STUDIES ON POLYANILINE AS ADSORBENT FOR DYE REMOVAL

A thesis submitted in the partial fulfillment of the requirements for the award of the degree

of

DOCTOR OF PHILOSOPHY

by

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NOVEMBER 2019

DELHI TECHNOLOGICAL UNIVERSITY

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DECLARATION

This is to certify that the work presented in this thesis entitled **“Studies on Polyaniline as Adsorbent for Dye Removal”** is original and has been carried out by me for the degree of **Doctor of Philosophy** under the supervision of **Dr. Raminder Kaur**, Assistant Professor, Faculty of Polymer Science and Chemical Technology, Department of Applied Chemistry. This thesis is the contribution of my original research work based upon the experimental studies. The contribution of others, wherever involved, has been cited and acknowledged.This thesis has been prepared in conformity with the rules and regulations of the Delhi Technological University, Delhi. To the best of my knowledge, the research work reported and results presented in this thesis have not been submitted either in part or full to any other university or institute for the award of anyother degree or diploma.

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled **“STUDIES ON POLYANILINE AS ADSORBENT FOR DYE REMOVAL”**by **Ms. Monika Duhan**, (Reg. No.:2K14/Ph.D./AC/02) in the partial fulfillment of requirements for the award of degree of **DOCTOR OF PHILOSOPHY**, is an authentic record of student’s own work carried by her under the supervision of **Dr.Raminder Kaur**, Assistant Professor, Departmentof Applied Chemistry, Delhi Technological University, Delhi. This work has not been submitted to any other institute or university for the award of any other diploma or degree.

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Dedicated

To

My Kids

Viraj Deswal

And

Vinaya Deswal

ACKNOWLEDGEMENT

It gives me immense pleasure to express my deep sense of gratitude and sincere thanks to my supervisor ***Dr. Raminder Kaur****, Department of Applied Chemistry, Delhi Technological University, Delhi, for her consistent guidance and encouragement from inception to completion of this thesis work. It has been an honor to be her Ph.D. student. She is an excellent supervisor and continuously encouraged and helped me for the achievement of goals of the research work. I am grateful for all her contributions in terms of time, suggestions, and constructive criticism and facilities to make my Ph.D.experience productive and stimulating.*

I owe my heart felt gratitude to the ***Prof. Yogesh Singh****, Honorable Vice Chancellor, Delhi Technological University for his kind permission and* ***Prof. S. G. Warkar,*** *Head, Department of Applied Chemistry, DTU for providing the necessary facilities to carry out this research work. I wish to express my sincere thanks from the deepest of my heart to* ***Dr. Saif Ali Chaudhary,*** *Associate Professor, Jamia Milia Islamia, Delhi for his help and providing valuable suggestions as and when needed during this research work.*

I am thankful to all faculty members, technical and non-technical staff of the department and my friends, seniors and fellow research students: ***Mr. Mukesh Kumar, Mr. Manjeet Malik, Ms. Anuja Agrawal, Mr. Surya Tanwar, Ms. Neelam Yadav, Ms. Babita Veer, Mr. Saurav, Mr. Suveen, Mr. Aayush Nagpal, Mr. Sharf Sidqui*** *for providing me endless encouragement, and support during the period of research work. I am heartfully thankful to* ***my in-laws*** *and my husband* ***Mr. Naveen Deswal*** *for giving me moral support, encouragement and help. I am indebted to* ***my parents****, my driving force for the completion of my research work.*

Finally, I am thankful to all who have helped me directly or indirectly in completion of this research. Above all, I owe to ***Almighty God*** *for granting me wisdom, health and strength to accept and overcome the challenges of the life.*

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ABSTRACT

Dyes are one of the major groups of water polluting chemicals among all water pollutants. Effluent from the textile industries contribute a huge amount of dyes which are not only highly toxic, but are also a matter of concern due to aesthetic point of view. They reduce the sun light penetration and photosynthesis, thereby increasing the biological oxygen demand and causing lack of dissolved oxygen that is vital to sustain aquatic life. The removal of the colouring materials and dyes from the effluent of textile industries is an extremely demanding task because pigments and dyes confront biodegradation and remains in the environment for long span of time. In spite of the primary recognition of polyaniline as a conducting polymer, it is now emerging as an adsorbent for the removal of dyes. This is due to its improved properties such as larger surface area, modified mechanical properties, low cost, high adsorption capacity, and ease of synthesis and exclusive oxidation/reduction and acid/base doping/de-doping chemistry. In the present studies, polyaniline (PANI) nanofibers (salt and base forms) were synthesised by using the interfacial polymerization method and further used as adsorbent for the eradication of different dyes from their aqueous solutions. The synthesized adsorbent was characterized by SEM, HRTEM, XRD, Zeta potential, BET and FTIR techniques. From morphology characterization (SEM and HRTEM) the size of the nanofibers was found to be 60 nm and XRD spectrum shows the amorphous nature of polyaniline with a little bit crystalline portion. Zeta potential testing indicated the positive charge on the salt form of polyaniline with positive value of zeta potential equal to10.1 mV. The UV- visible spectroscopy was used to analyze the un-adsorbed amount of the dyes. The kinetics of the adsorption of different dyes was studied using reported kinetic models such as Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion models. In addition, the Langmuir and Freundlich isotherm models were also studied to analyze the equilibrium data. The effects of different parameters such as contact time, initial dye concentration and pH were also studied. It has been seen that approx 95% methyl orange (MO) and 67% of methylene blue (MB) dye was removed by using salt form of polyaniline respectively and approx 91% of MB dye was removed by using base form of polyaniline at optimum conditions of adsorption parameters. Also, the investigation was carried out on structurically modified PANI nanofibers, modified by doping with phytic acid (PA) used to study the adsorption of methylene blue dye from aqueous solution. The doped adsorbent possessed negative charge on its surface with negative value of zeta potential equal to -2.06 mV. Approx 96% of methylene blue dye was removed by using doped polyaniline. The desorption study was also carried out to regenerate the exhausted polyaniline. Approx 86% of MB dye was recovered by using 95% ethanol solution in case of polyaniline base form and approx 65% of MB dye was recovered in case of PA doped PANI. Evidently, the PANI nanofibers are reported to be a novel adsorbent for removal of dyes.

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LIST OF ABBREVIATIONS

Symbol	**Notations**
BOD	Biochemical Oxygen Demand
TDS	Total Dissolved Solids
DO	Dissolved Oxygen
PA	Phytic Acid
PANI	Polyaniline
ES	Emeraldine Salt
EB	Emeraldine Base
PNFN	Polyaniline Nickel Ferrite Nanocomposite
PCSD1	Polyaniline Coated Sawdust of Wood
PCSD2	Polyaniline Coated Sawdust of Walnut
PNB	Polyaniline Nanotube Base
PAni/SD	Polyaniline Coated onto Wood Sawdust
MO	Methyl Orange Dye
OG	Orange G Dye
PTSA	p- Toulene Sulfonic Acid
CSA	Camphor Sulphonic Acid
PAn/SD	Polyaniline Coated Sawdust Composite
DG6	Direct Green 6 Dye
RO16	Reactive Orange 16
RB	Reactive Black
RV	Reactive Violet
AG	Acid Green 25
EBT	Eriochrome Black T
PANi-MMT	Polyaniline Momtmorrillonite Composite
MY	Mordant Yellow
MB	Methylene Blue
EY	Eosin Y
PPy	Polypyrrole
NT	Nanotubes

SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform Infrared
XRD	X-ray diffraction
BET	Brunauer–Emmett–Teller
R_L	Separation Factor
PNb	Polyaniline Nanofibers Base
PA doped PANI	Phytic Acid Doped Polyaniline
APS	Ammonium Persulphate

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

1.1.1 Water Pollution and Its Damaging Effects

Environmental pollution is becoming very problematic because of the steadily increasing world population, industrialization and global & environmental variations. Any type of pollution which perturbs the environment and human health is considered as the culprit for the environmental pollution. There is no denying of the fact that environment has to be protected and conserved, to make the future life possible. Among different types of pollutions; the water pollution is the major culprit for the environment deterioration, and thus, seeks immediate attention. When the quantity of any substance in the water increases to such an extent that it becomes harmful for the human beings and surrounding environment, then it is regarded as a pollutant. Pollutants at the low levels are not effective, as all the water bodies existing on the earth, have ability to clean up assertive amount of the pollution naturally by diluting and dispersing these pollution causing substances. But as the concentration or the quantity of the foreign substances gets increased, they start affecting the quality of the water [1]. The plants, animals and even the humans that consume such contaminated water may also get affected. It is indeed the quantity of the pollutant or the volume of the water body that determines the extent of the pollution. In addition to this, surface water pollution i.e. contamination of rivers, lakes, oceans etc., may also affect the underground aquifers, which, broadly termed as ground water [2]. The ultimate consequence of the pollution is the deterioration of the environment and the harm to the human beings. The main contributors of the water pollution are: domestic wastes including sewage; chemical wastes from industries including harmful chemicals, dyes, soaps and other chemicals; agriculture run-off including pesticides, insecticides, unused fertilizers; oil and the petroleum products from the refineries, oil wells or spell from the ships, radio-active wastes from the nuclear power plants and other types of wastes from the hospitals, process industries and other sources [3]. In addition to these, the discharge of huge amount of hot water from the thermal power plants and the commercial operations in water bodies also affect the environment, water animals and plants with thermal shock [1, 2].

Human health gets severely affected by the water pollution directly or indirectly. The consumption of the polluted water can cause many fatal diseases. Water pollution poses a threat to the environment and human beings by various means, such as, it may cause death of the aquatic animals, disrupt food chains, spread diseases and destroy ecosystems. In addition, the presence of organic compounds in the water body consumes a large sum of the dissolved oxygen for degradation, which in turn lowers its amount [4]. Health risks from the water pollution vary from area to area, depending upon the discharge of the effluent from different sources and the volume of the pollution causing agents. According to the reported work, the presence of more than 500mg/L of total dissolved solids (TDS) in any water body is the indication of the water pollution. The higher amount of TDS in water may disturb many ongoing physiological and biological processes in human body [5-7]. The toxic pollutants such as heavy metals and different types of chemicals may cause many toxicological effects on the human health and the aquatic ecosystem.

Throughout the last decades, the awareness about the water pollution has grown worldwide and several new remedial measures are proposed and implemented for the prevention and conservation of the available water resources [8, 9]. The environmental awareness is evidently one of the major concerns of today in all developed and developing countries. The different factors responsible for the water pollution are needed to deal wisely. The research, today, is more focused on the environmental friendly products and technologies. The need of the hour is to conduct technological and social investigation to conserve and improve the environment.

1.1.2 Effluent from the Industries

Hazardous waste released by the industries is the main focus of concern, as, if not remediated correctly, it can cause threat to the environment and the mankind. Since the industrial revolution had entered in the man's life, many things have revolutionary changed. But it also affected the nature and the environment in different ways [10]. Along with the many benefits from industries, many negative effects were also observed. The industries became one of the major contributors of water pollution, as they discharge numerous pollutants, which are very toxic in nature and affect the surrounding environment and human life adversely. Some industries use fresh water to bear away the industrial wastes including, mercury, nitrates, sulphur, lead, asbestos, petrochemicals and oils. All these remains ultimately get mixed with the water bodies. During the earlier times, only small factories were build-up to meet the requirements of the people, which generated a limited waste within the permissible limit of the self- cleaning capacity of the water bodies. But, as the time passed, these factories started to get converted into large industrial set-ups, which, knowingly or unknowingly, started polluting the water bodies, with their huge discharge of effluents [11].

Industries pollute the environment in many fronts. They contaminate the sources of drinking water with their untreated or partially treated wastewater, poison the air with the releases of harmful toxins and spoil the soil with burial of wasted chemicals and un-necessary by-products. In addition, the noise pollution is the major threat in this era of industrialization. Above all, sometimes, the industrial mishaps may also lead to the environmental disasters. The major causes of the industrial pollution which are ultimately responsible for the environmental degradation are: unplanned industrial growth, use of outdated technologies, inefficient waste disposal, lack of policies to control the pollution, low replenish rate of the resources leached from the natural world. The main categories of water pollutants which significantly affect the aquatic component of our bio-sphere are: a) Suspended solids and sediments, b) Inorganic pollutants, c) Organic pollutants, d) Pathogens, e) Radioactive pollutants, f) Nutrients and agriculture run-off, g) Thermal pollutants, and h) Oil [5,11].

- **Suspended Solids and Sediments:** This class of pollutants consists of eroded minerals from the land, slit and sand particles. These pollutants can reduce the sunlight penetration in the water body and can also destruct the normal aquatic life by their deposition in the water. In addition, if these deposited solids are organic in nature, they lead to the anaerobic conditions after their decomposition. The gills of fishes in water can be injured by these solid suspended pollutants.

- **Inorganic Pollutants:** Some non-biodegradable compounds from the industries, also contribute the water pollution. These pollutants comprise of inorganic salts, mineral acids, metals, trace elements, metal complexes with organic compounds, sulphates and cyanides, etc. These pollutants are dangerous if present in the appropriate amount in the water and pose a bad impact on the organisms in the environment.

- **Organic Pollutants:** In addition to the inorganic compounds coming from the industries, some organic compounds also enters the water resources in the form of pollutants and affects the quality of the water. These organic pollutants are classified as i) Oxygen Demanding Wastes-These pollutants are responsible for the depletion of the dissolved oxygen (DO) in the water because they need oxygen for their decomposition, by aerobic oxidation. ii) Synthetic Organic Compounds-Such as pharmaceuticals, food additives, plastics, solvents, synthetic pesticides, insecticides, soaps & detergents, paints, synthetic fibres and many volatile organic compounds in trace amount. These pollutants interfere with the microbial degradation during the self-purification process of the water body and also the quality of the water.

- **Pathogens**: The main sources of these pollutants are the sewage, poultries and the slaughterhouses. These pollutants include different types of bacteria and viruses, which can cause some fatal diseases.

- **Radioactive Pollutants**: The main sources of radioactive pollutants are nuclear power plants and nuclear reactors, testing of the nuclear weapons, mining and the processing of radioactive ores, industrial activities, medical institutes and research and development activities. They can cause serious problem after their deposition in the teeth and bones.

- **Nutrients**: Some nutrients such as nitrates and phosphorous comes from the effluent of the fertilizer industries and the agricultural run-off. These nutrients promote 'Eutrophication' and stimulate the growth of the algae and weeds in the water, which, in turn, decreases the amount of the dissolved oxygen in water, thus, act as pollutants. In addition to the aquatic life, human beings may also get affected by these pollutants, if polluted water is consumeddirectly.

- **Thermal Pollution**: The addition of the large quantities of hot water in any water body is the cause of the thermal pollution. The main culprits and contributors of the thermal pollution are commercial industries, nuclear power plants and thermal power plants. Thermal pollution affects the aquatic life in different ways, such as, increase in the bacterial activity, reduction in the DO level and cause thermal stratification in the water body.

- **Oil:** This water pollutant is present in nature itself and is degradable in the presence of the bacterial action. The major sources of this pollutant are; leakage of oil pipes, oil spills and waste from the refineries and industries. It separates the contact of water body with the air and results into the dropping of the dissolved oxygen (DO) in the water [12]. In addition, photosynthesis activity of the aquatic plants is also affected by this pollutant, because, it covers the entire surface water and reduces the sunlight transmission through the surface to the aquatic flora.

The textile sector, though, being a point of attraction from the last two decades, is one of the major culprits for the water pollution. This is due to the employment of large volumes of water for different processes of dyeing, for good quality fabric production [13, 14]. Water is used for different functions in the textile industries, like, 90-94% as process water, and 6-10% as cooling water. A noticeable change has been seen in the things with the discovery of synthetic dyes, such as, more colors fastness, production at low cost, brighter and easy application to the fabric, etc. However, these new changes made the world more advance and colourful, but at a hefty cost. The toxic chemicals used to produce synthetic dyes may cause cancer, or even death. Moreover, these dyes are responsible for the unwanted colour of the wastewater because of their recalcitrance behavior and resistance to the sunlight penetration in the water bodies [15]. Annual production of about 7×105 tonnes/year, has been reported for more than 100,000 different commercial dyes in the recent literature [16]. Dyes are the major group of polluting chemicals among the all water pollutants [17]. The effluent from the textile industries contains a large range of dyes and dye derivatives, surfactants, solvents, salts, suspended particles, acids or bases and additives, which makes it complex to treat prior to its disposal to water bodies [18]. As per the reported works, in addition to the different types of dyes (reactive, anionic, cationic, non-ionic and basic dyes), used in the textile industries, several other chemicals, that are used as wetting agents, softening, sizing agents, carriers, surfactants, etc., are also highly toxic, poorly biodegradable and persistent in the nature for long time periods and cause threat to the aquatic life [13, 19, 20]. However the exact data is unknown, more than 10,000 tonnes/year dyes are consumed around the world, and out of this amount, roughly, 100 tonnes /year of dye are lost in the textile effluent [21]. The synthetic dyes are used not only for the dying purpose in the textile industries [22], but are also playing role in different sectors of the progressive technology, such as leather tanning [23], cosmetic, food processing, rubber, plastics, dye synthesizing industries and printing [24-26], paper industries [27], ground water tracking [28], sewage [29], to determine the specific surface area of activated carbon [30], treatment of the wastewater [31] and many more sectors. This also aided in the amount of the colored effluent in the water bodies and leads to the water pollution [32, 33-35]. Different dyes employed in the textile industries are broadly categorized as: (a) Anionic dyes that include direct dyes, reactive dyes and acidic dyes. (b) Cationic dyes that include basic dyes. (c) Non-ionic dyes including dispersed dyes. The reactive and basic dyes are easily water soluble, cheaper to make, bright colored and easy to apply on the fabric, so, these dyes are generally preferred in the textile industries [36]. Type of the dye, and the dying process used to produce a colored fabric in the textile industries are the factors, on which the concentration of the unused dye in the wastewater depends. If the dying process used is improper and ineffective, usually about 25% of the total amount of dye gets lost in the wastewater and, thus, contribute as water pollutant. The effluent coming from the textile industries consists of high amount of COD and BOD, mineral oils, unused dyes and suspended solids etc.

1.1.3 Lethal Effects of Dyes

With increasing demands for more colorful textile products, the dyes are becoming an essential part of the modern life. But, it is not safe to overuse these chemical compounds, because of their adverse effects on the environment and mankind. Different dyes are reported to have different lethal effects. Anthraquinone containing dyes are difficult to degrade, and their impact in the water body remains for a long period of time [37]. Metal complex dyes (Fe, Co, Cr) are known for their carcinogenic nature, as the majority of dyes are chromium based [38-41]. The basic dyes, even in a very low concentration, can affect the visibility in the water, because of their high intensity of the colors [38, 40-46]. The absorption and reflection of the sunlight by the dyes hinders the penetration of the sunlight to the water body, and ultimately affect the aquatic life. Also, the presence of some metals and aromatics in the textile effluent may harm the aquatic life

[38-42, 47]. The toxicity of azo dyes, due to the presence of harmful amines, may affect the quality of the water [37, 48]. Due to the water-soluble nature of the reactive dyes, a small part of these may wash away during their use, and pollute the environment [49]. The reactive dyes, as reported in the literature, are very effective in dying purpose due to their formation of covalent bonds with the woolen, cellulose and PA fibers. The industry workers who deal directly with the reactive dyes are reported to suffer from respiratory diseases [40, 41]. Moreover, as dyes are quite stable chemically, resist breakdown and persistent in nature may have adverse impact on the environment, which remains for a long period of time. Even, after the breakdown, that took a long span to decompose. Above all, the breakdown products of dyes are highly toxic, mutagenic and carcinogenic to life [48, 50]. According to Central Pollution Control Board Ministery of Environment & Forests, the acceptable value of dye in the effluent should not to exceed, 400 mg/L [51] The dye concentration in the effluent of textile industries may vary from 2 mg/L to 2000 mg/L, but this is depend upon the processes carried out in the industry. Keeping these lethal effects of dyes in view, the necessary treatment of industrial effluent, especially that of textile industry, prior to its discharge in water body is very important. Though, it is possible to predict the toxicity of the dyes, the awareness among the workers and the users is the major requisite.

1.2 Methods Used for the Dye Removal

The removal of the colouring materials and dyes from the effluent of the textile industries is an extremely demanding task, because, the pigments and the dyes confront biodegradation and remain in the environment for long span of time [52, 53]. As the effluent from the textile industries and other provenances is loaded with huge amount of dyes, it needs necessary treatment, prior to the discharge in water bodies. Scientists have reported the use of many physical and chemical treatment processes to eradicate the dye content from the industrial effluent, such as coagulation, membrane separation, adsorption and advanced oxidation etc. [54]. Characteristics of the textile wastewater and the skill & ability of the operator are some factors which help to select the ideal treatment system. Literature provides the necessary information on the currently available water treatment techniques and also recommends many effective and economic alternatives for the dye removal and de-colorization of the effluent [55, 56]. The major treatment methods used in the industries for the dye removal are categorised into following classes:

i) Physical Methods:

- Coagulation /Flocculation
- Adsorption
- Ion Exchange
- Complexometric Techniques
- Membrane Separation

ii) ChemicalMethods

- Chemical Oxidation
- Irradiation

iii) Biological Methods

- Aerobic Treatments
- Anaerobic Techniques

iv) Electrochemical Methods

Every treatment process has few advantages and disadvantages, but in general, the environmentally safe and low cost treatment techniques are usually preferred [57, 58]. For example, as reported in some previous studies, azo dyes could be easily transformed into aromatic amine using direct anaerobic processes, because most of the azo dyes are not degraded efficiently by the biological treatments [59]. However, these treatment methods are profitable and effective only when the concentration of the solute in the wastewater is relatively high [60-62]. Another study recommended the adsorption as an effective and low cost alternate for the removal of dyes, for decolorization [37]. As evident from the literature, the extensive removal of the pollutants from the industrial effluent may not be possibly achieved via a single technique, as a single treatment applied is capable to remove only specific type of pollutant. Different physical and chemical treatment methods [63] employed to remove dyes from the industrial effluent are reported in Table 1.1. The advantages and drawbacks of these available and commonly practiced treatment processes have also been summarized.

Table 1.1 Different Effluent Treatment Techniques & their Advantages and Disadvantages [64].

Treatment Technique	Advantages	Disadvantages
Adsorption (Commonly used Adsorbent: Activated Carbon)	Effective removal of various kinds of dyes	Costly, Difficult to regenerate
Membrane Separation Method	Useful for almost all types of dyes	Production of the concentrated sludge
Ion Exchange Method	Easier adsorbent regeneration	Applicable to limited dyes
Irradiation	Laboratory level effective oxidation	High amount of dissolved O_2 required for the treatment
Electro Kinetic Coagulation Method	Low cost	More production of sludge

Oxidation Method	Easy to apply	Requires activation of H_2O
Ozonation Method	No increase in the volume of the effluent (ozone in gaseous form)	Short half-life(20 min)
Fenton’s Reagent	Effective decolorization of the soluble and insoluble dyes both	Sludge formation and its disposal
Electrochemical Degradation	No production of sludge, no use of chemicals	Less removal of dyes due to high flow rate
Photochemical Method	Less foul smell, no sludge production	High by-products production
Sod. Hypochlorite (NaOCl)	Azo-bond cleavage	Formation of aromatic amines
By White-Rot Fungi	Use of enzymes for degradation	Unreliable enzyme production
Microbial Culture of Mixed Bacteria	Achieveddecolourization almost in a day	Azo dyes not degraded under aerobic conditions
Adsorption by Biomass (living or dead)	Effective for dyes, affinity for microbial system	Useful only for some classes of dyes
Textile–Dye Bioremediation Systems	Decolourization of azo and other water soluble dyes	Production of methane and hydrogen sulphide gas

1.2.1 Removal of the Dyes by Adsorption

Among all the available treatment processes, the adsorption has been found to be a high calibre process because of the low cost, availability and effectiveness of the adsorbents; insensitivity to the toxic substances; feasibility and simplicity of design and operation [65-68]. Adsorption is a process in which the dissolved adsorbate molecules are attracted to the adsorbent surface by physical force or the chemical bonding. The factors such as contact time, temperature, pH, particle size and the surface area are the basis for the adsorption of the dyes, present as pollutant [69]. The attachment of the ionic and the molecular species bearing different functional groups is dependent on the nature of the interaction between the adsorbent and adsorbate molecules. It may be electrostatic interactions between oppositely charged sites at the adsorbent surface or it may be physisorption, due to the weak van der waals forces. It can be chemisorption, involving strong adsorbate-adsorbent bonding or may be a simple attachment of the adsorbate molecule at a definite site on the adsorbent surface [70]. When the adsorbent is not so costly, and do not require any prior treatment, the adsorption process seems to be quite effective [71]. In addition, the adsorption process is also fruitful when the biological treatment methods are not effective for the remediation of the industrial effluent [71, 72].

Classically, the most preferred adsorbent used for the removal of the dyes is activated carbon, due to its powerful adsorption capacity. As reported in literature, the activated carbon is capable to adsorb both, low and high molecular weight molecules, because of its porous structure and large surface area [70]. Although, the activated carbon has some advantages in terms of more surface area and highly porous structure, its boundless use is narrowed, because of its high cost and complicated preparation [73]. In addition, the activated carbon is non- selective in nature, and it is quite difficult to abstract the activated carbon from the solution, and its dumping may lead to the secondary pollution [70]. Many researchers are working on the development of a broad range of alternative adsorbentsfor the treatment of the wastewater, to substitute commercially available costly activated carbon. The main emphasis of the researchers is to develop new and novel alternative adsorbents, which have preferable performance characteristics, such as, larger surface area, modified mechanical properties, low cost, high adsorption capacity, simple preparation etc. In the recent past, many studies have been conducted, and, the researchers have developed a variety of adsorbents from different precursors, like, agriculture by-products, natural materials, solid wastes of industries, and have tested their possibility for the lowering the dye concentration from wastewater [74]. But many of these adsorbents have not been explored extensively at the industrial level due to some operational instability. Different adsorbents used for the dye removal from the industrial effluent are given in Table 1.2.

Table 1.2 : Different Adsorbents used for the Dye Removal from the Industrial Effluent.

Adsorbent	**Dye Used**	**Adsorption Capacity (mg g^{-1})**	**Reference**
1. Agriculture and Industrial Waste as Adsorbent			
Rice Husk	Indigo Carmine	65.90	[75]
Activated Carbon	Crystal Violet	64.80	[76]
Sugarcane Bagasse	Methylene Blue	34.2	[77]
Sugarcane Dust	Basic Green- 4	3.99	[78]
Cotton Waste	Basic Blue	277	[79]
Fly Ash	Brilliant Green	65.9	[80]
Sludge Ash	Reactive Blue -2	250	[81]
Sludge based Activated Carbon	Acid Rrown- 283	20.50	[82]
Activated Carbon (Chemviron GW)	Basic Red- 46	106	[82]
Sugar Industry Mud	Basic Red- 22	519	[83]
Activated Carbon (Jute Fiber)	Reactive Red	200	[84]

Metal Hydroxide Sludge	Reactive Red- 120	45.87	[85]
Charfines	Direct Brown	6.40	[86]
Waste Fe(III)/Cr(III) Hydroxide	Congo Red	44	[87]
Activated Carbon (filtrasorb 400)	Ramazol Reactive Black	434	[88]
Wheat Straw	Remazol Red	2.50	[89]
Corn-Cob Shreds	Remazol Red	0.60	[89]
Barley Husk	Congo Red	171	[90]
Slag	Basic Blue- 9	9.95	[91]
Core Pith	Acid Violet	1.60	[92]
Bamboo Dust Carbon	Methylene Blue	143.20	[93]
2. Fruits and Plants Waste as Adsorbent			
Orange Peel	Rhodamine B	3.22	[94]
Yellow Passion Fruit	Methylene Blue	16	[95]
Mandarin Peel	Methylene Blue	15.20	[95]
Banana Pith	Direct Red-28	18.20	[96]
Garlic Peel	Methylene Blue	142.86	[97]
Raw Date Pits	Methylene Blue	80.29	[98]
Bagasse Pith	Acid Blue- 25	21.70	[99]
Palm Fruit Bunch	Basic Yellow- 21	327	[100]
Jack Fruit Peel	Basic Blue- 9	285.71	[101]
Activated Desert	Methylene Blue	23	[102]

Plant			
Guava Leaf Powder	Methylene Blue	95.10	[103]
Tea Waste	Methylene Blue	85.16	[104]
Mango Seed Kernel	Methylene Blue	142.90	[105]
Jute Stick Powder	Rhodamine B	87.70	[106]
Tree Fern	Basic Red- 13	408	[107]
Saw Dust- Oak	Acid Blue -25	27.85	[108]
Wood	Basic Blue 69	77	[109]
Eucalyptus Bark	Remazol BB	34.10	[110]
Wood Chips	Remazol Red	2.80	[111]
Beech Sawdust (original)	Red Basic- 22	20.20	[112]
Saw Dust	Methylene Blue	62.40	[113]
3. Natural Inorganic Minerals as Adsorbent			
Clay	Methylene Blue	6.30	[114]
Sepiolite	Reactive Red- 239	108.80	[115]
Red Mud	Congo Red	4.05	[116]
Zeolite	Reactive Black- 5	60.50	[115]
Ca – Montmorillonite	Basic Green- 5	156.30	[117]
Ti – Montmorillonite	Basic Green- 5	170.50	[117]
Raw Kaolin	Methylene Blue	13.99	[118]
Calcined Alunite	Reactive Blue- 114	170.70	[119]
Halloysite Nanotubes	Methylene Blue	84.32	[120]
Dolomite	Brilliant Red	900	[121]

Diatomaceous Earth	Methylene Blue	198	[122]
Anion Clay Hydrotalcite	Acid Blue- 29	34	[123]
Bentonite – Na	Acid Blue- 193	67.10	[124]
Crude Clay	Basic Red- 46	54	[125]
Fly Ash	Reactive Blue- 21	106.71	[126]
Sepiolite	Reactive Blue- 21	66.67	[126]
Natural Zeolite	Basic Red- 46	8.56	[127]
Bentonite	Methylene Blue	33	[128]
Silica	Basic Blue- 3	11.16	[129]
4. Bioadsorbents for Dye Removal			
Chitin and Chitosan	Acid Green- 25	645.1	[130]
Chitosan Bead (crab)	Reactive Red- 222	1106	[131]
Peat	Acid Blue- 25	12.7	[109]
Chitosan Flake	Reactive Red- 222	339	[131]
White Rot Fungi	Remazol Black B	60	[132]
Fungus (*Aspergillus niger*)	Congo Red	14.72	[133]
Dried Seagrape	Astrazon Golden Yellow	35.5	[134]
Non-Cross-Linked Chitosan Beads	Reactive Red- 189	1189	[135]

1.3 Polyaniline: An Emerging Adsorbent

A variety of adsorbents have been used in the past for the eradication of dyes and toxins from the wastewater, including, activated carbon, natural clays [136,137], polymeric hydrogels [44,45], agriculture wastes and by-products [19], industrial chemical remains [138,139], modified clays, chitin and chitosan [71,37], starch and its derivatives [72,140], carbonized waste of wool [141] etc. The more details are provided in the Table 1.2. In last one decade, polyaniline (PANI), that is originally recognized and used as a conducting polymer [142, 143], has attracted the attention of many researchers as an emerging adsorbent. Polyaniline, in addition to its unique and attractive chemical stability [144], is also supported by the low cost of the raw material (aniline) and high yield of the polymerization reaction [144,145].

