# Chapter 1

# Introduction

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With increased industrialization the use of dyes for colorizing substances in textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries has increased which is leading to pollution.

## 1.1 Dyes

Dyes usually have a synthetic origin and complex aromatic structures which make them more stable and less biodegradable. More than 10,000 dyes are being used now days. Dyes are used to colorize other substances in textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries. 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 phenomena. Methylene blue has wider application such as it has medicinal usage, temporary hair colorant, auto - oxidizing agent. Although methylene blue 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. Release of dyes in water bodies also affects the aquatic life and food webs due to carcinogenic and mutagenic effects of synthetic dyes.

## 1.2 Removal of Dyes

The conventional methods of treating wastewater containing dyes are coagulation and flocculation, oxidation or ozonation, membrane separation, chemical precipitation, solvent extraction, reverse osmosis and adsorption. Among these adsorption is recognized as a promising technique due to its ease of operation, easy availability, simplicity of design, high efficiency, comparable low cost of application  in decoloration forms. Activated carbon is the most widely used adsorbent for removal of dyes, but its use is restricted due to its high cost. It has the advantage of exhibiting a high adsorption capacity for colour pollutants due to their high surface area or porous structure. Besides these physical characteristics, the adsorption capacity of a carbon produced from different sources with different ways is strongly influenced by the chemical nature of the surface. Although the determination of the number and the nature of the activated carbon groups began earlier, the precise nature of the group is not entirely established. Due to these, polar functional groups such as carboxyl, hydroxyl, aldehyde, ketones and anhydrides, the carbons have an acid-base character.

## 1.3 Adsorption

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent). Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon.

Recently, various low-cost adsorbents derived from agricultural waste or natural material, have been investigated intensively for dye removal from aqueous solutions. Many researchers have investigated the use of low cost and efficient alternative substitutes to remove dyes from wastewater. Some of these alternative adsorbents are palm ash and chitosan/ palm ash, shale oil ash, pomelo, de-oiled soya and bottom ash, sunflower seed shells and mandarin peelings, wheat husk, guava leaf powder and steel and fertilizer industries waste. Amine rich functionalized polymer poly-aniline synthesized on surface of jute fibre is employed from adsorption of MB from industrial effluents. The study was conducted through continuous column mode process. Study was carried out under several parameters that include initial pH, initial MB concentration, bed depth of reactors and influent flow rate of MB. The aim of this study was to evaluate the potential of PANI-jute for the removal of MB from aqueous solution. The effects of initial dye concentration, flow rate, and pH on MB adsorption were evaluated.

## 1.4 Objectives

After a thorough survey of the literatures, it can be observed that, there is an essential to study methylene adsorption on functionalized based polymers to remove maximum amount at rapidly in continuous column mode operation. The list of the objectives for the complete study is thereby listed.

1. To study the adsorption of MB by poly-aniline jute through continuous column process and analyzing the effect of the uncontrolled pH of the initial solution, effluent pH of the MB treated water.
2. Adsorption MB studies at various reactor bed depth, initial MB concentration and initial flow rate
3. Study on application of Bed Depth Service Time (BDST) model on adsorption of MB and Design of reactors for different flow rate and initial concentration using BDST.
4. Validation of BDST model and identification of loop holes of design reactor.
5. Study of desorption and reuse of poly- aniline jute.

# Chapter 2

# Literature Review

# Chapter 2

# Literature Review

## 2.1 Introduction

A dye is a colored, ionizing and aromatic unsaturated organic compounds that has an affinity to the substrate to which it is being applied. Dyes are applied to various substrates like textiles, leather, plastic, paper etc. It is generally applied in an aqueous solution, and requires a mordant to improve the fastness of the dye on the fiber. Dyes appear colored because they absorb some wavelengths of light more than others. Dyes must get completely or at least partially soluble in which it is being put to. The colored characteristic of a dye is due to presence of a substance called Chromophore. Dyes are aromatic compounds whose structures have aryl rings that has delocalized electron systems. These structures are said to be responsible for the absorption of electromagnetic radiation that has varying wavelengths, based upon the energy of the electron clouds. Chromophore makes the dyes able to absorb radiation. Chromophores acts by making energy changes in the delocalized electron cloud of the dye. This alteration invariably results in the compound absorbing radiation within the visible range of colours and not outside it. Human eyes detect this absorption, and responds to the colours. Chromophores are the atomic configurations which has delocalized electrons. Generally they are represented as carbon, nitrogen, oxygen and sulphur. They can have alternate single and double bonds.

## 2.2 Solubility and Cohesiveness

Auxochrome gives dye solubility and cohesiveness. Auxochromes has also the ability to intensify colors. It is a group of atoms which attaches to non-ionizing compounds yet has the ability to ionize. Auxochromes are of two types, positively charged or negatively charged.

Example: $-OH$, $-NHR$, $-Cl$, $-Br$, $-CH_3$, $-NO_2$, $-NR_2$, $-COOH$, $-NH_2$, $-SO_3H$

## 2.3 Classification of Dyes

Dyes can be classified based on different parameters like source of materials, chemicals present, nuclear structure and based on its use in industries.

### 2.3.1 Classification based on the source of materials

#### 2.3.1.1 Natural Dyes

Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources—roots, berries, bark, leaves, and wood—and other organic sources such as fungi and lichens.

#### 2.3.1.2 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, Sulphur, Disperse dye etc. Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Basic dyes are water-soluble cationic dyes that are applied to acrylic fibers, wool, silk and for coloration of paper. Direct dyes are neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate $Na_2SO_4$) or sodium carbonate ($Na_2CO_3$),used on cotton, paper, leather, wool, silk and nylon. Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. Vat dyes are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye. Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate, used for dyeing cotton and other cellulose fibers. Disperse dyes are developed for the dyeing of cellulose acetate, and are water insoluble.

These are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder, used dye nylon, dye polyester, cellulose triacetate, and acrylic fibres. Sulfur dyes are two part "developed" dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color, This is treated after with a sulfur compound in place to produce the dark black.

### 2.3.2 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, Anthraquinone dyes, derivatives of anthraquinone >C=O and >C=C Cyanine dyes, derivatives of phthalocyanine Diazonium dyes, based on diazonium salts, Nitro dyes, based on the $–NO_2$ nitro functional group, Nitroso dyes, are based on a –N=O nitroso functional, Phthalocyanine dyes used in textiles, derivatives of phthalocyanine >C=N used for paper.

### 2.3.3 Dyes according to the nuclear structure

Based on nuclear structure dyes are categorized as cationic and anionic.

### 2.3.4 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 Protein Textile Dyes, Cellulose Textile Dyes and Synthetic Textile Dyes.

## 2.4 Methylene Blue

Methylene blue (CI 52015) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. It appears as a solid, odourless, dark green powder, at room temperature yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of methylene blue. Methylene blue was first prepared in 1876 by German chemist Heinrich Caro (1834-1910). This compound is prepared by treating 4-aminodimethylaniline with hydrogen sulphide dissolved in hydrochloric acid, followed by oxidation with ferric chloride. Its structure is shown in Figure 2.1.:

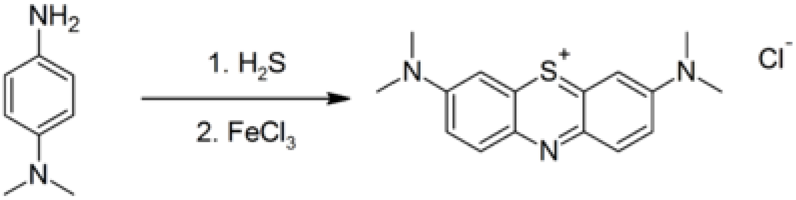

**Figure 2.1: Chemical Structure of Methylene Blue**

Methylene blue is a potent cationic dye with maximum absorption of light around 670 nm. The specifics of absorption depend on a number of factors, including protonation, adsorption to other materials, and metachromasy - the formation of dimers and higher-order aggregates depending on concentration and other interactions. Methylene blue shows a hormetic dose-response, with opposite effects at low and high doses. At low doses of the micro-gram level there have been shown to be improvements in memory consolidation, and there is a neuroprotective effect as well. It also has been shown that in low doses methylene blue protects the brain from disease by acting as an antioxidant in the mitochondria. Methylene blue is widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. Methylene blue is also a photosensitizer used to create singlet oxygen when exposed to both oxygen and light. It is used in this regard to make organic peroxides by a Diels-Alder reaction which is spinning forbidden with normal atmospheric triplet oxygen.

