THE PREPARATION OF CHITOSAN/PVA/ZEOLITE ELECTROSPUN COMPOSITE NANOFIBROUS MEMBRANE FOR HEAVY METAL REMOVAL APPLICATION

UMMA HABIBA

DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING SCIENCE

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR
2016

UNIVERSITI MALAYA
ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **UMMA HABIBA**

Registration/Matric No: **KGA130030**

Name of Degree: **Master of Engineering Science**
Title of Project Paper/Research Report/Dissertation/Thesis (“this Work”):

THE PREPARATION OF CHITOSAN/PVA/ZEOLITE ELECTROSPUN COMPOSITE NANOFIBROUS MEMBRANE FOR HEAVY METAL REMOVAL APPLICATION
Field of Study: **ADVANCE MATERIALS/ NANOMATERIALS**

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;
(2) This Work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya (“UM”), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate’s Signature Date

Subscribed and solemnly declared before,

Witness’s Signature Date

Name:

Designation:

ABSTRACT

Water is being polluted in many different ways. Moreover, existing water and wastewater treatment processes are going to exceed the limit for supplying sufficient water quality to meet the demands. More efficient water treatment membrane made of polymeric materials from renewable resources are necessary.

Chitosan is a biopolymer which is very well known for its biodegradability, nontoxicity, biocompatibility etc. As it is a partially deacetylated derivative of chitin, it behaves as polycationic in nature. Producing chitosan nanofiber via electrospinning is a challenge due to its polycationic behavior. In addition, limited solubility of chitosan and protonation of amino group decrease the electrospinnability of chitosan. To increase the electrospinnability, it is necessary to increase the degree of deacetylation and decrease the protonation of chitosan. In order to reduce the protonation of chitosan in acidic medium and water, blending with other polymer like PVA is helpful as it make hydrogen bond with amino group. Zeolite is widely being used for water treatment because of its molecular sieve structure. The objective of this study is to fabricate a novel chitosan/PVA/zeolite nanofibrous composite membrane via electrospinning process. Firstly, crude chitosan was hydrolyzed with NaOH for 24 hours to make the electrospinning feasible. Hydrolyzed chitosan was analyzed by FTIR. Consequently, degree of deacetylation and molecular weight of hydrolyzed chitosan was calculated. Analysis over hydrolyzed chitosan resulted in increase of degree of deacetylation. This will ease the electrospinning process. Next, 7 wt.% of hydrolyzed chitosan solution made by dissolving in 90% conc. acetic acid was blended with 8wt% of aqueous polyvinyl alcohol solution. Five electrospinning dope with the different weight ratio of chitosan/PVA was prepared, those are 50:50, 60:40, 70:30, 80:20 and 90:10. The electrospinning dope was then loaded in a syringe for electrospinning. Morphology of the electrospun products were studied by FESEM. FESEM analysis showed that chitosan/PVA with 50:50 weight ratio gave defect-free nanofibrous mat. Where, higher chitosan content in the blend solution lead to poor nanofiber. Therefore, 50:50 weight ratio of chitosan/PVA was selected as the polymer matrix for zeolite. Then, 1 wt % of zeolite was added to the blend solution followed by electrospinning process. The structure and elemental studies on the electrospun composite nanofiber was characterized with field emission scanning electron microscopy, X-Ray diffraction, Fourier transform infrared spectroscopy, swelling test and adsorption test. The result showed that chitosan/PVA/zeolite nanofibrous composite was successfully produced via electrospinning process. From the FESEM result, finer, beads free nanofiber with homogeneous size was electrospun. Fourier Transform Infrared spectroscopy test shown a strong bond between chitosan and zeolite. X-Ray diffraction spectra also showed strong interaction of chitosan and zeolite. Zeolite loses its crystallinity due to strong bonding with chitosan molecules. Swelling test showed no change in weight after immersing in distilled water, acidic and basic medium for 20 days. The isotherm models showed that the Langmuir model described the equilibrium data of Cr (VI), Fe (III) and Ni (II) adsorption. Adsorption capacity of the nanofiber was unaltered after 5 recycling runs which indicate the reusability of the chitosan/PVA/zeolite nanofibrous membrane.

ABSTRAK

Air dicemarkan melalui pelbagai cara. Selain itu, air yang sedia ada dan rawatan air sisa akan melebihi keperluan air yang bersih. Membran rawatan air yang lebih efisyen dan juga diperbuat daripada polimer yang boleh diperbaharui amat diperlukan.

Chitosan merupakan biopolymer yang diketahui sebagai polimer yang boleh biorosot, tidak toksik, dan sesuai untuk badan manusia. Atas sebab bentuk chitin yang terdapat dalam polimer tersebut, ia mempunyai sifat polikationik. Pembuatan nanofiber chitosan melalui electrospinning merupakan cabaran atas sebab sifat polikationik tersebut. Selain itu, kelarutan chitosan yang terhad serta pemprotonan kumpulan amino dalam chitosan menjejaskan electrospinning chitosan tersebut. Untuk menyenangkan electrospinning, peningkatan tahap penyingkiran kumpulan asetil dan penurunan pemprotonan kumpulan amino dalam chitosan diperlukan. Untuk menurunkan pemprotonan chitosan dalam pelarut yang berasid, pergabungan dengan polimer lain seperti PVA adalah bermanfaat kerana chitosan akan bentuk ikatan hydrogen dengan kumpulan amino. Zeolite luas digunakan untuk rawatan air atas sebab bentuk molekul yang bersifat tapisan. Objektif kajian ini ialah untuk reka membrane composit bernanofiber chitosan/PVA/zeolite yang novel melalui proses electrospinning.

Mulanya, chitosan mentah dihidrolisiskan dengan NaOH selama 24 jam untuk memastikan electrospinning boleh dilaksanakan. Chitosan yang telah dihidrolisiskan telah dianalisis dengan FTIR. Dengan ini, tahap penyingkiran asetil dan berat molekul telah dikira. Pengiraan menunjukkan peningkatan tahap penyingkiran kumpulan asetil. Ini akan menyenangkan proses electrospinning. Seterusnya, 7 wt% larutan chitosan yang telah dihidrolisiskan disediakan dengan penglarutan dalam 90% asid asetik pekat dan 8 wt% lartuan PVA. Lima nisbah chitosan/PVA digunakan untuk menghasilkan composit bernanofiber, iaitu 50:50, 60:40, 70:30, 80:20 dan 90:10. Larutan-larutan tersebut dimasukkan dalam picagari untuk electrospinning. Morfologi membran composit bernanofiber turut dianalisis dengan FESEM. FESEM menunjukkan bahawa chitosan/PVA dengan nisbah 50:50 mempunyai membran bernanofiber yang paling baik. Penggunaan chitosan yang lebih tinggi menyebabkan membran yang cacat. Dengan itu, nisbah 50:50 chitosan/PVA digunakan sebagai polimer matrix untuk zeolite. 1 wt% zeolite telah ditambah ke dalam larutan polimer dan diteruskan ke proses electrospinning. Melalui FESEM, *X-ray diffraction*, *Fourier transofmr infrared spectroscopy,* ujian bengkak dan ujian penjerapan, morfologi dan kajian elemen membran tersebut didapati. Keputusan menunjukkan bahawa halus, homogen nanofiber chitosan/PVA/zeolite yang bebas daripada kecacatan didapati. FTIR menunjukkan ikatan yang kuat antara chitosan dengan zeolite. XRD turut menunjukkan ikatan yang kuat antara chitosan dengan zeolite dan sebab itu, penghabluran zeolite menurun. Ujian bengkak menunujukkan tiada perbezaan dalam berat membrane tersebut selepas merendam dalam air suling, air berasid dan air alkali selama 20 hari. Model-model isoterma menunjukkan bahawa model Langmuir menjelaskan data keseimbangan penjerapan Cr (VI), Fe (III) dan Ni (II). Kapasiti penjerapan yang masih tidak berubah selepas penggunaan selama 5 kali menunjukkan membran chitosan/PVA/zeolite tersebut sesuai untuk diguna semula.

ACKNOWLEDGEMENTS

First and above all, I praise Allah, the almighty God for providing me this opportunity and granting me the capability to proceed successfully. This thesis appears in its current form due to the assistance and guidance of several people. I would therefore like to offer my sincere thanks to all of them.

I would like to express my deep thanks to my supervisors Dr. Amalina Muhammad Afifi and Dr. Ang Bee Chin for their supervision, support and guidance throughout the course of this research.

I would like to thank my friend Sepehr Talebian and Hossein Muhammad Khanlou for their unforgotten help in the laboratory.

Most importantly, I would like to express my deepest sense of gratitude to my mother, brothers, sister and my husband for the continued help, support and encouragement they always provide me.

I especially must restate my sincere appreciations to my Husband, Tawsif for unconditional love, continued support and help over the years.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

CNT	Carbon nanotube
DA	Degree of acetylation
DDA	Degree of deacetylation
FESEM	Field Emission Scanning Electron Microscopy
PVA	Polyvinyl Alcohol
RO	Reverse osmosis
TGA	Thermal Gravimetric Analysis
TFC	Thin film composite
TFN	Thin film nanocomposite
XRD	X-Ray Diffraction
1H NMR	Proton Nuclear Magnetic Resonance
13C NMR	Carbon-13 Nuclear Magnetic Resonance

CHAPTER 1: INTRODUCTION

1.1 Problem Statement

Water is an obligatory material for all life in the world. It is a precious resource which is being polluted every day. Contaminants of water are micro-organisms, organics, Heavy metals and toxicants. Though freshwater is a natural resource, the ability of these resources to sustain water quality at suitable level has become difficult because of increasing water pollution. Nowadays seeking ways of purifying water is one of the main concerns because of the lack of clean water resources. Remarkable amount of pollutants are discharged from all kinds of industries (M. A. Shannon et al., 2008). In addition, organic dyes and heavy metals come in contact with water from different industries, ternaries and pharmaceutical etc. (Carmen & Daniela, 2012). The increasing demand of water quality as well as emerging contaminants in water, guides to study the prevailing water treatment processes and introduce more efficient one. Growing pressure on water lead to thinking of using alternative and unusual water resources like wastewater, sea water, storm water and brackish water. Moreover, existing water and wastewater treatment processes are going to exceed the limit for supplying sufficient water quality to meet the needs. Therefore, it is very urgent to introduce water treatment procedure in the mostly affected areas.

Current improvement in nanotechnology suggests positive opening to develop next-generation water treatment processes. Our existing water treatment processes are no longer sustainable as it heavily depends on conveyance and centralized systems. Nanotechnology launched promising waste water treatment processes to overcome major problems in existing processes. Nanomaterials are being synthesized by different methods to get the desired properties. Usually the materials smaller than 100nm in at least one dimension are called nanomaterials. Some nanomaterials possess some promising properties that make them suitable for water treatment. In the last few decades, some processes such as reverse osmosis, flocculation (Golob, Vinder, & Simonič, 2005), bacterial action, adsorption (Annadurai, Ling, & Lee, 2008) and photocatalytic degradation (Tabatabaee & Abolfazl Mirrahimi, 2011) have been used. Among them, adsorption has been found to be more useful for simplicity of design, lower initial cost and manageability of operation. Adsorption of any species to a solid surface commonly results from Van der Waals attraction between adsorbate and adsorbent. However, higher adsorption can be a result of weak chemical bonding between adsorbate molecules and adsorbent. Functional polymers are potentials materials for water treatment. Its functional groups help to introduce more property to the parent material by modification of functional groups and introducing more active sites. Usually the adsorption process is limited by selectivity, active sites and kinetics of adsorbent. Appropriate nanomaterials can ensure high surface area, more active sites, porous structure and short intraparticle diffusion distance.