It is quite easy to oxidise or reduce PANI because of its rare electronic behavior, with its high electron affinity and low ionization energy. With its improved properties, such as larger surface area, modified mechanical properties, low cost, high adsorption capacity and simple preparation, polyaniline is now emerging as a novel adsorbent. Polyaniline in its different forms i.e. acidic (ES) and basic forms; PANI composites, coating of PANI on different solid substrates, salt form of PANI and doped PANI are reported to have been used as adsorbent for dyes and other organic compounds. Figure 1.1 represents the adsorption capacity of different forms of polyaniline for the methylene blue dye [146-149,]. The work done by the different researchers on polyaniline as adsorbent is summed up in Table 1.3.

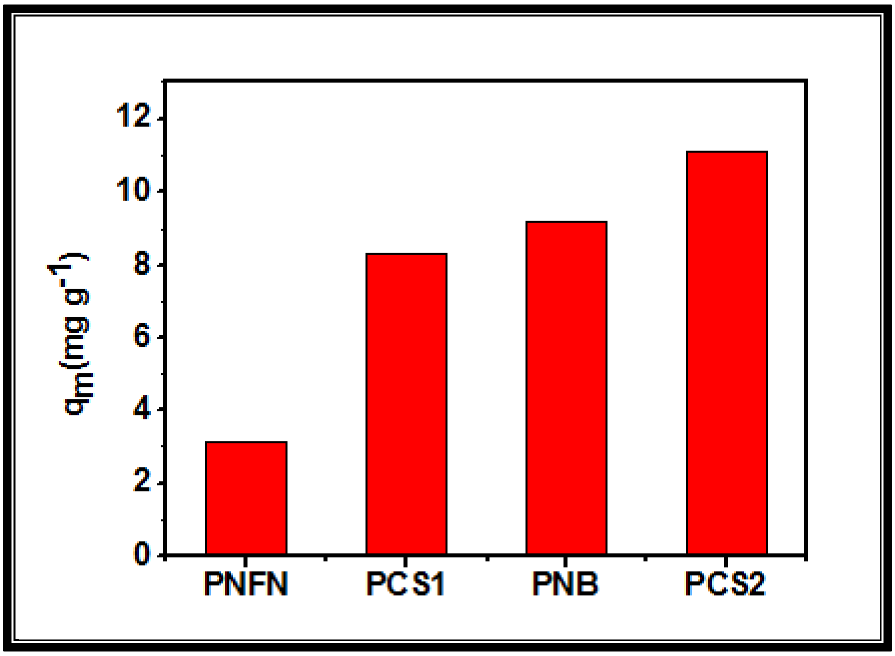

Figure 1.1: Adsorption Capacity of Different Forms of Polyaniline as Adsorbents for Methylene Blue Dye: Polyaniline Nickel Ferrite Nanocomposite (PNFN)[146], Polyaniline Coated Sawdust of wood (PCSD1)[147], Polyaniline Nanotube Base (PNB)[148], Polyaniline Coated Sawdust of walnut (PCSD2)[149].

Table 1.3: Work done by Different Researchers on Polyaniline as Adsorbent.

+

Adsorbent	**Dye Used**	**Adsorption Capacity (q_m)**	**Reference**
Removal of Dyes by Polyaniline			
PANI (Emeraldine Salt)	Indigo Carmine	99mg/g	[144]
Polyaniline Coated Sawdust	Acid Violet 49	192.31mg/g	[150]
p-Toulene Sulfonic Acid (PTSA) and Camphor Sulfonic Acid (CSA) Doped Polyaniline.	Orange G(OG)	0.22mg/g	[151]
Polyaniline Coated Sawdust	Direct Green 6	DG6- 217.39mg/g	[152]

Composite (PAn/SD)	Reactive Orange 16	RO16- 100mg/g	
Starch/Polyaniline Nanocomposite	Reactive Black Reactive Violet	RB-0.818 mmol/g RV- 0.786mmol/g	[153]
Polyaniline-Fe2O3 Magnetic Nano-Composite	Acid Violet 19	0.995mg/g	[154]
Polyaniline/Fe3O4 Nanocomposite	Titan Yellow	50mg/g	[155]
Polyanilline (PANI) Film Coated Sawdust	Methylene Blue	11.2mg/g	[156]
Pani/Al2O3 Composite	Tartrazine	6.25mg/g	[157]
Polyaniline Nanotubes Salt/Silica Composite	Acid Green 25 (AG)	6.896mg/g	[158]
Polyaniline-Montmorrillonite Composite	Congo Red	2.091mg/g	[159]
Nano -Polyaniline	Amido Black 10B	102.04mg/g	[160]
PANI-Mushroom Composite	Eosin Yellow	429.18mg/g	[161]
Removal of Metal Ions by Polyaniline			
Polyaniline/Coconut Shell–Activated Carbon (PANI/GAC) Composite	Cu(II)	38.97mg/g	[162]
Polyaniline/Humic Acid Composite	Hg(II) Cr(VI)	671mg/g -Hg(II) 150mg/g- Cr(VI)	[163]
Polyaniline/ Polystyrene Composite	Hg(II)	0.671 mol/g × 10^6	[164]

Polyaniline (PAn)/ Rice Husk Nanocomposite	Zn(II)	24.3mg/g	[165]
Polyaniline Synthesized on Jute Fiber	Cr(VI)	62.8mg/g	[166]
PANI/Wheat Bran	Cr(VI)	33.44mg/g	[167]
Polyaniline/Polyvinyl Alcohol (PANI/PVA) Composite	Cr(VI)	111.23mg/0.1g	[168]
PANI/ Saw Dust PANI/ Rice Husk	Cd (II)	PANI/ S.D-4.739mg/g PANI/R.H-5.128mg/g	[169]
Sulphuric Acid Doped PANI	Cr(VI)	95.79mg/g	[170]

1.3.1 Polyaniline in Dye Removal

The main driving force for the dye eradication by polyaniline is the interaction of positive fragment of PANI backbone with the dye molecule (negatively charged part) and basic site of PANI with positively charged dye [171]. A successful attempt of the use of polyaniline as adsorbent, as reported in literature, was achieved by the 100% removal of Eriochrome Black T (EBT) dye from its aqueous and methanolic solution by acidic polyaniline and emeraldine base at lower concentration of dye solutions. Adsorption was observed to have followed the first order and data was best fitted in Langmuir isotherm. The adsorption of EBT was found endothermic and entropy dominated. Different parameters such as particle size, adsorbent amount, dye concentration and contact time were reported to have significant effects on the adsorption of dye. Rate constant was evaluated and its value was found to be comparable with the recorded data for the adsorption of Chrome dye onto mixed adsorbent. Even the adsorption of the said polyaniline based adsorbent was found greater than the adsorption of Astrazone Blue dye on peat and Malachite Green dye onto activated slag and carbon. Adsorption from methanolic solution was reported as more endothermic than aqueous solution. It was also observed that the conductivity of PANI changed with adsorption [172]. In an another study, an adsorption of Sulfonated (anionic) dyes on Emeraldine salt (a form of the PANI) had been found to be influenced by the chemical interaction between the adsorbate and the adsorbent molecules. Figure 1.2 represents the variation of adsorption capacity of Congo Red dye by HCl and p-toluene sulphonic acid (PTSA) doped polyaniline (HCl/PTSA doped PANI) and polyaniline/ Chitosan composite (Pn/Ch composite) respectively [173,174-176]. As per the reported literature, this method of removal of anionic (sulfonated) dyes is quite new of its kind. A number of dyes had been used as adsorbate such as Methylene Blue, Coomassie Brilliant Blue R- 250, Orange G, Alizarin Cyanine Green, Remazol Brilliant Blue R and Rhodamine B for clearer prospect. According to the reported work, cationic or non-sulfonated dyes i.e. Methylene Blue and Rhodamine B were less adsorbed by the polyaniline salt, which, evidently indicated that the interaction between dye and PANI were chemical interaction i.e. interaction between the polar groups of sulfonated dyes and positively charged backbone of the PANI [156]. Dye adsorption onto PANI has been confirmed by UV-VIS spectra, in which a blue shift in the peaks had been noticed. Less adsorption had been observed in the case of the emeraldine base for sulfonated dyes. The data has been found to be supported by the Langmuir isotherm and the adsorption was reported to have followed a second order reaction kinetics. Considerable decrease in the conductivity of PANI has been observed after its exposure to the dye solution [177]. In the study of removal of Indigo Carmine dye from its aqueous solution using PANI-ES as an adsorbent, the data had been reported to be fitted well in the Langmuir's isotherm. According to the results of this work, with increased doping (with acid) of the polyaniline (Emeraldine Salt), with increased concentration of the acid, the extent of the positive charge on the PANI backbone is enhanced, which in turn, increase its dye adsorption capacity. Adsorption data of the concerned dye was observed to have followed the pseudo-second-order reaction kinetic [144].

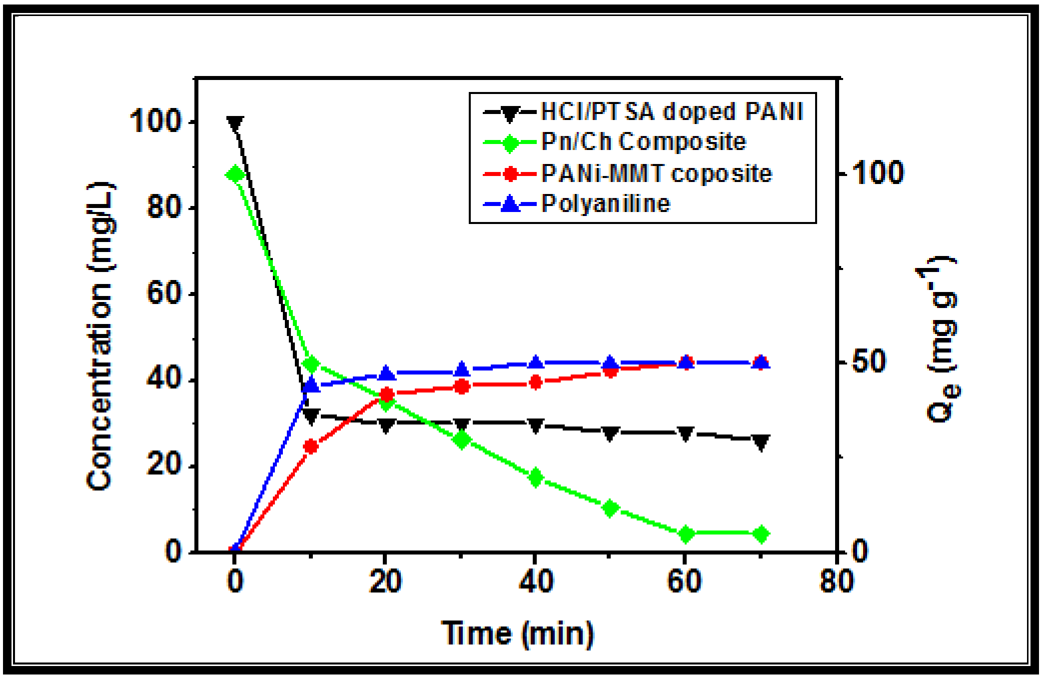

Figure 1.2: Variation in Adsorption of Congo Red Dye by HCl and PTSA Doped Polyaniline (HCl/PTSA doped PANI) [174], Polyaniline/ Chitosan Composite (Pn/Ch Composite) [178], Polyaniline [175] Polyaniline Momtmorrillonite Composite (PANi-MMT Composite) [176].

Some workers doped the PANI by using cheaper and environment friendly Potash Alum and used it for the adsorption of heteropolyaromatic (Methylene Blue), azo (Mordant Yellow-10, Orange-II) and xanthane (Rhodamine-B) dyes. Significant data was obtained for MY-10 and O-II i.e. anionic dyes. However, both MY and O-II dyes followed almost similar adsorption behavior initially, but with the progress of the reaction, more adsorption was observed in case of O-II than MY, as O-II dye was reported to attain a planar structure by intramolecular hydrogen bonding between –OH and –N=N- group. It had also been reported, that, 100 ppm initial dye concentration could be adsorb by using a comparatively lower amount of adsorbent i.e. 80 mg of doped PANI. Adsorption process of MY and O-II dyes on Potash Alum doped PANI had been observed to be endothermic. Adsorption data of both the dyes followed the pseudo-second-order model and supported Langmuir's isotherm model. Subsequent desorption study indicated that percentage of desorption of MY and O-II were 92 and 94% respectively at pH >11, which supported the excellent regenerative capacity of PANI as an adsorbent [179]. Figure 1.3 shows the adsorption of different dyes from the aqueous solution using polyaniline coated sawdust as an adsorbent [150 - 152,156,180]. As per the reported literature, the effect of the dopant was also studied for the adsorption of dyes on p-toulene sulfonic acid (PTSA) doped PANI and camphor sulfonic acid (CSA) doped PANI. A number of dyes were explored such as Methylene Blue, Orange G, Alizarin Cyanin Green, Rhodamine B, Remazol Brilliant Blue R, Malachite Green, and Coomassie Brilliant Blue R-250. The greater adsorption was seen in the case of CSA doped PANI than PTSA doped PANI because of the presence of more counter ions in case of CSA doped polyaniline as compared to PTSA doped PANI, that, increase the distance between the chains and, aided easier diffusion of anionic sulfonated dyes to the positively charged PANI backbone. A change in the conductivity (decrease) of PANI was also observed with adsorption of dyes in both the cases. Pseudo-second-order model described the adsorption behaviour of the dyes and the Langmuir model was fitted well to the adsorption data [181].

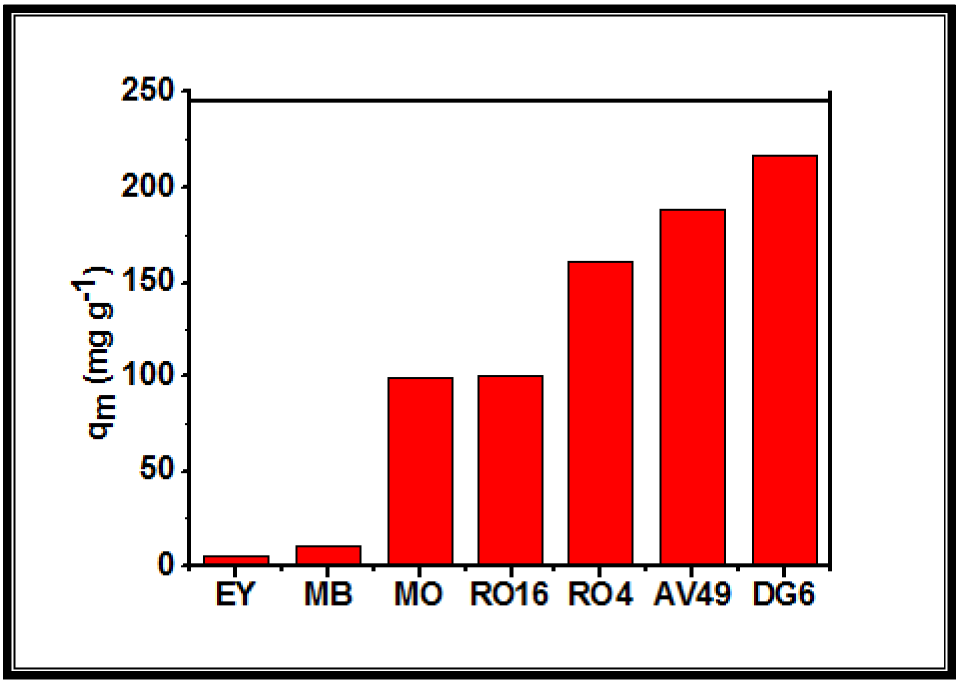

Figure 1.3: Adsorption Capacity of PANI Coated Sawdust for Different Dyes: Eosin Y (EY) [151], Methylene Blue (MB) [156], Methyl Orange (MO), Reactive Orange 16 (RO16) [152], Reactive Orange 4 (RO4) [180], Acid Violet 49 (AV49) [150], Direct Green 6 (DG6) [152].

Some researchers worked to remove Acid Green 25 (AG 25) dye from the effluent of textile industry by using polyaniline coated onto wood sawdust (PAni/SD). The parameters such as, contact time, initial dye concentration, temperature, pH of the test solution, amount of adsorbent dose etc. had been studied, and it was concluded that (PANI/SD) is an efficient adsorbent to remove the AG 25 from the wastewater in both batch and column systems. Moreover, the use of SD was discouraged, being non profitable adsorbent for the water treatment purpose. Adsorption process was observed as spontaneous and endothermic, at room temperature [182]. As per the literature, few researchers worked on the adsorption of Methyl orange (MO) dye from its aqueous solution by using polyaniline coated onto the sawdust (PANI/SD) as adsorbent. The adsorption efficiency of the PANI/SD was compared with the saw dust (without coating; SD) and activated carbon (granulated; GAC) in batch adsorption experiments. It had been observed that, the highest percentage of the adsorption of MO could be achieved at the pH values from 4 to 8. H-bonding existed between the MO and PANI which results into higher adsorption at PANI/SD than SD and GAC at pH= 4-8. Also, the presence of the strong intermolecular interactions between the Methyl Orange dye (diazo groups and imine groups) and the Polyaniline (imine and amino groups) reportedly enhance the percentage removal of the MO. The pseudo-second-order kinetics model was found to be best fitted to the adsorption data for all PANI/SD, GAC, SD. Significant results of this study were that, more than 80% of MO dye was recovered by using 0.1 M HCl solution in case of PANI/SD and nearly 90% of MO was recovered in case of SD by using 0.05 M solution of NaOH, but in case of GAC, only a little amount i.e. about < 5% of dye could be recovered. In another study, Eosin Y (EY) dye was removed by using two conducting polymers i.e. Polypyrrole (PPy) and Polyaniline (PANI), synthesized onto wood sawdust surface. Both column and batch systems were used to perform the adsorption experiments, at room temperature. The adsorption was not found pH dependent for a wide pH range i.e. 2-10, but a decrease in the adsorption had been noticed at the higher pH values (pH ≥12). Efficient removal of dye i.e. 96% was reported from PPy/SD column by using 0.05 M NaOH solution. The higher adsorption of EY (anionic dye) in acidic conditions was reported, which, is to be due to the more concentration of H^+ ions, that developed positive charge on the surface of the adsorbents, PPy/SD and PANI/SD and resulted into more attraction between adsorbate (EY) and adsorbents. But in case of alkaline solution, OH^- ions compete with EY, and a lower adsorption was observed. It has been found that, in addition to electrostatic interaction and H-bonding, ion-exchange reactions also played significant role to remove EY dye from its aqueous solution [151]. Another study conducted on the removal of anionic dye (Acid green 25) by using different adsorbents, such as, Polyaniline NT (nano tube) salt, conventional Polyaniline salt/silica composite and conventional Polyaniline salt. Among these adsorbents, Polyaniline NT salt/silica composite was reported as the best adsorbent and adsorbs comparatively more amount of dye per unit weight. The proposed order of the adsorption capacity of different polyaniline adsorbents was: Polyaniline NT salt/silica composite > Polyaniline NT salt > Conventional Polyaniline NT salt/silica composite > Conventional Polyaniline salt. The observed higher adsorption on Polyaniline NT salt/silica composite as compared to other concerned adsorbents was reported due to its higher surface area and availability of more binding sites. The adsorption was reported to be supported by the intraparticle diffusion and the surface adsorption, simultaneously [183]. The polyaniline doped with poly-acids were also reported for the enhanced removal of both anionic and cationic dyes from the aqueous solutions [184]. A study also reported the magnetically separation of Rh-B dye by using polyaniline-magnetite nanocomposite, synthesized by the swollen liquid crystal templates [158]. The removal of the basic blue dye with polyaniline / Magnetite composite was also reported in the literature. The increase in the surface area and the pore volume were responsible for the enhanced dye removal [186]. Polyaniline/ graphene oxide or polyaniline/ reduced graphene composites were also used for the remediation of Methylene Blue dye containing water [187].

1.4 Significant Findings from Literature

Polyaniline has found to be used by different researchers for the adsorptive removal of dyes and other chemicals from waste water. Originally regarded as a conducting polymer, with its unique properties, polyaniline has shown a potential to be used as an adsorbent. As per the reported studies, polyaniline due to its unique chemical stability, electronic behaviour and improved mechanical properties, is emerging as one of the inceptive adsorbent, especially for the dyes. Being derived from less costly raw materials; simple preparation; and high adsorption and regeneration capacity, polyaniline has shown its potential to be used as an adsorbent on commercial scale. Scientists are trying to explore the newly observed adsorption capacity of the polyaniline in its different forms i.e. acidic (ES) and basic forms of PANI; PANI composites, coating of PANI on different solid substrates, salt form of the PANI, doped PANI etc. In addition to its high surface area, that is modified to be used as adsorbent, its ability of being easy to oxidise or reduce, makes it more attractive for the selective removal of different charged moieties from the effluent. In the nutshell, polyaniline (PANI) and its derivatives have the calibre to replace the commercially available adsorbents with its unique properties, and excellent adsorptive and regeneration capacity.

1.5 Research Gaps

Although, different techniques have been used for the effluent water treatment to achieve the targeted separation, but these techniques also have some demerits, for e.g., incapability of treating large volumes, expensive, high pressures (membrane separation method),high sludge production, handling and disposal problems (Flocculation-Coagulation process), low decolourisation rate, generation of toxic substances, requirement of post treatment (Biological methods), high cost, expensive regeneration process, non-selectivity, more efforts to recover from waste products i.e. regeneration (Adsorption onto activated carbon).

During the last decades, a lot of studies on the dye adsorption by various non conventional adsorbents such as algae, fungi, industrial wastes, clays, polymers, metal oxides, composites, agricultural wastes etc. have been undertaken, in order to find out an alternate to the costly conventional adsorbent. The studies showed that the various adsorbents developed from the different origins, either organic or inorganic, show little or poor sorption potential for the removal of dyes as compared to commercial activated carbon, which also suffers from the difficulty of effective regeneration and higher production cost. Therefore, the search to develop an efficient adsorbents is still going on. Considering all these limitations, and operational difficulties, it has been observed that there is a need of an effective adsorbent with characteristics, such as low cost, good environmental stability, high surface area, easy to synthesise and regenerate. Polyaniline, a well known polymer, with its unique physicochemical nature and found to exhibit all these desired properties, seems to be a potential candidate to be used as an adsorbent for dye removal, from the wastewater. A very few studies, as reported from the literature also supported the idea.

Moreover, phytic acid (PA) doped polyaniline was not used by any researcher for the adsorptive removal of any dye from its aqueous solution. The PANI doped with PA seemed to be more effective adsorbent for basic dye (cationic dye) removal, because PA acid consolidated as anion to the backbone of PANI structure, during its in situ synthesis (polymerization of aniline). Doping with PA, not only modify the surface properties of PANI nanofibers, but it also interact with the dye molecules during the adsorptive removal of the same. The reaction between PA and PANI occurred via phosphate carboxyl group, preferably at the quinoid site of PANI backbone. Basically, during doping with PA, the nitrogen group of PANI got protonated to form doped PANI.

From the intensive literature studies on polyaniline as an adsorbent, it has been observed that:

1. In most of the studies, polyaniline is used in combination with other organic adsorbents, either as composite or as a film on some organic substrate. A very little adsorption studies have been carried out on the polyaniline in the direct state as received after synthesis.
2. No study has reported the use of nano-structured polyaniline (Nanofibers) as an adsorbent.
3. A very little studies have revealed the use of doped polyaniline as adsorbent for specific dyes.
4. No literature revealed the use of phytic acid doped polyaniline for the removal of any dye.

1.6 Research Objectives

The aim of this research work was **to conduct studies on polyaniline as adsorbent for dye removal.** Considering special properties of polyaniline, mainly due to extremely high surface to weight ratio, low density, large surface area to mass and high pore volume compared to conventional polymer and keeping in view that the properties of materials at the nanoscale are distinctly different from the bulk, the emphasis of the present studies is on the synthesis and exploration of the nano-stuctured polyaniline i.e. polyaniline nanofibers; as well as its modified form i.e. Phytic acid doped PANI nanofibers for the adsorption of anionic and cationic dyes. Broadly, I summarize my objectives of the research programme as:

1. Synthesis of polyaniline nanofiibers by using interfacial polymerization method and their characterization by using different techniques.
2. Adsorptive studies on the removal of anionic dye (methyl orange) and cationic dye (methylene blue) by using the emeraldine salt form of the polyaniline nanofibers.
3. Adsorption of cationic dye (methylene blue) by using the emeraldine base form of the polyaniline nanofibers.
4. Structural modification of polyaniline nanofibers by doping with phytic acid and studies on the adsorption of cationic dye (methylene blue) onto phytic acid doped polyaniline nanofibers.
5. Regeneration of the exhausted polyaniline using different solvents

1.7 Overview of the Thesis:

The objective of this thesis is to study the polyaniline as adsorbent for dye removal. The whole thesis is organized in SEVEN chapters. The **Chapter 1**of the thesis covers a comprehensive review on the pollution problems raised due to dyes and the utilization of polyaniline as adsorbent. The gaps in the already available literature have been discussed and the specific objectives to carry out this research work have been highlighted. The **Chapter 2** elaborates the experimental part which includes, the synthesis of emeraldine salt, emeraldine base and phytic acid doped polyaniline. The various characterization techniques used to characterize the synthesized adsorbent have also been discussed in this chapter. The **Chapter 3** deals with the removal of MO (anionic dye) by using emeraldine salt form of the polyaniline. This chapter explains the effects of different adsorption parameters, suitability of kinetic and isotherm models to the adsorption data. **Chapter 4** is about the studies conducted on the removal of cationic dye i.e. methylene blue dye (MB) by using the salt form of polyaniline. This chapter explains the kinetic and isotherm studies of the MB dye removal by nano-structured emeraldine salt. **Chapter 5** deals with the removal of methylene blue dye by using base form of the polyaniline nanofibers. The justification for the difference between percentage adsorption of dye with the nano-structured salt and base forms of the polyaniline has also been included. **Chapter 6** reveals the process of synthesis and characterization of the modified polyaniline nanofibers via the doping with phytic acid. The adsorptive studies of cationic dye (Methylene Blue) onto the phytic acid doped polyaniline nanofibers have been reported here. Lastly, Conclusion and future prospect of the study are included in the **Chapter 7,** which is followed by the **References**.

CHAPTER 2

MATERIALS AND METHODS

2.1 Raw Materials/Chemicals

The raw materials/ chemicals which were used for the preparation of nanostructured polyaniline and adsorption studies of dyes are listed below:

1. Aniline
2. Ammonium Persulphate
3. HCl
4. Toulene
5. Phytic Acid
6. Ethanol
7. Sodium Hydroxide
8. Ammonia
9. Methyl Orange Dye
10. Methylene Blue Dye

2.1.1 Specification and Sources of Raw Materials/Chemicals

Specification and sources of the raw materials and chemicals used to prepare polyaniline and their characterization is given in Table 2.1.

Table 2.1 Specification and Sources of Raw Materials/Chemicals

S. No.	Chemical	Sources	Specification
1.	Aniline	Sigma-Aldrich Inc., USA	AR Grade
2.	Ammonium Persulphate	Sigma-Aldrich Inc., USA	AR Grade
3.	HCl	Rankem India Pvt. Ltd, Gurugram	AR Grade
4.	Toulene	Central Drug House (P) Ltd, Delhi	AR Grade
5.	Phytic Acid	TCI Chemicals (India) Pvt. Ltd.	50% in Water
6.	Ethanol	Chang Yu Hi-Tech Chemicals, China	AR Grade
7.	Sodium Hydroxide	Central Drug House (P) Ltd, Delhi	AR Grade
8.	Ammonia	Thermo Fischer Scientific India Pvt. Ltd, Mumbai	AR Grade
9.	Methyl Orange Dye	Central Drug House (P) Ltd, Delhi	AR Grade
10.	Methylene Blue Dye	Central Drug House (P) Ltd, Delhi	AR Grade

2.1.2 Purity of Raw Materials/ Chemicals

The accuracy of the results depends not only on the accuracy of the instrument used or experiment performed, but also on the purity of the raw material used. The percentage purity of the raw materials/ chemicals is given in the Table 2.2.