In biology methylene blue is used as a dye for a number of different staining procedures, such as Wright's stain and Jenner's stain. Since it is a temporary staining technique, methylene blue can also be used to examine RNA or DNA under the microscope or in a gel: as an example, a solution of methylene blue can be used to stain RNA on hybridization membranes in northern blotting to verify the amount of nucleic acid present. While methylene blue is not as sensitive as ethidium bromide, it is less toxic and it does not intercalate in nucleic acid chains, thus avoiding interference with nucleic acid retention on hybridization membranes or with the hybridization process itself. Methylene blue is a component of a frequently prescribed urinary analgesic/anti-infective/anti-spasmodic known as "Prosed", a combination of drugs which also contains phenyl salicylate, benzoic acid, hyoscyamine sulfate, and methenamine. Methylene blue is a successful treatment for malaria. Methylene blue combined with light has been used to treat resistant plaque psoriasis, AIDS-related Kaposi's sarcoma, West Nile virus, and to inactivate staphylococcus aureus, HIV-1, Duck hepatitis B, adenovirus vectors, and hepatitis C. Phenothiazine dyes and light have been known to have virucidal properties for over 80 years. In some circumstances, the combination can cause DNA damage that may lead to cancer. Methylene blue has oxidizing agent properties, its effects as an oxidizing agent occurs only at very high doses. At pharmacologic doses it has reducing agent properties. It is owing to this reason that methylene blue is employed as a medication for the treatment of methemoglobinemia. Methylene blue (MB) is the most commonly used for dying 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. Therefore, many methods are available for the removal of dyes from industrial effluents. The conventional methods of treating wastewater containing dyes are coagulation and flocculation (E.Guibal et.al. 2007), oxidation (M. Fox et.al. 2004) , ozonation (Y. Nakamura et.al 1997), membrane separation(J.S. Wu et.al. 2008), electrochemical degradation (L. Fan et.al. 2008), chemical precipitation (M.X. Zhu et.al. 2007), biological degradation (G. Sudarjanto et.al 2006), reverse osmosis (Haigang Li et.al 2011), ultra filtration (Narjess Zaghbani et.al 2007) and adsorption(M Otero et.al 2003). Among these adsorption is recognized as a promising technique due to its ease of operation, easy availability, simplicity of design, high efficiency, comparable low cost of application in decolouration forms. Activated carbon (Nagarethinam Kannan et.al. 2001) is the most widely used adsorbent for removal of dyes, but its use is restricted due to its high cost. The adsorption characteristics of MB dyes on various adsorbents have been extensively investigated. Some of these alternative adsorbents are palm ash (J. T. Nwabanne et.al 2012) and chitosan (M.L.G. Vieira et.al 2014) / palm ash, cotton stalk (Hui Deng et.al 2011) ,shale oil ash, peanut hull (Dursun O¨ zer et.al 2007), rice husk (Upendra Kumar et.al. 2006), rice hull (K.S.Low et.al. 1999), pomelo, de-oiled soya and bottom ash (Puthiya Veetil Nidheesh et.al. 2012) sunflower seed shells and mandarin peelings, wheat husk, guava leaf powder (Runping Hana et.al 2009) and steel and fertilizer industries waste. 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 , but it is pro- hibitively 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, fibers, fruits peels, seeds and waste materials from forest industries such as sawdust, bark etc. have been used as adsorbents for the removal of dyes.

## 2.5 Source

Dyes are extensively used in many fields of up-to-date technology, in e.g., various branches of the textile industry, rubber industry, cement industry, ceramics, colorants for plastic industry, colorants for agricultural industry, printing inks, dyes in heat transfer printing, colorants for security printing, dyes for packaging sector, pigments in paints industry, dyes in medicine, glass, wire and cable industry, woodworking industry, the leather tanning industry, paper production, food, color photography, pharmaceuticals and medicine, cosmetic, hair colourings, wood staining, agricultural, biological and chemical research, light harvesting arrays, and photo-electrochemical cells (Kuhad et al., 2004; Couto 2009). Moreover, synthetic dyes have been employed for the efficacious control of sewage and wastewater treatment, for the determination of specific surface area of activated sludge for ground water tracing, etc (Forgacs et al., 2004). The largest consumer of dyes is the textile industry, accounting for 2/3$^{rd}$ of its market.

## 2.6 Effect of dyes on environment

Dyes are toxic, carcinogenic, mutagenic, and teratogenic effects on aquatic life and also on humans. When they remain in water systems, they cause aesthetic and environmental problems that affect water transparency and gas solubility. Dyes adsorb and reflect the sunlight entering water, thereby interfering with the aquatic species growth and hindering photosynthesis. Additionally, the can have acute and chronic effects on organisms depending on their concentration and length of exposure.

## 2.7 Removal techniques

### 2.7.1 Ion Exchange

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. The most widespread use of this process is in domestic water softening, where sodium ions from a cation-exchange resin replace the calcium and magnesium ions in the treated water and reduces the hardness of water. Ion exchange has been used in wastewater applications for the removal of nitrogen, heavy metals, and total dissolved solids. Materials used for the exchange of metals include natural zeolites, weak and strong cation-exchange resins, chelating resins where cations are exchanged with $Na^+$ and $H^+$ ions. The chemistry of the ion exchange process may be represented by the following equilibrium expression for the reaction of constituent A on the cation-exchange resin and constituent B in the solution.

$$nR^-A^+ + B^{+n} \leftrightarrow R_n^-B^{+n} + nA^+ \tag{2.1}$$

where, $R^-$ is the anionic group attached to an ion exchange resin.

The main advantage of ion exchange process is the availability of the large variety of specific resins from suppliers, each resin is effective in removing specific contaminants. Natural zeolites, clinoptilolite and chabazite have been used to treat wastewater with mixed metals ($Cr^{6+}$,

$Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$) (Ouki and Kavannagh, 1999). Chelating resins, such as amino-phosphonic and iminodiacetic resins, have been manufactured having a high selectivity for specific metals, such as $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cd^{2+}$ and $Zn^{2+}$. TP-207 is recommended by the Bayer company for selective removal of metal ions, particularly of $Pb^{2+}$ ions, (Bayer, 2000). The selectivity depends primarily on the nature and valency of the ions, the type of the resin, its saturation and the ion concentration in wastewater and typically is valid over a narrow pH range and the ion exchange process can be used with fluctuating flow rates (Metcalf and Eddy, 2003). Separation and recovery of mixed heavy metal ions ($Cu^{2+}$, $Cd^{2+}$, and $Ag^{2+}$) at each metal concentration of 0.0025 M using a cation-exchange resin in the presence of organic macrocations was studied (Amara and Kerdjoudj, 2004). The selectivity coefficient and the removal capacity of the resin for the ions in batch operations were determined and the kinetics of metal adsorption by both unmodified resin and resin modified with tetramethylammonium, tetrabutylammonium and polyethyleneimine were studied. After the adsorption of the organic macrocation, ion exchange capacity was varied and the rate of the ion exchange reaction of monovalent ions became slow, though exchange capacity for copper ions increased when the cation-exchange resin was modified in polyethyleneimine solution. Several stripping solutions were tested in batch experiments for the recovery of metals. Elution of $Cu^{2+}$ fixed on PEI-modified resin and unmodified resin with acids was almost 30% and 65% respectively.

To date, ion exchange has had limited application because of the extensive pretreatment requirement, concerns about the life of the ion exchange resins and the complex regenerated system required. Most of the ion exchangers are expensive and release other cations such as $H^+$ or $Na^+$ in aqueous solution, ion exchange processes are highly pH dependent, most metals bind at higher pH, due to less competition from protons for adsorption sites. High concentrations of influent total suspended solids can plug the ion exchange beds, causing 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 important factors that may limit the useful life and performance of ion exchange resin.

### 2.7.2 Reverse Osmosis

The reverse osmosis process is the reversal of flow through a semi permeable membrane from a high salinity or concentrated solution to the high purity or permeate stream on the opposite side of the membrane. Pressure is used as the driving force for the separation. The applied pressure must be in excess of the osmotic pressure of the dissolved contaminants to allow flow across the membrane as shown in the Figure 2.2. The rate of water transport is a function of the pressure applied, the apparent or differential osmotic pressure between the solutions (differential osmotic pressure is the difference between the absolute osmotic pressures of the two solutions), area and characteristics of the membrane and the solution temperature. Membranes commonly used are made of cellulose acetate, while membrane made of polyamides and composite materials are also available. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics.

Reverse osmosis is used worldwide primarily for desalination. In wastewater treatment, it is used for removal of dissolved constituents from wastewater remaining after advanced treatment with depth filtration or microfiltration. In reverse osmosis small particles are rejected by the water layer adsorbed on the surface of the membrane, which is known as dense membrane. Typically reverse osmosis can reject particles as small as 0.0001µm. (Metcalf and Eddy, 2003).

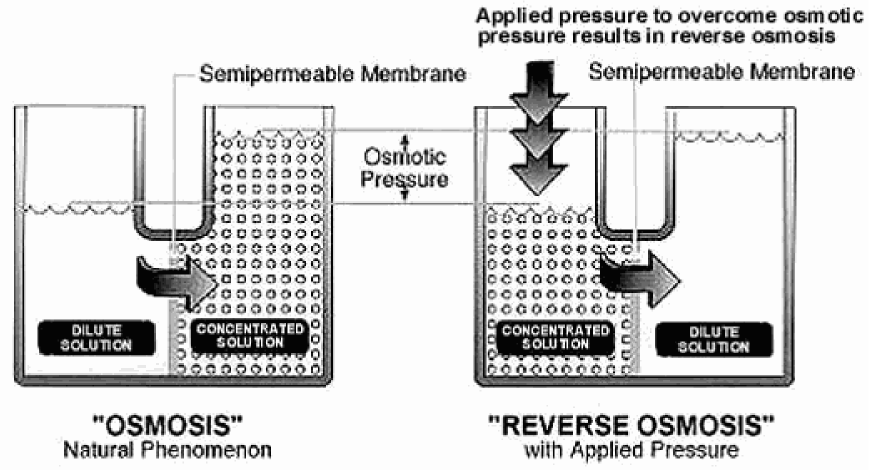

**Figure 2.2: Principle of osmosis and reverse osmosis (Source: Watson, 1999)**

The advantages of the reverse osmosis are it removes nearly all contaminant ions and most of the dissolved non ions, relatively insensitive to flow, operates immediately without any minimum break-in period. Operational simplicity and automation allow for less operator attention thus making reverse osmosis suitable for small system applications.