Nanofiber offers some promising properties such as light weight, porosity and high surface to volume ratio which is suitable to become adsorption. There are many nanofiber fabrication processes like drawing (Annadurai et al., 2008; Joachim, 1998), template synthesis (Feng et al., 2002; Martin, 1996), phase separation (Martin, 1996), self-assembly (Liu et al., 1999), melt blowing (Butin, Harding, & Keller, 1974; Ellison, Phatak, Giles, Macosko, & Bates, 2007), solution blow spinning (Medeiros, Glenn, Klamczynski, Orts, & Mattoso, 2009; Oliveira et al., 2011) and electrospinning (Deitzel, Kleinmeyer, Hirvonen, & Tan, 2001). Nowadays, electrospinning has become more popular as it can fabricate nanofiber below 100nm diameter (Bhattarai, Edmondson, Veiseh, Matsen, & Zhang, 2005; Jayakumar, Prabaharan, Nair, & Tamura, 2010; L. Li & Hsieh, 2006; Ohkawa, Minato, Kumagai, Hayashi, & Yamamoto, 2006). Electrospun polymer fiber has been successfully used in drug delivery (Sill & von Recum, 2008), tissue engineering (W. J. Li, Laurencin, Caterson, Tuan, & Ko, 2002) electronic devices (M. Y. Song, Kim, Ihn, Jo, & Kim, 2004) , water filtration (Aussawasathien, Teerawattananon, & Vongachariya, 2008; Gopal et al., 2006; S Ramakrishna et al., 2010) and so on. Among many applications, water treatment is one of the promising application because of its porosity and tunable pore size and larger surface area to volume ratio (Bognitzki et al., 2001; Hao Fong & Reneker, 1999; Huang, Zhang, Kotaki, & Ramakrishna, 2003). It is also highly permeable (Phillip Gibson, Schreuder-Gibson, & Rivin, 2001; PW Gibson, Schreuder-Gibson, & Rivin, 1999) and selective (Baker et al., 2008; Manesh, Santhosh, Gopalan, & Lee, 2007). Moreover, interconnected pore and smaller pore size implies more retention over dissolve particle in water (Burger, Hsiao, & Chu, 2006). These properties make the electrospun membrane very suitable for water treatment. But, it is defenseless against compaction and fouling during operation because of high porosity and surface area exposed to mechanical stress. Thus, selection of membrane materials needs to fulfil the filtration efficiency as well as mechanical strength.

Chitosan is promising polymer for drug delivery, tissue engineering, filtration and so on (Borchard, 2001). It is second most abounded bio materials in nature. It is being used widely for water treatment for its hydrophilicity, disinfection capacity, non-toxicity, adsorptivity, and biocompatibility. Being polycationic in nature it can bind metal ions and pathogens. It also reduces fouling and increase water flow rate (Desai et al., 2009; Jayakumar et al., 2010; J. Kim & Van der Bruggen, 2010). Presence of amino group ensures its multipurpose application (Martinová & Lubasová, 2008). Nonetheless, it is mechanically unstable and susceptible to swelling (Cooper, Oldinski, Ma, Bryers, & Zhang, 2013). Nowadays PVA, PEO, PVP, PET, PLA etc. are blended with chitosan to improve its mechanical property (Jayakumar et al., 2010). These polymers will form hydrogen bond with the chitosan and lead to a good mechanical property. In this study, chitosan was blended with PVA to improve the mechanical strength by making hydrogen bond with the amino group of chitosan. Meanwhile, it also helps to decrease the swelling rate. Moreover, PVA is nontoxic (Koski, Yim, & Shivkumar, 2004), biodegradable and soluble in acidic medium. PVA also reduce the crystallinity of chitosan network in some extent (J. H. Kim, Kim, Lee, & Kim, 1992). The strong hydrogen bond of PVA with functional group $–NH_2$ and NH-R lead to form good fibers (Pawlak & Mucha, 2003; Q. Li, 2010; Qi, Yu, Zhu, Chen, & Li, 2010). One of the important objective by adding PVA is to introduce more active sites (-OH groups) for adsorption (Tadros, 1974, 1978).

Although chitosan bind metal ions, a filler material can increase the adsorption property and mechanical strength. They are a few such as activated carbon (Demirbas, Kobya, Senturk, & Ozkan, 2004; Kula, Uğurlu, Karaoğlu, & Celik, 2008; Selvi, Pattabhi, & Kadirvelu, 2001), silica (Aguado, Arsuaga, Arencibia, Lindo, & Gascón, 2009), diatomite (Dantas, Neto, & Moura, 2001), appetite and perlite (Mathialagan & Viraraghavan, 2002).Among them zeolite was used to increase the absorptivity and mechanical strength of electrospun fiber. It is cheap and commonly used for water treatment. Zeolites are hydrated Aluminosilicated porous structure. This porous structure can accommodate different positively charged ion molecules, cation and organic molecules. It is mechanically strong, thermally stable and good adsorbent (Blocki, 1993). Most important character of zeolite for wastewater treatment is its hydrophilicity (Perminova, Hatfield, & Hertkorn, 2005) .Three-dimensional frameworks of SiO_4 and AlO_4 tetrahedral made the main structure of zeolite. The aluminum takes the center position of the tetrahedron of four oxygen atoms and negative charge is produced in the lattice by the isomorphous replacement of Si^{4+} by Al^{3+}. The exchangeable cation (sodium, potassium, or calcium) balance the net negative charge. These exchangeable cations are key factor for metal binding as they are also exchangeable with other cations such as lead, cadmium, zinc and manganese present in the water (Dahe, Teotia, & Bellare, 2012; Erdem, Karapinar, & Donat, 2004; Juang & Shiau, 2000; C.-F. Lin, Wu, & Lai, 2008).

Crosslinking of chitosan nanofiber is needed to improve chemical and mechanical stability in wet environment. Crosslinker such as glutaraldehyde (GA) (Chiou & Li, 2003; Jameela & Jayakrishnan, 1995; Schiffman & Schauer, 2007a, 2007b), genipin (Mi, Tan, Liang, Huang, & Sung, 2001), diisocyanates (Ngah, Endud, & Mayanar, 2002), and epoxides(Shauer & Schiffman, 2008) are being used. It also helps to decrease diameter of nanofiber (Austero, Donius, Wegst, & Schauer, 2012). In this study glutaraldehyde (GA) was selected.

1.2 Objectives

1. To fabricate chitosan/PVA/Zeolite nanofibrous composite membrane via electrospinning process.
2. To investigate the properties of the resulting nanofibrous composite membrane via FESEM, XRD, FTIR and Swelling test.
3. To evaluate the adsorption behavior of the nanofibrous composite membrane over Cr(VI), Ni(II) and Fe(III).

1.3 Thesis Overview

Chapter one of the thesis introduces the motivation, objectives and scope of the study. Chapter two represents literature review of background knowledge. Experimental and characterization details of the study have been discussed in chapter three. Experimental study has three parts; first one discusses the hydrolysis of the chitosan, second discuss the electrospinning and morphology of chitosan/PVA nanofiber and third discuss the electrospinning and characterization of chitosan/PVA/zeolite composite nanofibrous membrane.

1.4 Scope of Work

The study focus on the fabrication and characterization of chitosan/PVA/zeolite electrospun nanofibrous membrane and its adsorption behavior on Cr (VI). Fe (III) and

Ni (II). Adsorption capacity was not evaluated in different pH and temperature. This study explores the resulting nanofiber as a faster heavy metal ion removal agent. One minute of contact time in adsorption study provide a significant information about the adsorption capacity of the resulting nanofiber membrane. The working capacity of this membrane can be tested in subsequent research to prove it as an attractive material for desalination.

CHAPTER 2: LITERATURE REVIEW

2.1 Chitosan

Chitosan is a polycationic, non-toxic, biodegradable polysaccharide which is deacetylated unit of chitin. Chitin is the second most plentiful polysaccharide found in the nature. It is extracted from exoskeleton of crab, crustaceans and shrimp shells, insects, fungal mycelia (Cauchie, 2002; Roberts, 1992) and wastes of mushrooms such as Agaricus bisporus (Wu, Zivanovic, Draughon, & Sams, 2004). Chitosan is a copolymer of N-acetyl-D-glucosamine and D-glucosamine. Here, the D-glucosamine is the deacetylated unit which depends on the degree of deacetylation (DDA) of chitin to chitosan. Chitosan has pKa near 6.5 and soluble in acidic solutions as some of the amine groups become protonated (Sorlier, Denuziere, Viton, & Domard, 2001). The positively charged fraction of repeat units is a function of the solution pH and degree of deacetylation (DDA). A higher degree of deacetylation means chitosan backbone contains larger number of positively charged groups. Chitosan has several unique properties which are suitable for water treatment. It has the ability to adsorb metal ions from solution and to hinder the maturation of a wide variety of bacteria, yeasts and fungi (Desai et al., 2009). The amino group of chitosan becomes positively charged in aqueous medium. Positively charged amino of chitosan interact with the negatively charged components in the microbial cell membranes. Barrier property of microbial is altered for the binding between chitosan and cell wall components. Thus, it causes leakage of intracellular components and prevents entry of nutrients (Helander, Nurmiaho-Lassila, Ahvenainen, Rhoades, & Roller, 2001), which cause the death of the cell. The antimicrobial effectiveness of chitosan depends on degree of deacetylation, pH, molecular weight and crystallinity of chitosan as well as microbial buffer solution temperature (Lim & Hudson, 2003).