Table 2.2 Purity of Raw Materials/ Chemicals

S. No.	**Raw Material/Chemical**	**Percentage Purity**
1.	Aniline	≥ 99.5%
2.	Ammonium persulphate	≥ 98%
3.	HCl	36.5-38% (w/w)
4.	Toulene	≥ 98%
5.	Phytic Acid	50% (w/w)
6.	Ethanol	≥ 99.9%
7.	Sodium Hydroxide	≥ 98%
8.	Ammonia	25-30% (w/w)
9.	Methyl Orange Dye	≥99%,
10.	Methylene Blue Dye	≥ 99%

2.2 Research Methodology

The methodology employed to achieve the objectives of the research is divided into the following sections:

- ✓ Synthesis of polyaniline nanofibers (salt and base form) by using interfacial polymerization method
- ✓ Synthesis of structurally modified polaniline nanofibers by doping with phytic acid.
- ✓ Characterization of synthesized (salt, base and doped) polyaniline nanofibers.

- ✓ Adsorption studies (batch adsorption, kinetic studies and isotherm studies) of anionic and cationic dyes onto salt, base & doped forms of polyaniline nanofibers and optimization of different adsorption parameters i.e. contact time, initial dye concentration and pH.
- ✓ Desorption studies to regenerate the exploited adsorbent.

2.2.1 Synthesis of Polyaniline Nanofibers (Salt and Base Form) by Using Interfacial Polymerization Method

A simple approach was used to synthesize polyaniline nanofibers with high yield via oxidative polymerization reaction. The nterfacial polymerization method [188], instead of conventional polymerization technique was employed for the synthesis of polyaniline nanofibers in bulk quantities. It is a simple unstirred polymerization in an acid-aqueous solution without the aid of additives. In brief, 0.32 mol of the monomer (aniline) was dissolved in the toluene (organic solvent) in a beaker, to prepare the organic phase. 0.08 mol of ammonium persulphate (APS; oxidant) was dissolved in a 1M HCl aqueous solution, in an another beaker to form aqueous phase. APS solution was then added dropwise to the organic phase within a specific period of time. After mixing of these two solutions (phases), pure nanofibers were formed at the interface of this biphasic system. The reaction mixture was kept unruffled for next 20 h, then was filtered and washed with distilled water several times. The synthesized adsorbent is the salt form of the polyaniline. To obtain the base form of polyaniline, the reaction mixture was treated with 1M ammonia. The blue coloured compound, thus, obtained was dried at 60^{o} C for 24 h. Polyaniline nanofibers base (PNb) in the powder form was obtained.

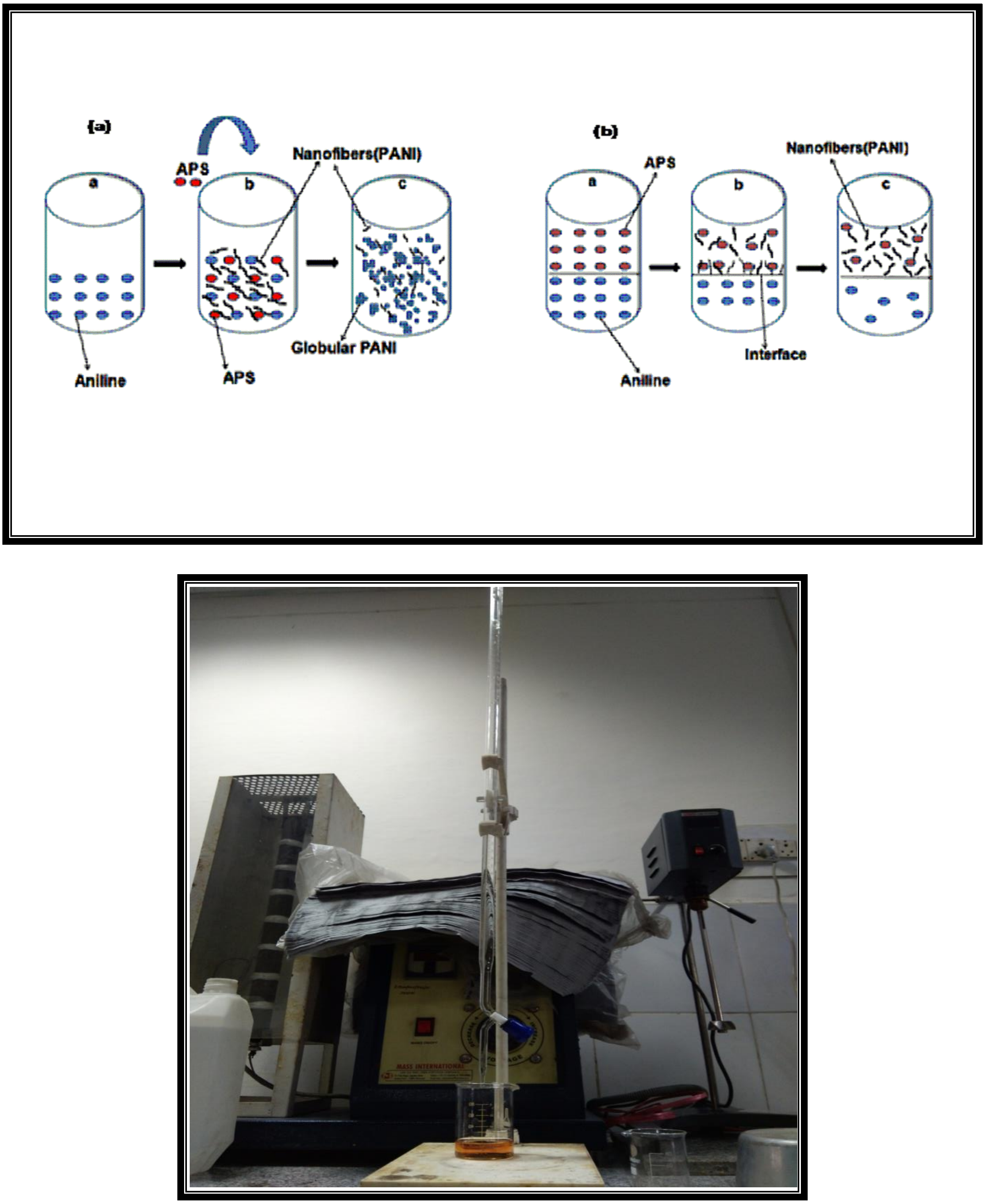

Figure 2.1: (a) Synthesis of Polyaniline Agglomerates by Conventional Method using 1M HCl Solution; (b) Synthesis of Nanofibers by Interfacial Polymerisation Method using 1M HCl as Aqueous Layer and Toluene as Organic Layer[188]; and (c) Experimental Set –Up of Polyaniline Nanofibers Synthesis in Laboratory.

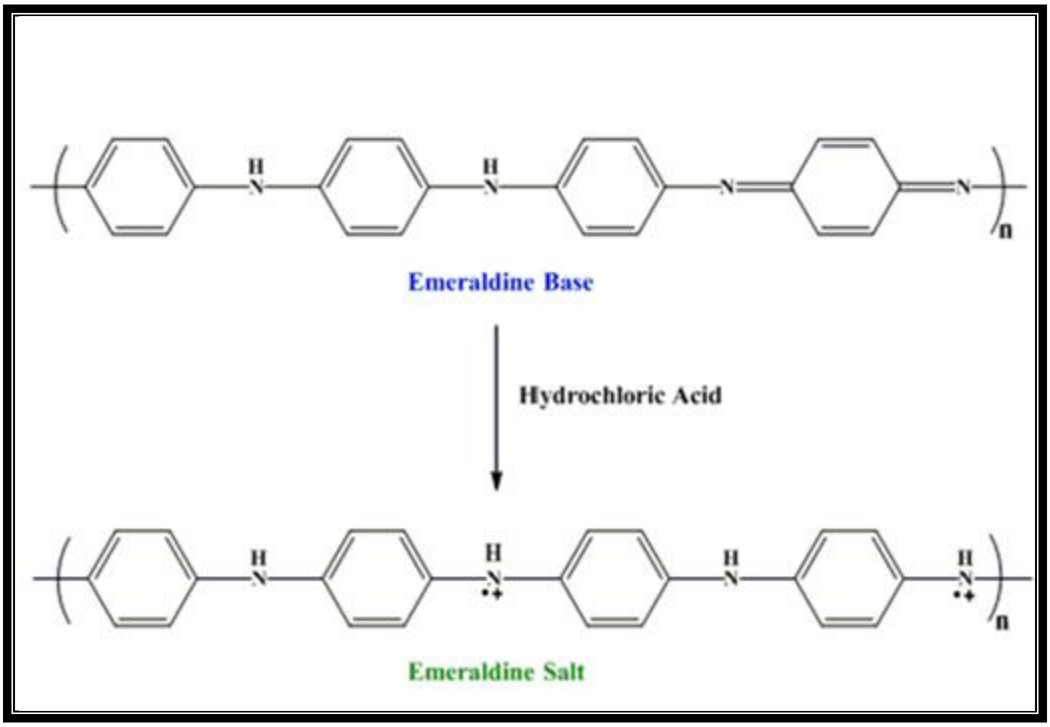

Figure 2.2: Chemical Structure of Polyaniline (Emeraldine Base) and Transformation to a Conductive Salt by Prototonation in an Acid Medium.

2.2.2 Synthesis of Structurally Modified Polyaniline Nanofibers by Doping with Phytic Acid

Structural modification of the PANI nanofibers has been carried out using pythic acid (PA). A 50 wt % solution of phytic acid was used for the synthesis of PA doped PANI nanofibers by oxidative polymerization of aniline (monomers). In brief, the solution-I was prepared by dissolving 0.46 mL phytic acid (dopant) and 0.45 mL aniline (monomer) in 2 mL of distilled water and the solution-II was prepared by dissolving 0.285 g of APS into 1 mL of distilled water. Then solution-II was added to the solution-I and the mixture was agitated for a period of 1 minute. As reaction (polymerization) proceeded, a noticeable change in colour of the solution (from brown to dark green) was observed. The reaction mixture was then kept undisturbed at 4^0C for 24 h, and washed with distilled water several times and dried in oven at 60^0C for 24 h to obtain powdered PA doped PANI nanofibers.

2.2.3 Characterization of Synthesized (salt, base &doped) Polyaniline Nanofibers.

The synthesized (salt, base & doped) polyaniline nanofibers were characterized by using different techniques such SEM, HRTEM, FTIR, XRD, BET, ZETA potential etc.

2.2.3.1 SEM Analysis

Scanning Electron Microscope (SEM) (S-3700N; Hitachi, Japan) was used to examine the morphology and texture of the resulted polyaniline. The samples were gold-sputter coated to render them electrically conductive and then scanned at an accelerating voltage of 15 kV. Image processing was conducted by using in-built software SEM data manager of Hitachi PC-SEMs.

Figure 2.3: Scanning Electron Microscope (Hitachi S-3700N)

2.2.3.2 TEM Analysis

The size of the synthesized adsorbent was characterized by TEM (Transmission Electron

Microscopy). Dispersed (in ethanol) PANI samples were transferred to a copper grid and imaging was carried out on F 30 S twin 300 HRTEM at 300 kV.

Figure 2.4: Transmission Electron Microscope

2.2.3.3 FTIR Analysis

Nicolet 380 FT-IR spectrophotometer was used to obtain the FTIR spectra of the synthesized adsorbent (polyaniline) within 400-4000 cm^{-1} region at room temperature by preparing KBr pellet.

Figure 2.5: FTIR (Nicolet 380) Spectrometer

2.2.3.4 XRD Analysis

X-ray diffraction (XRD) patterns of PANI powder were obtained by using BRUKER D8 ADVANCE diffractometer by employing CuKα (Kα –1.54056 Å) radiation. The diffractometer study was conducted at 40mA and 40 kV. The scanning step was 0.02^0 in 2θ with a dwell period of 0.5s per step.

Figure 2.6: X-Ray Diffractometer (BRUKER D8 ADVANCE)

2.2.3.5 BET Analysis

Surface area analyzer (Micromeritics ASAP 2010) was used to determine the BET surface area of the prepared polyaniline.

2.2.3.6 ZETA Potential Analysis

The Zeta potential measurement of the synthesized PANI nanofibers (ethanol dispersion) was carried out by using Malvern Zetameter.

2.2.3.7 Electrical Conductivity Analysis

Four point probe technique with digital micro voltmeter (DMV-00), low current source (LCS-02) and PID controlled oven (PID-200) was used to measure the electrical conductivity of the polyaniline sample (in pellet form) at room temperature.

Figure 2.7: Four Probe Digital Conductivity Meter

2.2.3.8 XPS Analysis

XPS analysis was done by using PHI 5000 Versa Probe III to determine the composition of prepared adsorbent.

2.2.3.9 UV – Visible Analysis

Agilent Technologies Carry Series UV-Vis spectrophotometer was used to study the adsorption of dye on polyaniline within 200 – 800 nm region of wavelength.

Figure 2.8: UV – Vis Spectrophotometer (Agilent Technologies Carry Series)

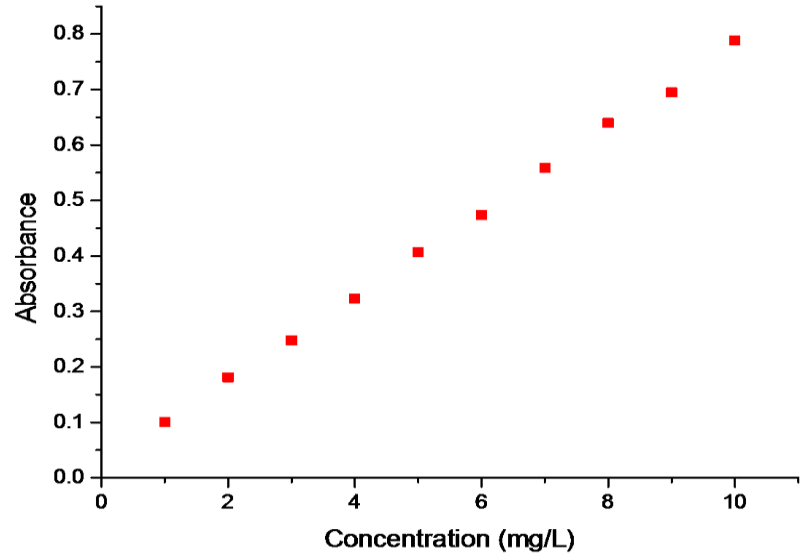

Figure 2.9: Calibration Curve of Methyl Orange Dye

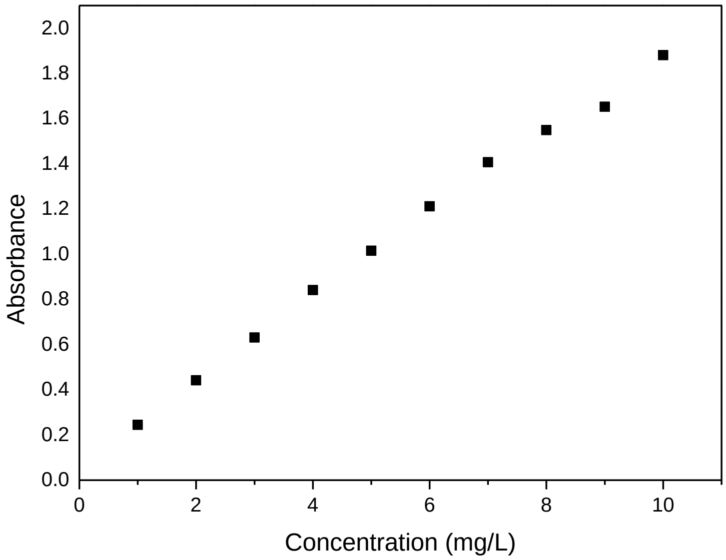

Figure 2.10: Calibration Curve of Methylene Blue Dye

2.2.4 Adsorption studies (batch adsorption, kinetic studies and isotherm studies) of anionic and cationic dyes onto salt, base & doped forms of polyaniline nanofibers and optimization of different adsorption parameters i.e. contact time, initial dye concentration and pH.

2.2.4.1 Batch Adsorption Studies

An apropos amount of dye was dissolved in distilled water to prepare the stock solution for the experiments. Further, different concentration solutions, as needed, were prepared by diluting the stock solution with distilled water. The adsorption experiment was performed by agitating the appropriate amount of the adsorbent with a definite volume of dye solution in a shaker incubator, at a fixed speed, for a fixed interval of time. Then the reaction mixture was centrifuged at 6000 rpm for 15 minutes. The un-adsorbed dye was estimated by using UV- Visible spectroscopy at suitable maximum wavelength. Prior to testing, the standard solutions of dye were used for the calibration of the UV-Visible spectrophotometer.

Analogous absorption for the individual concentrations was obtained at λ_{max} of dye. By plotting the data between concentration and absorbance, a linear regression curve was obtained. The following equations were used to calculate the adsorption capacity and adsorbed percentage of dye onto polyaniline respectively:

$$Q = \frac{(C_o - C_e)V}{m} \tag{2.1}$$

$$\%A = \frac{C_o - C_e}{m} \times 100\% \tag{2.2}$$

where, Q (mg/g) is the adsorption capacity, C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), V (L) is the volume of the solution used and m (g) is the mass of adsorbent used.

2.2.4.2 Kinetic Studies

While designing any adsorption system, the determination of the rate of the reaction is the most important step. The rate expression of any reaction is derived from the kinetic study of the reaction system. Analysis of the experimental data for an adsorption process can be carried out by using different available rate models such as a) Pseudo- first order model, b) Pseudo- second order model, and c) Intraparticle diffusion model to depict the experimental data. In detail:

2.2.4.2.1 Pseudo-First-Order Model:

The linearized form of the Lagergrane pseudo-first-order model [189] is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2.3}$$

Where,

q_t = adsorption capacity at time, t (mg/g)

q_e = adsorption capacity at equilibrium (mg/g)

k_1 = the rate constant of adsorption (1/min)

and, t = contact time (min).

A plot of log (q_e−q_t) versus t gives a straight line with slope equal to k_1 and intercept equal to q_e respectively.

2.2.4.2.2 *Pseudo-Second-Order Model:*

The linearized form of the Lagergren pseudo-second-order model [189] is as below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2.4)$$

Where,

q_t = adsorption capacity at time, t (mg/g)

q_e = adsorption capacity at equilibrium (mg/g)

k_2 = second order adsorption rate constant, (g /mg/ min)

$k_2 q_e^2$=h i.e. the initial rate constant (cat t→0), (mg/ g /min)

and t = contact time (min).

A plot of t/q_t versus t gives a straight line with slope equal to q_e and intercept equal to $k_2 q_e^2$ respectively.

2.2.4.2.3 *Intraparticle Diffusion Model:*

According to this model, the adsorption takes place in many steps such as:

1. Transport of adsorbate molecules from the bulk aqueous phase to the surface of the adsorbent.
2. Transfer of adsorbate molecules from the surface of the solid adsorbent into the interior of the pores.

As reported in literature, in the adsorption process that follows intraparticle diffusion, the adsorption occurs in proportional with $t^{1/2}$. The intraparticle diffusion model is expressed by the following equation [190]:

$$q_t = k_{id} t^{0.5} \tag{2.5}$$

Where,

q_t =adsorption capacity at time t (mg/g)

$t^{0.5}$ = Half-life period/time (min)

and, k_{id} = rate constant of intra-particle diffusion (mg/g $min^{0.5}$)

A plot of q_t versus $t^{0.5}$ gives a straight line with slope equal to k_{id}. To determine the rate of adsorption, the experimental data obtained is tested for all the available models. The best fit rate equation is determined on the basis of the linear regression correlation coefficient values i.e. R^2 value obtained. The higher value of R^2 is the indication of good fit.

2.2.4.3 Isotherm Studies

The interactions between adsorbate and adsorbent can be well described by the adsorption isotherms. Various isotherm models were proposed in past to explain the adsorption behavior of different adsorbents [191]. The mechanism of the adsorption can be studied by fitting the experimental data in different types of already established isotherm models, and the interactions between the surface of the adsorbent & adsorbate particles and the nature of the adsorption i. e. multilyered or monolayer adsorption can be predicted. In addition, the removal capacity of any adsorbent can be measured to some extent by adsorption isotherms. Among all these models, Langmuir and Freundlich isotherm models are extensively used to explain the adsorption behavior of any dye onto an adsorbent.

2.2.4.3.1 Langmuir Isotherm Model:

The Langmuir isotherm model is found to be best fitted when monolayer adsorption has been taken place. It is based on the assumption that, the adsorption takes place at specific homogeneous sites within the adsorbent, forming a single layer over the adsorbent surface. The Langmuir's isotherm is governed by the following equation [192]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \tag{2.6}$$

Where,

C_e = Concentration of dye adsorbed at equilibrium (mol/L)

q_e = Amount of dye adsorbed at equilibrium (mg/g)

q_m = Langmuir monolayer adsorption of dye (mg/g)

and b = Langmuir's constant

On plotting C_e/q_e versus. C_e, a straight line is obtained, with slope equal to q_m and intercept equal to b respectively.

The separation factor, R_L (dimensionless) can be determined by following expression:

$$R_L = \frac{1}{1 + bC_0} \tag{2.7}$$

Where,

C_0 =Initial dye concentration.

The recommended value of R_L, for the favourable adsorption lies between 0 and 1.

2.2.4.3.2 Freundlich Isotherm Model:

Similar to the Langmuir model, the Freundlich Isotherm model is also based upon the assumption of monolayer adsorption. It is best fitted for an adsorption on the heterogeneous surface having unequal active sites and different energies of adsorption. The linearized equation for the Freundlich isotherm model [193] is given as:

$$\log q_e = \log K_f + n_h \log C_e \tag{2.8}$$

Where,

q_e = Amount of dye adsorbed at equilibrium (mg/g)

C_e = Concentration of dye adsorbed at equilibrium (mol/L)

K_f and n_h are the Freundlich coefficients.

A plot of log q_e versus log C_e gives a straight line with slope equal to n_h and intercept equal to K_f respectively.

2.2.4.4 Optimization of different adsorption parameters i.e. contact time, initial dye concentration and pH.

The effects of different adsorption parameters have been studied for the adsorptive removal of dyes onto polyaniline during this study.

2.2.4.4.1 Effects of Contact Time

The effect of contact time can be studied by keeping all other parameters constant and varying the time of the reaction for a fixed period.

2.2.4.4.2 Effects of Initial Dye Concentration

The effect of initial dye concentration on adsorption can be studied by varying the concentration of the dye within a suitable range and keeping all other parameters constant.

2.2.4.4.3 Effects of pH

The effect of pH of solution on dye removal can be studied by varying the pH of the reaction mixture from 2-11 and keeping all other adsorption parameters at constant value.

2.2.5 Desorption Studies to Regenerate the Exploited Adsorbent.

Desorption of dyes from the exhausted adsorbent was also carried out by using different solvents such as: water, 0.1 M NaOH, 0.1 M HCl and 95% Ethanol solution. Batch experiment was used to perform this reaction. In brief, a specific amount of the dye loaded polyaniline was treated with a fixed volume of the above solvent in shaker incubator for a specific period of time and then centrifuges the reaction mixture at 6000 rpm for 15 minutes. Analysis of supernatant gave the estimation of recovered dye.

CHAPTER 3

STUDIES ON THE REMOVAL OF METHYL ORANGE (ANIONIC DYE) BY USING POLYANILINE NANOFIBER SALT

The aim of this study is to utilize the salt form of polyaniline nanofibers (PANI nanofibers) to remove an anionic dye i.e .methyl orange (MO), from its aqueous solution. The emeraldine salt (a form of polyaniline) was synthesized by interfacial polymerization method directly. During the synthesis, the insulating form of polyaniline i.e. emeraldine base can be easily converted into a conducting form (emeraldine salt) by simple protonation in the presence of an acid, which generates a positive charge on the backbone of polyaniline. The effects of important adsorption parameters such as contact time, pH and initial dye concentration have been studied. Reaction kinetics is investigated by using different kinetic models. Different isotherms are used to analyze the experimental adsorption data. Chemical structure of methyl orange dye is shown in Figure 3.1.

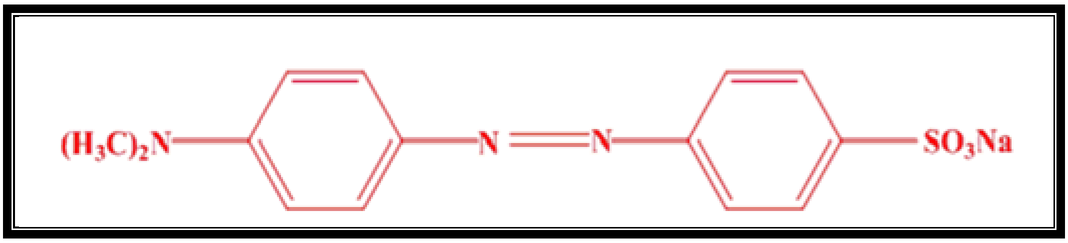

Figure 3.1. Molecular Structure of Methylene Blue Dye.

3.1 Synthesis of Polyaniline Nanofibers (PANI Nanofibers)

PANI nanofibers were synthesised by interfacial polymerisation method using a biphasic system constituting of organic phase (aniline in toluene) and aqueous phase (ammonium persulphate (APS) in aqueous HCl solution). The molar ratio of the aniline to APS taken was 4:1 and maintained throughout the reaction. The obtained emeraldine salt was characterised for its size, surface area, morphology and structure prior to be used as adsorbent.

3.2 Batch Adsorption Studies

Stock solution of known concentration was prepared by dissolving methyl orange (MO) dye in double distilled water. The desired solutions of different concentration were prepared by diluting this stock solution. Batch mode adsorption experiment was performed by agitating 50 mg (0.05 g) of adsorbent with 100 mL of dye solution in a shaker incubator at a speed of 250 rpm. After a specified period of time, the mixture was withdrawn and centrifuged at 6000 rpm for 15 minutes. The un-adsorbed amount of dye was estimated at 463 nm by analysing the supernatant liquid using UV- visible spectrophotometer (Agilent Technologies Carry Series), at room temperature. The UV-Visible spectrophotometer was calibrated prior to use with the help of standard solutions of MO dye. Analogous absorption for individual concentrations was obtained at λ_{max} 463 nm. By plotting the data between concentration and absorbance, a linear regression curve was obtained. The following equation was used to calculate the adsorbed amounts of methyl orange on PANI nanofibers:

$$q = \frac{(C_o - C_e)V}{m} \tag{3.1}$$

Where, q (mg/g) is the amount of MO dye adsorbed onto unit weight of the adsorbent, C_o is the initial dye concentration (mg/L), C_e is the dyeconcentration at equilibrium (mg/L), V (L) is the volume of the solution used during experiment and m (g) is the mass of the adsorbent used.

3.3 Results and Discussion

3.3.1 Structural Characterization of PANI Nanofibers

3.3.1.1 FTIR

Figure 3.2 shows the main characteristic peaks of FTIR spectra of polyaniline (emeraldine salt). The peak obtained at 3250 cm^{-1}represents the N-H stretching of the structure [194]. The absorption band at 2933cm^{-1} is due to the asymmetric stretching mode of C-H aromatic bond [195]. The peak at 1561 cm^{-1}and 1485 is attributed to the quinoid and benzenoid ring structure within the sample [196]. The C-N stretching of the secondary amines is confirmed by the peak at 1286 cm^{-1}. Absorption band observed at 1073 cm^{-1} is due to the C-H bending vibration. The absorption band lies at 690 $cm^{-1}$is attributed to 1, 4 di-substituted benzene [197].

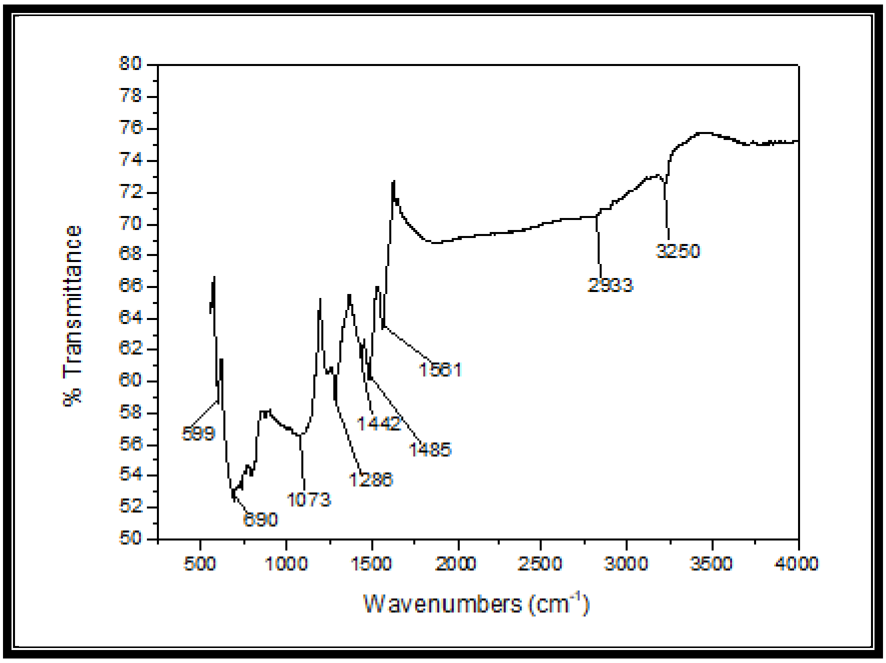

Figure 3.2: FTIR Spectrum of Polyaniline Salt

3.3.1.2 XRD

The X- ray diffraction pattern (at room temperature) of the synthesized polyaniline nanofibers (Figure 3.3) shows three different peaks (about $2\theta = 11.5^0$, 17.9^0 and 24^0). The peaks, at about 17.9^0 and 24^0 are due to periodicity parallel and perpendicular to the main chain of the adsorbent respectively and the broad peak at about $11.5^0$is attributed to the scattering from the parallel orientation of the polymer chain. Debye Scherer equation (as given below) was used to calculate the crystal size of the polyaniline.

$$D = \frac{K\lambda}{(\beta cos\theta)} \tag{3.2}$$

Where β is FWHM i.e. full width half maximum and k is Bragg's constant (0.9). According to the observed peaks (due to quinonoid and benzenoid groups) in XRD pattern, PANI nanofibers are dominantly amorphous in nature. However, a smaller crystalline part was also recorded by measuring the crystallinity degree (%) of the sample. The percentage crystallinity of the PANI nanofibers is observed to be 29% (measured by using X' Pert Highscore, version 2.1 software)with a crystal size of 3.81 nm. The similar studies were also carried out by Morsi and Elsabee [198].

