be studied.
- 3.** Performance evaluation of the reactor when employed with actual industrial wastewater.

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## REFERENCES

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