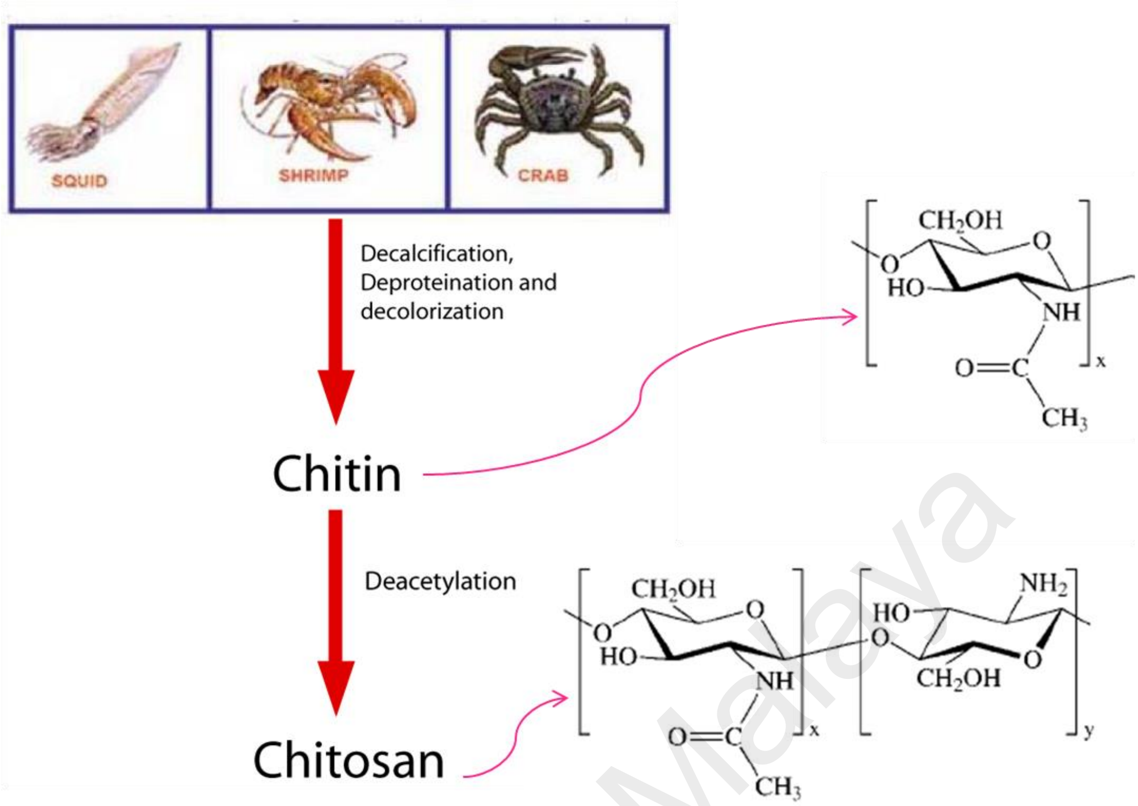


Figure 2.1: Chitin and chitosan molecule

2.1.1 Properties

The properties of chitosan depends on the degree of deacetylation of chitosan. Degree of deacetylation of chitosan depends on processing parameters and conditions under which it is processed. This is because, the amount of free amino groups in the polymer chain is controlled by the degree of deacetylation. The free amino groups of chitosan becomes positive in acidic medium. The amino group along with the hydroxyl group ensures functionality of chitosan which turns it to be a very reactive polysaccharide. Chitosan's polycationic behavior helps to establish electrostatic interactions with different atom and molecules. The amount of functional groups generated by deacetylation and other processing condition allow for making active sites which is also helpful for solubility (Şenel & McClure, 2004). It is a semicrystalline polymer. Deacetylated unit of low molecular weight chitin is used to obtain the Single crystals of chitosan (Cartier, Domard, & Chanzy, 1990). It crystalize in an orthorhombic unit cell ($P2_12_12_1$) with dimensions a 0.807 nm, b ¼ 0:844 nm, c ¼ 1:034 nm. It is a two-chain orthorhombic unit cell where two chains are arranged in antiparallel mode (Ogawa, 1991; Ogawa, Yui, & Miya, 1992).

2.1.1.1 Solubility of Chitosan

The solubility of chitosan depends on its degree of deacetylation, distribution of the acetyl groups along the main chain and the molecular weight (Aiba, 1991; Kubota & Eguchi, 1997). Usually, an irregular structure is obtained after deacetylation due to semicrystalline character of initial polymer. The degree of ionization of chitosan molecule in the acidic medium depends on the pH and the pK of the acid. It was examined by the role of the protonation of chitosan on solubility in the presence of acetic acid (M Rinaudo, Pavlov, & Desbrieres, 1999) and hydrochloric acid (Rinaudc, Pavlov, & Desbrieres, 1999). Chitosan is soluble at acidic medium. The required amount of acid to dissolve depends on the quantity of chitosan (M Rinaudo et al., 1999). The required concentration of protons in the acidic solution is at least equal to the concentration of -NH_2 units. In actual fact, the solubility is a highly unfavorable parameter to control. It depends on the degree of deacetylation, intra-chain H bonds involving the hydroxyl groups, distribution of acetyl groups along the chain and the ionic concentration of chitosan as well as property of the acid used for protonation.

2.1.1.2 Degree of Deacetylation of Chitosan

The degree of deacetylation (DDA) is one of the important properties for chitosan. It determines the applicability of chitosan. It helps to recognize whether the biopolymer is chitin or chitosan. It should be equal or higher than 40% for defining chitosan (Peter, 1995). It also have a remarkable role in determining the applicability of chitosan. Moreover, the physical, chemical and biological properties of chitosan such as the tensile strength of films (Mima, Miya, Iwamoto, & Yoshikawa, 1983), ability to chelate metal ions (Tan, Khor, Tan, & Wong, 1998), reactivity and solubility (Duarte, Ferreira, Marvao, & Rocha, 2002) are influenced by DDA.

2.1.2 Applications

Many interesting properties of Chitosan like biodegradability, natural and abundance origin, reactivity, etc. make it a useful material in agricultural, food processing, nutritional enhancement, cosmetics and waste water treatment.

2.1.2.1 Agricultural Applications

Chitosan is a biodegradable and nontoxic biopolymer. Therefore, it can be used in agriculture. It was reported that chitosan can be used for seed coating, fertilizer and time released drug application. The use of chitosan in these areas has shown to increase the amount of crops produced by improving germination, rooting and leaf growth, while reducing the occurrence of fungal infections and diseases (Şenel & McClure, 2004).

2.1.2.2 Wastewater Treatment

Chitosan can be used in wastewater treatment in different ways. It can be used as flocculent to clarify water, adsorbent and chilling agent to remove organic elements and metal ion, respectively (Marguerite Rinaudo, 2006). –OH and $–NH_2$ are the two functional group of chitosan that role as active sites in different reactions and bonding. Chitosan’s functional groups and natural chelating properties make chitosan useful in wastewater treatment by allowing for the binding and removal of metal ions such as copper, lead, chromium, mercury, and uranium from wastewater. It is also to remove other negatively charged solids from wastewater effluents (Q. Li, Dunn, Grandmaison, & Goosen, 1992).

2.1.2.3 Food Industry Applications

Chitosan’s chelating properties and high functionality make it valuable in several applications within the food industry such as binding with and removing certain elements, particles, and materials such as dyes and fats from foods. The antibacterial and antifungal properties found in chitosan can also be used during the storage and preservation of food (Q. Li et al., 1992).

2.1.2.4 Medical Applications

Chitosan can be functioned to different forms. This ability makes it a useful polymer in the medical application. Application of chitosan has been reported in orthopedic, periodontal, and tissue engineering, wound healing, and drug delivery (Khor & Lim, 2003).

2.2 Polyvinyl Alcohol

Polyvinyl Alcohol is a biodegradable synthetic polymer. It is non-toxic, biocompatible and hydrophilic (Zheng, Du, Yu, Huang, & Zhang, 2001). It is composed of 1, 3-diol linkages [-CH_2-CH (OH)-CH_2-CH (OH)-]. In some cases, few percentage of 1, 2-diols [-CH_2-CH (OH)-CH (OH)-CH_2-] can be present depending on the condition of the polymerization of vinyl ester precursor (Hallensleben, 2000). PVA is water soluble (XingYu Chen, Hou, Yang, & Xu, 2016). PVA is widely used in different industries such as in medical (Kanamoto, Kiyooka, Tovmasyan, Sano, & Narukawa, 1990; Y. Wang & Hsieh, 2008), packaging (Kunugi, Kawasumi, & Ito, 1990) and building industries (Grubb & Kearney, 1990). PVA can be modified by pre- or post-polymerization techniques to enhance to its desired property. (Lyoo, Blackwell, & Ghim, 1998).

2.2.1 Chitosan/PVA Blend

PVA is a most common polymer additive that is blended with chitosan to make nanofiber (L. Li & Hsieh, 2006). PVA can ease the electrospinning process of nanofiber fabrication. PVA and chitosan both is soluble in diluted acetic acid. Therefore, miscibility of chitosan and PVA solution become easier (Park, Jeong, Yoo, & Hudson, 2004). PVA can reduce the crystallinity in the chitosan network and make strong hydrogen bond with functional group –NH_2 and NH-R present in chitosan (Pawlak & Mucha, 2003; Qi et al., 2010). For lower composition of PVA, hydrogen bond is made with CH_2OH group of chitosan. CH_2OH group of chitosan is more available for interaction, as it shows free rotation. As the PVA increases, it start to make bond with NH_2 groups. This formation helps in electrospinning of chitosan. Although PVA is soluble in water, its combination with chitosan renders the latter insoluble by forming a hydrogen bond. PVA also increases the adsorption property of chitosan (Muhd Julkapli, Akil, & Ahmad, 2011). In strengthen the chitosan by making –H bonding with the amino group of chitosan molecule and also introduce more active sites for dye adsorption.

2.3 Zeolite

Zeolites are hydrated Aluminosilicated porous structure. This porous structure can accommodate different positively charged ion molecules, cation and organic molecules .Zeolite is cheap and available in large amount in the earth. It is mechanically strong, thermally stable and good adsorbent (Misaelides, 2011). The uptake of metal cations from solutions by the zeolites is affected by a variety of factors such as the temperature, the solution pH, the presence of competing cations and complexing agents (Colella, 2007).

2.3.1 Properties of Natural zeolite

Different kinds of zeolite can be found all around the world. But all zeolite have the common framework. It consists of three common component named aluminosilicate framework, exchangeable cations and zeolitic water. Here is the usual chemical formula of zeolite:

$$M_{x/n}\,[Al_xSi_yO_{2(x+y)}]\cdot pH_2O \ldots\ldots\ldots\ldots\ldots\ldots 2.1$$

Where, M represent cations like Na, K, Li, Ca, Mg, Ba and Sr, n is the charge of cations, y/x = 1-6 and p/x = 1-4. The main framework of zeolite is the tetrahedron. Usually, a silicon or aluminum atom occupy the centre of the tetrahedron and four oxygen atoms are settled at the vertices. Though SiO_4 tetrahedron is neutral, lattice becomes negative when Si^{4+} is replaced by Al^{3+} in the center of a tetrahedron. The negative charge is neutralized by cations like sodium. The aluminosilicate framework is the most conserved and stable component and defines the structure type. The water molecules can be present in voids of large cavities and bonded between framework ions and exchangeable ions via aqueous bridges. The water may serve as bridges between different exchangeable cations. Zeolites are capable of exchanging ions with external medium, which is the significant characteristic of zeolite. Ion exchange proceeds in an isomorphous fashion. Several factors control the ion-exchange behavior of natural zeolite such as charge density of the anionic framework, the framework structure, ionic charge, ion size and shape and concentration of the external electrolyte solution (Kalló, 2001). Due to the formation environment, natural zeolite has varying chemical composition and cation-exchange capacity.