Various reverse osmosis systems were used for removals of metal ions from wastewater. 97.0% and 98.5% removals with the effluent concentrations of 3.5 mg/L and 1.8 mg/L of Cu2+ and $Cd^{2+}$ ions respectively were achieved by using high pressure spiral-wound polyamide membrane reverse osmosis system (Qdais and Moussa, 2004). For the mixed metals (250 mg/L each of $Cu^{2+}$ and $Cd^{2+}$) of 500 mg/L, more than 99% removal of each was reported. Removals of $Ni^{2+}$ and $Zn^{2+}$ ions by thin film reverse osmosis membrane system was studied by Ipek (2005) with initial $Ni^{2+}$ and $Zn^{2+}$ concentrations of 169 mg/L and 170 mg/L and reported 99% removals of both. In the pretreatment units of filtration and granular activated carbon adsorption 23-25% of $Ni^{2+}$ and 25-45% of $Zn^{2+}$ were removed. It was also observed that the increase in the influent conductivity did not have a significant effect on metal removal, however presence of EDTA improved metal removal efficiencies.

The limitations of reverse osmosis are membrane fouling and deterioration with time resulting from deposition of soluble materials, organic matters, suspended and colloidal particles and other contaminants. To prevent frequent fouling of membrane, high level of pretreatment is necessary. This method is expensive compared to conventional treatment, as high capital and operating costs are requried by the high energy input to develop pressure needed to operate. Managing the wastewater (brine solution) is also a potential problem.

### 2.7.3 Electrodialysis

The principle of electrodialysis involves removal of ionic components from an aqueous solution through ion exchange membranes using an electrical driving force. The wastewater to be treated is pumped through a membrane stack, which consists of alternately placed anionic and cationic selective membranes separated by gasket frames and plastic spacers with positive electrode (anode) at one end and negative electrode (cathode) at the other end. In order to transfer the electric current and to remove gases produced by electrode reactions, the electrode chambers are rinsed with an electrolyte solution. When a DC voltage is applied across the electrodes, the electrical potential created, causes anions to move in the direction of the anode and cations to move in the direction of the cathode and the ion-selective membranes form barriers to ions of opposite charge. Thus the anions attempting to migrate to the anode, permeate through the anion exchange membrane but are stopped by the cation exchange membrane, similarly cations trying to migrate to the cathode are stopped by the anion membrane after permeating through the cation exchange membrane, resulting in concentration and dilution in adjoining cells. The principle of the electrodialysis process is illustrated in Figure 2.3, which shows a schematic diagram of a typical electrodialytic cell arrangement consisting of a series of anion and cation-exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. The advantages of the electrodialytic technique for removal of metals are low effluent concentrations are possible, process is relatively insensitive to flow and total dissolved solids level, the metal removal degree can be controlled by adjusting the flow rates of the solutions and the metals removed might be reused (Velizarova *et al*., 2002). Maximum $Cu^{2+}$ removals of 95% and 97% from initial concentrations of 1000 mg/L were achieved by two types of commercial membranes at $60^{o}$ C temperature, flow rate of 4.2 mL/min and voltage of 30 volts (Mohammadi *et al*., 2004). It was also observed that when membranes were paired with higher ion exchange capacity, metal removal efficiencies improved.

Problems associated with the electrodialysis include chemical precipitation of salts with low solubility on the membrane surface and clogging of the membrane by residual colloidal particles. High level of pretreatment is required to reduce membrane fouling. High capital and operating costs are also necessary.

Removal of MB was studied by Mahmoud et.al by electro-coagulation technique using iron electrodes. The study deals with the enhancement of removal of Methylene Blue dye by using an electromagnetic field during the electro-coagulation process. Effects of electrolyte concentration, dye concentration, intensity and the direction of the electromagnet on the decolorization efficiency have been investigated. The formed ferric hydroxide flocs trap colloidal particles and make solid–liquid separation easier during the next stage. The electro-coagulation stages must be optimized in order to design an economically feasible process. The results showed that the optimum electrolysis was 10–20 min at a current density of 8 mA/cm$^2$, while the optimum concentration of the electrolyte (NaOH) was found to be 2 wt.% when the dye concentration was 50 mg/L. The utilization of an electromagnetic field enhanced the dye removal due to the induced motion of paramagnetic ions inside the solution.

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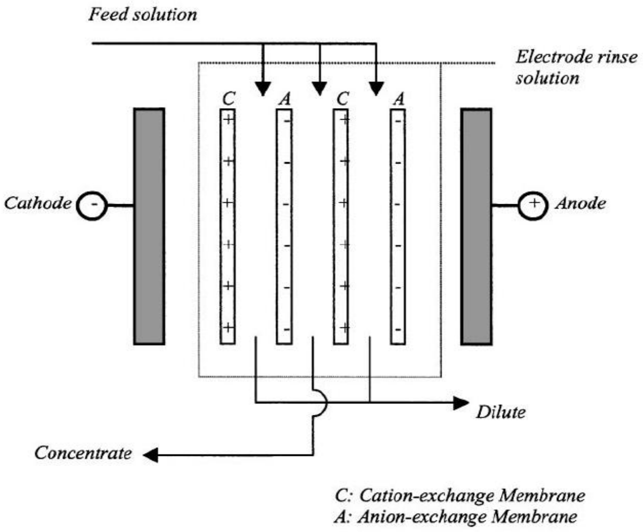

**Figure 2.3: Schematic diagram of electrodialysis process (Zhiqiang and Admassu, 2000)**

A study was done on removal of MB by micellar enhanced ultra filtration with mixed surfactants by Huang et.al. Micellar enhanced ultra filtration (MEUF) has been extensively applied to the separation of organic solutes or heavy metal ions from water, but the feasibility and efficiency of removing them simultaneously via MEUF have been seldom researched. In this study, removal of MB with MEUF by the binary mixture of sodium dodecylsulfate (SDS) and polyoxyethylene octyl phenyl ether (TritonX-100) was investigated. Similar study was done by Jiang et.al. using high-performance porous spherical or octapod-like single-crystalline $BiVO_4$ photo catalysts for the removal of methylene blue under visible-light illumination.

Another study was done on removal of methylene blue using two zeolites prepared from naturally occurring Egyptian Kaolin by Jamil et.al. MB removal was investigated using synthetic solutions at initial concentrations 15 mg/L of MB at constant temperature and pH (25 ± 0.1 °C and 7.5 ± 0.2) respectively. The removal efficiency was determined at different contact times and different zeolite doses. Another study was done by Wang et.al. using Fe(II)Fe(III)-LDHs prepared by co-precipitation method in a heterogeneous-Fenton process for removal of Methylene Blue.

Out of all methodology used for removal of MB Adsorption is the most effective. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent). Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon.

A study was carried by Ghaedi et.al on acceleration of MB adsorption on to activated carbon prepared from dross licorce by ultrasonic. Results indicated that optimum condition as 20 mg/L of MB concentration, pH 7 for sample solution, dosage of adsorbent 0.2g was applicable for removal of MB upto 95% at 16 min with high adsorption capacity. Another study on adsorption of MB on adsorbent materials using cotton stalk, sulphuric acid treated cotton stalk and phosphoric acid treated cotton stalk from aqueous solution. Compared with cotton stalk prepared activated carbon, less specific surface area and more functional group on these adsorbents were found. Results indicated that Freundlich was best suited isotherm for sulphuric acid CS and Langmuir for CS and phosphoric acid CS.

Low cost adsorbent were also employed such as garlic peel for removal of MB from aqueous solution Hameed et.al. Experiments were carried out with initial concentration (25-200 mg/L) at pH 4 – pH 12. Equilibrium adsorption time of 210 minute was reported with 0.3g dose of garlic peel. Equilibrium data fitted very well with Freundlich isotherm equations. Another study was made of liquid –phase adsorption of MB using cedar sawdust and crushed brick by Hamdaoui. Experiments were carried out for aqueous solution 40 mg/L. It was observed that with increase in solution temperature the dye removal decreased and optimum pH value for dye adsorption was observed at pH 7. Results indicate that Freundlich is less suitable than Langmuir isotherm.

Enhanced adsorption of MB from aqueous solution by chitosan- g – poly ( acrylic acid)/ vermiculite hydrogel composites was reported by liu et.al**.** Experiments were carried out considering pH of dye solution, contact time etc. and observed that it follows Langmuir isotherm. Another study was done using dehydrated peanut hull for removal of MB adsorption from aqueous solution by ozer et.al. Experiments were carried out for various parameter such as initial MB concentration, pH etc. Results of the experiment suggested that it follows Langmuir model

The presence of functional groups such as amines, sulphonyl, carboxyl, etc is responsible for dye adsorption by such low cost materials. To improve the uptake of adsorbent researchers have impregnated functionalized chemicals on surface of support base. Further, the synthesis of purely functionalized polymers became a recent trend for adsorption of dyes. Poly-aniline is an eco-friendly polymer which is widely employed for adsorption of heavy metals from wastewater. The presence of unpaired $sp^3$ hybridized electrons enables the binding of cationic ions through coordinate bond. Therefore, it is important to analyze and study the adsorption of MB by poly-aniline polymer.

Batch process data has several limitations to predict the performances in practical situation such as actual industrial wastewater treatment plant where continuous reactors replaced batch operation. Besides, in batch mode adsorption process, adsorption equilibrium is achieved and the adsorption characteristics were analyzed by isotherms. However, in fixed-bed column, the adsorption zone or mass transfer zone keeps moving through the bed and the fluid and solid phase in that zone are never able to achieve equilibrium. Adsorption efficiency by column mode depends on flow rate, bed height and influent adsorbate initial concentration.