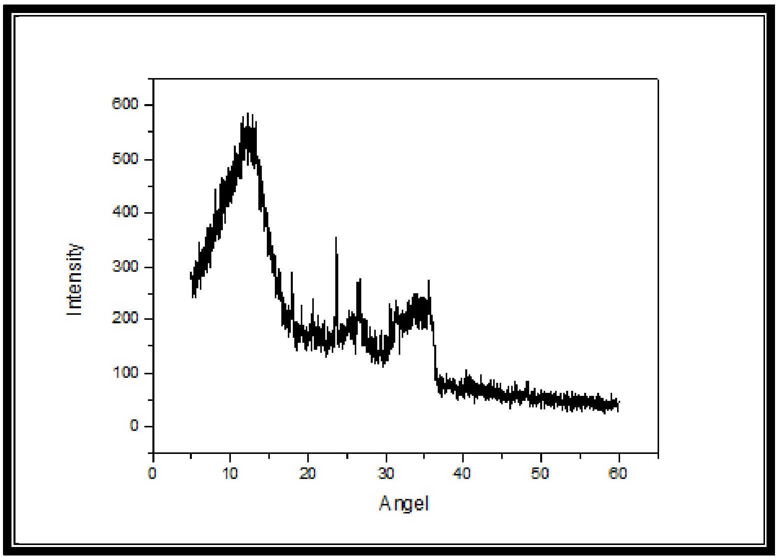

Figure 3.3: X-ray Diffraction Pattern of Polyaniline Nanofibers at Room Temperature.

3.3.2 Morphology

3.3.2.1 SEM, HRTEM and SAED Studies

The results of the scanning electron microscopy (SEM) (Figure 3.4a and 3.4b) shows the surface morphology of the polyaniline synthesized by the conventional and the interfacial polymerization methods respectively. Conventionally synthesized polyaniline results into agglomerates (because of the secondary growth of synthesized nanofibers), but the pure nanofibers are obtained in case of the interfacial polymerization method due to suppression of secondary growth in biphasic system. The average diameter of the synthesized PANI nanofibers was found to be 60 nm. The above results are in synchronization with the reported work on synthesis of PANI nanofibers i.e. 30-60 nm [199] and 50-80 nm [196] by interfacial polymerization. The fibrous nature of the polyaniline was also confirmed by HRTEM analysis (Figure 3.4 c). The HRTEM image shows the nano-range structure of polyaniline with a rough surface. The selected area electron diffraction (SAED) pattern of the synthesised PANI nanofibers (Figure 3.4 d) displays their composition. As clear from the Figure 3.4 d, many small-sized PANI nanocrystals are present in the polyaniline nanofiber which confirms its polycrystalline structure. Figure 3.4e shows the SEM analysis of the PANI nanofibers after adsorption. It is clear from the Figure 3.4e that, the diameter of the PANI nanofibers got increased, post adsorption of MO dye.This increase in diameter of the nanofibers post adsorption is attributed to the attachment of dye molecules to the backbone of polyaniline nanofibers due to the electrostatic interaction between dye molecules and the surface of the adsorbent.

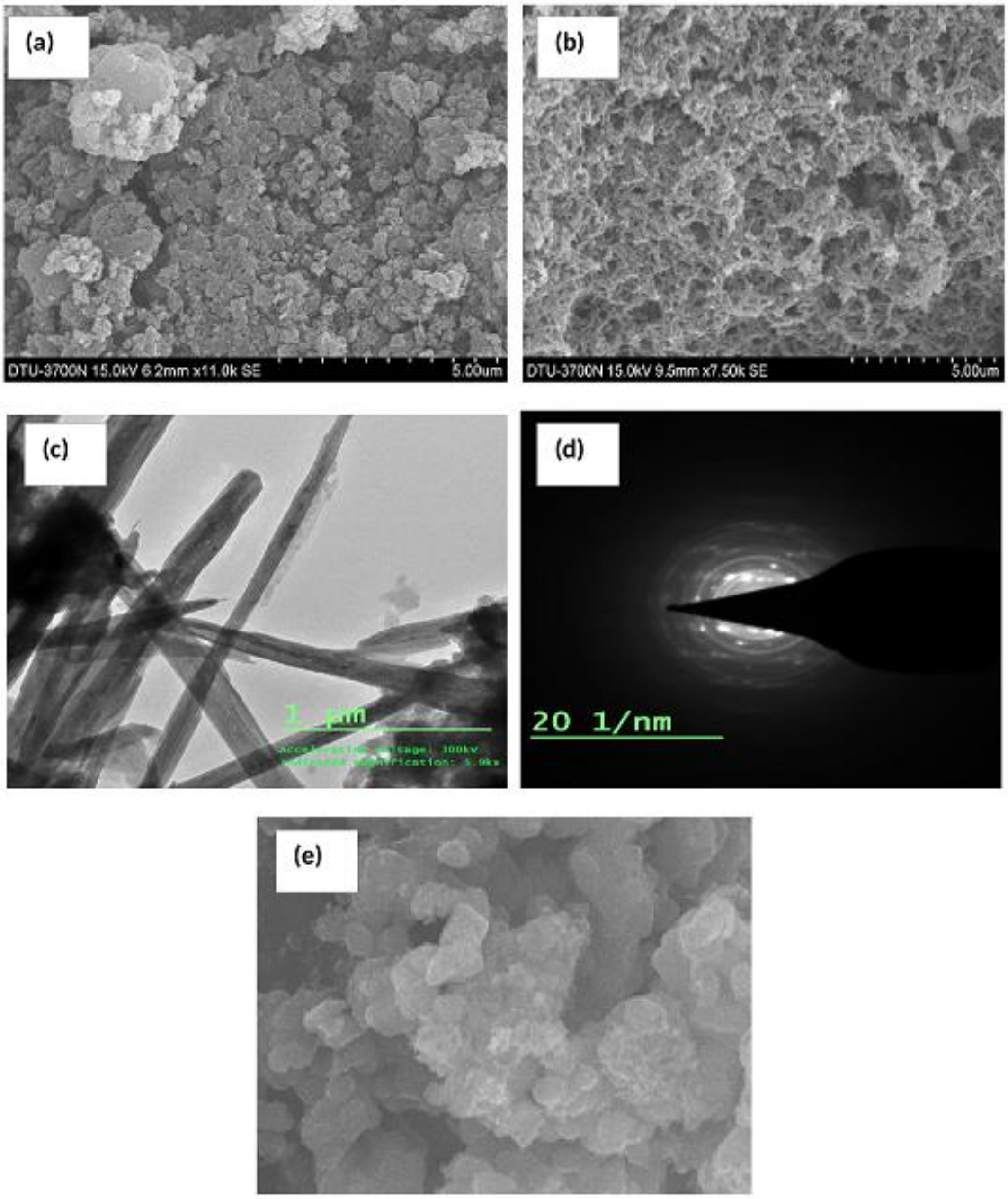

Figure 3.4: Structural Studies of Polyaniline:(a) SEM of Conventionally Synthesized Polyaniline, (b) SEM of Polyaniline Synthesized by Interfacial Polymerization Method, (c) HRTEM of Polyaniline Nanofibers, (d) SAED Pattern and (e) SEM Image of Polyaniline Nanofibers (synthesized by interfacial polymerization) Loaded with Methyl Orange Dye after Adsorption.

3.3.2.2 BET Analysis

BET surface area of the synthesised PANI nanofibers was obtained by using surface area analyzer. As expected, the BET surface area of the nanostructured polyaniline (48.83 m^2 /g) is much more (nearly 4 times) than that of conventionally synthesized polyaniline powder (13.65 m2/g).The higher surface area of the nanostructured polyaniline is due to smaller diameter of the nanofibers(inverse relationship between diameter and surface area of nano materials), which is not in the case of the conventionally synthesized polyaniline. This enhanced surface area of the adsorbent, i.e. PANI nanofibers is responsible for increased adsorption capacity of the PANI nanofibers in addition to the electrostatic forces of attraction between the positively charged backbone of polyaniline and negative group on the dye molecules.

3.3.2.3 ZETA Potential Analysis

The Zeta potential measurement of the synthesized PANI nanofibers (ethanol dispersion) was carried out by using Malvern Zetameter (Figure 3.5). It has been noticed that the adsorbent (PANI nanofibers) possesses positive charge on its surface with positive value of zeta potential equal to10.1 ± 2.96 mV. This result is also supported by the reported literature **[**200**].**

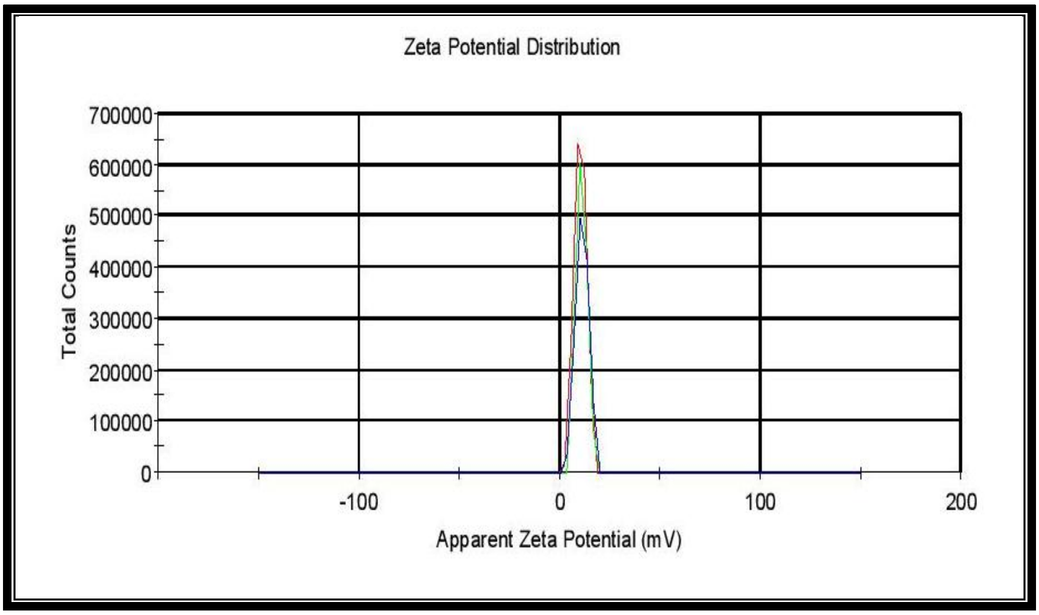

Figure 3.5: ZETA Potential Measurement of Polyaniline Nanofibers Salt

3.3.2.4 Electrical Conductivity

Four point probe technique was used to measure the electrical resistance of the PANInanofibers at room temperature. Further, conductivity of the PANI nanofibers was obtained using the value of this electrical resistance. The equation used to measure the conductivity is

$$\sigma = \frac{1}{\pi/_{ln2}} R\ d \qquad (3.3)$$

Where $\left(\frac{\pi}{ln2} R\right)$is the sheet resistance and, d is the thickness of the polyaniline pellet. The conductivity of the pellet was measured at different voltages (0.006 mA, 0.008 mA, 0.01 mA and 0.012 mA respectively). The conductivity of the salt form of the polyaniline was found to be 0.98 S/cm which is less than that of electrochemically synthesised PANI. But this value also supports the fact that, salt form of polyaniline has been synthesized in this experiment. The result coordinates well with the reviewed literature [195].

3.3.3 Kinetic Studies

The analysis of the adsorption process is carried out by the investigation of the adsorption kinetics. The experimental data is depicted by using different models such as a) Pseudo- first order model, b) Pseudo- second order model, c) Intra-particle diffusion model.

3.3.3.1 Pseudo- First- Order Model

Pseudo-first-order model is dependent on the hypothesis that the adsorption process iscontrolled by weak interactions i.e. physical interactions between the adsorbent and the adsorbate. The following equation represents the linearized form of the pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (3.4)$$

Where q_t and q_e are the quantities (mg /g) of dye (MO) adsorbed on PANI nanofibers at time t (min) and at equilibrium respectively and k_1 (1/min) is the pseudo-first-order adsorption rate constant. For this study, resulted $q_e = q_{80}$ i.e. at 80 minutes of contact time. The values of k_1 and q_e were evaluated from the slope and the intercept of the straight line obtained by plotting log (q_e-q_t) vs t, using experimental data, as shown in Figure 3.6 a. All the parameters are tabulated in the Table 3.1.

3.3.3.2 Pseudo-Second-Order Model

Pseudo-second-order model is depends on the assumption that the adsorptive removal of a component (dye) from its solution occurs by chemisorption process.The following expression shows the linearized form of the pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3.5}$$

where k_2(g /mg/min) is second order adsorption rate constant; $k_2q_e^2$=h (mg /g/min) is the initial rate constant (at t→0) and other symbols such as t, q_t and q_e have their usual meaning (Table 3.1).The values of $k_2q_e^2$ and q_e can be calculated respectively from the intercept and the slope of the straight line i.e t/q_t vs t as shown in Figure 3.6 b.

3.3.3.3 Intra-Particle Diffusion Model

Adsorption is a multilayer process and involves transit of dye molecules from aqueous solution to the adsorbent surface. Along with the exterior coverage of the adsorbent surface, interior diffusion may also occur through the pores of the adsorbent.So, to understand the mechanism of the diffusion of MO dye molecules into polyaniline, an another model i.e. intra-particle diffusion model have been used in this study, which is represented by the following equation [201]:

$$q_t = k_i t^{0.5} + C \tag{3.7}$$

Where, k_i is the intra-particle diffusion constant (mg/g/min$^{0.5}$); C, is the boundary layer thickness and q_t and t have usual meanings. The occurrence and effect of the pore diffusion was analyzed by plotting q_t vs $t^{0.5}$as shown in Figure 3.6 c. In anticipation with the previous literature [202] including four different steps for intra-partical diffusion, i.e. i,) bulk diffusion ii) film diffusion iii) intra-particle diffusion and iv) chemical reaction (between adsorbate and adsorbent at active sites of adsorbent), it is evident from the curve in (blue colored) Figure 3.6 c, that, there is an initial increase in the slope of graph with increase in the dye concentration, thus, representing the fast adsorption, followed by some augmented line slope, resulting from high MO concentrations due to high interaction of MO and PANI nanofibers. After the complete coverage of the available active sites, MO molecules start to move into the pores of the polyaniline due to the involvement of intra-particle diffusion, as evident from third portion of the curve with flat slope and finally attain equilibrium (i.e. with very low MO concentration), as evident from the slope of the curve at last (fourth) portion. So, it could be concluded that the actual adsorption process involved both the surface adsorption as well as intra-particle diffusion of MO dye molecules. Similar results have been reported in the previous literature for the removal of MO dye from its aqueous solution by using chitosan/ Al_2O_3/ magnetite nanoparticle composite [203]. The values of k_i and C were evaluated respectively from the slope and intercept of the closely fitted straight line (red coloured).

Though, the R^2 value of pseudo-first-order model is 0.947, but this is lesser than that of pseudo-second-order model. Also, the calculated q_e value for pseudo-first-order model is much different from the experimental q_e value, which shows that the pseudo-first-order model is not preferably followed by the adsorption of MO onto PANI nanofibers. As evident from Table 3.1, the regression constant value in case of pseudo-second-order model is highest (R^2=0.996), which represents the much better fitness of this model to the experimental adsorption data. In addition, the calculated q_e value significantly agreed with the experimental q_e value, which, evidently indicated that the adsorption of Methyl Orange dye on PANI nanofibers follows the pseudo-second-order model predominantly. In spite of a good value of the regression constant (i.e.R^2 value) for intra-particle diffusion model, the plot is not passing through the origin, which showed that the adsorption of MO onto polyaniline cannot be explained only by intra-particle diffusion model, but also involves chemical interaction (chemisorption) between adsorbent and adsorbate, as supported by the fitness of pseudo-second-order model.

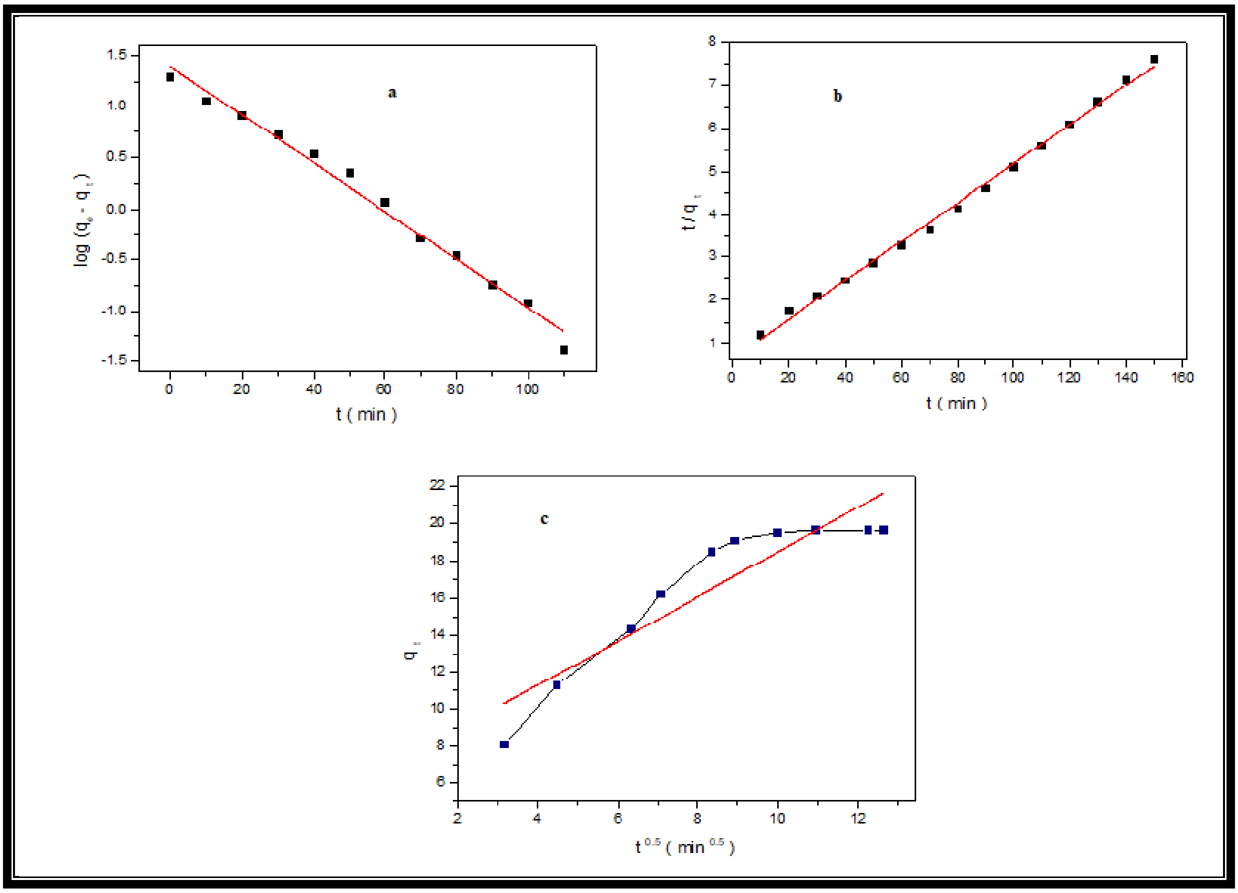

Figure 3.6: Kinetic Studies of Adsorption of Methyl Orange Dye by Polyaniline Nanofibers Salt : (a) Pseudo-First-Order Model, (b) Pseudo-Second-Order Model and (c) Intraparticle Diffusion Model

Table 3.1: Rate Constants Values for Adsorption of Methyl Orange (MO) Dye on PANI Nanofibers salt for Different Kinetic Models.

Kinetic Models	Parameters		R^2 value
Pseudo-first-order	k_1 (1/min)	0.0457	0.947
	q_e, exp (mg /g)	19.66	
	q_e,cal(mg/ g)	23.13	
Pseudo-second-order	k_2 (g/ mg $^{/}$ min)	0.00160	0.996
	q_e, cal (mg/ g)	22.26	
Intraparticle Diffusion	k_i (mg min$^{0.5}$ / g)	1.202	0.858
	C	6.461	

3.3.3.4 Effect of Contact Time

Kinetic studies of MO adsorption onto PANI nanofibers were conducted to study the effect of contact time on MO adsorption (initial dye concentration- 7 mg/L, pH ~7, room temperature) (Figure 3.7a). The uptake process of dye was very rapid at the initial stage of the reaction (for initial 40 minutes) and henceforth, the rate of dye removal was noted to be very slow and attained equilibrium after 80 minutes of contact time. The initial higher rate of adsorption of MO dye is due to the availability of more active sites, which further, decreased with time and the equilibrium was attained after a span of time.

3.3.3.5 Effect of Initial Dye Concentration

The effect of initial dye concentration on adsorption (Figure 3.7b) was studied by varying the initial concentration of MO dye from 2-10 mg/L. There is apparently an increased MO adsorption onto polyaniline, with increase in initial dye concentration. This is due to the fact that, the more dye molecules present in the system exert more driving forces to overcome the mass transfer resistance among solid and aqueous phases. After a specific initial dye concentration, i.e. 7mg /L (present study), no significant change in thje adsorption of MO has been observed. So, 7mg /L value is the equilibrium concentration for the present research work. The results obtained are supported by the analogous studies from the literature [204].

3.3.3.6 Effect of pH

The effect of pH on MO adsorption was studied by varying the reaction solution pH from 3-11 and keeping all other parameters constant (Figure 3.7c). It has been observed that the maximum adsorption of MO dye occurred within a range of pH value from 5 to 8. As seen from the plot, the value of q_t decreased with change in pH value beyond this range on both sides (lower and higher pH value). This behaviour could be explained on the basis of ionisation of the MO dye molecules and the changes in adsorbent surface with pH of the reaction mixture. Basically, MO dye molecule has two groups i.e. sulphonate group and amine group, and their ionization depends upon the pH of the solution. Amine group gets protonated at lower pH (in acidic medium), but remains unaffected in neutral and basic medium. So, in acidic medium, protonation of amine and sulphonate groups increase the positive charge density of the reaction solution and hence less adsorption of MO has been observed. Further, at higher pH value (beyond 8), due to the presence of more OH^- groups in the solution, which compete with mo dye moieties and hence, less adsorption of MO dye molecules have been observed. On the other hand, the MO dye molecule possesses significantly negative charge at neutral pH (or nearly neutral pH values; ranges from 5-8) and shows maximum MO adsorption. Moreover, as the emeraldine salt and the emeraldine base forms of the polyaniline exist at lower (acidic) and higher (alkaline) pH values respectively, the emeraldine salt form get converted to emeraldine base at neutral pH (~7) value [205]. Since, the MO dye exists as an anionic moiety and polyaniline possesses significantly positive charge in the pH value ranging from 5-8, the maximum adsorption has been occurred between this range of pH values, due to the existence of electrostatic force of attraction between MO dye and PANI nanofibers.

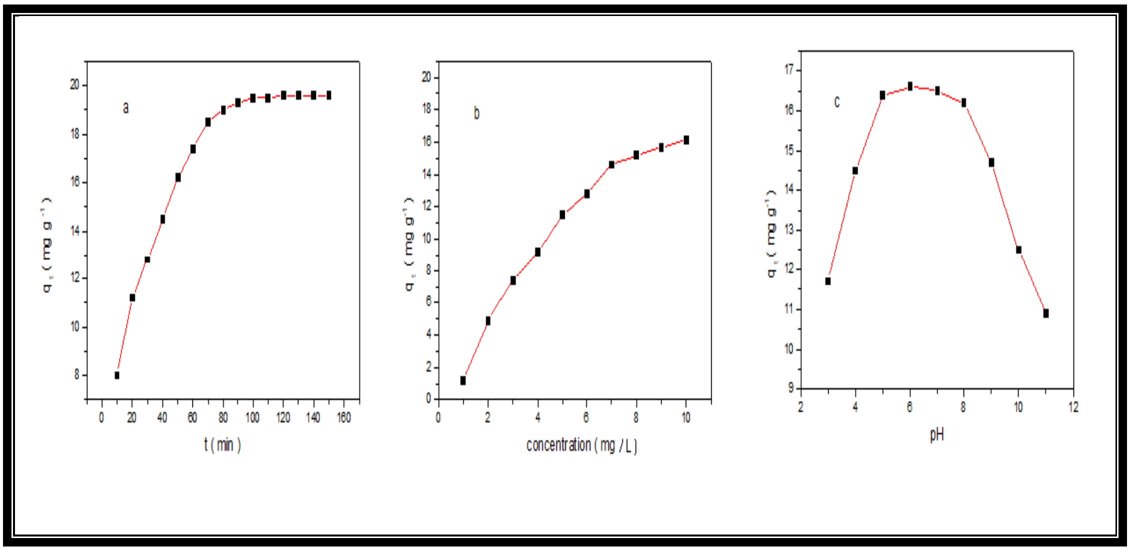

Figure 3.7: Variation of Methyl Orange Dye Adsorption onto Polyaniline with (a) Contact Time, (b) Initial Dye Concentration and (c) pH of the Solution.

3.3.4 Isotherm Studies

Adsorption system can be designed or optimised by the isotherm studies which define the relationship between the concentration of dissolved dye and the amount of the adsorbent at equilibrium. Different adsorption isotherm models have been tested to analyze the results obtained from the adsorption of the methyl orange (MO) dye onto PANI nanofibers salt, such as Langmuir and Freundlich isotherm models.

3.3.4.1 Langmuir Isotherm Model

Langmuir adsorption isotherm model assumes that there are fixed number of adsorption sites available on the surface of an adsorbent, and hence, only a monolayer adsorption takes place. The observed energy of adsorption is not dependent on the surface coverage in this case.The equation for the Langmuir isotherm model is as below [192]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \tag{3.8}$$

Where, C_e and q_e are the concentration and the amount of dye adsorbed at equilibrium respectively. q_m is the Langmuir monolayer adsorption of dye and b is the Langmuir constant. The suitability of the fitness of experimental data in this model is tested by plotting C_e/q_evs.C_e and the best fitted straight line obtained is shown in Figure 3.8a. The values of q_m and b are obtained from the slope and the intercept of the straight line respectively. The values of all the parameters are reported in Table 3.2. The adsorption efficiency is predicted from the separation factor R_L. The dimensionless separation factor (R_L) has the following expression:

$$R_L = \frac{1}{1 + bC_0} \tag{3.9}$$

Where, C_0 is the initial dye concentration. The values of R_L and q_m are 0.071 and 25 mg /g respectively. As the recommended value of R_L for the favorable adsorption lie between 0 and 1, the observed value of R_L, in the present study indicates a favorable adsorption of MO onto PANI nanofibers salt.

3.3.4.2 Freundlich Isotherm Model

Non-specific adsorption of methyl orange dye onto polyaniline was studied by Freundlich adsorption isotherm model. This model assumes that the adsorption occurs on a heterogeneous surface in spite of homogeneous surface, and the active sites and their energies distribute exponentially. The linearized form of Freundlich isotherm is represented by the equation as given below [193]:

$$\log q_e = \log K_f + n_h \log C_e \tag{3.10}$$

Where, K_f and n_h are the Freundlich coefficients. The best fitted straight line was obtained by plotting log $q_e$vs log C_e (Figure 3.8 b) and the values of K_f and n_h were obtained from the intercept and the slope respectively. The values of R^2, K_f and n_h are given in Table 3.2. Freundlich isotherm model is seemed to be the best-fitted isotherm model with the value of the regression coefficient, R^2=0.91. So, it could be concluded that, the multilayer adsorption on the heterogeneous surface of the polyaniline nanofibers has taken place during this adsorption experiment.

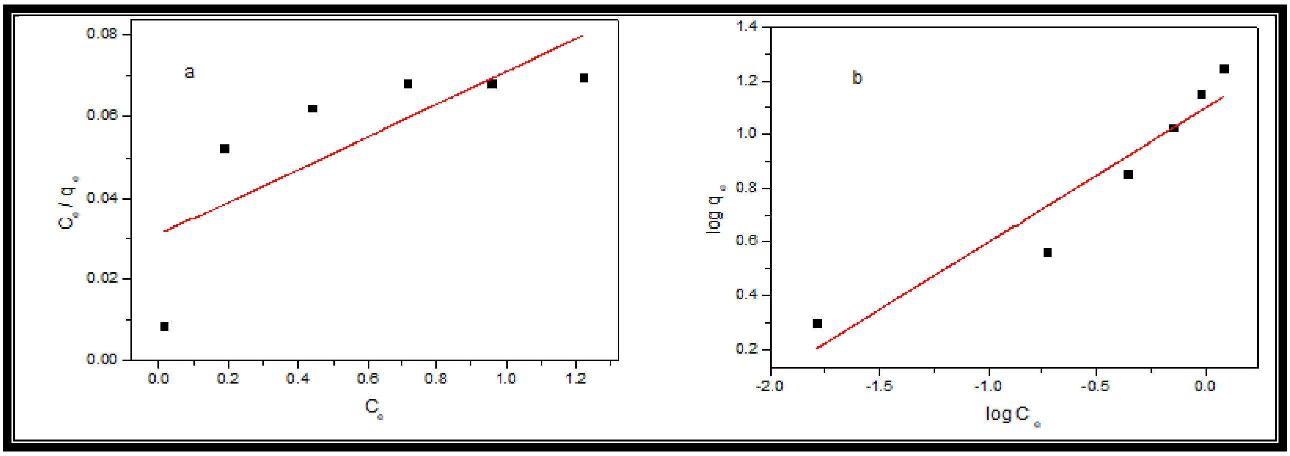

Figure 3.8: Isotherm Studies: (a) Langmuir Isotherm and (b) Freudlich Isotherm Plots for Methyl Orange Adsorption by Polyaniline Nanofibers Salt.