2.3.2 Decontamination by Zeolite

Zeolite has a unique structure that make it a proper material for decontamination. It has been widely used as adsorbents because of its ion exchange capability and molecular sieve properties. It is a common material in purification and separation technologies. Water contains different organic and inorganic pollutants. Zeolites are being used for removal of organic dyes, heavy metal ion such as Fe (III), Zn (II), Cr (VI) etc. and other pollutants. The purification of waters and the treatment of industrial and urban wastewaters are further fields of applications of natural zeolite (Colella, 2007). Natural zeolites were mainly investigated and applied as adsorbent for ammonium from urban as well as for heavy metals and dyes from industrial wastewaters. Wastewater treating facilities utilizing natural zeolites are already in operation in many countries. Natural zeolite is also used for the reduction of heavy metals and petroleum products in motorway storm waters (Pitcher, Slade, & Ward, 2004). In this section, application of zeolite as a purifier will be discussed.

2.3.2.1 Removal of Ammonium

Ammonium is nitrogen ion form pollutant comes from municipal sewage, fertilizer factory effluent and agricultural wastes into the water. Ammonia causes depletion of dissolve oxygen, fish toxicity and eutrophication of lakes and rivers. Higher concentration of ammonium can worsen the problem. Natural zeolite is an effective adsorbent for removal of ammonium from water. It can remove as much as 30.6 mg/g of ammonium. (S. Wang & Peng, 2010).

2.3.2.2 Removal of Heavy Metal Ions

Water pollution by heavy metal is increasing day by day because of increasing different kinds of industries. The contamination by heavy metal is becoming a major concern because of its toxicity. It has been reported that many heavy metal ions are causing dangerous diseases. It was reported that zeolite is robust adsorbent for metal ion removal (Kalló, 2001; Kesraoui-Ouki, Cheeseman, & Perry, 1994). However, most of research concentrated on single metal ion. But real wastewater can contain several metal ions at a time. Ion-exchange kinetics of zeolite is an important factor for removal of heavy metal ions. Many analysis have revealed that adsorption mechanism of heavy metal ions usually follow two kinetic models, pseudo-first-order or pseudo-second-order. It is observed that the kinetics of heavy metal ion adsorption depends on respective metal ions and type of zeolite (S. Wang & Peng, 2010). Cation selectivity of zeolite is an important parameter. Among different heavy metal ions, Pb has the prominent affinity for ion exchange for almost all kinds of zeolites. It is also seen that the ion concentration and solution pH has effects on the ion-exchange selectivity. Therefore, several factors are needed to be considered in real wastewater treatment process (S. Wang & Peng, 2010).

2.3.2.3 Removal of Inorganic Anions

The acid ions such as NO_3^-, SO_4^{2-}, PO_4^{3-}, F^-, ClO_4^-, CN^- are largely present in wastewater. These ions are very harmful as they are reason of pollution at high content. Other toxic species are Cr(VI) with CrO_4^{2-}, $Cr_2O_7^{2-}$ forms, As(V) with $H_2AsO_4^{2-}$, $HAsO_4^-$, and As(III). They are harmful for human body. Currently, ion-exchanged zeolite and surfactant-modified forms are being used for removal of these anions (S. Wang & Peng, 2010).

2.3.2.4 Removal of Organic Contaminants

The removal of organic contaminants in a cheaper process is a problem even though a large number of systems are being used with adsorption techniques. Adsorption is becoming popular because of simplicity of design, lower initial cost and ease of operation. Dyes are common pollutants organic pollutant present in wastewater, which are mainly discharged with the effluent from textile, printing, food and leather industries. Different kinds of dyes including basic, acidic, reactive, and dispersive dyes are being used. Dyes have very adverse effect to environment. It affect the nature of the water by hindering sunlight penetration into the water and decreasing the photosynthetic reaction. Some dyes are also toxic and even carcinogenic (S. Wang, Boyjoo, Choueib, & Zhu, 2005). In the past decade, several research have been conducted using natural zeolites for dye adsorption. (Alpat, Özbayrak, Alpat, & Akçay, 2008; Karadag, Akgul, et al., 2007; Karadag, Turan, Akgul, Tok, & Faki, 2007; S. Wang & Ariyanto, 2007; S. Wang & Zhu, 2006). It is discovered that natural zeolites are effective adsorbent for cationic dye due to the cation-exchange characteristic. They also shows low adsorption capacity towards anionic dyes. After surfactant modification, natural zeolites will be good adsorbents for anionic dye adsorption (S. Wang & Peng, 2010).

2.4 Water Pollution

Water pollution is the contamination of natural water by physical, chemical, radioactive or pathogenic microbial substances. It is contaminated by both natural reasons and man-made activities. Polluted water is the reason of illness and even lethal diseases. Various microbes present in water can causes many threatening diseases like Schistosomaisis, Dracunculiasis, Amebiasis, Cholera, Typhoid etc. (Hunter, 2003). Different metal ions like Cr, Pb, As, Zn, Co, Cu and Ni are contaminant of water (Argun

& Dursun, 2008). These contaminants can cause severe health problem. This situation is more severe in developing country and industry area .Predominant impact of water pollution upon environment includes soil pollution, increasing species mortality rate, loss of ecosystem and biodiversity. There are several natural causes of water pollution. Some natural causes of water pollution are volcanic eruptions, sedimentation from severe rainfall, storm, earthquake and algae blooms from natural causes and etc.

2.4.1 Classes of Water Pollutants

Water is being polluted from different sources. There are different kinds of pollutants which are being discharged in the water. Among them, chemical water pollutants are very dangerous as most of them have negative effect on human body as well as environment. There are many chemical pollutants which come to environment from different natural and man-made sources. Among them, Some common names of chemical contaminants are mercury emerging from mining activity (Malm, 1998), chlorinated organic molecules originated from water treatment plants, nitrogen compounds applied for agricultural purposes or various acids from of different manufacturing activities (Kumazawa, 2002; Rogers, 1996).

Physical water pollutants are not so harmful as pathogens or chemical to environment or human health. They are some physical factors such as temperature change and larger particles. Although they are not toxic, it can cause various harmful effects. Sediment load and rubbish like plastic bags, bottles etc. can be classified as physical pollutants. This kinds of pollution have very negative effects on the metabolism and food cycle of marine life in adverse ways (Clark, 1969).

Radioactive substances are mainly chemical pollutants. They have smallest contribution to water pollution. Radioactive materials rarely discharged to water from nuclear plants. It is discharged from agricultural firm like tobacco farming. Usually, radioactive materials come into the environment as a result of contamination of phosphate fertilizer from these firming (Ahmed & El-Arabi, 2005; Fávaro, 2005).

Pathogens are common microbes that pollute water. Untreated sewage and surface runoff from intensive livestock grazing are main source of pathogens. Giardia lamblia is an example of disease agents which can cause diarrhea, abdominal cramping and many more health problem. It is a parasitic protozoan, usually present in fecal material of animal and humans. It is peculiarly insidious, because of its immunity from ordinary sewage treatment process (Sahlström, Aspan, Bagge, Danielsson-Tham, & Albihn, 2004).

2.4.2 Causes of Water Pollution

2.4.2.1 Industrial Waste

Different kinds of industries such as textile industries, pharmaceutical industries, tannery polymer, ceramic and steel manufacturing industries produce large amount of waste and by-products which contains harmful chemicals and other pollutants. Pharmaceutical wastes are very toxic and complex among other industrial waste (Seif, Joshi, & Gupta, 1992). Some common pollutants are mercury, metal ions, sulphur, asbestos, dyes, nitrates and many other harmful chemicals. Many industries do not have proper waste management system and discharge the effluent in the environment which cause water pollution as well as soil pollution. The waste is moved into the natural water resources like rivers and canal via drainage system. In many countries, the waste is directly released to water sources. These chemicals can change the color of water and temperature and cause Eutrophication. Therefore, natural environment of water resources can be destroyed. It is a treat to the flora and fauna of the water.

2.4.2.2 Sewage and Wastewater

The sewage and waste water that is produced by each household is chemically treated and released into the sea. The sewage water is source of several harmful microbes and chemicals which are root cause of many dangerous health problems. Pathogens are known as a common water pollutant. Microorganisms in water are known to be causes of some very deadly diseases and become the breeding grounds for other creatures that act like carriers. These carriers inflict these diseases via various forms of contact onto an individual. A common example of this process would be Malaria.

2.4.2.3 Mining Activities

Mining is the technique of extracting coal and minerals from underground. This process brings different harmful element to the contact of ground water. Different components which are taken out in the crude form carries hazardous chemicals. These hazardous components mix with water and may cause different health problems. Generally, mining activities discharge sulphides and several metal wastes from the rocks.

2.4.2.4 Marine Dumping

The rubbish assemble by every household in the form of aluminum, paper, glass, rubber, plastic and food are dump into the river and sea in many countries. This kind of object need from 2 weeks to 200 years to be decomposed or degraded. These objects not only the reason of water pollution but also harm a threat to the marine life sustainability in the sea.

2.4.2.5 Accidental Oil Leakage

Oil spill is a matter of concern as large amount of oil enters into the natural water. Oil does not dissolve in the water. Therefore, it hampers the natural environment of marine wildlife including fish, birds and sea otters. The oil can be spilled by accident its carriage ship and can be a threat to the marine species depending on the toxicity of pollutants and amount of oil.

2.4.2.6 Burning of Fossil Fuels

Fossil fuels are made by natural processes from dead organisms. Fossil fuels contains large amount of carbon. Coal and oil are two common fossil fuels which are burnt for different purposes. It produce large amount of ash in the atmosphere. Ash contains different hazardous chemicals that mixed with water vapor and causes acid rain.

2.4.2.7 Chemical Fertilizers and Pesticides

Chemical fertilizers and pesticides are applied to save crops from bacteria and insects. These chemical substances are beneficial for the plants maturation. But, they have negative effects on environment. When these chemical substances mixes with water, it become very harmful for plants and animals present in the water. Also, when it rains, the chemicals mix up with rainwater and flow down into rivers and canals which pose serious damage for aquatic animals.

2.4.2.8 Global Warming

An increase in earth’s temperature due to greenhouse effect results in global warming. Increasing temperature has many adverse effect on environment. One of them is increasing temperature of water. It causes death of aquatic animals and marine species which later results in water pollution.

2.4.2.9 Animal Waste

Animal waste can contain different harmful microbes. It often washed away to the river and canal by rain water. Thus, water quality is diminished. This water can cause different water borne diseases like cholera, jaundice, diarrhea, dysentery and typhoid.

2.4.2.10 Underground Storage Leakage

Coal, petroleum, chemical and different hazardous products are transform through underground pipes. Accidentals leakage may contaminate the soil and consequently the water.

2.5 Heavy Metal Ions

The term heavy metal refers to any metallic chemical element that is toxic or poisonous at even low concentrations. Among different pollutants, heavy metal ions are very dangerous because of its toxicity carcinogenic behavior (Fu & Wang, 2011). Besides, it is nondegradable in the environment and cannot be decomposed (Mapanda, Mangwayana, Nyamangara, & Giller, 2005). Several metal ions can be present in the water such as Cr (VI), Cr (III) (Anderson, Meyer, & Mayer, 1973), As (V) (Silver & Phung, 1996), Cu (II), Co (II), Ni (II), Fe (III), Mn (II) (Nies, 1999), Hg (II), Zn (II), Cd (VI) , Pb (II) (Hahne & Kroontje, 1973), Se (VI) (Whanger, 1992) and Tl (VI) (Alluri et al., 2007).These ions can cause different diseases like throat dryness, lung tumors, damage of organs including kidneys and heart, tooth decay, gastroenteritis symptoms and so on. Heavy metal are present in the nature. It comes to water sources via geochemical process. Besides, several man made activities such as construction, manufacturing, agriculture, mining and transportation cause addition of heavy metal ions into the water resources. Fig 2.2 represents the heavy metal content in the waste water effluents released from different industries of Taloja Industrial Estate of Mumbai for the Assessment years 1999-2000.