# Chapter 3

# Materials and Methods

# 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 column and analytical techniques.

## 3.1 Materials

Aniline ($C_6H_5NH_2$) purchased from Merck was purified by distilling over KOH pellets to distilled and purified. Ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] and 1,4-phenylenediamine [$C_6H_8N_2$] required for synthesis of polyaniline were directly used as received. Thus lower metal concentrations for calibration were obtained by series dilution of standard solution using dilution factor of 10. Mineral acids used during the experiments were procured from Merck, India, and used as received. All chemicals and reagents used were of analytical grade purity and distilled water prepared in laboratory was used for all dilutions and reagents preparations. Support materials for adsorbent- Jute were obtained from jute bags which were purchased from local market and washed with detergents to remove dirts. Then these were dried and chopped into fibers of 0.5-1.0 cm length and used in the present work. Stock solutions for MB ions, acid/base of different strength and buffers were prepared at regular intervals.

## 3.2 Polymer synthesis and adsorbent preparation

In this study, polymers was synthesized on support materials and employed as adsorbent.

### 3.2.1 Synthesis of short chain polyaniline polymer on surface of jute fibers

In order to prepared the polymer, aniline ($C_6H_5NH_2$) was oxidized 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 g, 21.5 mmol) and 1,4-phenylenediamine (0.330 g, 3.05 mmol) were dissolved in 66 mL of 1 M HCl (aq.). The reaction was controlled in 0- 5 °C using ice tray arrangement 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. Complete deprotonation of PANI-jute, alkali treatment was given by soaking PANI-jute in 1 M $NH_4OH$ 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 raw jute fibers and PANI-jute are shown in Figures 3.2 (a & b).

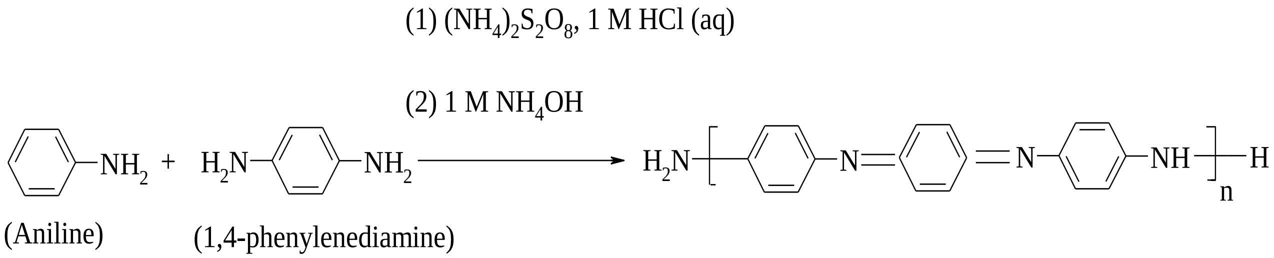

Figure 3.1: Synthesis scheme of short chain polyaniline

**Figure 3.2(a & b): Raw jute and PANI - jute**

## 3.3 Adsorption studies with Methylene blue dye

Adsorption study with methylene blue dye has been performed in continuous column using PANI-Jute. This study was carried out using synthetic wastewater containing methylene blue.

### 3.3.1 Continuous column experiment set up

The fixed bed column study with PANI-jute was conducted using a column made of PVC pipe of 3.5 cm dia and 80 cm length. Column was packed with adsorbent, PANI-jute till 60 cm depth, with outlets at every 15cm. The set up of experiments is shown in Figure 3.3-3.5. Outlets were made using ball pens and pipes of inner dia 0.8cm at 15cm intervals. Solution is filled in the column till 10cm above first outlet to maintain the hydraulic loss. To maintain the hydraulic loss the pipe at the outlet is arranged so as to achieve the desired flow rate at the outlet. A raw jute plug was provided at the bottom to support the adsorbent bed as well as to prevent leakage of solution and adsorbent. The presence of air gaps within the packed adsorbent caused inefficiency of maintaining the flow rate and inefficient adsorption. To ensure that there are no air gaps present the adsorbent packed column was firstly packed by pressing the adsorbent in the column using a rod and secondly, was wetted by filling with methylene blue solution for 5 hour prior to starting of the experiment. In the experiment influent containing methylene blue was pumped using Miclins peristaltic pump PP30 at a constant flow in the column. Flow rate was cross checked at the exit of the column at regular intervals of 30 minutes to prevent and minimize the flow rate fluctuations in column.

## 3.4 Column Experiment

### 3.4.1 Experimental set up

In order to study the removal of methylene blue in fixed bed column, column experiments were conducted with varying pH, influent concentration, flow rate and bed depth. Treated solution samples were collected from the exit of column at different depths at predetermined time intervals. The absorbance of these materials was measured using Spectrophotometer 169, Systronics.

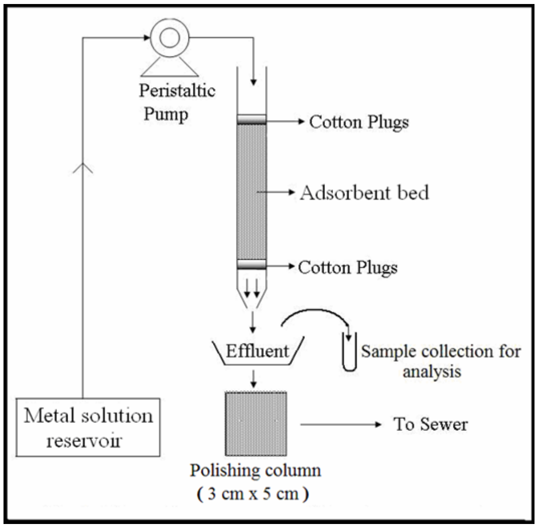

**Figure 3.3: Schematic arrangement of experimental set up for column study**

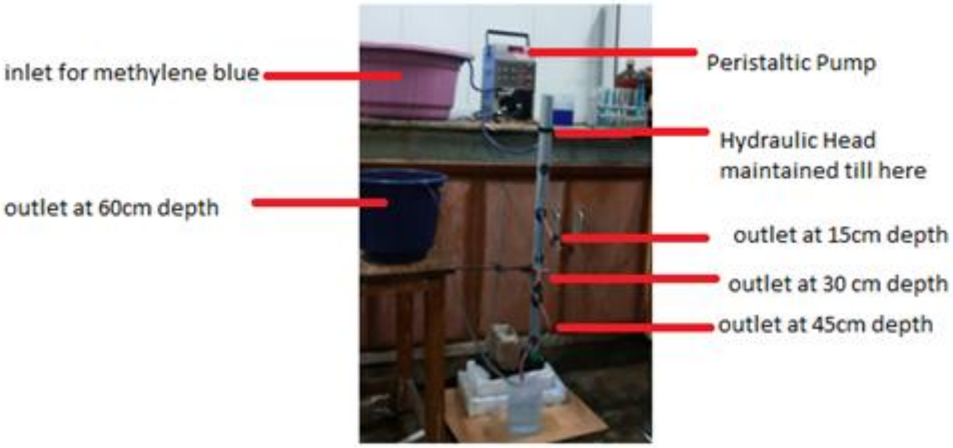

**Figure 3.4: Experimental set up for column study**

### 3.4.2 Experimental Anaylysis

Generally, the performance of the column bed is described through Generally the performance of the column bed is described through the concept of breakthrough curve, which is obtained by plotting throughput volume ($V_t$) at any time (t) versus effluent methylene blue concentration (C). Throughput volume was calculated using equation (3.1).

$$V_t = Q.t \tag{3.1}$$

where Q is the volumetric flow rate (mL/min).

(i) Bed Depth Service Time (BDST) model

The Bohart-Adams equation can be represented as (Bohart and Adams 1920):

**Figure 3.5: Schematic arrangement of running experiment**

$$Ln(\frac{C_o}{C_b}-1)=Ln(e^{k_{ads}N_o(Z/u)}-1)-k_{ads}C_o t_S \tag{3.2}$$

Further, Hutchins (1973) modified the Bohart–Adams equation and presented a linear relationship between the bed depth and service time (equation 3.2) which requires only three fixed bed tests to collect the necessary data.

$$t_S=\frac{N_o Z}{C_o u}-\frac{1}{k_{ads}C_o}Ln(\frac{C_o}{C_b}-1) \tag{3.3}$$

where, $t_s$ is the service time at breakthrough point (h), $N_o$ the dynamic bed capacity (mg $L^{-1}$), Z the packed-bed column depth (cm), u the linear flow rate (cm/h) defined as the ratio of the volumetric flow rate Q ($cm^3$/h) to the cross-sectional area of the bed A ($cm^2$), $C_o$ and $C_b$ are respectively the influent and the breakthrough adsorbate concentration (mg/L) and $k_{ads}$ the adsorption rate constant (L/mg.h). Plotting service time ($t_s$) versus bed depth (Z) will generate a straight line equation having slope of ($N_o/C_o$.u) and intercept of $(-)\frac{1}{k_{ads}C_o}Ln(\frac{C_o}{C_b}-1)$. Critical bed depth ($Z_o$) represents the theoretical minimum depth of column that would be able to prevent the adsorbate concentration from exceeding $C_b$. It is obtained when breakthrough is immediate and it can be calculated by substituting $t_S = 0$ in equation 3.3 as shown below:

$$Z_0 = \frac{u}{k_{ads}\ N}\left(\frac{C_0}{C_b}-1\right) \tag{3.4}$$

According to BDST model equation (2.25), the data collected from one flow rate experiment can predict the system with different flow rate. When an experiment conducted at flow rate $Q_1$, yields an equation of the form

$$t_s = a_1Z + b_1$$

the predicted equation for new flow rate $Q_2$, is given by:

$$t_s = a_2Z + b_1 \quad \text{and}$$

$$a_2 = a_1\left(\frac{Q_1}{Q_2}\right)$$

where, $a_1$ and $a_2$ are the slopes at flow rate $Q_1$ and $Q_2$ respectively. However the intercept $b_1$ remained same since it is independent of flow rate in linearized BDST equation. BDST model can also be used to design systems for treating other influent solute concentrations using the data of a previous laboratory experiment of one influent solute concentration. When an experiment conducted at initial concentration $C_1$, yields an equation of the form

$$t = r_1X + s_1$$

the predicted equation for new flow rate $Q_2$, is given by:

$t = r_2X + s_2$ and

The new slope and intercept values can be determined as:

$$r_2 = r_1\left(\frac{C_1}{C_2}\right)$$

$$s_2 = s_1\frac{C_1}{C_2}\left(\frac{\mathrm{Ln}\left[C_2/C_F)-1\right]}{\mathrm{Ln}\left[C_1/C_b)-1\right]}\right)$$

where, $r_1$ and $r_2$ is slopes at influent concentration $C_1$ and $C_2$ respectively, $s_1$ and $s_2$ are intercepts at influent concentration $C_1$ and $C_2$ respectively, $C_F$ is effluent concentration at influent concentration $C_2$ and $C_b$ is effluent concentration at influent concentration $C_1$.

### 3.4.3 Operational problems

During the setting of setup as well as while running the experiment there were many issues that came across. Firstly, the fibres at top needed to be clogged using cotton plugs so that fibres do not float when influent flows through the reactor. Secondly, the calibration of peristaltic pump was required to be done for maintaining a constant desired flow rate of influent. In order to do so tubing factor of the pipe was calculated using the set flow rate in peristaltic pump and the obtained flow rate.

### 3.4.4. Desorption:

For desorption experiment, a solution of 0.1 M HCL was fed into the reactor as desorbent. Inorder to concentrate more MB in lesser desorbents, a flowrate of 2 ml/min was maintained for the desorption of MB from PANI-jute.

# Chapter 4

# Result and Discussion

# Chapter 4

# Result and Discussion

## 4.1 Effect of pH

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The optimization of pH also can reveal the mechanism of binding dye on adsorbent in the process is chemically predominant adsorption. As such the pH effect study is mostly conducted in batch mode operation due to the controllability of the solution pH. Since the batch processes are mostly replaced by continuous process in industrial effluent treatment, optimization of pH is studied here in continuous mode itself where pH is not controlled once it is fed to the reactor. To study the effect of various pH, experiments were conducted with various pH of pH 2, 4, 6 and pH 8 with constant flow rate of 20 mL/min and initial MB concentration of 20 mg/L. The findings are shown in Figure 4.1. It was observed that the reactor at pH 2 got exhausted at 25 h and pH 4 reactor at 28 h.

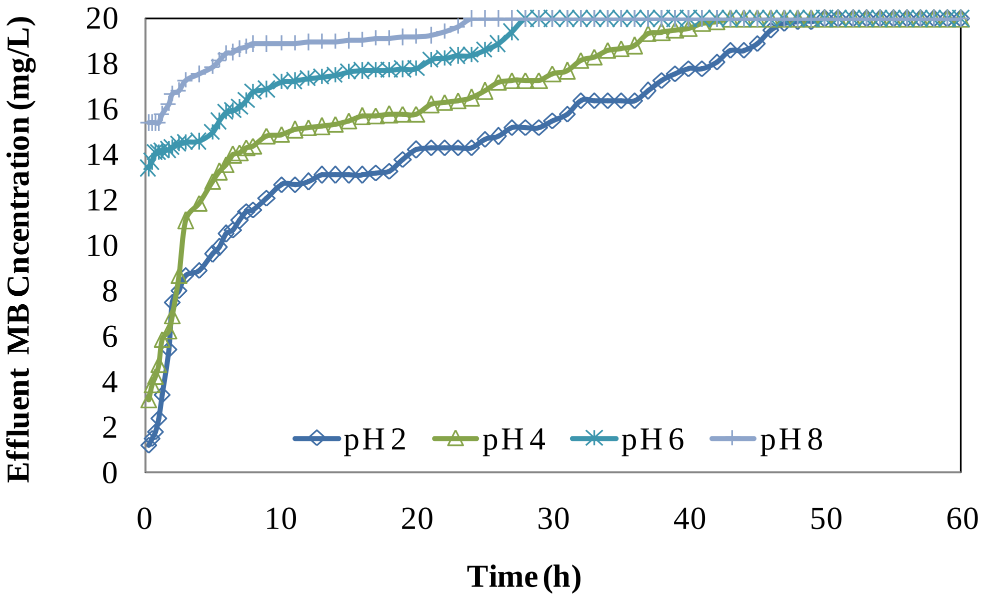

Figure 4.1: Effect of pH on MB adsorption

With further decrease in pH, exhaustion time increase from 42 h for pH 6 to maximum of 50 for reactor with pH 8. However during the experiment, effluent pH was observed to increase slightly towards basic. The profiles of effluent pH is shown in Figure 4.2 The surface property of the PANI-jute adsorbent led to increase the pH. It is known that ionic dyes MB upon dissolution release colored ions in solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge which is in turn influenced by the solution pH. At acidic pHs, the positively charged species start dominating and the surface tend to acquire positive charge while the adsorbate species MB are still negatively charged. As the adsorbent surface is positively charged the increasing electrostatic repulsion between positively charged adsorbate species and positively charged adsorbent particles would lead to decreased adsorption of dye cations. At higher pH, the surface of MB particles become negatively charged, which enhances the positively charged MB cations through electrostatic forces of attraction (Ncibi et al., 2007; Yasemin, 2006). Similar trend was observed for adsorption of methylene blue onto yellow passion fruit peel (Pavan et al., 2008) and methyl violet onto sunflower seed hull (Hameed, 2009).

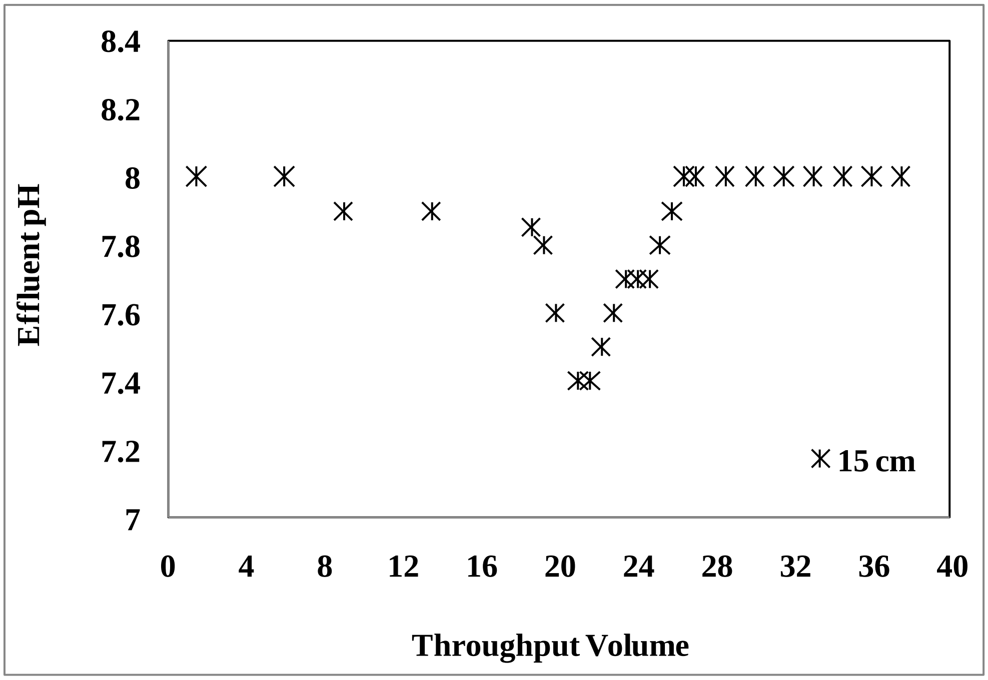

**Figure 4.2: Effluent pH profiles on MB adsorption**

## 4.2 Effects of bed depth

To study the effects of bed depth, three column with bed depth of 15, 30 and 45 cm were employed. Initial concentration of MB was 5 mg/L and flow rate was maintained at 5 ml/min. The findings of the study is shown in Figure 4.3.