Table 3.2: Different Adsorption Isotherm Parameters of MO onto PANI Nanofibers Salt.

Isotherms	**Isotherm constant**	**R^2 value**
Langmuir	q_m(mg g) 25 b(L /mg) 1.29 R_L 0.071	0.61
Freundlich	K_f 12.56 n_h 1.99	0.91

It has been observed that the adsorption of Methyl Orange dye onto PANI nanofibers has followed the following order of isotherm model: Freundlich > Langmuir. The isotherm study has concluded that the Freundlich isotherm model is best fitted to the adsorption data of the Methyl Orange dye onto Polyaniline nanofibers (R^2= 0.91) and the non-specific adsorption has been occurred. This inference is also acceptable due to the presence of electrostatic interactions between negatively charged group (SO_3^-) on MO dye and positive charge (NH^+) on polyaniline backbone. Moreover, among different researchers, who had studied the adsorption of methyl orange dye onto different adsorbents, most of them reported that the adsorption data is fitted to the Freundlich model, thus, indicating, a multilayer adsorption of dye onto heterogeneous surface of the adsorbent [206,207].

The comparative study for MO dye removal by different adsorbents (Table 3.3) and different forms of polyaniline (Table 3.4) shows that the synthesized adsorbent in this work i.e. PANI nanofibers salt is superior as compare to other adsorbents. So, it was concluded that the nano-fibrous form of polyaniline is efficient and effective for the adsorptive removal of acidic dye (MO dye) from its aqueous solution.

Table 3.3: Adsorption of MO Dye by Using Different Types of Adsorbents.

S.No.	Adsorbent	Q_m (mg /g)	[Reference]
1	Carboxylate group functionalized multi-walled Carbon Nanotubes	5.580	[208]
2	Camel Thorn Plant	16.67	[209]
3	Ferric Oxide–Biochar Nano-Composites derived from Pulp and Paper Sludge (Fe2O3–BC)	16.05	[210]
4	Unactivated Biochar (BC)	16.05	[210]
5	Date Stones Activated Carbon	3.07	[211]
6	Kaolinite	1.24	[212]
7	Metakaolinite	3.07	[212]
8	Activated Geopolymer	0.33	[212]
9	Activated Geopolymer	15.78	[213]
10	Dragon Fruit (*Hylocereusundatus*) Foliage	19.1	[214]
11	Polyaniline nanofibers	25	Present work

Table 3.4: Removal of MO Dye by using Different Forms of Polyaniline.

S. No.	Adsorbent	Adsorbent dose (g)	Volume of dye solution (ml)	Initial dye concentration	Contact Time (min)	Adsorption (%age or mg/ g)	References
1	Polyaniline doped with oxalic acid	0.03	25	4×10^{-4} M	300	92%	[215]
2	Polyaniline Microsphere	0.05	25	1000 mg/ g	120	154.56 mg/g	[216]
3	Pani/SD composite	0.8	50	50 mg /g	60	99 mg/ g	[217]
4	Polyaniline nanofibers	0.05	100	10 mg /g	80	25 mg /g	Present work

3.3.5 Mechanism of Adsorption of MO on PANI Nanofiber Salt

The adsorptive removal of any pollutant depends upon the nature of the adsorbate, adsorbent composition and the reaction solution environment. The mechanism of adsorption is quite complicated due to the involvement of one or more interactions such as: hydrogen bonding; acid-base interactions; ion exchange; electrostatic interactions; complex formation; precipitation or simple physical adsorption [218]. In this study, it is expected that,methyl orange dye got dissociated into X-SO_3^- (X is organic part of dye molecule) and Na^+ moieties after dissolution in the water. During adsorption, X-SO_3^- interact with NH^+ group of the polyaniline backbone. Thus, the electrostatic interactions are preferably involved in MO adsorption onto PANI nanofibers. The present adsorption experiment was found to have followed the pseudo-second-order model, which indicated the presence of the chemical adsorption during this experiment. Apart from the outer surface adsorption of MO dye onto PANI nanofibers, diffusion of dye ions into the pores of adsorbent was also observed. Figure 3.9 showing the π-π interaction, H- bonding and electrostatic interactions between polyaniline salt and methyl orange dye.

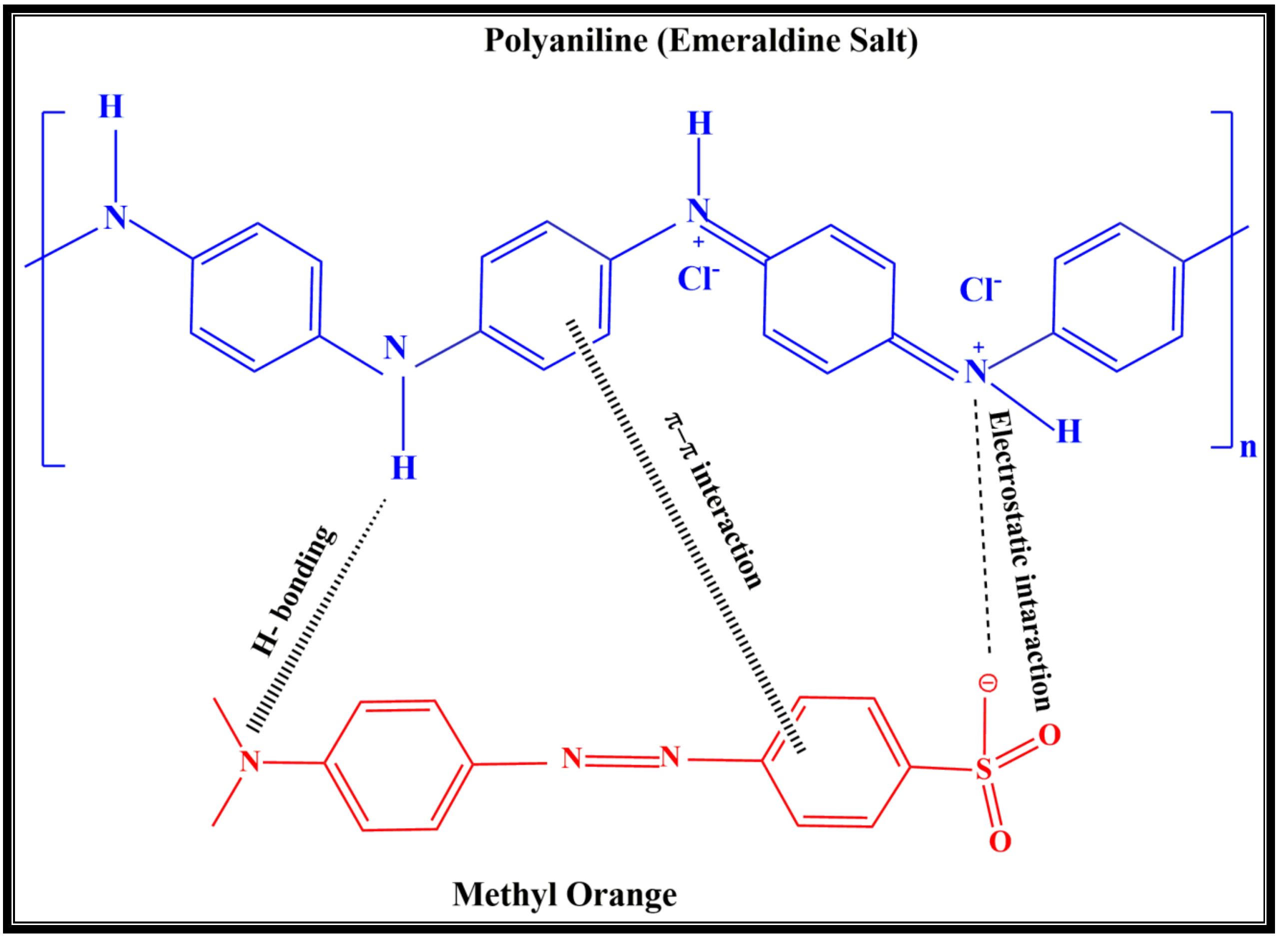

Figure 3.9: Schematic Diagram of Interaction between Polyaniline Salt and Methyl Orange Dye

3.4 Significant Findings

In this research work, the polyaniline nanofibers were used as a novel adsorbent to remove the methyl orange dye from its aqueous solution. Polyaniline nanofibers were synthesised by the interfacial polymerization method. Further, the synthesized adsorbent was characterized by SEM, HRTEM, XRD, Zeta potential, BET and FTIR techniques. The SEM results indicated the nano-range of the synthesized fibrous polyaniline which was further confirmed as of 60 nm in diameter by HRTEM. The BET analysis reported the enhanced (approx. 4 times) surface area of the PANI nanofibers (48.83 m^2 /g) as compared to the conventional polyaniline (13.65 m^2 /g).This enhanced surface area aided into more adsorption of MO dye on this nanostructured form of polyaniline. UV- visible spectroscopy was used to analyze the un-adsorbed amount of dye.

Batch adsorption experiments were used to study the kinetics of the adsorption system. The kinetics of the adsorption of dye was studied using different kinetic models such as Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion models. It has been observed that the Pseudo-second-order model was best fitted to the adsorption data of MO which indicated the involvement of chemisorption in the removal of methyl orange dye by polyaniline nanofibers salt. It has been seen that intra-particle diffusion is also playing a significant role in the adsorption along with chemisorption asthe value of the regression coefficient obtained for the best fitted straight line for intra-particle diffusion model is significantly high i.e. $R^2= 0.858$. In addition, Langmuir and Freundlich isotherm models were also used to analyze the equilibrium data. The best fitting of the data was observed with the Freundlich model. So, it can be concluded that the adsorptive removal of the methyl orange dye occurred on the heterogeneous surface of the polyaniline and there is a formation of multilayer during this adsorption experiment. The effects of different parameters such as contact time, initial dye concentration and pH were also studied and the equilibrium values of these parameters are found to be 80 minutes, 7 mg/L and pH~7 respectively. Approx 95% of MO dye was eradicated from its aqueous solution by using salt of polyaniline. From this study, it is evident that polyaniline nanofibers can be used as an efficient adsorbent for the removal of acidic dyes from the wastewater. The studies can further be scaled-up on the pilot and commercial scale for the combating of water pollution by cause of the presence of harmful dyes.

CHAPTER 4

ADSORPTION OF METHYLENE BLUE DYE (CATIONIC DYE) ONTO SALT FORM OF POLYANILINE NANOFIBERS

The emeraldine salt form of the polyaniline has positive charge on its backbone. Along with this positive charge, it also has lone pair of electrons on the alternate nitrogen atoms of the structure, so, it can also be employed as an adsorbent for the removal of cationic dyes. The driving force for that is the interaction between the positive charge of the dye and lone pair of electrons of nitrogen. This present study has been conducted to explore the adsorption capability of the polyaniline nanofibers (salt) for the removal of the methylene blue dye (cationic dye) from its aqueous solution. The molecular structure of methylene blue dye is as shown in Figure 4.1.

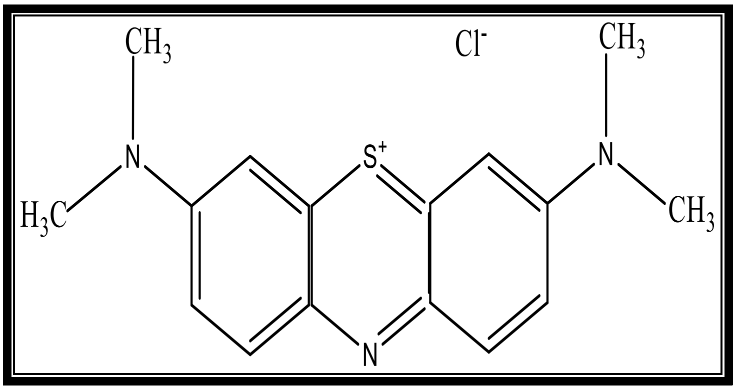

Figure 4.1: Molecular Structure of Methylene Blue Dye.

4.1 Batch Adsorption Studies

The stock solution (known concentration) of Methylene Blue dye was prepared in distilled water. A range of dye solutions, with distinct required concentrations, were prepared by diluting this stock solution. The batch experiment was enacted by agitating 0.05 g of the adsorbent with 100 mL of the dye solution in a shaker incubator at a speed of 250 rpm. After a specified period of time, the mixture was withdrawn and centrifuged at 6000 rpm for 15 minutes. The un-adsorbed amount of dye was predicted at 664 nm by analyzing the supernatant liquid using UV-visible spectrophotometer (Agilent Technologies Carry Series). The following equation was used to determine the adsorbed amounts of methylene blue on the PANI nanofiber salt:

$$q = \frac{(C_o - C_e)V}{m} \tag{4.1}$$

Where q (mg/g) is the amount of methylene blue dye adsorbed onto unit weight of the adsorbent, C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), m (g) is the mass of the adsorbent used and V (L) is the volume of the solution used.

4.2 Results and Discussion

4.2.1 Kinetic Studies

The most vital step during the designing of any adsorption system is the estimation of the rate of reaction. The rate expression of any reaction is derived from the kinetic studies of the reaction system. Various rate models have been used to analyze the experimental data of the adsorption process such as: a) Pseudo- first order model, b) Pseudo- second order model, c) Intraparticle diffusion model. In detail:

4.2.1.1 Pseudo-First-Order Model

The linearized form of the Lagergrane pseudo-first-order model [189] is:

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

Where,

q_t = adsorption capacity at time, t (mg /g)

q_e = adsorption capacity at equilibrium (mg /g)

k_1 = the rate constant of adsorption (1/min)

and t = contact time (min).

A plot of log (q_e−q_t) versus t (Figure 4.2 a), gives a straight line with slope equal to k_1 and intercept equal to q_e respectively. As seen from the figure, the Pseudo-first-order model is not preferably followed by this adsorption experiment, because R^2=0.91 value is low. Also, the calculated q_e value is much different from the experimental q_e value as reported in Table.4.1.

4.2.1.2 Pseudo-Second-Order Model

The linearized form of the Lagergren pseudo-second-order model [189] is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4.3}$$

Where,

q_t = adsorption capacity at time, t (mg /g)

q_e = adsorption capacity at equilibrium (mg /g)

k_2 = second order adsorption rate constant, (g /mg/min)

$k_2 q_e^2$=h i.e. the initial rate constant (cat t→0), (mg /g/min)

and t = contact time (min).

A plot of t/q_t versus t (Figure 4.2 b), gives a straight line with slope equal to q_e and intercept equal to $k_2 q_e^2$respectively. The regression constant value (R^2=0.99) represents the fitness of the model to the adsorption of methylene blue dye onto PANI nanofibers. In addition, the calculated q_e value (2.624) significantly agreed with the experimental q_e value (2.54), which, indicate that the adsorption of methylene blue dye on polyaniline follows the pseudo-second-order model predominantly.

4.2.1.3 Intraparticle Diffusion Model

According to this model, the adsorption takes place in many steps, such as:

1. Transport of the adsorbate molecules from the bulk aqueous phase to the surface of the adsorbent.
2. Transfer of the adsorbate molecules from the surface of the solid adsorbent into the interior of the pores.

As per the reported literature, in the adsorption following the intraparticle diffusion, the adsorption occurs in proportional with $t^{1/2}$. The intraparticle diffusion model is expressed by the following equation [190] :

$$q_t = k_{id}t^{0.5} \tag{4.4}$$

Where,

q_t =adsorption capacity at time t (mg /g)

$t^{0.5}$ = Half-life period/time (min)

and, k_{id} = rate constant of intra-particle diffusion (mg /g/min$^{0.5}$)

A plot of q_t versus $t^{0.5}$(Figure 4.2 c) gives a straight line with slope equal to k_{id}.As the regression constant value (R^2 =0.80) is not so high in this case, it can be concluded that,the adsorption of methylene blue onto polyaniline is not following this model preferably. In addition, sincethe plot is not passing through the origin; it is evident that the adsorption of methylene blue cannot be explained only by intraparticle diffusion model.

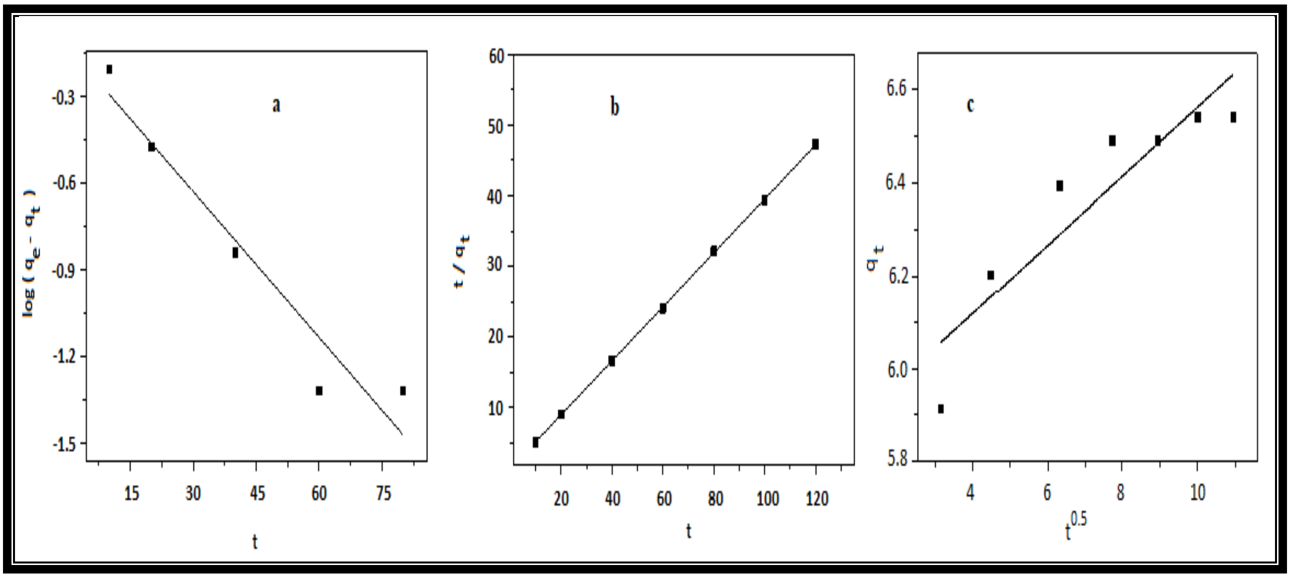

Figure 4.2. Kinetic Studies: (a) Pseudo-First-Order Model; (b) Pseudo-Second-Order Model and (c) Intraparticle Diffusion Model.

From the kinetic studies, it is concluded that the adsorption data was best fitted to the pseudo-second- order model, with the higher value of regression constant i.e. R^2 =0.99. Other models are also found satisfactory to some extent, by this adsorption system. The order of fitness of all three models is as: Pseudo- second- order > Pseudo- first- order > Intraparticle diffusion. All the adsorption parameters are given in Table.4.1.

Table 4.1 . Adsorption Parameters for Different Kinetic Models(MB onto PANI Salt)

Kinetic Models	**Parameters**		**R^2 value**
Pseudo-first-order	k_1 (1/min)	0.036	0.91
	q_e, exp (mg/ g)	2.54	
	q_e, cal (mg/ g)	0.75	
Pseudo-second-order	k_2 (g/ mg/ min)	0.204	0.99
	q_e, cal (mg/ g)	2.62	
Intraparticle Diffusion	k_i(mg $min^{0.5}$/ g)	0.073	0.80
	C	5.821	

4.2.1.4 Effect of Contact Time

The batch experiments were performed to study the removal of methylene blue dye by polyaniline nanofibers with respect to contact time (initial dye concentration- 6 mg/L, pH ~7, room temperature). Figure 4.4a shows the variation of the percentage adsorption of methylene blue dye onto polyaniline nanofibers with contact time. At the initial stage of the removal process, a rapid increase in the percentage removal of dye has been observed. But, it apparently decreased with the passage of time, and finally, an equilibrium state was achieved at 60 minutes. The initial rapid adsorption is due to the availability of sufficient active sites on the surface of the polyaniline, which, decreased with time. Further, after the achievement of equilibrium, the adsorption was found to have taken place at almost constant rate, and dye molecules probably started to move into the adsorbent matrix, through diffusion. It has been observed that about 67% of dye gets adsorbed at equilibrium stage at a contact time of 60 minutes. So, the equilibrium time for adsorption, in this study is 60 minutes. These results are comparable with other study reported in the literature [219].

4.2.1.5 Effect of Initial Dye Concentration

Among all the adsorption parameters, the initial dye concentration is one of the important parameter to be studied which affects the adsorptive removal of dye by an adsorbent. The effect of the initial dye concentration of methylene blue on the adsorption was carried out by varying the initial concentration (1-10mg/L) and keeping all other parameters as constant (contact time-60 min, pH~7, room temperature). Figure 4.4b shows the decrease in percentage dye removal of methylene blue with respect to increase in initial dye concentration of the solution. The higher adsorption at initial stage of the reaction is because of more number of active sites are available at the initial stage to interact with the dye molecules. But as time passes, the availability of active sites goes on decrease, because the active sites are fixed but the number of dye molecules goes on increase and hence adsorption percentage at higher concentration will decrease and Finally, the adsorption reactin attain equilibrium.The equilibrium concentration of this work was obtained to be 6mg/L. The previous literature studied also reported the similar pattern of results for different dyes [220-221].

4.2.1.6 Effect of pH

The effect of pH on MB adsorption was studied by varying the reaction solution pH from 2-10 and keeping all other parameters constant (initial dye concentration-6 mg/L, contact time- 60 min, room temperature) (Figure 4.4c). It has been observed that the maximum adsorption of MO dye occurred between the pH ranges 6-8, and become constant with further increase in this pH value. This can be attributed to the existence of emeraldine base form of the polyaniline at about neutral pH of solution. At neutral pH polyaniline possessed lone pair of electrons on nitrogen atoms and hence, remove more dye at this pH value. Also, at lower pH values, the presence of more H^+ ions in the reaction mixture, compete with the positively charged dye molecules, so less adsorption is occurred.

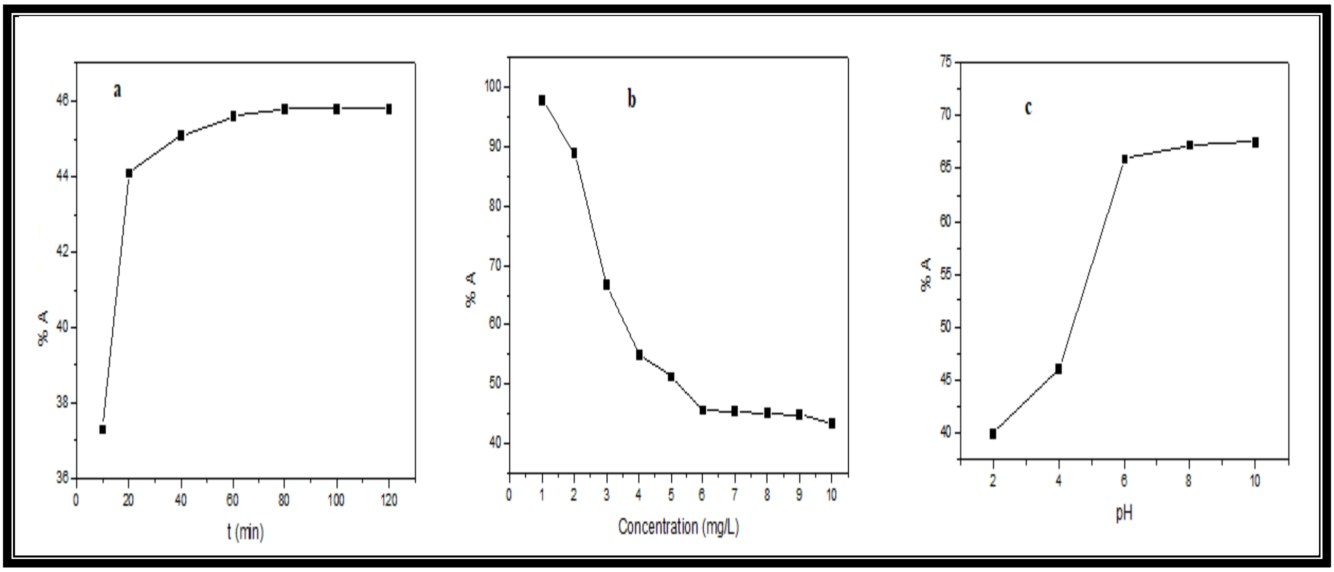

Figure 4.3. (a) Effect of Contact Time; (b) Initial Dye Concentration of Dye and (c) pH of Solution on the Adsorption

4.2.2 Isotherm Studies

Various isotherm models were proposed in past to explain the adsorption behaviour of different adsorbents [222]. The mechanism of the adsorption can be studied by fitting the experimental data in different types of adsorption isotherms available. The interactions between the adsorbing species and the adsorbent can be well described by the adsorption isotherms. Depending upon the interactions between the surface of the adsorbent & the adsorbate particles, and the nature of the adsorption i.e. multilayered or monolayer adsorption, the results can be compared with these already established isotherms and proposed mechanism of adsorption can be predicted. In addition, the removal capacity of any adsorbent can be measured by the adsorption isotherms. Among all the reported isotherm models, the Langmuir and Freundlich isotherm models are being tested to explain the adsorption behavior of polyaniline for methylene blue i.e.

4.2.2.1 Langmuir Isotherm Model

1. The Langmuir isotherm model is found to be best fitted, when monolayer adsorption has been taken place. It is based on the assumption that the adsorption takes place at specific homogeneous sites, within the adsorbent, thus forming a single layer over the adsorbent surface. The Langmuir's isotherm is governed by the following equation [192]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \tag{4.5}$$

Where,

C_e = Concentration of dye adsorbed at equilibrium (mol /L)

q_e = Amount of dye adsorbed at equilibrium (mg /g)

q_m = Langmuir monolayer adsorption of dye (mg /g)

and b = Langmuir's constant

The separation factor, R_L (dimensionless) can be determined by following expression [223]:

$$R_L = \frac{1}{1 + bC_0} \tag{4.6}$$

Where,

C_0 =Initial dye concentration.

The recommended value of R_L, for the favourable adsorption lies between 0 and 1.

The R_L value for the adsorption of MB onto PANI nanofibers salt is found to be 0.3. Since, the obtained value of R_L lies in the recommended range, therefore the adsorption of methylene blue onto polyaniline is favorable for Langmuir isotherm. A straight line was obtained by plotting a graph between C_e/q_e versus C_e (Figure 4.3a), from where the values of q_m and b can be calculated, by slope and the intercept respectively. Moreover, the values of the all adsorption parameters are tabulated in Table 4.2. The R^2 value (0.83) indicated well fitness of this model to the adsorption data.

4.2.2.2 Freundlich Isotherm Model

The other model tested is the Freundlich Isotherm model, which is based upon the assumption that, the adsorption takes place at the heterogeneous surface, and, the active sites are independent to each other. The linearized equitation for the Freundlich isotherm model [193] is given as:

$$\log q_e = \log K_f + n_h \log C_e \tag{4.7}$$

Where,

q_e = Amount of dye adsorbed at equilibrium (mg /g)

C_e = Concentration of dye adsorbed at equilibrium (mol /L)

K_f and n_h are the Freundlich coefficients.

A plot of log q_e versus log C_e (Figure 4.3 b), gives a straight line with slope equal to n_h and intercept equal to K_f respectively. The values of R^2, K_f and $n_h$obtained are 0.94, 1.43 and 1.78 respectively (Table.4.2). Some another studies also reports the same pattern of fitness of the adsorption data [224].

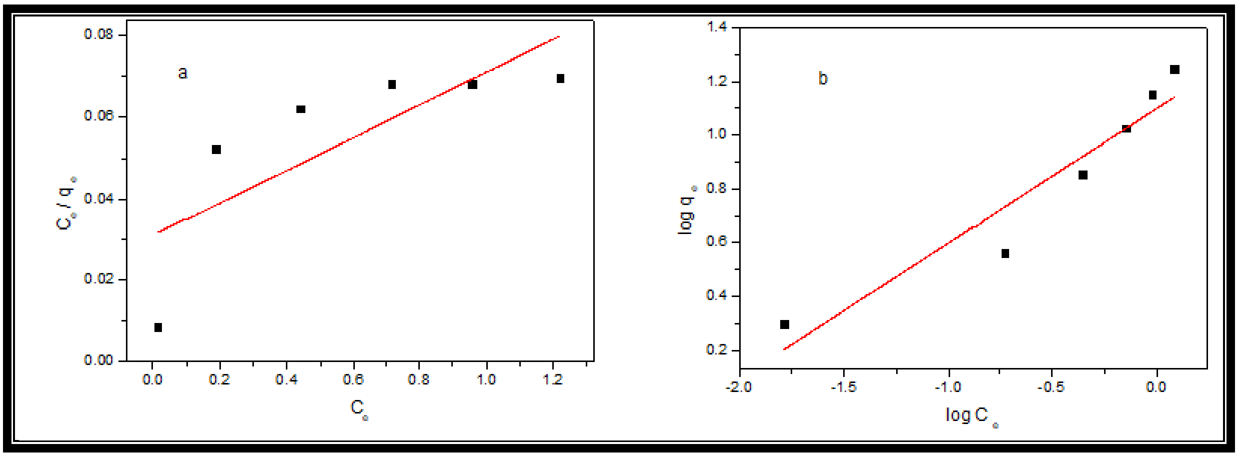

Figure 4.4. Isotherm Studies : (a) Langmuir Isotherm Model and (b) Freundlich Isotherm Model of Methylene Blue on Polyanilne Nanofibers Salt.