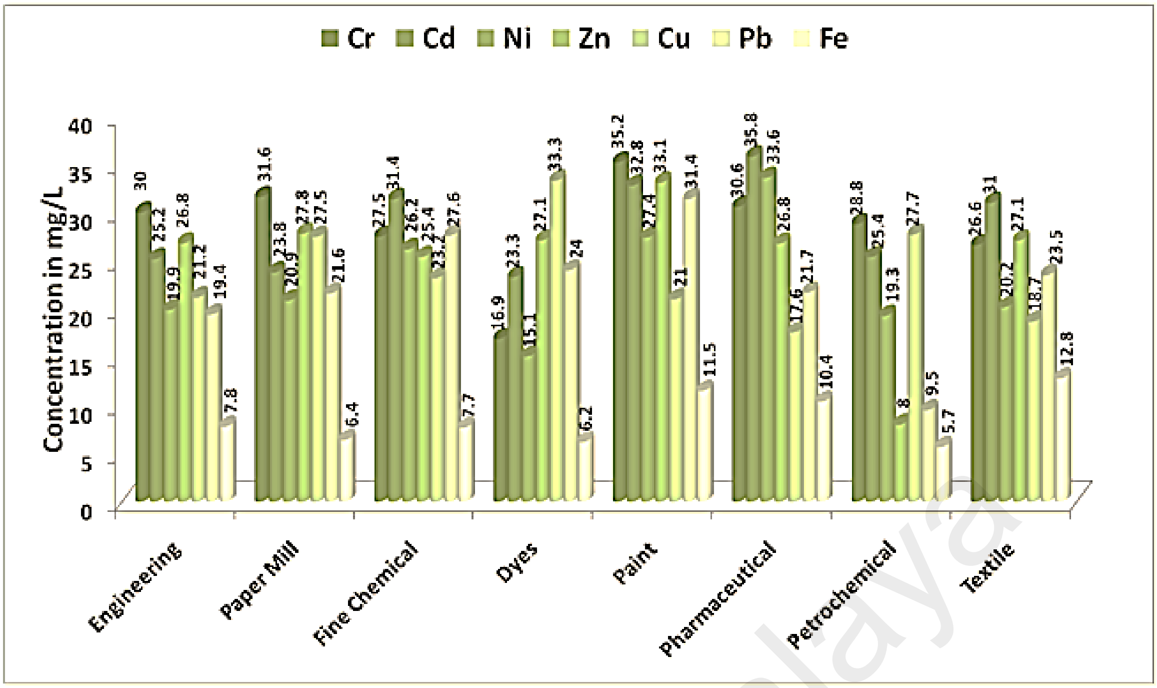


Figure 2.2: Average variation in Heavy metal content in the waste water effluents released from different industries of Taloja Industrial Estate of Mumbai for the Assessment years 1999-2000 (Lokhande, Singare, & Pimple, 2011)

2.5.1 Chromium (VI)

Hexavalent chromium, Cr (VI) means any compound containing the element chromium in the +6 oxidation state. It does not freely prevail in nature. Main chromium mineral is chromite ($FeCr_2O_4$). Chromium metal and Cr (III) are not considered harmful material for health. But Cr (VI) is toxic and carcinogenic (Barceloux & Barceloux, 1999).

Figure 2.3: Potassium Chromate

It come in contact with water when it is discharge from several industries. Different industries like chrome plating, textile dye industries, wood preservation , pigment production, stainless-steel production, petroleum refineries, and leather tanning use Cr (VI) as chromate and dichromate (Sultan & Hasnain, 2005; Thacker, Parikh, Shouche, & Madamwar, 2006). These industries discharge effluent which contains Cr (VI). These effluent cause pollution of soil and water. Cr (VI) is recognize as genotoxic carcinogenic material (Cancer & Organization, 1990). It increases the risk of lung cancer and can cause ulcers in the stomach (Dupont & Guillon, 2003). Cr (VI) is also toxic to animals and plant because of its high oxidative property(Cutting et al., 2010). According to WHO and USEPA, acceptable concentration of Cr (VI) is 50 and 100 $\mu g \cdot L^{-1}$, respectively (Lv, Xu, Jiang, Tang, & Xu, 2012). But, concentration of Cr (VI) is higher than the acceptable value in Cr (VI) containing wastewater (Z. Wang, Ma, Chen, & Zhao, 2008).

Figure 2.4: Tannery waste, containing hexavalent chromium and azodyes, Ranipet, India

2.5.2 Nickel (II)

Nickel is a metallic element with symbol Ni. Usually, it is a two valent element, but other oxidation state can exist. It has many recognizable industrial uses. It is used in stainless steel, rechargeable battery, welding products, electroplating industries, nickel steel and different special alloys (Davis, 2000). A research study on effluent of Taloja industrial belt of Mumbai showed that Ni (II) content was 33.6 mg/L which is very high from the acceptable value (Lokhande et al., 2011). It can contaminate drinking water by leaching from the pipe and fittings (Organization, 2004). It was reported that nickel leaching can be up to 6 µg/L from new stainless steel pipe (Organization, 2004). Acceptable level of nickel consumption is 0.2 µg/m^3 (Kasprzak, Sunderman, & Salnikow, 2003). High dose is dangerous for life and health because of its acute toxicity and carcinogenicity.

Figure 2.5: Electroplating Industry waste water (Md. ashikur & Rabia 2014)

2.5.3 Iron (III)

Iron is an essential material for human nutrient. Acceptable level of iron consumption is 10-50 mg/day (Organization, 1988). According to European Legislation, acceptable iron content in drinking water is 200 μg/L (Sieliechi, Kayem, & Sandu, 2010).Consumption dose as low as 60mg/kg of body weight can cause death (El-Harbawi et al., 2010). Excessive iron in the blood can cause damage of cells of gastrointestinal tract (Sieliechi et al., 2010). It was reported that excessive iron can cause Alzheimer's disease (Ong & Halliwell, 2004). Interaction between iron and cholesterol causes oxidative damage leading to atherosclerosis and neurodegeneration. Excessive iron in selective regions of the brain may be involved in the neurodegenerative disorders (Perez et al., 2010). A research study on effluent of Taloja industrial belt of Mumbai showed that Iron content was 12.8 mg/L which is very high from the acceptable value (Lokhande et al., 2011). Iron can be responsible for diphasic shock and anorexia. Iron also deposit in pipelines which make problem in water supply. It combine with oxygen to make reddish particles. These debris can cause metallic taste to water (Zamzow & Murphy, 1992).

Figure 2.6: Cadmium, zinc, copper, and iron stain the Animas River in Colorado

Iron can be present in tape water. Exposure to a combination of water and oxygen causes iron to deteriorate; the casings and pipes of a well water supply have a passing acquaintance with both factors. If the casings and pipes contain iron, the acquaintance leads to this deterioration. Rust, the natural by-product of iron corrosion, flakes off the well's components and into the water traveling from the well to our taps. Possibility of iron contaminant become higher when iron pipes are used (Jin, Wu, Zhang, & Guan, 2014). More specifically, the main source of an appreciable iron entry into a municipal water supply is through pipeline corrosion, metal finishing and galvanized pipe manufacturing (Zuane, 1990).

Figure 2.7: Iron in tape water

2.6 Water Treatment

Water treatment is a process to remove all the undesirable element present in the water to have acceptable quality of water for drinking, household and other application. Usually, water is polluted by the contaminants like pathogen, metal ions, detergent, disinfection by product, chemical compound, petroleum (gasoline, diesel), sediment, fertilizer, chemical waste etc. Among them, metal ions are very dangerous as they are carcinogenic and cannot be decomposed. There are three kinds of technology for water treatment: chemical method, physical method and biological method. Some examples of chemical methods are flocculation, coagulation, ion-exchange, precipitation, electroflotation etc. (S. H. Lin & Chen, 1997). Usually, chemical methods are rapid and efficient process. There is no loss of adsorbent materials. But, the limitation of these process are high energy and chemical cost. Besides, accumulation of concentrated sludge creates a disposal problem (Robinson, McMullan, Marchant, & Nigam, 2001). Physical methods of water treatment are membrane filtration, eletrodialysis, reverse osmosis and adsorption. Physical methods are more advantageous as there is no sludge production and little consumption of chemical. But it is economically unfeasible and creates by-products. Besides, reproducibility of adsorbent is challenging (R. S. Bai & Abraham, 2003). Biological methods are adsorption by microbial biomass, fungal decolorization, bioremediation systems and microbial degradation. These processes are economically attractive but slow.

2.7 Wastewater Treatment

Wastewater treatment is a different from water treatment. It gives attention to disposal rather than use. Water reclamation implies avoidance of disposal by use of wastewater as a raw water supply. Main objective of water and wastewater treatment is to remove impurities or pollutants present in the water. But, typical water treatment processes may not be suitable for wastewater treatment. Because it may contains inert, highly toxic and inhibitory organic compounds (Chakinala, Gogate, Burgess, & Bremner, 2008; Oller, Malato, & Sánchez-Pérez, 2011) Several processes are discussed below.

2.7.1 Adsorption process

Adsorption is a process of separating or collecting soluble particles from a solution by an interface which is called adsorbent. The Adsorption process can have three steps which vary with type of adsorbent: 1) transfer of the adsorbate molecule to the adsorbent wall, 2) diffusion of adsorbate through the adsorbent if it is porous and 3) removing of adsorbate molecule from the solution by making bond between adsorbate and adsorbent. It can be classified as chemical and physical adsorbent. Usually, physical adsorption is caused by Van der Waals attrition force between adsorbate and adsorbent. In case of chemical adsorption, there is a chemical reaction or interaction between adsorbent and adsorbate (Metcalf, 1991). Many adsorption process are reversible. It means adsorbate can be separated from the adsorbent by desorption process. There are several reason of desorption. Most common two is displacement by other compound or decrease in effluent concentration (Snoeyink, 1990). Desorption is very useful phenomenon as it help to recover the adsorbed important metal ion which is applicable in mining belt (Benavente, Moreno, & Martinez, 2011). On the other hand, it ensure reusability of adsorbent (Jing, Zhou, Song, & Dong, 2011).

2.7.2 Phase Separation

Phase separation are applied to an intermediate phase in a water treatment sequence during oxidation or polishing. Impurities are transferred into a non-aqueous phase. In a primary stage of phase separation, floating, visible and heavy materials are removed from the water. Sedimentation and filtration are two common examples of phase separation. Solids and non-polar liquids can be isolated from wastewater by sedimentation process. In this process, gravity is used for separation when density differences are enough to overcome dispersion by turbulence. Gravity separation techniques are used as primary treatment of wastewater of sewage. In this process, heavy solids are accumulated on the bottom of a special container such as quiescent settling basin. Nowadays, skimmers are being used with complex clarifiers to concurrently separate floating grease. Grease can contain solids like feathers, wood chips and soap scum. (Weber, 1972). Colloidal suspensions of fine solids may be removed by filtration. Fine physical barriers distinguished from coarser screens or sieves by the ability to remove particles which are smaller than the openings (through which the water passes) (Weber, 1972).