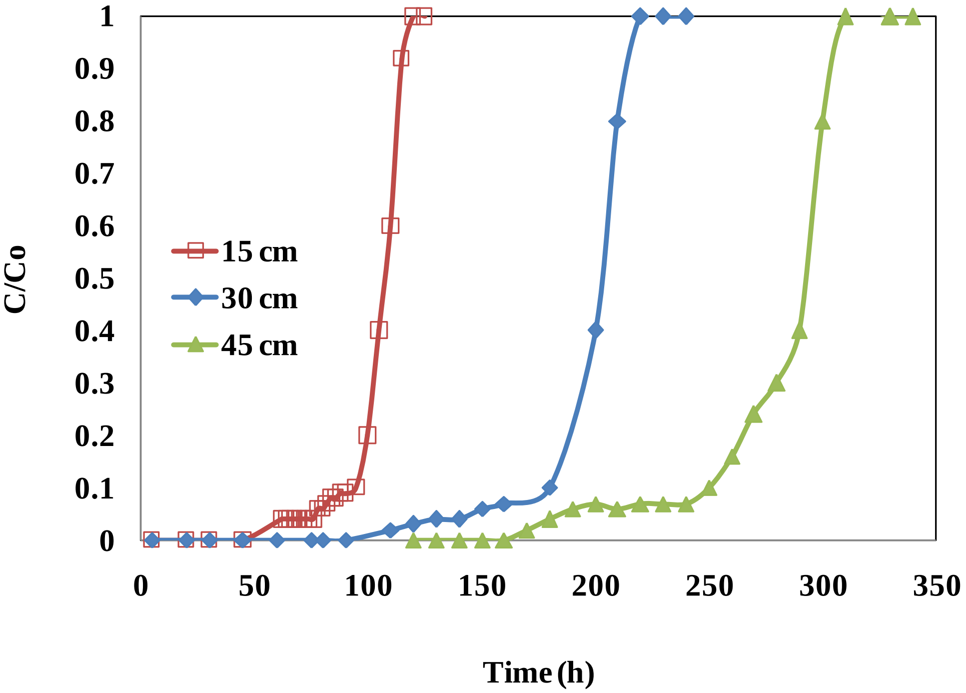

**Figure 4.3: Effect of bed depth on MB adsorption**

It can be seen that breakthrough which is considered of 5% of the influent methylene blue concentration were achieved at 60,130,190 hrs for reactor bed depth of 15,30 and 45 cm respectively, with the increase in amount of MB. Therefore, their respective throughput volumes are 18, 39, and 57 L respectively. The adsorption of column was observed at 120, 210 and 320 hr for bed depth of 15, 30 and 45 cm respectively. Regarding the nature of the breakthrough a sharp wave front were observed for bed depth of 15 and 30 cm whereas the wave front of 45 cm depth was a bit shallow, probably running the reactor for more than 300 hrs lead to some operational error along with maintenance. This may lead to shallow wave front of 45cm bed depth.

The amounts of MB adsorbed were evaluated to be 150 mg, 320 mg, and 460 mg of MB by three reactor depth of 15, 30 and 45cm respectively. Since 15 cm of bed depths have PANI-jute of amount 27gm. Therefore, the average uptake capacity is around 6 mg of MB/gm of PANI-jute. The mechanism of adsorption is continuous column process is through the formation of mass transfer zone unlike equilibrium achievement in batch process. Therefore, the amount of MB adsorbed will be lesser in continuous column process then batch process.

## 4.3 Application of BDST model

In order to predict the column reactor for different higher initial MB concentration of 20 mg/L, BDST model has been employed. A graph between bed depths and breakthrough time from the observation of initial column run of initial MB of 5 mg/L and flow rate of 5mL/min was plotted. It is shown in Figure no 4.4.

Correlation coefficient ($R^2$) of 0.998 suggests the applicability of BDST model for the adsorption of MB by PANI-jute through continuous column process. The obtained linear equation is

$$t = M_1 Z + C_1$$

or

$$t = 4.333 Z - 3.33 \qquad (4.1)$$

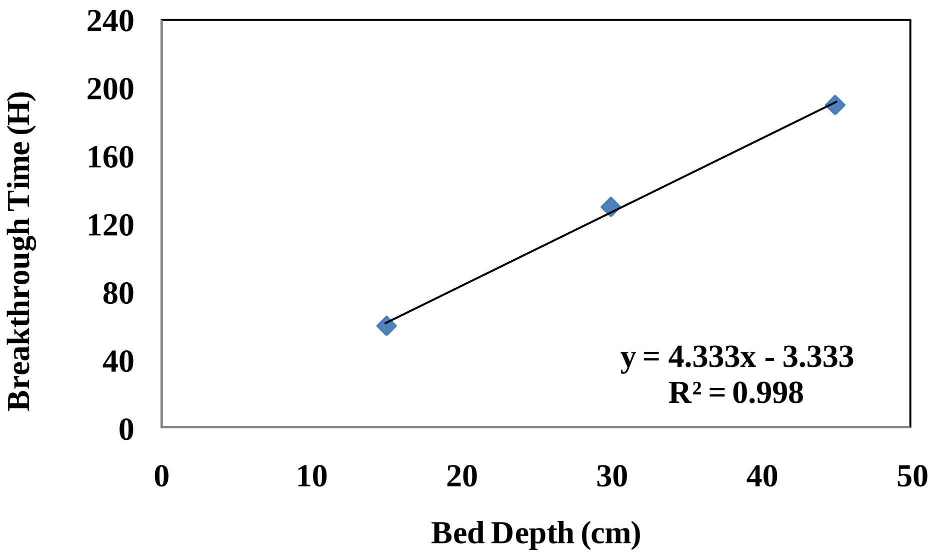

**Figure 4.4: Application of BDST model on MB adsorption**

**Table 4.1 :BDST Data for experimental data for $C_o$ = 5 ppm, Q = 5 ml $min^{-1}$**

| $C_t$ | $C_o/C_t$ | a, min $cm^{-1}$ | b,min | F ($\times 10^{-3}$) ,cm $min^{-1}$ | $N_o$($\times 10^{-3}$), mg $l^{-1}$ | $K_{ads}$, l $mg^{-1}$ $min^{-1}$ |
|---|---|---|---|---|---|---|
| 0.2 | 25 | 4.333 | -3.333 | 0.1299 | 2.8136 | 0.1907 |
| 1 | 5 | 4.333 | -3.333 | 0.1299 | 2.8136 | 0.0831 |
| 4.6 | 1.0869 | 4.333 | -3.333 | 0.1299 | 2.8136 | -0.1466 |

### 4.3.1 New initial MB concentration

Predicting the new model for new concentration of MB 20 mg/L using the model for flow rate of MB 5 ml/min, the eq 4.1 becomes

$$t = M_2 Z + C_2 \qquad (4.2)$$

where, $M_2 = M_1 \frac{C_{01}}{C_{02}} = 4.333 * \frac{5}{20} = 1.0832$

$$C_2 = C_1 \left(\frac{C_{01}}{C_{02}}\right) \left(\frac{\ln\left(\frac{C_1}{C_b}-1\right)}{\ln\left(\frac{C_2}{C_f}-1\right)}\right) \qquad (4.3)$$

$C_2 = 3.33 \times \frac{5}{20} \times \left(\frac{\ln\left(\frac{20}{1}-1\right)}{\ln\left(\frac{5}{0.5}-1\right)}\right)$

$C_2 = 1.1157$

Hence, the equation of BDST model for 20 mg/L becomes:

$$t = (1.0832 \times Z) - 1.1157 \quad (4.4)$$

**Table 4.2 :BDST Data for experimental data for $C_o$ = 20 ppm, Q = 5 ml min$^{-1}$**

| $C_t$ | $C_o/C_t$ | a, min cm$^{-1}$ | b,min | F ($\times10^{-3}$), cm min$^{-1}$ | $N_o$($\times10^{-3}$), mg l$^{-1}$ | $K_{ads}$, l mg$^{-1}$ min$^{-1}$ |
|---|---|---|---|---|---|---|
| 4 | 5 | 1.0333 | 5.6667 | 0.1299 | 2.6839 | -0.0064 |
| 15 | 1.33 | 1.0333 | 5.6667 | 0.1299 | 2.6839 | 0.0079 |
| 19 | 1.05 | 1.0333 | 5.6667 | 0.1299 | 2.6839 | 0.0029 |

For a column depth 15, 30 and 45 cm, the breakthrough concentration time as per the BDST model are evaluated and shown in Table 4.1:

**Table 4.3: Comparison of Predicted and experimental data of BDST from initial MB 20 mg/L and flow rate 5 mL/min**

| **S No** | **Depth (cm)** | **Time Predicted (h)** | **Time Experimental (h)** | **$\lambda^2$** |
|---|---|---|---|---|
| 1 | 15 | 15.13 | 21 | 1.64 |
| 2 | 30 | 31.38 | 37 | 0.85 |
| 3 | 45 | 47.63 | 52 | 0.37 |

To validify the applicability of BDST model not only the value of $R^2$ is accounted for. Therefore, we run the experiment again for flow rate of 5 mg/L and concentration of 20 mg/L for different bed depth of 15, 45 and 60 cm. The findings are shown in Figure 4.5 & 4.6.

It can be seen that breakthrough which is considered of 5% of the influent methylene blue concentration of 20 mg/L (ie. 1 mg/L or $C/C_o = 0.05$) were achieved at 21, 37, 52 hours for reactor bed depth of 15, 30 and 45 cm respectively. Therefore, their respective throughput volumes are 6.3, 11.1, and 15.6 l respectively. The difference in breakthrough time between experimental and predicted is analyzed by Chi square test which is defined by the following equation 4.5. (Ho et al, 2005)

$$\lambda^2 = \Sigma \frac{(t_e - t_p)^2}{t_p} \qquad (4.5)$$

The Chi square test results are incorporated in Table 4.1. It can be seen that with error of only 1.64 and lesser, the predicted value are much acquainted with experimental value suggesting the well applicability of BDST.