Table 4.2 Different Adsorption Isotherm Parameters of Methylene Blue by Polyaniline Nanofibers Base.

Isotherms	Isotherm constant		R^2 value
Langmuir	q_m b R_L	4.6 0.55 0.002	0.83
Freundlich	K_f n_h	1.41 1.90	0.94

So, the isotherm studies concluded the following order of fitness of isotherm models to the adsorption data of MB on PANI nanofibers salt, based upon the values of the regression constant i.e. Freundlich model > Langmuir model. This observation is in synchronization with the reported results in the literature. The literature studies show that, the most of the adsorptive removal of dyes from their aqueous solutions followed the Freundlich isotherm model [211,225,226]. The best fitness of the Freundlich model indicates the multilayer adsorption of the MB dye onto the heterogeneous surface of the PANI nanofibers salt.

4.3 Significant Findings

PANI nanofibers had been synthesized by a much familiar method i.e. Interfacial polymerization. The characterization of the synthesized polyaniline nanofibers was carried out by using FTIR, SEM, HRTEM and BET and the UV-visible spectroscopy was used to study the uptake of the dye (MB) by PANI nanofibers. SEM results indicated the nano range of the synthesized fibrous polyaniline, which was further confirmed, of 60 nm in diameter by HRTEM. BET analysis reported the enhanced surface area of the PANI nanofibers as compared to the conventional polyaniline (approx. 4 times). This enhanced surface area aided into more adsorption of MB dye on this nanostructured form of polyaniline. The batch adsorption experiments were carried out to study the kinetics of the dye removal process. Three kinetic models were used during this work: Pseudo-first-order, Pseudo-second-order and Intraparticle diffusion models. It has been observed that the Pseudo-second-order model is best fitted to the adsorption data, which indicates the involvement of chemisorption process in the removal of methylene blue dye. It has been noticed that intraparticle diffusion has taken place along with other mechanisms, but this is the not only one mechanism observed, to remove the dye from its aqueous solution. The order of fitness of these models to the adsorption data is as follow: Pseudo- second- order > Pseudo- first- order > Intraparticle diffusion. In addition, two isotherm models were tested to analyze the equilibrium data i.e. Langmuir and Freundlich models, which followed the following order of fitness: Freundlich > Langmuir model. As stated above, the best fitting of the data was observed with Freundlich model, which suggested the multilayer formation of the MB dye on the heterogeneous surface of the polyaniline. The effects of the parameters such as: contact time, initial dye concentration and pH of the solution were also studied, and the obtained equilibrium values of these parameters are 60 minutes, 6mg/L and 7 respectively. About 67% of mehylene blue dye was removed at equilibrium during this work. So, PANI nanofibers can remove basic dyes to some extent.

CHAPTER 5

ADSORPTIVE STUDIES ON THE REMOVAL OF CATIONIC (METHYLENE BLUE) DYE BY USING BASE FORM OF THE POLYANILINE NANOFIBERS

The emeraldine base form of the polyaniline nanofibers was prepared by treating the emeraldine salt form of polyaniline nanofibers with 1M ammonia solution. The polyaniline nanofibers base (PNb) is neutral in nature and possess lone pair of electrons on nitrogen atoms, which is favourable for cationic dyes removal. This is attributed to the more interaction between positive charge on the cationic dye and the lone pair of electrons on nitrogen atoms of the polyaniline structure. The current study is focused on the use of polyaniline nanofibers base (PNb) for the adsorptions of basic dye i.e. Methylene Blue (MB), from its aqueous solutions, by exploiting the unique physicochemical properties of polyaniline. The effects of different adsorption parameters such as contact time, pH and initial dye concentration have also been studied. The reaction kinetics has been investigated by using different kinetics models. Different isotherms are used to analyse the experimental adsorption data.

5.1 Synthesis of Polyaniline Nanofibers Base

Polyaniline nanofibers were synthesized by interfacial polymerization method [188]. In brief, 0.32 mol of monomer (aniline) was dissolved in toluene in a beaker to form the organic phase. The aqueous phase was formed by dissolving 0.08 mol of APS in 1M HCl solution in another beaker. The APS solution was added drop-wise to the organic phase, within a specific period of time. Then the reaction mixture was kept unruffled for 20 h. The content was then filtered and washed with distilled water several times. To obtain the base form of polyaniline, the reaction mixture was treated with 1M ammonia. The blue colored compound, thus, obtained was dried at 60^{o} C for 24 h. Polyaniline nanofibers base (PNb) in the powder form was obtained.

5.2 Batch Adsorption Studies

The capability of PNb to remove MB from its aqueous solution was measured by performing the adsorption batch experiments. An apropos amount of methylene blue dye was dissolved in distilled water to prepare the stock solution for the experiments. Further, different concentration solutions, as needed, were prepared by diluting the stock solution with distilled water. The adsorption experiment was performed by agitating the 0.05 g of the adsorbent with a 100 mL volume of dye solution in a shaker incubator, at a fixed speed, for a fixed interval of time. Then the reaction mixture was centrifuged at 6000 rpm for 15 minutes. The un-adsorbed dye was estimated by using UV- Visible spectroscopy at 664 nm. The standard solutions of methylene blue dye were used for the calibration of the UV-Visible spectrophotometer. Analogous absorption for individual concentrations was obtained at λ_{max} 664 nm. By plotting the data between concentration and absorbance, a linear regression curve was obtained. The following equations were used to calculate the adsorption capacity and adsorbed percentage of MB dye onto PNb respectively:

$$Q = \frac{(C_o - C_e)V}{m} \tag{5.1}$$

$$\%A = \frac{C_o - C_e}{m} \times 100\% \tag{5.2}$$

where, Q (mg/gm) is the adsorption capacity, C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), V (L) is the volume of the solution used and m (g) is the mass of PNb used.

5.3 Results and Discussion

5.3.1 Characterization of Polyaniline Nanofibers Base

5.3.1.1 XRD

The nature of PNb (crystalline or amorphous) was determined by XRD (Figure 5.1). The pattern shows two diffraction peaks at 2θ values of 21.6^0 and 22.2^0respectively.The crystal size of the prepared PNb was found to be 3.5nm as calculated from Debye Scherer equation and the nature of adsorbent was observed as amorphous, with a little bit crystalline portion. Literature studies also support the above results [227].

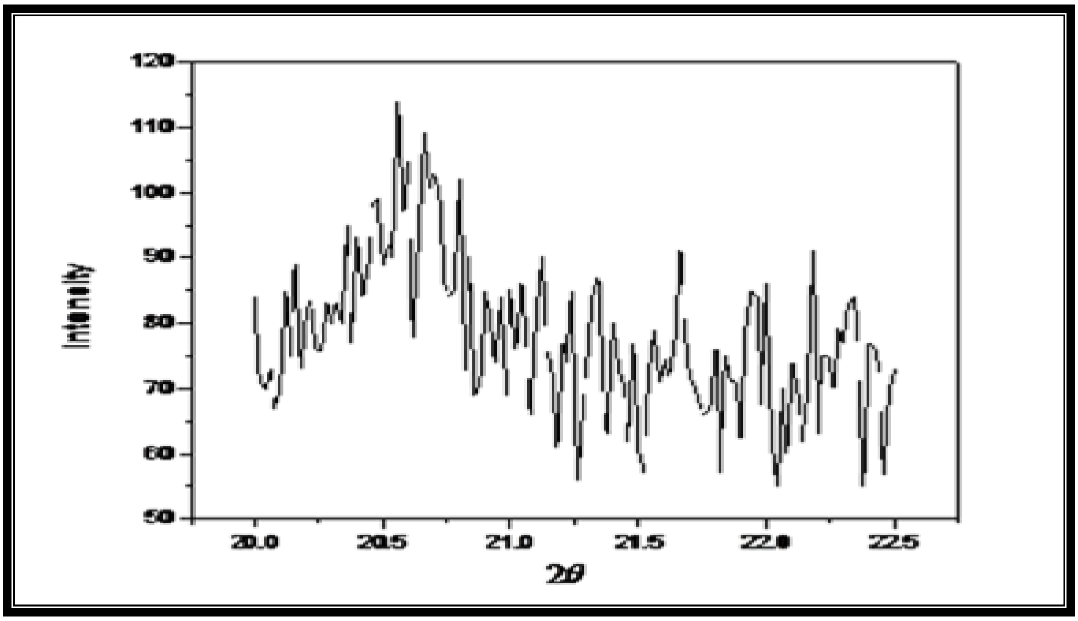

Figure 5.1: XRD Pattern of Polyaniline Nanofibers.

5.3.1.2 FTIR

FTIR spectra of polyaniline (Figure 5.2) synthesised by the interfacial polymerization method explains the molecular structure of the same. N-H stretching of the structure is represented by peak obtained at 3250 cm^{-1}. The absorption band centred at 2981cm^{-1} is due to the asymmetric stretching mode of C-H of aromatic bond. Bands at 1567 cm^{-1} and 1489 cm^{-1} are attributed to the C=C stretching mode of quinoid and benzenoid ring respectively, indicating that the structure of the polyaniline is in emeraldine form. The absorption peak at 1444 cm^{-1} is because of C=N aromatic stretching. C-N stretching of secondary aromatic amine was shown by a band at 1288 cm^{-1}, whereas vibration band at 1144 cm^{-1} is attributed to C-H in plane bending. Vibration peaks at 820 cm^{-1} and 740 cm^{-1} is due to C-H out of plane deformation in 1,4 di-substituted benzene ring. All the above given vibration bands of polyaniline are also confirmed by the reported literature studies [228, 194,197].

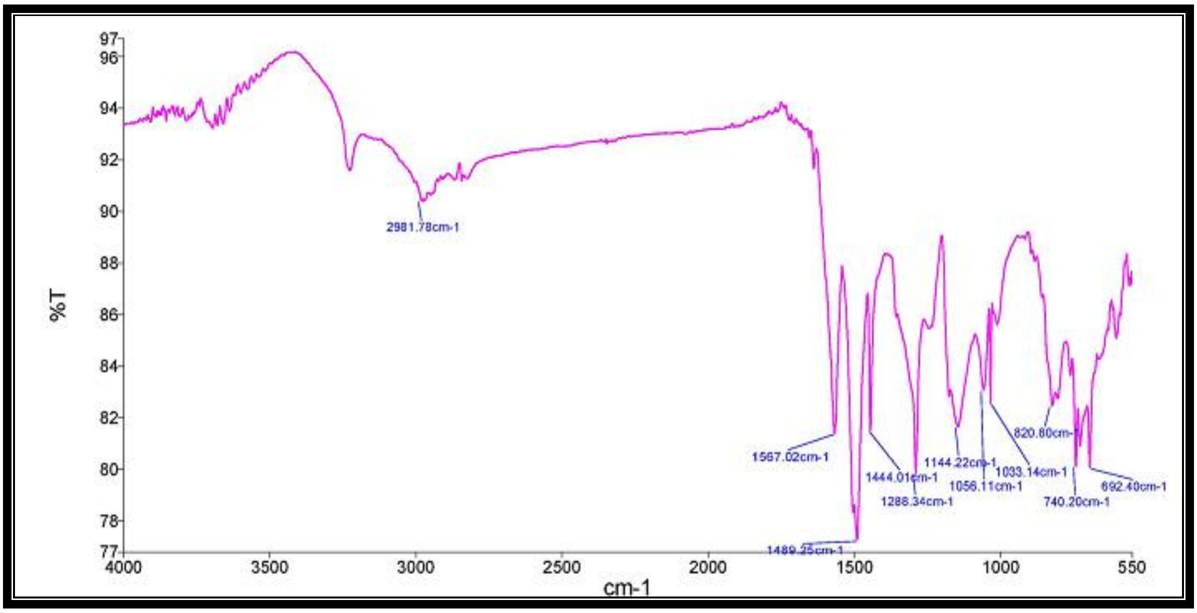

Figure 5.2: FTIR Spectra of Synthesized Polyaniline Nanofibers.

5.3.1.3 SEM and HRTEM

The result of SEM analysis (Figure 5.3a) shows the surface morphology of synthesized PNb. The average diameter of PANI nanofibers prepared during this work was found to be 60 nm. Moreover, the observed result is in synchronization with another research report from previous literature studies [196]. The synthesized PNb was further analyzed by using HRTEM technique (Figure 5.3b). The HRTEM images confirmed the structure of the PNb in nano-range with a rough surface.

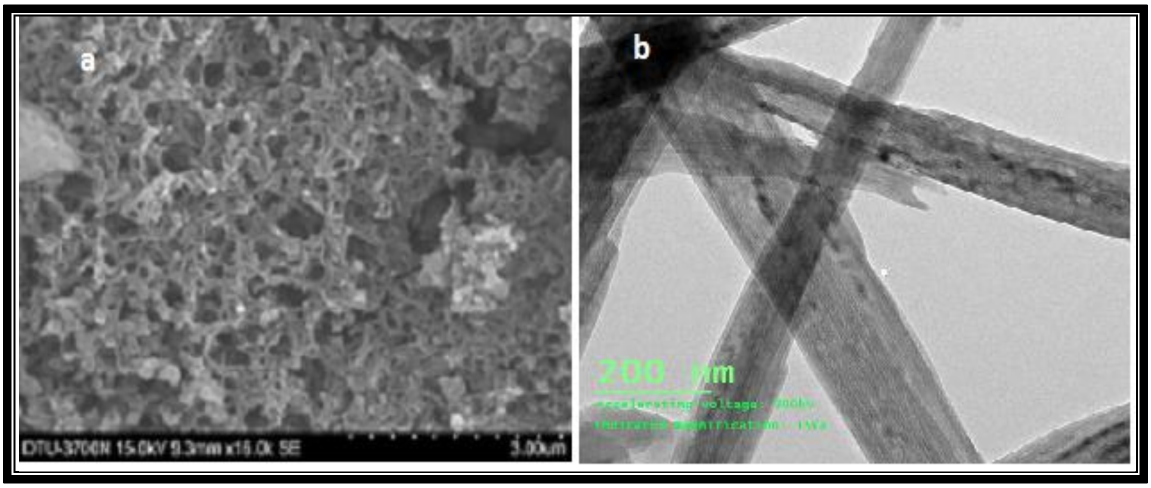

Figure 5.3: (a) SEM Image and (b) HRTEM Image of Polyaniline Nanofibers Base (PNb).

5.3.1.4 BET Analysis

The synthesized polyaniline nanofibers were characterized by surface area analyzer. As per the results of surface area analyzer, the surface area of PNb was found to be higher as compared to conventionally synthesized polyaniline. Table 5.1 shows the surface area, pore volume and pore diameter of nanostructured and conventional polyaniline. The higher surface area of the PNb is quite beneficial for the adsorption of MB onto polyaniline.

5.3.1.5 Electrical Conductivity

The result of the four probe technique shows that the synthesized PNb have less electrical conductivity (2.3×10^{-2} S/cm) as compare to the salt form of the polyaniline. The similar results were also reported by a research group, for the emeraldine base form of the polyaniline [229].

Table 5.1. BET Analysis Data of the MB Adsorption onto Polyaniline Nanofibers Base (PNb).

Adsorbent	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Average Pore Diameter (nm)**
Polyaniline Nanofibers	48	1.0256×10^{-2}	15.7
Conventional Polyaniline	14	2.638×10^{-3}	34.4

5.3.2 Kinetic Studies

The kinetic study of dye removal by adsorption is important due to the reason of its control over the equilibrium time and the efficiency of the adsorption process. It is also helpful to explain the mechanisms of the adsorption. Three different kinetic models were used to study the rate of dye uptake on the polyaniline nanofibers, i.e. the pseudo-first order model [230] the pseudo-second order model [231] and intra-particle diffusion model.

5.3.2.1 Pseudo- First Order Model

The following equation represents the pseudo-first order model:

$$\log(\mathrm{Q_e} - \mathrm{Q_t}) = \log \mathrm{Q_e} - \frac{\mathrm{K_1 t}}{2.303} \tag{5.3}$$

Fitting of adsorption data to the pseudo-first order model was examined by plotting a graph of log (Q_e-Q_t) vs t, as presented in Figure 5.4a, where Q_e and Q_t are the amount (mg/g) of methylene blue dye adsorbed on the polyaniline nanofibers at equilibrium and at time t (min) respectively. K_1 (l/min) is the adsorption constant for pseudo-first order model. The slope and the intercept of the graph (Figure 5.4 a) provided the values of K_1 and Q_e respectively. The values of the above adsorption parameters are given in Table 5.2. As shown in the table, the value of correlation coefficient is 0.91 for this adsorption process. But, the values of calculated and experimental Q_e do not coincide with each other. So, it could be concluded that this particular model is not followed by this adsorption system preferably.

5.3.2.2 Pseudo- Second Order Model

Another adsorption model studied for adsorption of MB on PNb is the pseudo-second order model, which is related with the quantity of dye adsorbed at the equilibrium and on the surface of polyaniline (Figure 5.4 b).The following equation represents the pseudo-second order model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{5.4}$$

The plot of t/Q_t vs t is a straight line, where Q_t, Q_e and t have their usual meanings and K_2 (g/mg min) is the rate constant for the pseudo-second order model. The values of above parameters are presented in Table 5.2. As observed, the values of calculated and experimental Q_e agrees with each other and the R^2 value is reportedly equal to 0.99. So, we can assume that the adsorption data for MB onto PNb is best fitted in this model. Moreover, this fitting of adsorption data also indicates that chemisorptions played significant role during this adsorption experiment.

5.3.2.3 Intraparticle Diffusion Model

The intra-particle diffusion model was also studied to comprehend the adsorption process of MB onto PNb. This model can be represented by the following equation:

$$Q_t = K_i t^{0.5} + C \tag{5.5}$$

Where,K_i (mg/g $\text{min}^{0.5}$) is the rate constant for the intra-particle diffusion, C is the boundary layer thickness and Q_t and t have usual meanings. A plot of Q_t against $t^{0.5}$ (Figure 5.4c) gave the values of rate constant of and boundary layer thickness from slope and intercept respectively.

The values of all the parameters are given in Table 5.2.

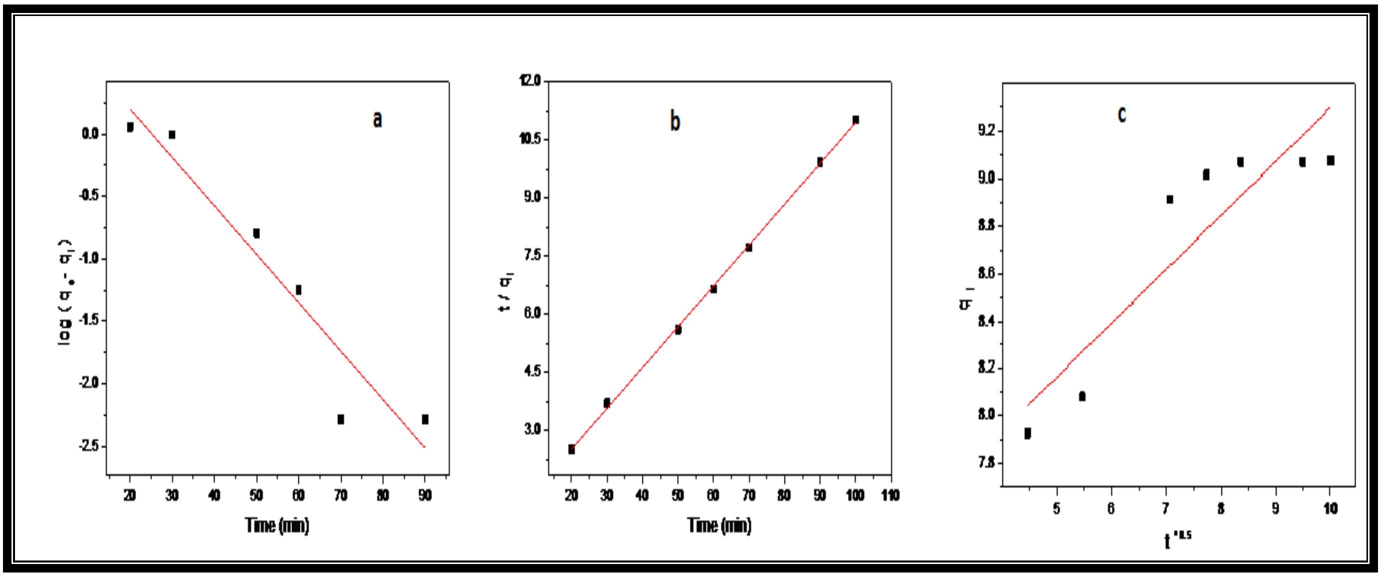

Figure 5.4: Kinetic Studies: (a) Pseudo-First Order Model; (b) Pseudo-Second Order Model and (c) Intra-Particle Diffusion Model.

Table 5.2. Adsorption Parameters for Different Kinetic Models (MB onto PANI Base).

Kinetic Models	**Parameters**	**R^2 value**
Pseudo-first-order	k_1(1/min) 0.087 q_e,exp (mg/ g) 8.63 q_e,cal (mg/ g) 9	0.91
Pseudo-second-order	k_2 (g/ mg /min) 0.0046 q_e, cal (mg/ g) 9.52	0.99
Intra-particle Diffusion	k_i (mg $min^{0.5}$/ g) 0.22 C 7.02	0.82

But the intra-particle model is not the only model followed by the adsorption of MB on PNb, because the best fitted straight line (Figure 5.4c) does not pass through the origin. Moreover, the value of R^2 (0.82) also indicated that this model is not preferably followed by the adsorption of MB onto PNb, but play a significant role in combination with some other mechanism (s).

5.3.2.4 Effect of Contact Time

As the adsorption process is significantly influenced by the contact time, the effect of contact time on the adsorption of MB onto PNb was studied (initial dye concentration -6 mg/L, pH ~7, room temperature) (Figure 5.5a). As apparent from the figure, the adsorption of MB from its aqueous solution increased with increase in contact time. It has been observed that about 79% of the dye was adsorbed within first 20 minutes and an equilibrium stage (91% removal) was attained after 60 minutes. So, the optimized equilibrium contact time for the present study is 60 minutes. Previous literature also reported the similar results [219].

5.3.2.5 Effect of Initial Dye Concentration

The effect of initial dye concentration on adsorption of MB on PNb (Figure 5.5b) was also studied by varying the initial concentration of methylene blue dye (2-10mg/L) and keeping all other parameters constant (pH~7, room temperature, contact time - 60minutes). It could be seen from the figure that, the adsorption percentage decreases with increase in initial dye concentration. This is due to the availability of more uninhabited active sites on the adsorbent surface in case of lower initial dye concentration. But at higher initial dye concentration, number of active sites is fixed but number of dye molecules is higher. Hence, results into less adsorption of MB at high dye concentration. On the other hand, the amount of dye adsorbed at equilibrium is increased with an increase in initial dye concentration. This can be explained on the basis of the driving forces provided by the dye molecules that defeats the resistance to the mass transfer (of dye molecules) among solid and aqueous phases. Moreover, there is apparently increased interaction between dye molecules and adsorbent with increase in initial dye concentration. After a specific initial dye concentration i.e. 6mg/L, no significant change in adsorption of MB has been observed. So, 6 mg/L value is the equilibrium concentration for the present research work. Some other studies have been reported the similar pattern of results for different dyes such as methyl violet, methyl orange and reactive blue 221 [219-221].

5.3.2.6 Effect of pH

The effect of pH on MB adsorption onto polyaniline base was studied by varying the reaction solution pH from 2-10 and keeping all other parameters constant (initial dye concentration- 6 mg/L, contact time- 60 minutes, room temperature) (Figure 5.5c). Maximum adsorption was noted between pH values of 6-8. At lower pH value, the protonation of polyaniline base occurres, due to which, positive charge appears on the polyaniline and hence less adsorption takes place at lower pH of the solution. But in alkaline medium i.e. at higher pH, predominantly base form exists, which results into more dye removal.

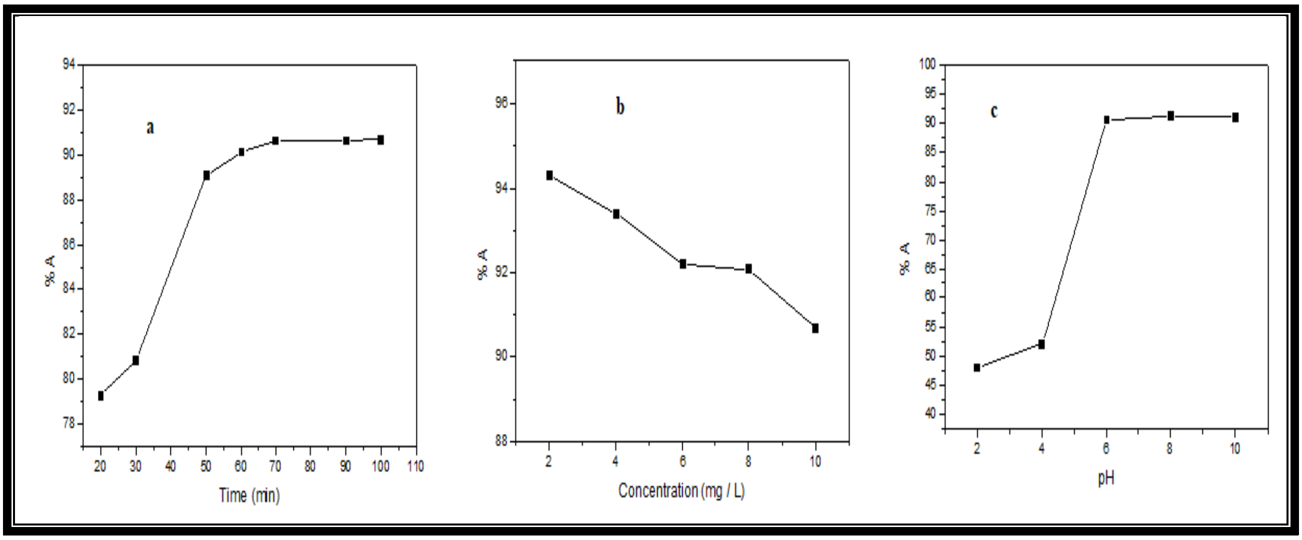

Figure 5.5: Effects of Adsorption Parameters on Removal of Methylene Blue Dye: (a) Contact Time; (b) Initial Dye Concentration and (c) pH of Solution.

5.3.3 Isotherm Studies

Adsorption isotherms are principally used to understand the distribution of the adsorbate over the adsorbent and subsequently for the designing of an adsorption system. The adsorptive behavior of MB onto PNb has been studied by using two isotherm models: Langmuir and Freundlich isotherm models.

5.3.3.1 Langmuir Isotherm Model

The Langmuir isotherm model is based on the assumption that the adsorption of dye has taken place on a homogenous surface with the formation of a monolayer [192] The linear form of Langmuir isotherm [232] is as follows:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{1}{Q_m} C_e \tag{5.6}$$

Where, Q_m (mg/g) is the maximal capacity of the adsorption analogous to the exhaustive monolayer coverage, b (L/mg) is the Langmuir constant, C_e and Q_e are the dye concentration (mg/L) and adsorbed amount (mg/g) at equilibrium respectively. The liner plot of the Langmuir model (Figure 5.6 a), provides the values of Q_m and b from the slope and the intercept respectively. In addition, the values of all adsorption parameters are tabulated in Table 5.3. The R^2 value (=0.66) undoubtedly indicated that this model is not best fitted to the adsorption data of the MB onto PNb. The favourability of the isotherm is also confirmed by the dimensionless factor (R_L), calculated from expression 5.7 below:

$$R_L = \frac{1}{1+bC_o} \tag{5.7}$$

The R_L-value (=0.26) from this model shows the feasibility of the adsorption process, but the removal of MB on PNb cannot be explained by Langmuir isotherm preferably.

5.3.3.2 Freundlich Isotherm Model

Another isotherm model studied is the Freundlich isotherm model. This model assumes that the adsorption occurs on a heterogeneous surface in spite of a homogeneous surface and the active sites on the adsorbent are not equal. Freundlich isotherm is expressed by the following equation [193]:

$$\log q_e = \log K_f + n_h \log C_e \tag{5.8}$$

Where, K_f and n_h are the Freundlich constants and K_f is an indicator of the maximum adsorption capacity; Q_e and C_e have their usual meanings. Figure 5.6b shows the $\log Q_e$ vs $\log C_e$ relationships for the adsorption of MB onto PNb. This model is seemed to be the best-fitted isotherm model with the value of the regression coefficient, R^2=0.98. The values of all the parameters are given in Table 5.3. So, it could be concluded that the multilayer adsorption on the heterogeneous surface of polyaniline nanofibers base has been taken place during this adsorption experiment.

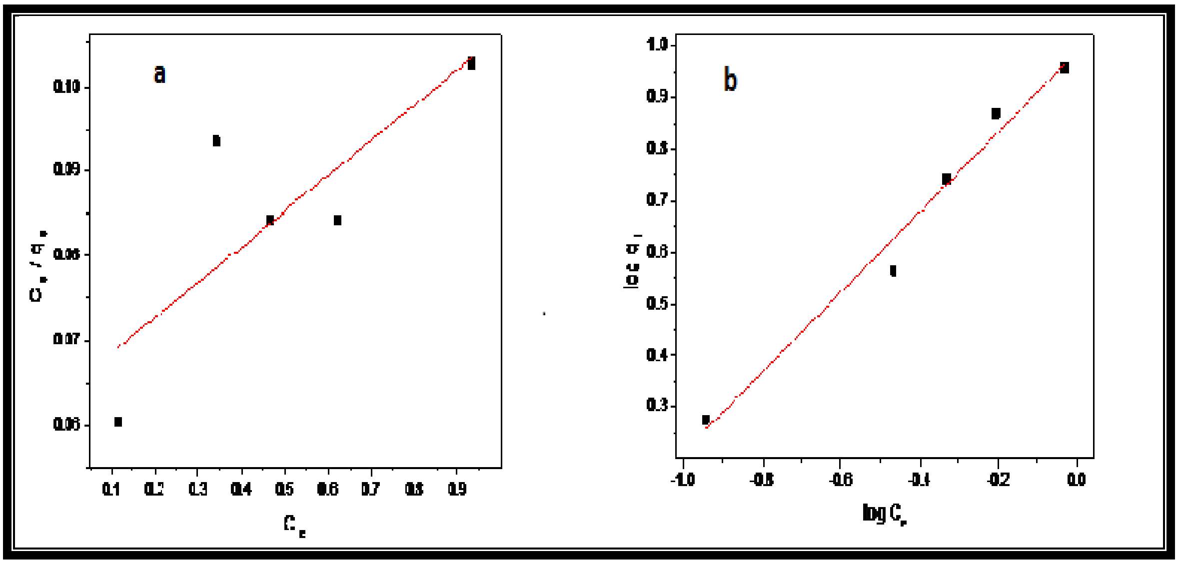

Figure 5.6: Isotherm Studies: (a) Langmuir Isotherm Model (b) Freundlich Isotherm Model.