2.7.3 Oxidation

Oxidation can reduce the biochemical oxygen requirement of wastewater. Thus, it helps to diminish the toxicity of several contaminates. Secondary treatment converts some impurities to carbon dioxide, water, and biosolids. In the recent years, advanced oxidation processes has been introduced for wastewater treatment. Two types of processes are available called heterogeneous (photocatalyst and iron based) and homogenous (ozone and ultraviolet (UV)/H_2O_2) (Linden & Mohseni, 2014). It is recognized as a tool to destroy recalcitrant compounds or, at least, to transform them into biodegradable species (Ribeiro, Nunes, Pereira, & Silva, 2015). Two examples of oxidation are biochemical oxidation and chemical oxidation. Biochemical oxidation is a secondary treatment of dissolved colloidal organic compounds. It was usually used for the treatment of agricultural wastewater, industrial wastewaters and sewage (Balmat, 1957; Butterfield, Purdy, & Theriault, 1931; Butterfield, Ruchhoft, & McNamee, 1937). On the other hand, chemical oxidation is usually used as post treatment process after biochemical oxidation (Weber, 1972). It can remove some unaffected organic pollutants remaining after biochemical oxidation. Ozone, chlorine or hypochlorite is added to wastewater for disinfection of bacteria and microbial pathogens by chemical oxidation.

2.7.4 Polishing

Polishing is used as post treatment or independent treatment process for industrial water treatment in some extent. Chemical reduction or pH adjustment minimizes chemical reactivity of wastewater following chemical oxidation (Weber, 1972).

2.8 Nanotechnology in Water Treatment

Nanomaterials are being used widely for water treatment and wastewater treatment. Different kinds of nanomaterials have been designed for removal of organic and inorganic solutes, toxic metal ions and microorganisms from the water (Cloete, 2010). Nanomaterials have some stunning properties to remove contaminants from water. It is considered to be a dynamic research area for water treatment (Cloete, 2010; Karn, Kuiken, & Otto, 2009).

At present, nanotech-based technologies such as adsorption, reverse osmosis, nanofiltration and ultrafiltration membranes etc. are being applied in water treatment. Indeed, different nanofibers, carbon nanotubes and various nanoparticles are the products used for water treatment (Celik, Park, Choi, & Choi, 2011; Pradeep, 2009; X. H. Qin & Wang, 2006; Savage & Diallo, 2005). Nanotechnology is used for water treatment expecting more efficient action to remove pollutants such as bacteria, virus and heavy metals which are difficult to be removed from water if using convectional water treatment systems. Nanomaterials have higher surface areas. It helps to increase reactivity, dissolution and adsorption of contaminants (Qu, Alvarez, & Li, 2013).

2.8.1 Nano-adsorbent

Adsorption is an important step to remove pollutants form water. Usually, it is applied as a polishing step. Limitation of ordinary adsorbents are lack of selectivity, insufficiency of the surface area or active sites and the adsorption kinetics. Nano-adsorbents are attracting attention because of its large surface area to volume ratio which can ensure efficient adsorption associated with adsorption active sites. Other important factors of nano-adsorbents are tunable pore size and short intraparticle diffusion distance which can accelerate the adsorption process.

2.8.1.1 Carbon Based Nano-adsorbents

CNTs are very efficient for removing various organic chemicals. It is a robust adsorbent for different organic chemicals (Bo Pan & Xing, 2008). Mainly, the larger surface to volume ration is the reason of this high adsorption capacity to the chemicals. Moreover, the multiple interactions between CNT and pollutants accelerate the process. CNTs are hydrophobic in nature because of its graphitic surface. In any aqueous medium, CNTs are susceptible to form bundles or aggregates because of its hydrophobicity. As a result, the effective surface area is reduced. On the other hand, CNT aggregates accommodate interstitial spaces and channels, which act as very energetic active sites for high adsorption for organic molecules (B. Pan, Lin, Mashayekhi, & Xing, 2008). It also can accommodate large quantity of micropores unreachable to large organic molecules (Ji, Chen, Duan, & Zhu, 2009). It can be concluded that CNTs are superior to other materials because of its higher adsorption capacity. It is also good adsorbent for several larger sized organic molecules as a result of more accessible and active adsorption sites and porosity.

Activated carbon has some limitation. Low adsorption affinity for low molecular weight polar organic compounds is a vital limitation. On the other hand, CNTs can adsorb different polar organic molecules. There are some factors such as π-π interactions, electrostatic interaction and hydrogen bonding which speed up the process. (Yang & Xing, 2010). The π electron rich CNT surface is very active during any adsorption process. It helps to make π-π interactions with organic molecules with polar aromatic compound and C=C bonds (W. Chen, Duan, & Zhu, 2007; D. Lin & Xing, 2008). Organic compounds which have -COOH, -OH, -NH_2 functional groups could also form hydrogen bond with the graphitic CNT surface which donates electrons (Yang, Wu, Jing, & Zhu, 2008). The adsorption process is accelerated by electrostatic interaction between adsorbate and adsorbent specially for positively charged organic molecules (Ji et al., 2009).

Oxidized CNTs can adsorb metal ions very efficiently with higher removal rate. The major adsorption sites of CNTs are functional groups such as hydroxyl (-OH), carboxyl (-COOH) and phenol for metal ion adsorption. Another important fact is that all the functional groups are present in the surface which increase the possibility of interaction between CNT and contaminants. The adsorption process mainly comprises of electrostatic attraction and chemical bonding (Rao, Lu, & Su, 2007). As a consequence, the adsorption capacity of CNTs can be enhanced significantly by surface oxidation. It has been confirmed by different studies that adsorption capacity of CNTs is higher than activated carbon for heavy metal ions like Cu (II), Cr (VI) Pb (II), Zn (II) etc. (Y. H. Li et al., 2003; Lu, Chiu, & Liu, 2006). Moreover, active adsorption sites and tiny intraparticle diffusion distance speed up the adsorption process. Therefore, activated carbon can be consider as an alternative agent for adsorption.

2.8.1.2 Metal Based Nano-adsorbents

There are several metal oxides that can act as effective adsorbent for organic dyes, heavy metal ions and other pollutants. Some familiar adsorbents are alumina, iron oxide, zeolite and titanium oxide. The adsorption mechanism is basically monitored by ineraction between pollutants ion present in the water and the oxygen of metal oxides (Koeppenkastrop & De Carlo, 1993). Adsorption can be completed by single step or two-step process. In single stage process, direct adsorption is occurred at the surface of adsorbent. As for two-step process, initial adsorption of pollutants ions on the exposed surface of adsorbent. Last step of this process is intraparticle diffusion along with micropore walls. (Trivedi & Axe, 2000). It was reported that arsenic adsorption capacity of nano-magnetite increased to 100 times as particle size was decreased from 300 to 11 nm (Yean et al., 2005). Specific surface area was increased as the particle size was decreased. Therefore, increasing in adsorption can be ascribed to the increase in specific surface area (Auffan et al., 2009; Auffan et al., 2008). Metal based nanomaterials have shown its efficiency for removal of heavy metal ions such as arsenic, lead, mercury, copper, cadmium, chromium, nickel. Its potentiality to remove metal ion is higher activated carbon (Sharma, Srivastava, Singh, Kaul, & Weng, 2009). Among them, remarkable results was observed for arsenic removal. Though, activated carbon is an efficient adsorbent for several organic and inorganic pollutants, it shows limited adsorption capacity for arsenic, especially for As (V) (Daus, Wennrich, & Weiss, 2004). Several metal oxide nanomaterials including nano sized magnetite and TiO_2 have shown arsenic adsorption performance superior to activated carbon (Deliyanni, Bakoyannakis, Zouboulis, & Matis, 2003; Mayo et al., 2007). Suitable porous materials like activated carbon can accommodate metal (hydr)oxide nanoparticles. These nanoparticle impregnated porous structure can be used to remove arsenic as well as organic co-contaminants (Hristovski, Nguyen, & Westerhoff, 2009; Hristovski, Westerhoff, Möller, & Sylvester, 2009).

2.8.1.3 Polymeric Nano-adsorbents

Dendrimers are designed adsorbents for removing different organic pollutants and heavy metal ions present in the water. Inner shell of dendrimers are hydrophobic. It is useful for adsorption of organic contaminates from water. Besides, the outer part or branches of these adsorbents are designable for acting as an adsorbents of heavy metal ions. Several phenomena or factor can be involved in the adsorption process including hydrogen bonding, complexation, hydrophobic effect and electrostatic cooperation (Crooks, Zhao, Sun, Chechik, & Yeung, 2001). It was reported that, a dendrimer-ultrafiltration scheme was made adsorption of heavy metal ions (Diallo, Christie, Swaminathan, Johnson, & Goddard, 2005). Complete removal of Cu (II) was observed by PAMAM dendrimer

2.8.1.4 Membranes and Membrane Processes

Membranes make a physical obstacle for pollutants based on their size. As the key component of water treatment and reuse, they provide high level of automation, require less land and chemical use, and the modular configuration allows flexible design (Qu, Brame, Li, & Alvarez, 2012). One of the significant limitation of membrane is high energy consumption in pressure driven membrane process. Another problem is intrinsic tradeoff between membrane permeability and selectivity. Membrane fouling adds to the energy consumption and the complexity of the process design and operation. Furthermore, it decreases the lifespan of membranes. The performance and efficiency of any membrane systems is mainly controlled by the membrane material. Introduction of functional nanomaterials into membranes can improve the membrane permeability, longer life span, fouling resistance, mechanical and thermal stability. Moreover, functional nanomaterials can contribute for contaminant degradation and self-cleaning.

2.8.1.5 Thin Film Nanocomposite Membranes

Thin film nanocomposite has several important properties for water treatment. In this case, main concern is the introduction of proper nanomaterials like TiO_2, Ag, SiO_2 and zeolites into the membrane. There are two common process for introduction of nanomaterials named surface modification and mixing with the casting solution. Among various dopants, currently zeolites are attracting attention. They have exhibited their potentiality in improving membrane property. The addition of nano-zeolites leads to more permeable, negatively charged, and thicker polyamide active layer (Mary L Lind et al., 2009). One study revealed that water permeability increased up to 80% over the TFC membrane as well as the salt rejection predominantly preserved (93.9±0.3%) (B.-H. Jeong et al., 2007). Another study reported that adding 0.2 wt% of nano-zeolites(250 nm) to membrane ensured higher permeability and better salt rejection (>99.4%) than ordinary RO membranes (Mary Laura Lind, Eumine Suk, Nguyen, & Hoek, 2010). The hydrophilic porous structure of nano-zeolites generate favorable paths for water. However, water permeability increased even with pore-filled zeolites, although less than the pore-open ones, which could be attributed to defects at the zeolite-polymer interface. Zeolite has been used as a bearer of antimicrobial dopants such as Ag+, which imparts anti-fouling property to the membrane (Lind et al., 2009b). The zeolite doped TFN technology has reached the initial phage of commercialization. A membrane named Quantum Flux is commercially available. It can filtrate wastewater using reverse osmosis process.