Above this, the adsorption exhaustion the of column reactor were observed at 110, 205 and 305 h for bed depth of 15, 30 and 45 cm respectively.

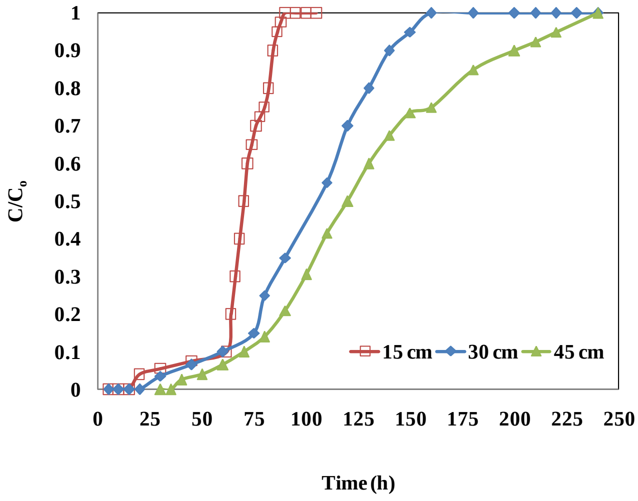

**Figure 4.5: Profiles for effluent MB at flow rate 5 mL/min and initial MB 20 mg/L.**

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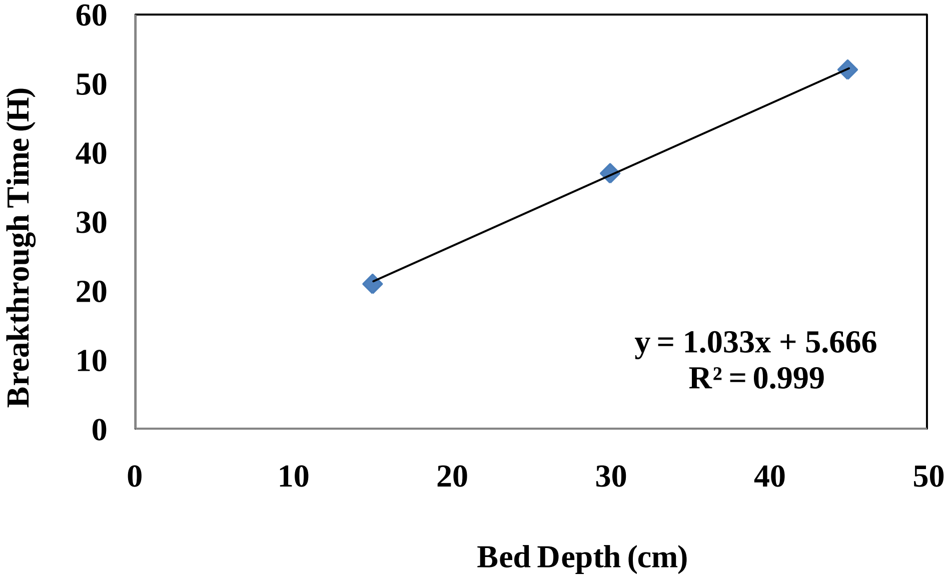

**Figure 4.6: BDST. model for MB concentration 20 mg/L and flow rate 5 mL/min**

From Figure 4.6, it can be seen that breakthrough which is considered of 5% of the influent methylene blue concentration were achieved at 21, 37, 52 hrs for reactor bed depth of 15, 30 and 45 cm respectively, with the increase in amount of MB. Therefore, their respective throughput volumes are 6.3, 11.1 and 15. 6 L for bed depth of 15, 30 and 45 cm bed depth respectively. Regarding the nature of the breakthrough a sharp wave front were observed for bed depth of 15 and 30 cm whereas the wave front of 45 cm depth was a bit shallow, probably running the reactor for more than 90 h lead to some operational error along with maintenance. This may lead to shallow wave front of 45 cm bed depth. Regarding the nature of the breakthrough curve, 15 cm bed depth achieves a sharp wave front suggesting immediate adsorption. Such sharp front S Curve is not the case for bed depth of 30 cm and 45 cm bed depth. Probably, leakage and operation problem, non-uniform and inconsistent packing at higher depth may be the probable reason. Also running the reactor for more than 250 hours lead to some operational error along with

### 4.3.2 New higher flow rate

Further to study the applicability of BDST model for prediction of new reactor for higher flow rate, i.e. 20 mL/min, there are two approaches. First, prediction using BDST model from experimental data of experiment conducted with initial flow rate of 5 mL/min and initial MB concentration of 5 mg/L and secondly from experiment conducted with initial flow rate of 5 mL/min and initial MB concentration of 20 mg/L.

For the predicted from experiment of flow rate 5 mL/min and intial MB 5 mg/L, firstly we, predict to flowrate of 5 mL/min and initial MB 20 mg/L. From then on further prediction using equation of BDST becomes

$$t = M_3 Z + C_2$$

$$t = M_1 \left(\frac{Q_1}{Q_2}\right) Z + C_2$$

$$t = 1.0832 \left(\frac{5}{20}\right) Z - 1.1157$$

$$t = 0.2708 Z - 1.1157$$

For a column depth 15, 30 and 45 cm, the breakthrough concentration time as per the BDST model are evaluated and shown in Table 4.1:

Secondly, the prediction for MB 20 mg/L and flowrate 20 mL/min is straight executed from experimental value of MB 20 mg/L and flow rate 5 mL/min. A graph between bed depths and breakthrough time is already shown in Figure 4.4. The obtained linear equation for flow rate of 5mg/L and concentration of 20 mg/L is

$$t = 1.033 Z + 5.666$$

Now, predicting the BDST model for different flow rate i.e. 20 mg/L, the model equation becomes

$$t = M_3\left(\frac{Q_1}{Q_2}\right) Z + C$$

$$t = 1.033\left(\frac{5}{20}\right) Z + 5.666$$

$$t = 0.25825\ Z + 5.666$$

For a column depth 15, 30 and 45 cm, the breakthrough concentration time as per the BDST model are evaluated and shown in Table 4.2.

To validate the applicability of BDST model not only the value of $R^2$ is accounted for. Therefore, we run the experiment again for flow rate of 20 mg/l and concentration of 20 mg/l for different bed depth of 15, 45 and 60 cm. The findings are shown in Figure 4.7. It can be seen that breakthrough which is considered of 5% of the influent methylene blue concentration were achieved at 6, 11 and 15 h for reactor bed depth of 15, 30 and 45 cm respectively, with the increase in amount of MB. Therefore, their respective throughput volumes are 1.8, 3.3 and 4.5l respectively. To further study the comparison between the experimental and predicted value of breakthrough time, Chi square test were carried out and the values were incorporated in table. 4.2 For both the prediction from initial MB concentration of 5 mg/L and initial MB 20 mg/L, the chi square error and not high with below 2. However the predicted values were deviated on both sides of the experimental value. Such well prediction strongly suggests the applicability of BDST model for breakthrough time of 5%.

Regarding the nature of the breakthrough a sharp wave front were observed for bed depth of 15 and 30 cm whereas the wave front of 45 cm depth was a bit shallow, probably running the reactor for more than 25 hrs lead to some operational error along with maintenance. This may lead to shallow wave front of 45cm bed depth.

**Table 4.4 :BDST Data for experimental data for $C_o$ = 20 ppm, Q = 20 ml $min^{-1}$**

| $C_t$ | $C_o/C_t$ | a, min $cm^{-1}$ | b,min | F ($\times 10^{-3}$), cm $min^{-1}$ | $N_o$($\times 10^{-3}$), mg $l^{-1}$ | $K_{ads}$, l $mg^{-1}$ $min^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 20 | 0.3 | 1.6667 | 0.5195 | 3.117 | -0.0101 |
| 9 | 2.22 | 0.3 | 1.6667 | 0.5195 | 3.117 | -0.1509 |
| 19.5 | 1.026 | 0.3 | 1.6667 | 0.5195 | 3.117 | 0.0082 |

**Table 4.5 : BDST predicted breakthrough time and experimental time for higher flowrate**

| S No | Depth (cm) | Time Experimental (h) | Time Prediction 1 (h) | $\lambda_1^2$ | Time Predicted 2 (h) | $\lambda_2^2$ |
|---|---|---|---|---|---|---|
| 1 | 15 | 6.00 | 2.94 | 1.53 | 9.53 | 2.07 |
| 2 | 30 | 11.00 | 7.00 | 1.45 | 13.41 | 0.52 |
| 3 | 45 | 15.00 | 11.07 | 1.09 | 17.23 | 0.33 |

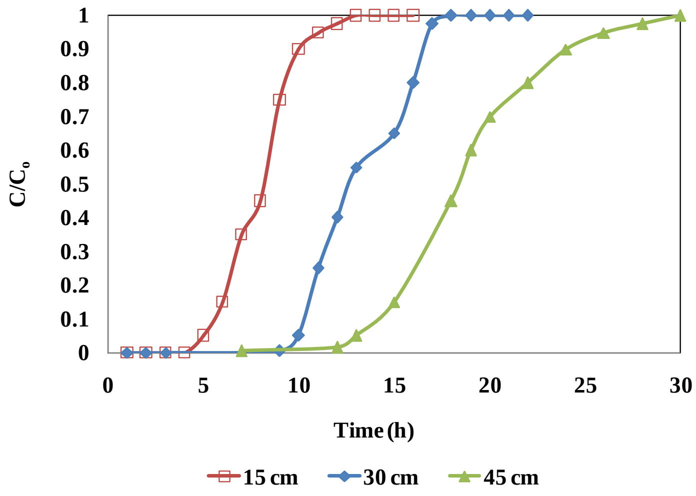

**Figure 4.7: BDST model for MB concentration 20 mg/L and flow rate 20 mL/min.**

## 4.4 Desorption

The adsorption of methylene blue by PANI-jute being strongly chemical adsorption, there is a possibility of recovering back the adsorbed MB ions by some desorbent. The optimum pH was occurred in basic pH range through formation of coordinate bond and electrostatic attraction between OH- ions on surface of PANI-jute and cationic MB. Therefore, the desorbent to be employed should be acidic solution to protonate the adsorbent and repels the cationic MB dyes. Desorption of MB would enable the reuse of the reactor also and further increase its overall capacity. To study the desorption, 0.1 M of HCl solution was fed at low flow rate of 2 mL/min and set up is shown in Figure 4.8. Lower flow rate will enable more contact time and release more MB ions. The findings of the desorption study is shown in Figure 4.9.