Table 5.3 Different Adsorption Isotherm Parameters of Methylene Blue by Polyaniline Nanofibers Base.

Isotherms	Isotherm constant		R^2 value
Langmuir	q_m	24.3	0.66
	b	0.64	
	R_L	0.26	
Freundlich	K_f	9.72	0.97
	n_h	1.29	

5.3.4 Interaction between Methylene Blue Dye and Polyaniline Base

The adsorption of methylene blue dye onto polyaniline base form is occurred mainly by the involvement of electrostatic interaction between positive charge of the dye and lone pair of electrons present on the nitrogen atom of the polyaniline backbone, H-bonding and π-π interactions. Figure 5.7 shows the schematic representation of these interactions. The positively charged moiety of the methyl blue dye interact with lone pair of amine nitrogen of the backbone of polyaniline base (electrostatic interactions) and π-π interactions exists between aromatic rings of polyaniline and methylene blue dye. Also, the H- bonding between two participants enhances the removal of MB by PNb.

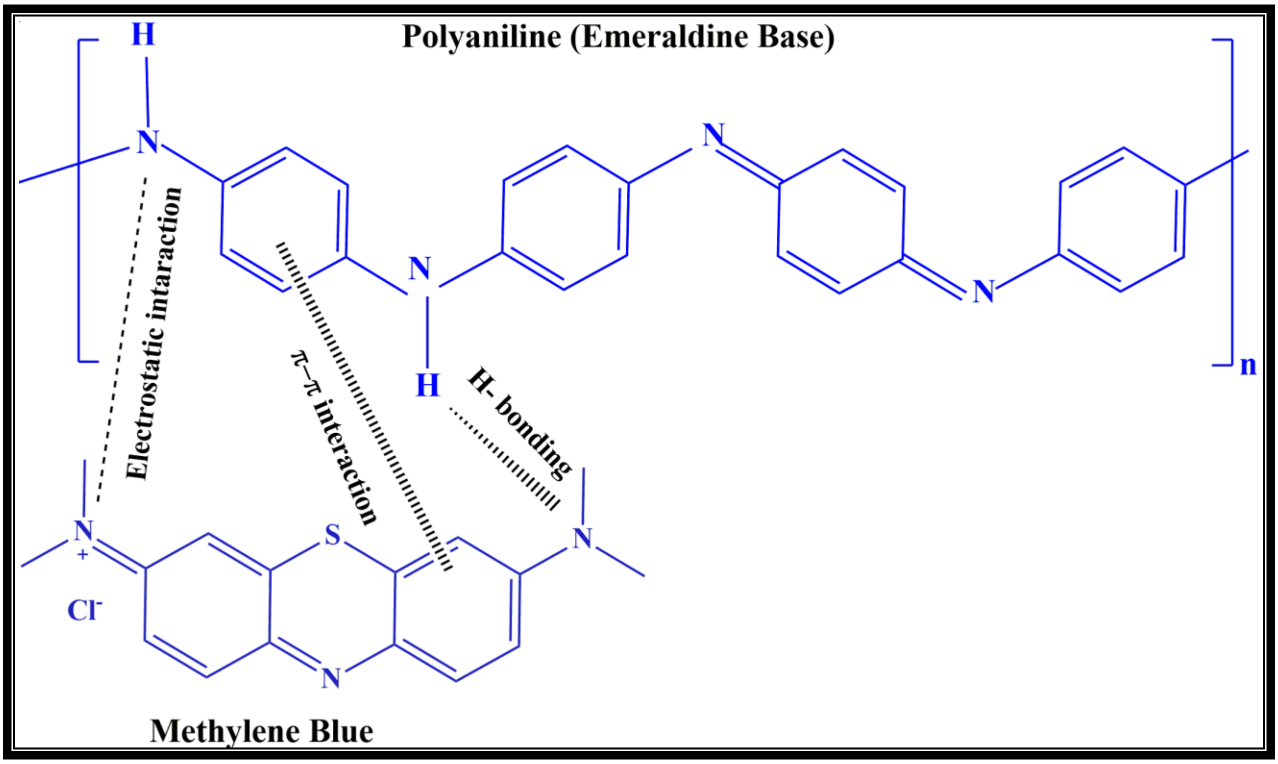

Figure 5.7: Schematic diagram of Interaction between Polyaniline Base and Methylene Blue Dye

5.4 Desorption study

Desorption studies on the exhausted adsorbent were carried out during this research work to utilize the exhausted adsorbent reusable and to make the process more cost effective. For this, the MB loaded polyaniline was treated with different solvents (water, 0.1M NaOH, 0.1M HCl and 95% Ethanol) to regenerate the exhausted adsorbent. Among the above solvents, ethanol (95%) was found to be most effective and almost 86 % of the dye was recovered.

5.5 Significant Findings

In this research work, base form of polyaniline nanofibers was used as a novel adsorbent to remove the methylene blue (cationic dye) dye from its aqueous solution. Polyaniline nanofibers were synthesized by the interfacial polymerization method. The synthesized adsorbent was characterized by SEM, HRTEM, XRD, Four Probe technique, surface area analyser and FTIR techniques. The UV- visible spectroscopy was used to analyze the un-adsorbed amount of the dye. Batch adsorption experiments were used to study the kinetics of the adsorption system. The kinetics of the adsorption of dye was studied using different kinetic models such as the pseudo-first-order, the pseudo-second-order and the intra-particle diffusion models. It has been observed that the pseudo-second-order model was best fitted to the adsorption data of the MB onto PNb, which indicated that the removal of methylene blue dye by polyaniline nanofiber base is by chemisorption process. It has been seen that intra-particle diffusion is also playing a significant role in the adsorption of dye, along with chemisorption, as the value of the regression coefficient obtained for the best fitted straight line for intra-particle diffusion model is significantly high i.e. R^2= 0.82. In addition, both Langmuir and Freundlich isotherm models were also used to analyze the equilibrium data. The best fitting of the data was obtained with the Freundlich model. It can be concluded that the adsorptive removal of the methylene blue dye occurred on the heterogeneous surface of the polyaniline and there is a formation of multilayer during this adsorption experiment. The obtained value of isotherm Langmuir capacity (Q_m) was 23.4mg/g. The effects of different parameters such as contact time, initial dye concentration and pH were also studied and the equilibrium values of these parameters are found to be 60 minutes, 6 mg/L and pH 6-8 respectively. Approx 91% of MB dye was removed by polyaniline nanofibers base. The desorption study revealed that almost 86% of methylene blue dye could be recovered from dye loaded polyaniline. The regenerated adsorbent was found to be efficient for 4 more cycles, prior to being discarded. From this study, it is evident that base form of polyaniline nanofibers can be used as an efficient adsorbent for the removal of basic dyes from the wastewater.

CHAPTER 6

SYNTHESIS AND CHARACTERIZATION OF THE MODIFIED POLYANILINE NANOFIBERS VIA DOPING WITH PHYTIC ACID AND ADSORPTIVE STUDIES OF CATIONIC DYE (METHYLENE BLUE) ONTO IT

In the recent past, polyaniline (PANI) has attracted the attentions of many researchers as an emerging adsorbent. Due to the ease of structural modification (via doping) of the PANI, its use as adsorbents is growing popular in comparison to the conventional adsorbents in wastewater treatment. The molecular structure of PANI contains nitrogen atom within its backbone to which different functional groups can be attached during doping to modify its surface properties, which may result into enhanced dye removal [233].Out of the available dopants, phytic acid (PA) can be considered as a good dopant because: i) it is natural (phytates in plant extracts and legumens), low cost, non-polluting and innocuous [234]. ii) It can be used as a substituent of HCl for the synthesis of polyaniline nanofibers by oxidation mechanism [235] iii) It is a cyclic compound with six phosphate carboxyl groups, which heighten the binding rapport for pollutants [234, 236]. Owing to the above properties, the doping of PANI with PA seemed to be more effective for the basic dye (cationic dye) removal, because PA acid consolidated as anion to the backbone of PANI structure, during in situ synthesis (polymerization of aniline) using PA solution[237]. PA doping not only modify the surface properties of PANI nanofibers, but also interact with the dye molecules during the adsorptive removal of the same. The reaction between PA and PANI occurred via phosphate carboxyl group, preferably at the quinoid site of the PANI backbone. Basically, during doping with PA, the nitrogen group of the PANI got protonated to form doped PANI.As per the reported literature; one PA molecule can be combined minimum with two PANI molecules and act as crosslinker along with a doping agent, and form a net-like structure [238]. Methylene blue is one of the significant dyes used in the textile industries; it also has some other applications in different fields like medical science, biology and chemistry etc. Even though it is not very hazardous, some serious diseases (hypertension, dizziness, vomiting, anaemia and nausea etc.) can be induced after its long period exposure.

Already reported literature studies have revealed that PA and PA-salts have been used for the remediation of effluent rich with heavy metals (Cu^{2+}, Cd^{2+}, Zn^{2+}) [234], but till date, no studies have been reported on the dye removal treatment of wastewater by using PA doped PANI nanofibers. So, the present study is carried out with an aim to use the PA doped PANI nanofibers for the removal of MB (cationic dye) from its aqueous solution. The synthesized PA doped PANI is characterized by SEM, HRTEM, FTIR, BET, XPS, Zeta potential and XRD. The UV-visible spectrophotometer was used to investigate the concentration of the un-adsorbed MB in the residual solution. The adsorption studies were performed by varying the adsorption parameters (contact time and initial MB dye concentration and pH of solution). Various kinetic models were used to analyze the mechanism of the reaction. The isotherm study was carried out to understand the relation between the amount of doped PANI and MB dye by using Langmuir and Freundlich models. Finally, desorption study was also conducted by using different solutions. The synthesized PA doped PANI nanofibers were found to be novel and efficient adsorbent for MB (cationic dye) removal.

6.1 Synthesis of PA Doped PANI Nanofibers

Phytic acid solution is used for the synthesis ofPA doped PANI nanofibers by oxidative polymerization of aniline (monomers). In brief, prepare solution-I, by dissolving 0.46mL phytic acid (dopant) and 0.45 mL aniline (monomer) in 2 mL of distilled water and solution-II, by dissolving 0.285 g of ammonium persulphate (APS) into 1mL of distilled water. Then add solution-II to solution-I and agitate the mixture for a period of 1 minute. As the reaction (polymerization) proceeded, a noticeable change in the color of the solution (from brown to dark green) is observed. Then keep the reaction mixture at 4^0C for 24 h undisturbed. Wash the synthesized PA doped PANI nanofibers with distilled water several times and dry the obtained powder in oven at 60^0C for 24 h.

6.2 Batch Adsorption Studies

An emphatic amount of MB dye was dissolved in distilled water to prepare the stock solution for the experiment. Further, different concentration solutions, as needed, were prepared by diluting the stock solution with distilled water. The adsorption experiment was performed by agitating the 0.05 g of the adsorbent with a 100 mL of dye solution in a shaker incubator, at a speed of 250 rpm, for a specified interval of time. Then the reaction mixture was centrifuged at 6000 rpm for 15 minutes. The un-adsorbed dye was estimated by using UV- Visible spectroscope at 664 nm. The standard solutions of methylene blue dye were prepared for the calibration of the UV-Visible spectrophotometer. Analogous absorption for individual concentrations was obtained at λ_{max} 664 nm. By plotting the data between concentration and absorbance, a linear regression curve was obtained. The following equations were used to calculate the adsorption capacity and adsorbed percentage of dye onto PA doped PANI nanofibers respectively:

$$Q = \frac{(C_o - C_e)V}{m} \tag{6.1}$$

$$\text{Percentage Adsorption} = \frac{C_o - C_e}{m} \times 100\% \tag{6.2}$$

Where, Q (mg/gm) is the adsorption capacity, C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), V (L) is the volume of the solution used and m (g) is the mass of PA doped PANI nanofibers used.

6.3 Result and Discussion

6.3.1 Interaction between PA Doped Polyaniline and Methylene Blue Dye

The radical polymerization method was used for the synthesis of nanofibers of PANI. Basically, the conventional oxidant, APS (radical initiator) was used to initiate the process, by pulling out an electron from each monomer unit (aniline) and form radical cation. This radical cation of aniline can be exists into three resonating structures which combines into a head-to-tail manner to form the PANI Chain [239]. The secondary amine of PANI backbone, act as a doping site at which different types of ions, molecules and functional groups can be attached to modify the surface of the synthesized PANI nanfibers. In current study, the Phytic acid (PA) used as the dopant, contains six phosphoric groups with hydroxyl and oxygen (PA$^-$) at terminal sites. These added active sites of PA increase the adsorption capacity of the synthesized doped PANI nanofibers, hence, resulting in more efficient adsorbent for dye removal. A schematic representation of the interaction between the methylene blue dye (MB) and the phytic acid doped polyaniline (DPANI) is as shown in Figure 6.1.

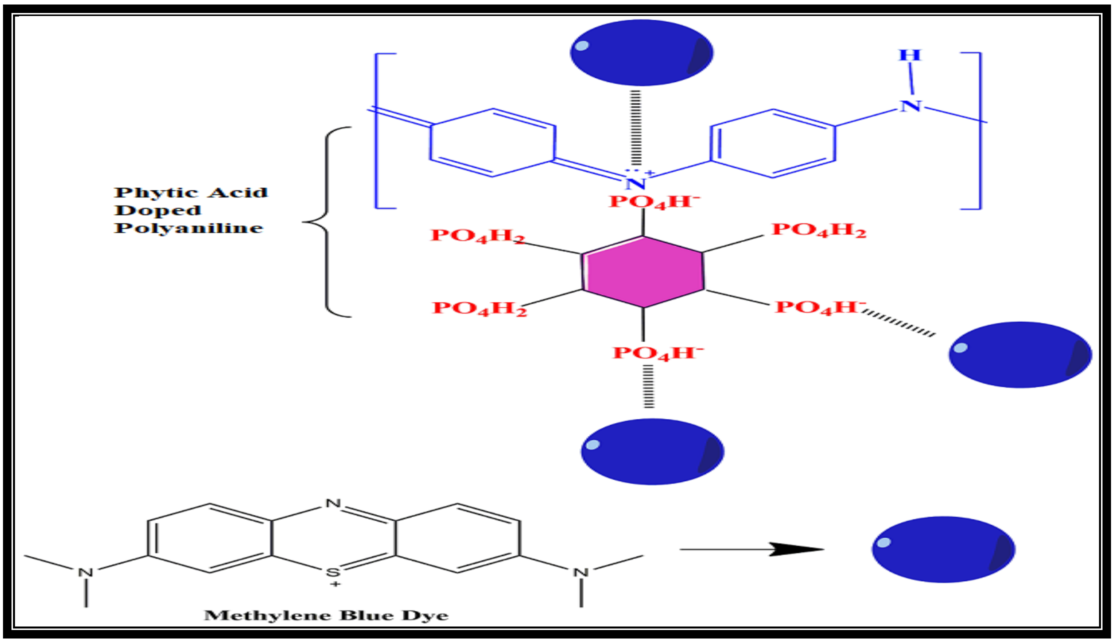

Figure 6.1: A Schematic Representation of the Interaction between MB Dye and Phytic Acid Doped Polyaniline

6.3.2 Characterization of PA Doped PANI Nanofibers:

6.3.2.1 FTIR

FTIR spectra of synthesized PA doped PANI nanofibers (Figure 6.2) explains the molecular structure of the same,between the wavelength range of 4000 cm^{-1} to 500 cm^{-1} (more or less similar to undoped emeraldine salt form of PANI). A characteristic broad absorption band for N-H stretching of the structure was obtained at 3441.4 cm^{-1}[240]. The peaks at 1571.8 cm^{-1} and 1496.4 cm^{-1} are attributed to the C=C stretching mode of quinoid and benzenoid ring respectively, indicating that the structure of the polyaniline is in emeraldine form [241]. The absorption peaks at 1230.0 and 1301.5 cm^{-1} are attributed to C=N and C-N stretching vibration (secondary amine) respectively [241]. The vibration bands at 824.0 and 1145.5 cm^{-1} are attributed to out-of-planeand in- plane bending of C-H bond respectively [242]. The peak at 692.9 cm^{-1} obtained due to out-of-plane deformation of phenylene ring [242]. The vibration peaks at 506.8 cm^{-1} and 754.7 cm^{-1} are due to C-H bond bending vibrations in 1,4 di-substituted benzene ring [241]. In addition to these common vibration peaks of emeraldine PANI, some specific peaks at 597.1, 937.2 and 1613.0 cm^{-1} are attributed to the P-O bending vibration, P-O-C symmetrical vibration and P=O stretching vibrations respectively. These peaks indicated that, PANI nanofibers were doped with a consequential amount of PA, without any change in the molecular structure of nanofibers during synthesis.

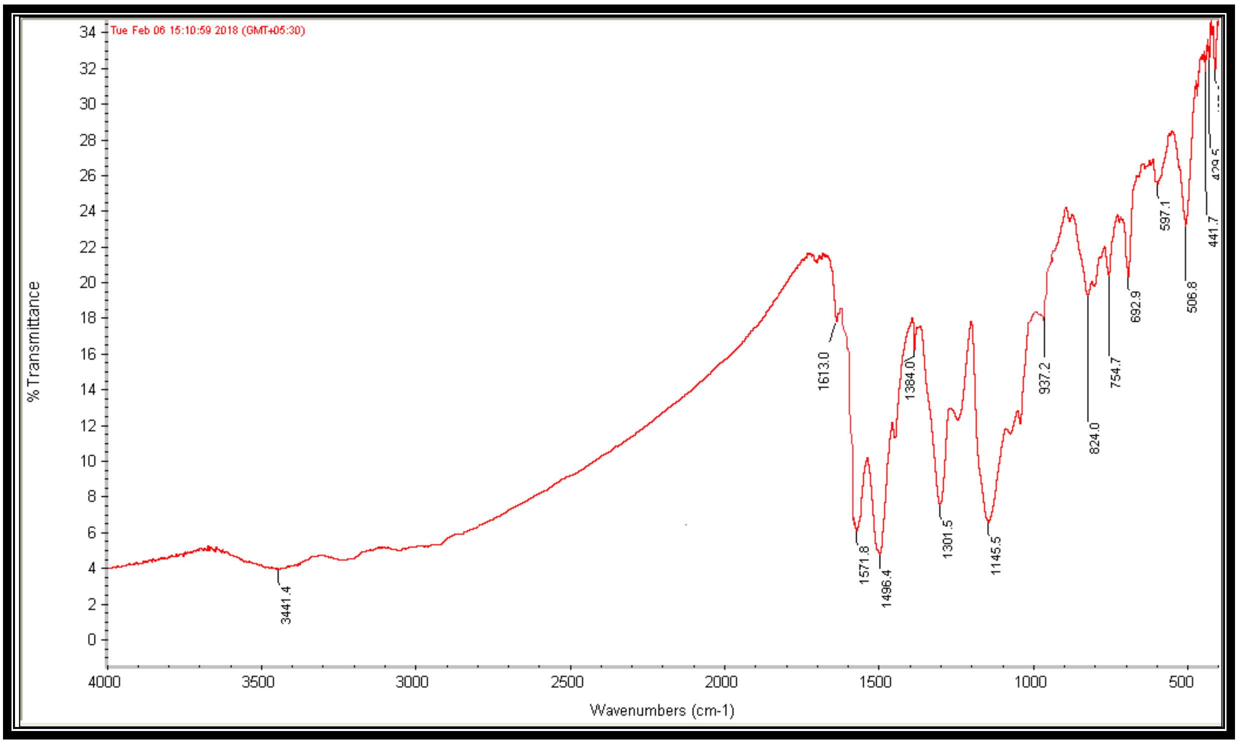

Figure 6.2: FTIR Spectra of Phytic Acid Doped Polyaniline Nanofibers.

6.3.2.2 XRD

The nature of PA doped PANI nanofiber (either crystalline or amorphous) and crystallite size was determined by XRD technique (Figure 6.3).The XRD pattern shows a broad band with peaks at 2θ values of 20^0 and 25^0, which indicated a major amorphous portion of PA doped PANI nanofibers with very little crystalline nature. The crystal size of the prepared PA doped PANI nanofibers was found to be 3.5 nm as calculated from Debye Scherer Equation (Eq. 6.3, below). The literature studies also support the above result [243].

$$D = \frac{K\lambda}{(\beta COS\theta)} \qquad (6.3)$$

Where, β is FWHM i.e. full width half maximum and k is Bragg’s constant (0.9), λ is wavelength of X-ray radiation (0.154 nm) and θ is the Bragg’s angle.

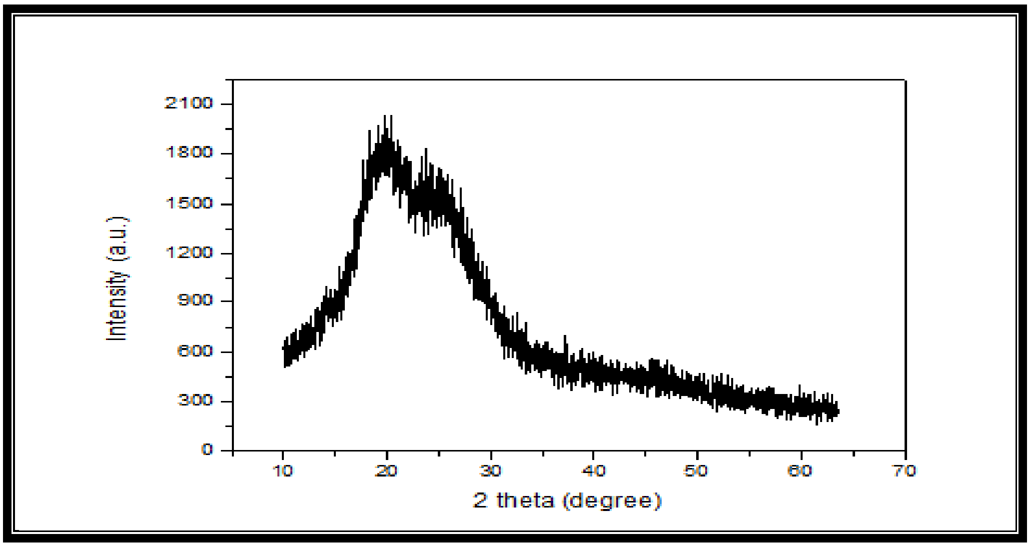

Figure 6.3: XRD Pattern of Phytic Acid Doped Polyaniline Nanofibers.

6.3.2.3 SEM and TEM

The result of SEM (Figure 6.4a) shows the heterogeneous surface morphology of PA doped PANI nanofibers. This heterogeneous surface morphology of PA doped PANI nanofibers are due to the monomer's unidirectional head-to-tail attachment with each other during polymerization (free radical mechanism). The average diameter of PA doped PANI nanofibers, as prepared in this work, was found to be 60 nm. The synthesized PA doped PANI nanofibers were further analyzed by using HRTEM technique (Figure 6.4b). HRTEM images confirmed the nano-range structure of doped PANI.

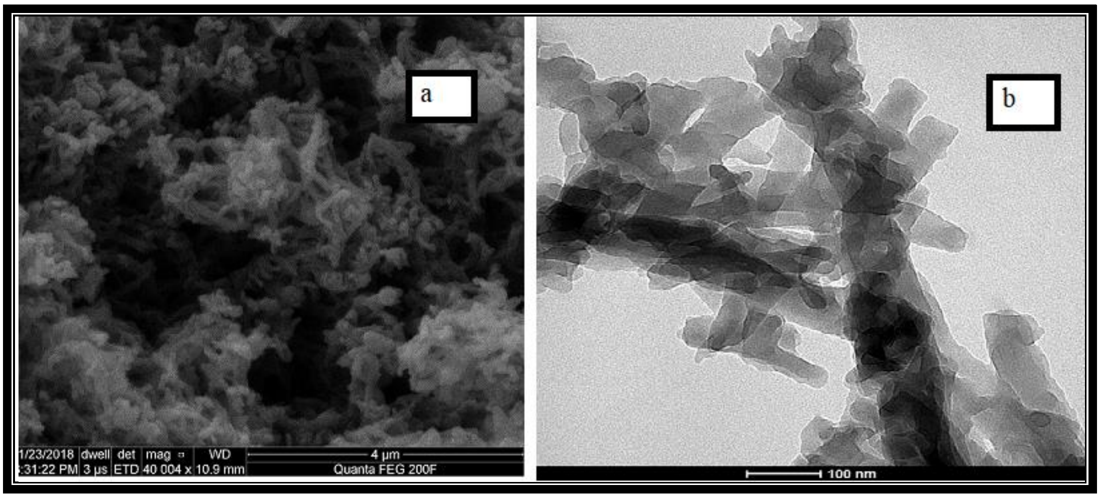

Figure 6.4: (a) SEM Image and (b) HRTEM Image of Phytic Acid Doped Polyaniline Nanofibers.

6.3.2.4 BET Analysis

The synthesized polyaniline nanofibers were characterized by surface area analyser. As per the results of surface area analyser, the surface area of PA doped PANI nanofibers was found to be higher as compared to conventionally synthesized polyaniline. Table 6.1 shows the surface area, pore volume and pore diameter of nanostructured and conventional polyaniline. The higher surface area of the synthesized nanostructured doped PANI is quite beneficial for the adsorption of MB.

6.3.2.5 ZETA Potential Analysis

The ZETA potential measurement of the phytic acid doped polyaniline nanofibers (ethanol dispersion) was carried out by using Malvern Zetameter (Figure 6.5). It has been noticed that the doped adsorbent possessed negative charge on its surface with negative value of Zeta potential equal to -2.06 mV.

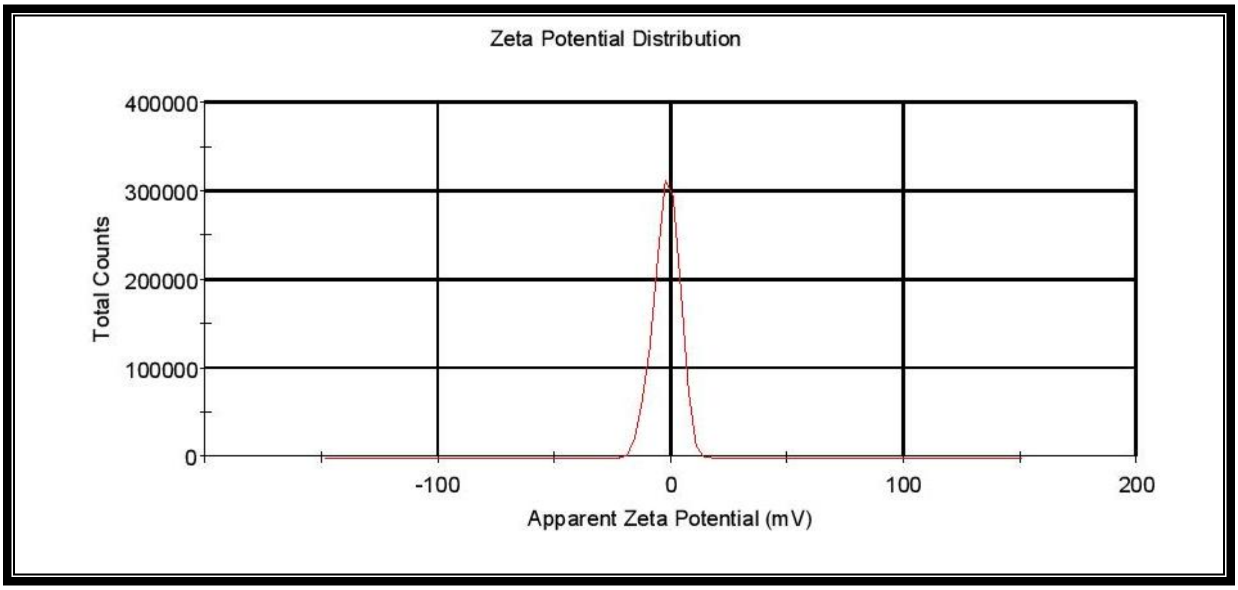

Figure 6.5: ZETA Potential Measurement of Phytic Acid Doped Polyaniline Nanofibers

Table 6.1. BET Analysis Data of the MB Adsorption onto Phytic Acid Doped Polyaniline Nanofibers.

Adsorbent	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Average Pore Diameter (nm)**
Phytic Acid Doped Polyaniline Nanofibers	33	9.6154×10^{-2}	11.7
Conventional Polyaniline	14	2.638×10^{-3}	34.4

6.3.2.6 XPS Analysis

XPS characterization was done to determine the composition of the synthesised adsorbent (PA doped PANI). The PA doped PANI shows three characteristic peaks (Figure 6.6a), which centred at binding energies of 286, 401 and 532 eV, which are attributed to the presence of C1s, N1s and O1srespectively. Figure 6.6b shows the presence of phosphorous in the synthesised adsorbent with the clearly observed peak for the P2p, at the binding energy of 135 eV. These results clearly indicated that a substantial amount of phosphoric compound was doped to the polyaniline.