2.8.1.6 Nanofiber Membranes

Nanofiber is defined as a fiber having diameter in nanometer range. It has important properties like permeability, interconnected porosity, selectivity, high surface area to volume ratio, light weight etc. Some common processes for nanofiber fabrication are melt blowing, meltspinning, jetspinning, force spinning and electrospinning. Among them, electrospinning is a popular process because of its simplicity, efficiency and cheap which can fabricate nanofibers with diameter below 100 nm using various polymer and polymer matrix composites (Cloete, 2010; D. Li & Xia, 2004). The electrospun nanofibers have smaller diameter, high specific surface area to volume ratio and complex pore structures. Its morphology including diameter and diameter distribution, composition, secondary structure, and spatial alignment of electrospun nanofibers can be easily manipulated for specific applications (D. Li & Xia, 2004). Even though nanofiber membranes are being commercially utilized for air filtration, their prospective utilization in water treatment is still undeveloped. Nanofiber membranes can remove very small particles from water at a very high rejection rate with less fouling (Seeram Ramakrishna et al., 2006). Electrospun nanofiber membrane can ensure retention of micro-particle/nanoparticle with higher elastic modules, compaction resistance (S. Homaeigohar, Koll, Lilleodden, & Elbahri, 2012; Sawada et al., 2012) , high ductility and longer life span (Maximous, Nakhla, Wan, & Wong, 2010). In addition, ceramic particles and functional nanomaterials can be easily introduce into the spinning solutions to fabricate composite nanofibers (D. Li & Xia, 2004). The exceptional properties of electrospun membrane make it an ideal platform to synthesize a multifunctional media for water treatment. For example, by implementing ceramic nanomaterials or any adsorbent agents on the nanofiber scaffold, removal capacity of nanofiber can be increased. It has been revealed by notable number of research studies that membranes can act as multifunctional barrier over pollutants by adding nanomaterials in the membrane. Hydrophilic metal oxide nanoparticles such as Al_2O_3, TiO_2, and zeolite etc. are widely being used for such application. antimicrobial nanoparticles (e.g., nano-Ag and CNTs), and (photo) catalytic nanomaterials (e.g., bi-metallic nanoparticles, TiO_2). The objective of introducing hydrophilic metal oxide to nanofiber is to diminish the possibility fouling during operation by increasing the hydrophilicity of the membrane. It has been shown that the addition of metal oxide including alumina (Maximous, Nakhla, Wong, & Wan, 2010), silica (Bottino, Capannelli, D'asti, & Piaggio, 2001), zeolite (Pendergast, Nygaard, Ghosh, & Hoek, 2010) and TiO_2 (Bae & Tak, 2005) to polymeric membranes can increase membrane surface hydrophilicity, water permeability, or fouling resistance. Moreover, these particles can help to improve the mechanical and thermal strength of polymeric membranes, lowering the effect of heat and compaction on membrane permeability (Ebert, Fritsch, Koll, & Tjahjawiguna, 2004; Pendergast et al., 2010)

2.9 Electrospinning

Electrospinning is a method of producing very fine fiber with high surface area to volume ratio. Electrospun fiber has been used in scaffolds engineering, filtration technology, wound healing and medical application due to their interesting characteristics.The set up consists of a spinneret, a high voltage power supply and a grounded collector. Electric potential is applied between the spinneret and the target collector. After a certain value of electrostatic force which can overcome the surface tension of electrospinning solution, a charged fluid jet is ejected from the tip of cone (Bognitzki et al., 2001; Hao Fong & Reneker, 1999; Huang et al., 2003; Zong et al., 2002). The polymer to be electrospun is dissolved in a suitable solvent to prepare electrospinning solution. A grounded metal plate or rotating drum is used as a target collector. The electrode is connected to the tip of the metal needle. The process is schematically illustrated in Fig. 2.8.

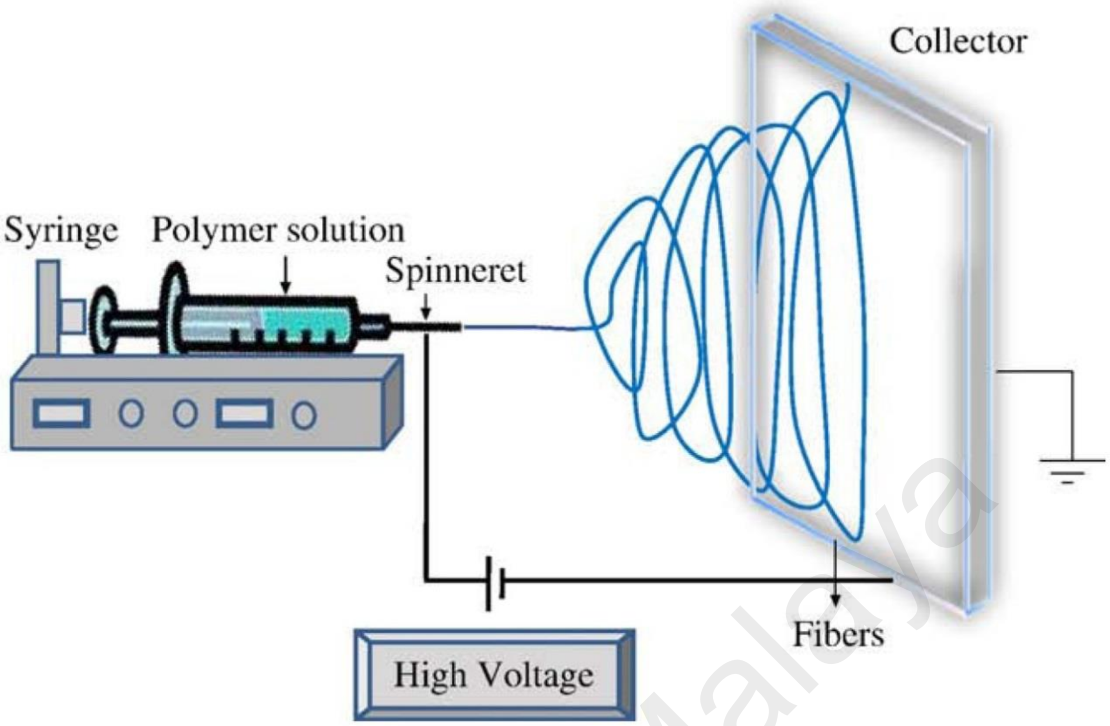


Figure 2.8: Schematic diagram of electrospinning equipment (Zhu & Chen, 2013)

2.9.1 Electrospinning Mechanism

A static electric force is responsible for electrospinning a polymer solution to fiber. At first, a syringe or capillary tube is loaded with polymer solution. Then, electric field is applied between a conducting capillary (needle or spinneret) and collector plate or rotating drum. The polymer solution is sustained in a droplet shape by surface tension. When appropriate voltage is applied to overcome the surface tension a jet comes out of it (D. Li & Xia, 2004).

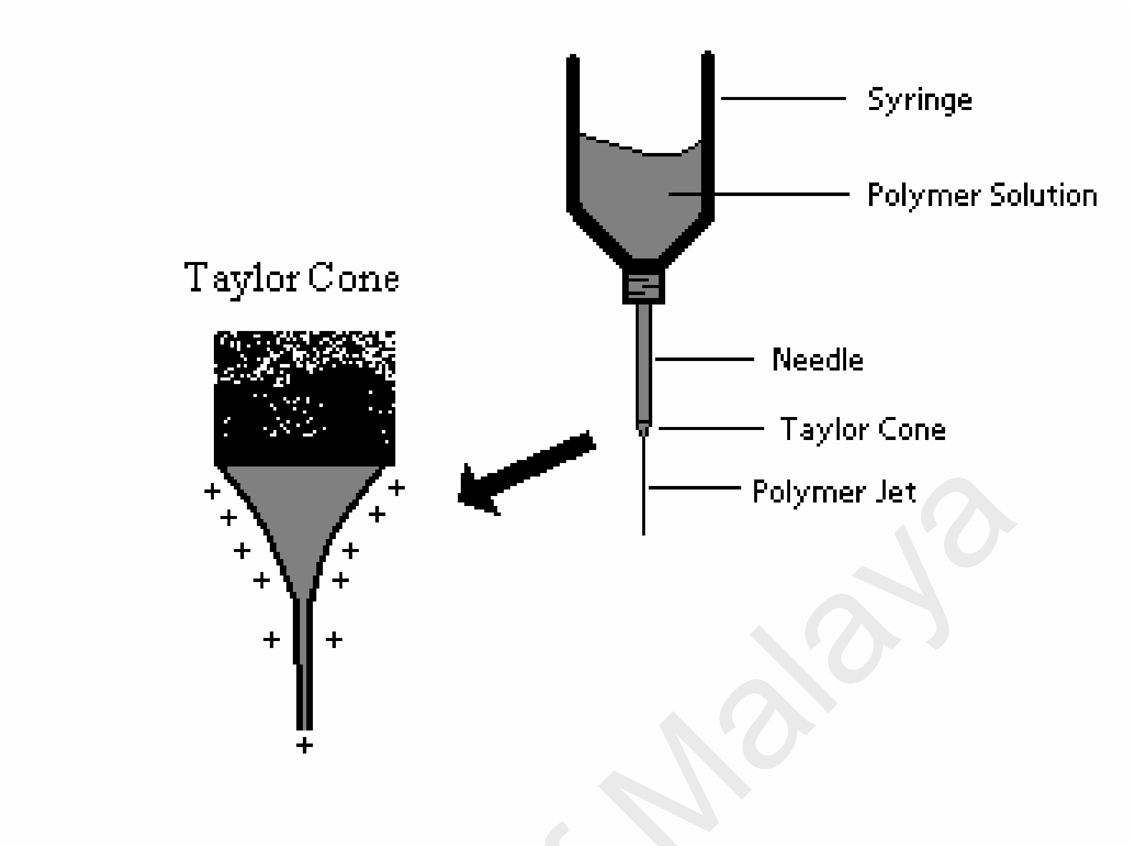


Figure 2.9: **Taylor cone formation and origin**

Electric field causes the spherical droplet to transform into a conical shape. This is known as the Taylor cone (see Figure 2.3). The force from the electric field causes the solution to be drawn out towards the collector. In this stage, internal and external charges cause the liquid jet to be whipped around the field as it accelerates towards the grounded collector. This action is responsible for the evaporation of the solvent. Simultaneously, it causes stretching and sliding of polymer chains. This whipping motion helps the fibers to have diameters in nanometer range (Huang et al., 2003; Subbiah, Bhat, Tock, Parameswaran, & Ramkumar, 2005).