**Figure 4.8: Experimental setup showing desorption**

During the first throughput volume of 750 mL, ie 6 hours period, a very concentrated solution of dye was released. The concentration of MB ranges from 1200 - 1300 mg/L. The ability of the PANI-jute to release such concentration in acidic solution suggests its strong ion exchanger behavior. The initial concentration was also observed to concentrate from 5 mg/L to 1300 mg/L. The degree of concentration is evaluated to be 1300/5, ie 260 times. Probably lower flowrate may still be tried and results higher concentration. With lapse of time, throughput volume increase to 1.6 L whereas the initial concentration decreased to 50 mg/L which concentration capacity is still 10 times. However to achieve dilute or almost insignificant amount of dye, ut still consumes another 1 L of desorbent. Thus the first 1 L desorbent desorbs 1300 mg of MB dyes, whereas the last 1 L desorbent desorbs near about 50 mg.

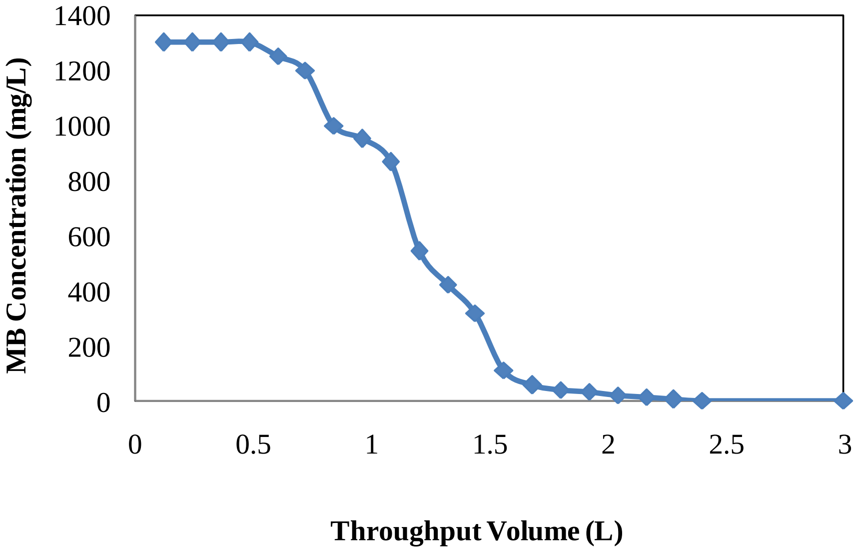

**Figure 4.9: Profiles of desorption**

### 4.5 Reuse of column reactor

The reusability of a column reactor is a very important prospect for every reactor. Through reuse, adsorption capacity can be increased. Above this, the synthesis of adsorbent polymer will also be minimized. In order to evaluate the reusability of poly-aniline bed reactor, the exhausted reactor after desorption is further subjected for 2nd cycle of adsorption. The experiments were conducted with initial MB of 5 mg/L and flow rate of 5 ml/min. The breakthrough curve of the experiments at bed depth of 15, 30 and 45 cm are shown in Figure 4.10 and experimental set up for reuse is shown in Figure 4.11. The breakthrough time at 5% for bed depth of 15, 30 and 45 cm are 0.7, 1.7 and 2.6 h respectively. The efficiency were reduced probably due to some sites in adsorbent which are still occupied by MB of the initial first cycle. However sharp wave front with vertical breakthrough was obtained suggesting the immediate chemical adsorption of the adsorbent.

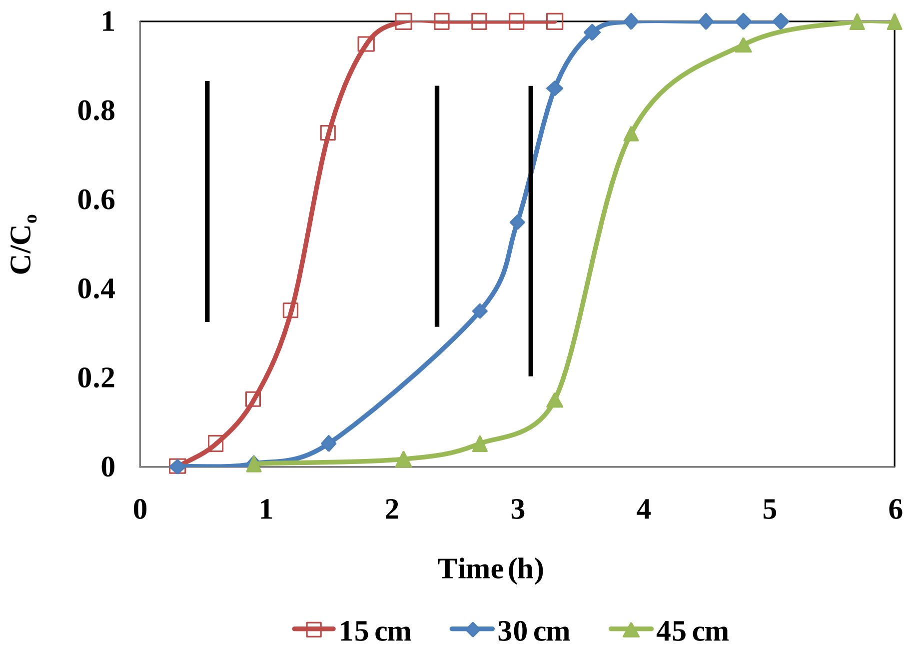

**Figure 4.10 : BDST model for Reuse of filter beds for adsorption at MB concentration 5mg/l and flow rate 5ml/min.**

**Figure 4.11: Experimental setup showing the reuse of adsorbent for adsorption**

# Chapter 5

# Conclusion and Recommendation

# Chapter 5

# Conclusion and Recommendations

## 5.1 Conclusion

Main conclusions drawn from the study are:

1. Optimum adsorption of methylene blue occurs at basic pH of 7-8 with breakthrough time of 50 h. Removal decreases in acidic as well as basic pH.
2. With increase in bed depth the adsorption of methylene blue increased.
3. With increase in influent concentration the breakthrough time for different bed depth decreases as more MB ions are to be adsorbed for same bed depth as was 60,130 and 190 hrs for 15,30 and 45 cm at 5ppm which reduced to 21, 37, and 52 h, respectively for 20 ppm at flow rate of 5 mg/l.
4. With increase in flow rate of MB ions, the adsorption capacity increased and the percentage removal decreased and it was observed that the diffusion of MB ions is higher at low flow rate and lower at high flow rate. At 5mg/l flow rate throughput volume was 6.3, 11.1 and 15.6 l for 15, 30 and 45 cm bed depth, respectively which reduced to 1.8, 3.3 and 4.5 l respectively for 20 mg/l at initial concentration of 20 ppm.
5. BDST model was made using experimental data for $C_o$ 5 ppm and flow rate of 5 mg/l, $C_o$ 20 ppm and flow rate of 5 mg/l and for $C_o$ 20 ppm and flow rate of 20 mg/l.
6. Two BDST model was made using initial concentration of 5 mg/l and flow rate of 5mL/min and initial concentration of 5 mg/L and flow rate of 20 mL/min for initial concentration of 20 mg/L and flow rate of 20 mL/min. The comparison was made between experimental data and BDST model of 5mg/l initial concentration and 5 mL/min flow rate and BDST model of 5mg/l initial concentration and 20mL/min flow rate. The chi square value obtained for first comparison are 1.57, 1.45 and 1.09 and for second comparison are 2.07, 0.52 and 0.33 bed depth of 15,30 and 45cm, respectively. Thereby validifying the BDST model.
7. Column was successfully desorbed using 0.1 M HCl at 2 ml/min which concentrated the initial concentration of methylene blue 5mg/l to almost 1300mg/l.

8. Reusing the adsorbent for $C_o$ 5ppm and flow rate of 5 mg/l was conducted which ensured the effective removal of MB with breakthrough time of 0.7, 1.7 and 2.6 h for 15, 30 and 45 cm bed depth, respectively.

## 5.3 Recommendation

1. Poly-Aniline Jute fiber may be used as adsorbent for removal of methylene blue dye in industry .
2. BDST model can be used to design column for higher initial concentration and flow rate.
3. Adsorbent can be successfully desorbed and reused for removal of dyes for more than one cycle.

## 5.2 Scope of further studies

1. Further study can be conducted with larger column size and higher initial concentration of methylene blue.
2. Performance evaluation of the reactor column with actual industrial wastewater needs to be studied.
3. Performance evaluation of the reactor when employed with actual industrial wastewater.

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