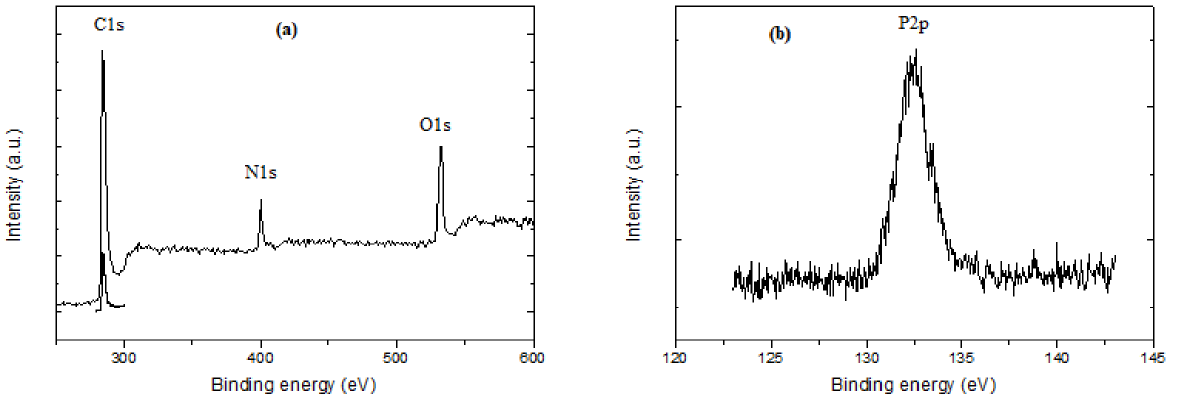

Figure 6.6: XPS Analysis of Phytic Acid Doped Polyaniline.

6.3.3. Kinetic Studies

The kinetic study of dye removal by adsorption is important due to the reason of its control over the equilibrium time and the efficiency of the adsorption process. It is also helpful to explain the mechanism of the adsorption process. Three different kinetic models were used to study the rate of dye uptake on the PA doped PANI nanofibers, which are as follows: the pseudo-first order model, the pseudo-second order model and the intra-particle diffusion model.

6.3.3.1 Pseudo- First Order Model

The following equation represents the pseudo-first order model:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303} \qquad (6.4)$$

Fitting of the adsorption data to the pseudo-first order model was analyzed by plotting a graph of log (Q_e-Q_t) vs t relationships as presented in Figure 9a, where Q_e and Q_t are the amount (mg/g) of MB dye adsorbed on PA doped PANI nanofibers at equilibrium and at time t (min) respectively. K_1 (l/min) is the adsorption constant for pseudo-first order model. The slope and the intercept of the graph (Figure 6.7a) provided the values of K_1 and Q_e respectively. The values of the above adsorption parameters are given in Table 6.2. As shown in the table, the value of correlation coefficient is 0.92 for this adsorption process, and the values of calculated and experimental Q_e do not coincide with each other. So, it could be concluded that this particular model is not followed by this adsorption system preferably.

6.3.3.2 Pseudo- Second Order Model

Another adsorption model studied for the adsorption of MB on PA doped PANI is the pseudo-second order model, which is related with the quantity of dye adsorbed at the equilibrium and on the surface of polyaniline (Figure 6.7 b). The following equation represents the pseudo-second order model:

$$\frac{T}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{6.5}$$

The plot of t/Q_t vs t is a straight line curve, where Q_t, Q_e and t have their usual meanings and K_2 (g/mg min) is the rate constant for the pseudo-second order model. The values of above parameters are represented in Table 6.2. As observed, the values of calculated $Q_{e\ cal.}$ (2.92) and experimental $Q_{e\ exp.}$ (2.88) agreed with each other and the R^2 value is reportedly equal to 0.99. So, we can assume that the adsorption data for MB onto PA doped PANI is best fitted in this model. This fitting of adsorption data also indicates that chemisorption played significant role during this experiment.

6.3.3.3 Intraparticle Diffusion Model

The intra-particle diffusion model was also studied to understand the adsorption process of MB dye onto PA doped PANI nanofibers. This model assumes that the dye molecules that are adsorbed on the surface of doped PANI nanofibers are diffused into interstitial sites of the adsorbent, but the formation of any bond (physical or chemical) with adsorbent in interstitial sites is a limiting step. This model can be represented by the following equation:

$$Q_t = K_i t^{0.5} + C \tag{6.6}$$

Where, K_i (mg/g $min^{0.5}$) is the rate constant for the intra-particle diffusion, C is the boundary layer thickness and Q_t and t have usual meanings. A plot of Q_t against $t^{0.5}$ (Figure 6.7c) gave the values of rate constant of and boundary layer thickness from slope and intercept respectively. The values of all the parameters, so obtained, are given in Table 6.2. But the intra-particle model is not the only model followed by the adsorption of MB on PA doped PANI nanofibers because the best fitted straight line (Figure 6.7c) does not pass through the origin. Moreover, the value of R^2 (0.93) also indicated that this model is not preferably followed by the adsorption of MB onto PA doped PANI nanofibers, but plays a significant role in along with other mechanism (s).

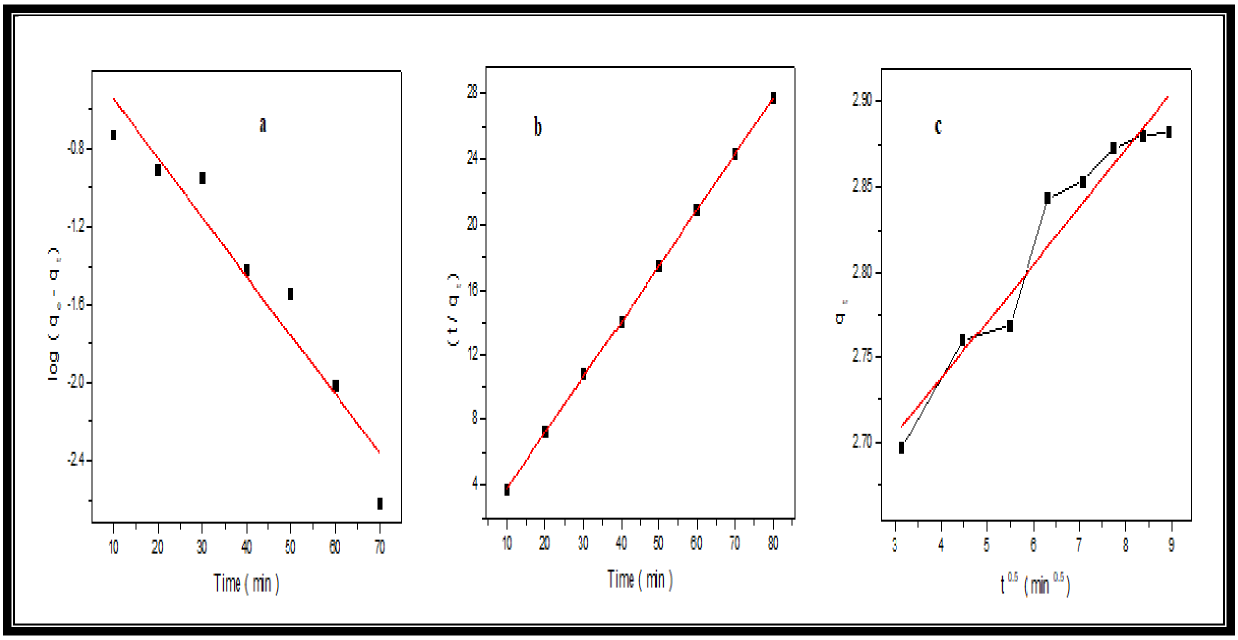

Figure 6.7: Kinetic Studies: (a) Pseudo-First-Order Model; (b) Pseudo-Second-Order Model and (c) Intra-Particle Diffusion Model.

Table 6.2. Rate Constants Values for Adsorption of Methylene Blue Dye on Phytic Acid Doped PANI Nanofibers for Different Kinetic Models.

Kinetic Models	**Parameters**		**R^2 value**
Pseudo-first-order	k_1(min^{-1}) q_e,exp(mg g^{-1}) q_e,cal(mg g^{-1})	0.048 2.88 0.33	0.92
Pseudo-second-order	k_2(g mg^{-1} min^{-1}) q_e,cal(mg g^{-1})	0.047 2.92	0.99
Intraparticle Diffusion	k_i(mg min$^{0.5}$ g^{-1}) C	0.033 2.603	0.93

6.3.3.4 Effect of Contact Time

As the adsorption process is significantly influenced by the contact time, it is quite interesting to study the effect of contact time on the adsorption of dye by varying the time of adsorption from 20-120 minutes (initial dye concentration- 7 mg/L, pH- 8.5, room temperature) (Figure 6.8a). The ease of PA doped PANI to remove MB from its aqueous solution was measured by performing the adsorption batch experiments. As shown in figure, the removal of MB from its aqueous solution was increased with increase in contact time. It has been observed that about 92% of the dye was adsorbed within first 20 minutes and an equilibrium stage (96% removal) was attained after 60 minutes. So, the optimized equilibrium contact time for the present study was 60 minutes.

6.3.3.5 Effect of Initial Dye Concentration

The study of the effect of initial dye concentration on adsorption (Figure 6.8b) is also a very important factor to understand the adsorption process, which is carried out by varying the initial concentration of MB dye (2-10mg/L) and keeping all other parameters constant (contact time -

60 minutes, pH- 8.5, room temperature). It could be seen from the figure that, the adsorption percentage decreases with increase in initial dye concentration. This is due to the availability of more uninhabited active sites on the adsorbent surface in case of lower initial dye concentration. But at higher initial dye concentration, almost complete coverage of active sites has been achieved, hence, a lessMB adsorption has been observed. On the other hand, the amount of dye adsorbed at equilibrium is increased with an increase in initial dye concentration. This can be explained on the basis of the driving forces provided by the dye molecules that defeats the resistance to the mass transfer (of dye molecules) among solid and aqueous phases. Moreover, there is apparently an increased interaction between dye molecules and the adsorbent, with increase in the initial dye concentration. After a specific initial dye concentration i.e. 7mg/L, no significant change in the adsorption of MB has been observed. So, 7mg/L value is the equilibrium concentration for the current research work. Some other studies have been reported the similar pattern of results for different dyes such as methyl violet, methyl orange and reactive blue 221 [220, 221].

6.3.3.6 Effect of pH

The pH of reaction solution in an adsorption process is an important parameter of concern because the nature of the surface of the adsorbent gets changed with the pH of the solution [244]. So, the study of the pH variation on the dye removal efficiency of adsorbent is a very important in adsorption study. The effect of solution pH on MB removal by PA doped PANI nanofibers was studied (between pH value 2-11) to optimize the pH value for this study (contact time- 60 minutes, initial dye concentration- 7 mg/L, room temperature) (Figure 6.8c).The significant effect of pH on MB adsorption was observed between 6-8 pH values. In case of PA doped PANI nanofibers, the deprotonation of PA’s phosphoric groups occurred, depending upon the pH of the reaction solution. At a medium pH value, some of the phosphoric groups get deprotonated

(Hydrogen + dihydrogen phosphates), while at higher pH, more or all phosphoric groups changed to phosphates with more negative sites on the adsorbent. Hence, higher MB adsorption is achieved at higher pH value and finally equilibrium is attained at pH~8.5.

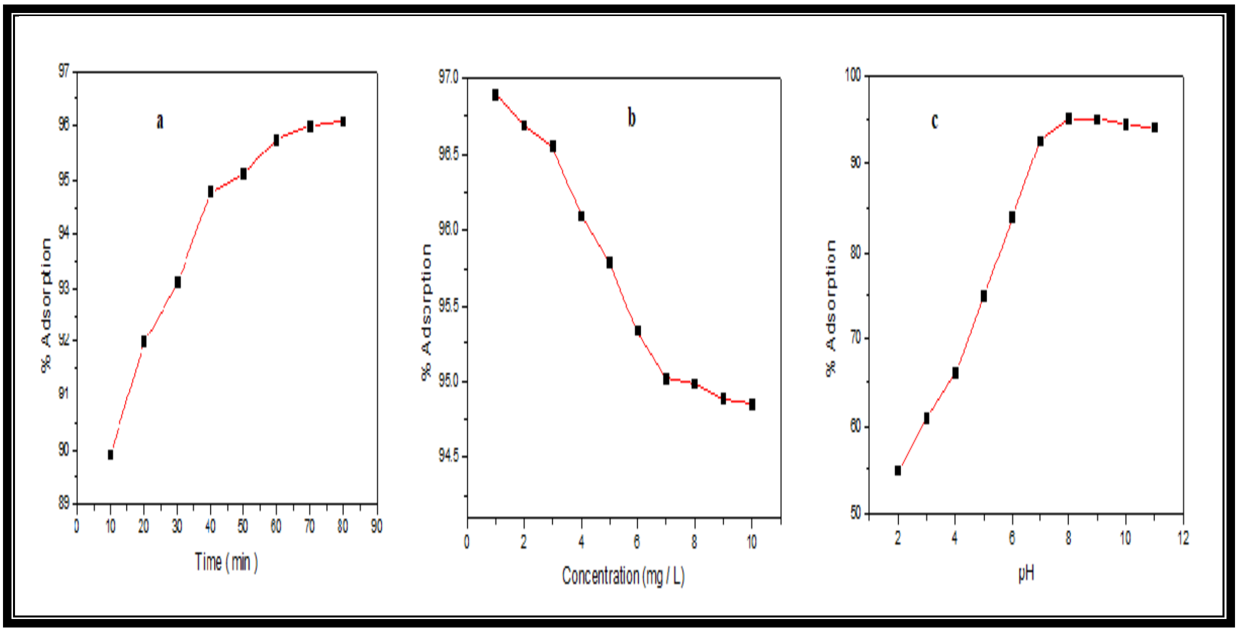

Figure 6.8: Effects of Adsorption Parameters on Removal of Methylene Blue Dye: (a) Contact Time; (b) Initial Dye Concentration and (c) Solution pH.

6.3.4 Isotherm Study

Adsorption isotherms are principally used to understand the distribution of the adsorbate over the adsorbent and subsequently for the designing of an adsorption system. The adsorptive behaviour of MB onto PA doped PANI nanofibers have been studied by using two isotherm models: Langmuir and Freundlich isotherm models.

6.3.4.1 Langmuir Isotherm Model

The Langmuir isotherm model is based on the assumption that the adsorption of dye has taken place on a homogenous surface with the formation of a monolayer [192]. The linear form of Langmuir isotherm is as follows:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{1}{Q_m} C_e \qquad (6.7)$$

Where, Q_m(mg/g) is the maximal capacity of adsorption analogous to the exhaustive monolayer coverage, b (L/mg) is the Langmuir constant, C_e and Q_e are the dye concentration(mg/L) and the adsorbed amount (mg/g) at equilibrium respectively. The liner plot of Langmuir model (Figure 6.9a) provides the values of Q_m and b from the slope and the intercept respectively. The values of the all adsorption parameters are tabulated in Table 3. The R^2 value (0.70), undoubtedly indicated that this model is not best fitted to the adsorption data of the MB dye onto PA doped PANI nanofibers. The favourability of the isotherm is also confirmed by the dimensionless factor (R_L), calculated from equation below:

$$R_L = \frac{1}{1 + bC_o} \qquad (6.8)$$

As per the R_L value (0.005), this model shows the feasibility of the adsorption process, but the removal of MB on DPANI cannot be explained by Langmuir's isotherm preferably.

6.3.4.2 Freundlich Isotherm Model

Another isotherm model studied is the Freundlich isotherm model. This model assumes that the adsorption occurs on a heterogeneous surface in spite of a homogeneous surface, and, the active sites on the adsorbent are not equal [193]. Freundlich isotherm is expressed by the following equation:

$$\log q_e = \log K_f + n_h \log C_e \qquad (6.9)$$

Where, K_f and n_h are the Freundlich constants and K_f is an indicator of the maximum adsorption capacity; Q_e and C_e have their usual meanings. Figure 6.9b shows the log Q_e vs logC_e relationship for the adsorption of MB onto PA doped PANI nanofibers. This model is seemed to be the best-fitted isotherm model with the value of the regression coefficient, R^2= 0.99. The values of all the parameters are given in Table 6.3. So, it could be concluded that the multilayer adsorption of

MB on the heterogeneous surface of the PA doped PANI has been taken place during this adsorption experiment. A similar study has also been reported in the literature for the removal of the Methyl Orange dye by polyaniline nanofibers [245].

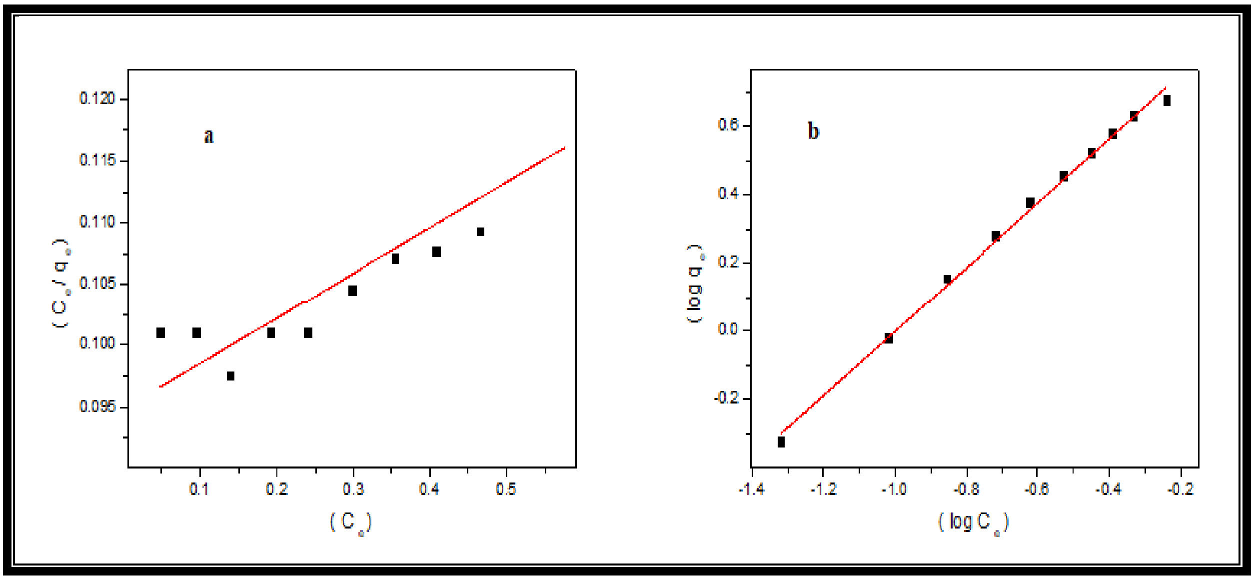

Figure 6.9: Isotherm Studies: (a) Langmuir Isotherm Model (b) Freundlich Isotherm Model.

Table 6.3. Different Adsorption Isotherm Parameters of Methylene Blue onto Phytic Acid Doped PANI Nanofibers.

Isotherms	Isotherm constant	R^2 value
Langmuir	q_m 43.4 b 0.23 R_L 0.005	0.70
Freundlich	K_f 10.02 n_h 0.99	0.99

6.4 Desorption Study

Desorption study was carried out to make the adsorbent reusable and to make the process cost effective. In this study, the MB dye loaded PA doped PANI nanofibers were treated with different solvents (water, 0.1M NaOH, 0.1M HCl and 95% Ethanol) to regenerate the exhausted adsorbent.Among theabove solvents, ethanol (95%) was found to be more effective and almost 65% of the dye was recovered.

6.5 Significant Findings

A polymeric based novel adsorbent has been developed for the absorptive removal of cationic (methylene blue) dye. The adsorbent was synthesized by a simple oxidative mechanism (free radical mechanism) using phytic acid solution. The preparation of doped PANI nanofibers was evidenced by different analysis such as: FTIR, XRD, ESEM, HRTEM, XPS and BET etc. The UV- visible spectroscopy was used to analyze the un-adsorbed amount of dye. The PA doped PANI nanofibers showed a significantly improved MB removal as compared to its conventional counterpart because of the presence of more active sites on the surface of the concerned adsorbent due to the presence of phosphoric groups of phytic acid moiety. In addition, the higher MB adsorption at higher pH is also due to the automatic deprotonation of the dihydrogen phosphate groups. This resulted into more negative sites in basic conditions and hence, more MB adsorption occurred. Batch adsorption experiments were used to study the kinetics of the adsorption system. The kinetics of the adsorption of dye was studied using different kinetic models such as Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion models. It has been observed that the Pseudo-second-order model was found to be best fitted to the adsorption data of the MB onto PA doped PANI nanofibers, which indicated that the removal of MB dye occurred by chemisorption process. It has been seen that intra-particle diffusion is also playing a significant role in the adsorption along with the chemisorption, as the value of the regression coefficient obtained for the best fitted straight line, for intra-particle diffusion model, is significantly high i.e. R^2= 0.93.In addition, both Langmuir and Freundlich isotherm models were used to analyse the equilibrium data. The best fitting of the data was observed with the

Freundlich model. It can be concluded that the adsorptive removal of the MB dye occurred on the heterogeneous surface of the synthesized doped adsorbent and there is a formation of multilayer during this adsorption experiment. The obtained value of isotherm Langmuir capacity (Q_m) was 43.4mg/g. The effect of different adsorption parameters i.e. contact time, initial dye concentration and solution pH were also studied and the equilibrium values of these parameters are found to be 60 minutes, 7 mg/L and 8.5 respectively. Approx 96% of MB dye was removed by using PA doped Polyaniline. Desorption study revealed that almost 65% of MB dye could be recovered by using 95% ethanol as a solvent, from dye loaded PA doped PANI nanofibers. From this study, we concluded that, the surface improvement of PANI nanofibers by doping resulted in high rates of cationic dye adsorption and can be further explored at commercial scale for dye removal from industrial effluent.

CHAPTER 7

CONCLUSIONS AND FUTURE PROSPECTS

7.1 Conclusions

The solicitation of polyaniline as an adsorbent has gained admiration from recent few years only. Though, originally regarded as a conducting polymer, polyaniline, with its unique properties has shown a potential to be used as an adsorbent. As per the reported studies, polyaniline due to its unique chemical stability, electronic behavior and improved mechanical properties is emerging as one of the inceptive adsorbent, especially for the dyes. Being derived from less costly raw materials, simple preparation, high adsorption and regeneration capacity, polyaniline has shown its potential to be used as an adsorbent on commercial scale. This newly observed adsorption capacity of polyaniline, has been explored by different researchers, for the absorptive removal of dyes and other chemicals from waste water,in its different forms i.e. acidic (ES) and basic forms of PANI; PANI composites, coating of PANI on different solid substrates, salt form of the PANI, doped PANI etc. In addition to its high surface area, that is modified to be used as adsorbent, its ability of being easy to oxidize or reduce makes it more attractive for the selective removal of different charged moieties from the effluent.

- In the present study, polyaniline nanofibers (salt, base and doped forms) were synthesized bythe interfacial polymerization method and used for the adsorptive removal of both cationic and anionic dyes.
- The synthesized adsorbent was characterized by SEM, HRTEM, XRD, Zeta potential, BET and FTIR techniques.
- The SEM results indicated the nano-range of the synthesized fibrous polyaniline which was further confirmed as of 60 nm in diameter by HRTEM.
- The BET analysis reported the enhanced (approx. 4 times) surface area of PANI nanofibers

($48.83\ m^2g^{-1}$) as compared to conventional polyaniline ($13.65\ m^2g^{-1}$).This enhanced surface area aided in more adsorption of dye onto this nanostructured form of polyaniline.

- The UV- visible spectroscopy was used to analyze the un-adsorbed amount of dye.
- Batch adsorption experiments were used to study the kinetics of the adsorption system for both cationic and anonic dyes.the kinetics of the adsorption of dyes was studied using different kinetic models such as Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion models.
- It has been observed that in all the adsorption system, Pseudo-second-order model was best fitted to the adsorption data which indicated the involvement of chemisorption in the removal of dye by polyaniline nanofibers.
- The intra-particle diffusion is also playing a significant role in the adsorption along with chemisorptions.
- Langmuir and Freundlich isotherm models were studied to analyse the equilibrium data. The best fitting of the data was observed with the Freundlich model, in all the cases. So, it can be concluded that the adsorptive removal of the dyes occurred on heterogeneous surface of the polyaniline, and there is a formation of multilayer during the adsorption experiment.
- The effects of different parameters, such as, contact time, initial dye concentration and pH were also studied.
- About 95% of methyl orange dye was removed by emeraldine salt form of the polyaniline and 91% of methylene blue dye was removed by emeraldine base form of polyaniline. This removal is attributed to the interaction between opposite charges of the polyaniline salt and the methyl orange (anionic) dye in former case and interaction between lone pair of electrons of nitrogen atom of base form of polyaniline and methylene blue (cationic) dye in later case.
- Only 67% of methylene blue dye was removed by salt form of polyaniline, this is because of less interaction between the two participants.

- The PANI nanofibers were structurally modified by doping for studying the effect of doping on adsorption capacity of the concerned polymer. The phytic acid doped polyaniline was synthesized to enhance the selective adsorptione of the cationic dyes (Methylene Blue in present study).
- The adsorbent was synthesized by a simple oxidative mechanism (free radical mechanism)using phytic acid solution.
- The preparation of the doped PANI nanofibers was evidenced by different analysis such as: FTIR, XRD, ESEM, HRTEM, XPS and BET etc.
- The PA doped PANI nanofibers showed a significantly improved MB removal as compare to its conventional counterpart because of the presence of more active sites on its surface, due to the phosphoric groups of phytic acid moiety.
- The higher MB adsorption at higher pH is also due to the automatic deprotonation of the dihydrogen phosphate groups which resulted into more negative sites, in basic conditions, and hence, more MB adsorption occurred.
- The Pseudo-second-order model was best fitted to the adsorption data of the MB onto PA doped PANI nanofibers, which indicated that the removal of MB dye occurred by chemisorption process.
- It has been seen that intra-particle diffusion is also playing a significant role in the adsorption along with the chemisorptions in MB removal by PA doped PANI.
- Both Langmuir and Freundlich isotherm models were also studied to analyse the equilibrium data. The best fitting of the data was achieved with the Freundlich model fron which it was concluded that the adsorptive removal of the MB dye occurred on the heterogeneous surface of the synthesized doped adsorbent and there is a formation of multilayer during this adsorption experiment.
- Approx 96% of methylene blue dye was removed by using phytic acid doped polyaniline at

optimum adsorption parameters.

- The desorption study revealed that almost 65% of MB dye could be recovered by using 95% ethanol as a solvent, from dye loaded PA doped PANI nanofibers.
- The surface improvement of PANI nanofibersby doping, resulted in high rates of cationic dye adsorption and can be further explored at commercial scale for dye removal from industrial effluent.
- The present study has been conducted on the lab scale and approximately 90-96 % of dye removal was observed.
- From these studies, it is evident that polyaniline nanofibers can be used as an efficient adsorbent for the removal of acidic as well as basic dyes from theiraqueous solution.
- For higher dye concentrations, the higher dosage of the adsorbent can be employed to remediate the effluent up to an acceptable standard, which can be calculated by scale-up studies.
- In the nutshell, polyaniline (PANI) and its derivatives have the caliber replace the commercially available adsorbent with its unique properties and excellent adsorptive and regeneration capacity.

7.2 Future Prospects

Polyaniline Nanofibers with higher surface area can be used for more dye removal (salt-acidic dyes, base- basic dyes and doped- selective dye removal).Polyaniline Nanofibers can be applicable at industrial level because of its lower synthesis cost, easy synthesis and effective adsorptive capacity. Phytic Acid doped Polyaniline can be used for the selective cationic dye removal.The adsorption capacity of Polyaniline Nanofibers can be enhanced by making the composites or by coating with appropriate substrate. Doping of PANI can be carried out by some other acids such as mercaptoacids etc. Polyaniline (salt and base) and doped Polyaniline can be used for metal ion removal from aqueous solution.

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LIST OF PUBLICATIONS

S. No.	Title of the Paper	Name of the authors	Name of Journal	Indexing status of Journal with indexing agency
1.	PHYTIC ACID DOPED POLYANILINE NANOFIBERS: AN ADVANCED ADSORBENT FOR METHYLENE BLUE DYE REMOVAL	**Monika Duhan** and Raminder Kaur	Environmental Nanotechnology Monitoring and Management (Elsevier)	SCI Scopus (Elsevier)
2.	ADSORPTIVE REMOVAL OF METHYL ORANGE WITH POLYANILINE NANOFIBERS: AN UNCONVENTIONAL ADSORBENT FOR WATER TREATMENT	**Monika Duhan** and Raminder Kaur	Taylor & Francis	SCI Clarivate Anlytics
3.	ERADICATION OF METHYLENE BLUE DYE ONTO POLYANILINE NANOFIBERS BASE BY USING KINETIC AND ISOTHERM MODELS	**Monika Duhan** and Raminder Kaur	Under review (Environmetrics)	SCI Wiley
4	POLYANILINE AS AN INCEPTIVE DYE ADSORBENT FROM EFFLUENT (**Book chapter**)	Raminder Kaur and **Monika Duhan**	Advanced Materials for Wastewater Treatment	Martin scrivener Publisher, Wiley
5.	REMOVAL OF CATIONIC DYE (METHYLENE BLUE) BY USING POLYANILINE NANOFIBERS (EMERALDINE SALT) : KINETIC AND ISOTHERM STUDIES	**Monika Duhan** and Raminder Kaur	Sustainable Technologies for Environmental Management 2019	
6.	ADSORPTIVE REMOVAL OF METHYLENE BLUE BY POLYANILINE NANOFIBERS	**Monika Duhan,** Raminder Kaur and Aayush Nagpal	NFEST 2018 International Conference	
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8.	POLYANILINE NANOFIBERSAS AN EMANATING ADSORBENT FOR DYE REMOVAL FROM EFFLUENT	**Monika Duhan** and Raminder Kaur	NANO INDIA 2017	

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