2.9.2 Electrospinning Process Parameters

Though the electrospinning process is simple, fabrication of nano-sized fiber with uniformity depends on numerous variables. There are two types of parameter named solution parameter and machine parameter. Solution parameters include polymer type, concentration of solution, type of solvent, solvent concentration, viscosity, molecular weight of the polymer, conductivity and surface tension. Machine or process parameters include electric field strength, flow rate, distance from the capillary to the collector, shape and movement of the collector, room temperature, and humidity (Huang et al., 2003; D. Li, Ouyang, McCann, & Xia, 2005) Viscosity of polymer solution is a notably crucial parameter and significantly dominated by polymer concentration. A minimum amount of polymer chains is a prerequisite to be present to ensure chain entanglement and fiber production (Frenot & Chronakis, 2003; D. Li & Xia, 2004). Increasing polymer concentration increases the number of polymer chains present in solution. Meanwhile, viscosity is also increased which causes obstacle to flow through a needle. Therefore, electrospinning is hampered (Frenot & Chronakis, 2003; D. Li & Xia, 2004).

2.9.2.1 Effect of Applied voltage

During electrospinning, high-voltage power supply create a flow of current through the solution to be electrospun via metallic needle. This effect cause a spherical droplet of solution to be deformed into a Taylor cone. Finally, electrospinning is started from a stable Taylor cone to form nanofibers at a suitable voltage (Fig. 2.10 a–c) (Laudenslager & Sigmund, 2012). The application of high voltage to the polymer solution held by its surface tension creates a charge on the surface of the liquid. Reciprocated charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical drop formed at tip of the needle tip gets converted into conical shape Critical value of applied voltage can vary for different polymer. The formation of smaller-diameter nanofibers with an increase in the applied voltage is attributed to the stretching of the polymer solution in correlation with the charge repulsion within the polymer jet (Sill & von Recum, 2008). Usually, beads or beaded nanofibers are formed when applied voltage is higher than critical value. Formation of nanofiber with increased diameter or defects like beads at higher voltage are attributed to increase in the jet velocity and decrease in the size of the Taylor cone at the same flow rate. It was reported by Deitzel et al. that increase in the voltage caused bead formation using poly(ethylene)/water solution (Deitzel, Kleinmeyer, Harris, & Tan, 2001). Moreover, increase of diameter with increasing applied voltage also reported which is attributed to an increase in the jet length (Fig. 2.10) (Baumgarten, 1971).

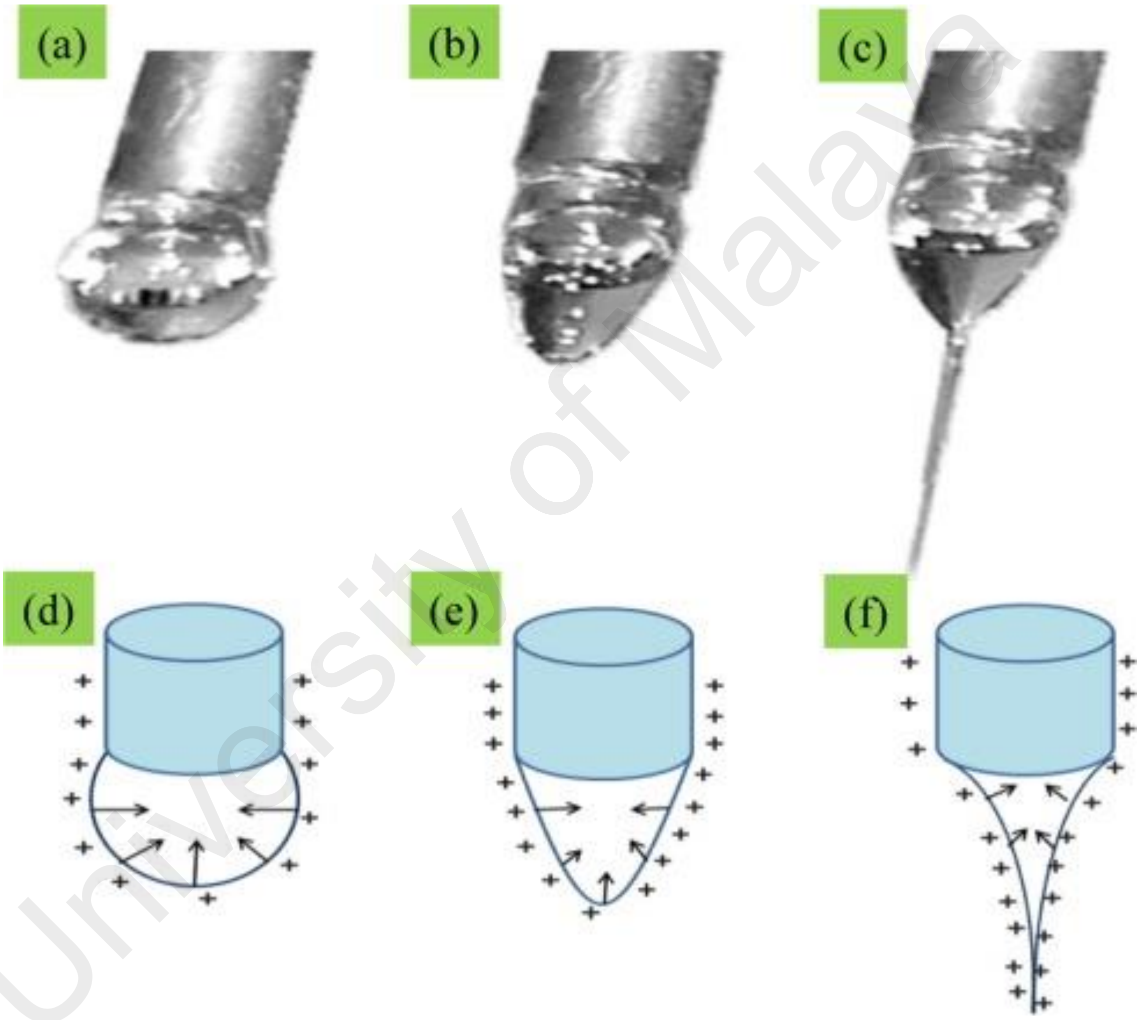


Figure 2.10: (a–c) three stage deformation of the polyvinylpyrrolidone droplet under the influence of increasing electric field, (d–f) the mechanism of the effect of charges on the polymeric droplets (Laudenslager & Sigmund, 2012) .

2.9.2.2 Effect of Solution Feed Rate

Feed rate or flow rate is an important parameter in electrospinning. Morphology of electrospun nanofiber depends on it. Suitable feed rate of a polymer solution can help in producing bead free uniform nanofiber. The critical value of feed rate varies with polymer solution. Flow rate above critical value can be a reason of bead formation in the fiber matrix. It was reported that bead less nanofibers of polystyrene was fabricated at feed rate 0.07 mL/min, while bead was observed at 0.10 mL/min. Feed rate beyond critical value can cause increase in pore size and diameter because of incomplete drying of nanofiber jet (Megelski, Stephens, Chase, & Rabolt, 2002). Therefore, a balance in feed rate is required to maintain a balance between the leaving polymer or polymer blend solution and replacement of that solution with a new one during jet formation (Megelski et al., 2002; Zeleny, 1935). This will also allow the formation of a stable jet cone and sometimes a receded jet (a jet that emerges directly from the inside of the needle with no apparent droplet or cone). Receded jets are not stable jets, and during the electrospinning process, these jets are continuously replaced by cone jets. As a result of this phenomenon, nanofibers with a wide range diameter are formed (Fig. 2.11f) (Zargham, Bazgir, Tavakoli, Rashidi, & Damerchely, 2012). In addition to bead formation, in some cases, at an elevated flow rate, ribbon-like defects (Megelski et al., 2002) and unspun droplets (Fig. 2.11g) have also been reported in the literature (Zargham et al., 2012). Higher feed rate cause non-evaporation of the solvent and inadequate stretching of the solution. These effects are possible reason of formation of beads, ribbon-like structure and increase in diameter (Z. Li & Wang, 2013). The presence of the unspun droplets is attributed to the influence of the gravitational force (Zargham et al., 2012). Surface charge density is another important factor that can cause defects in nanofiber. Reduction in the surface charge density allow merging of nanofiber during electrospinning towards the grounded collector. This merging of nanofibers facilitates the formation of garlands (Reneker, Kataphinan, Theron, Zussman, & Yarin, 2002).

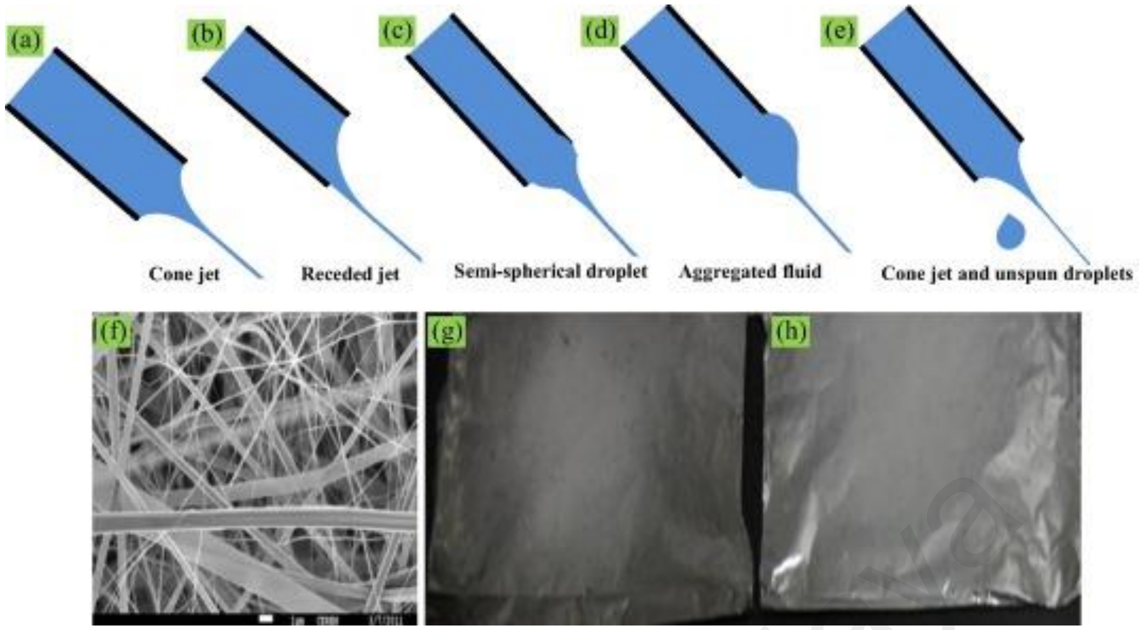


Figure 2.11: (a-e) Formation of various jets with increasing flow rate, (f) the SEM image of nanofiber, (g) the digital images show solution drop and (h) electrospun fibers of chitosan deposited on aluminum foil of nylon 6 (Zargham et al., 2012).

2.9.2.3 Effect of needle to collector distance and needle diameter

One of the important parameter of electrospinning is the distance between needle tip and collector. Morphology of nanofiber membrane can be varied by changing this parameter. It also varies with other polymer like other parameter such as the applied electric field, viscosity, and flow rate. Distance can affect the deposition time, instability interval and evaporation rate of solvent (Matabola & Moutloali, 2013). Therefore, a critical distance need to maintain for a particular polymer to get defect free and uniform nanofiber. (Bhardwaj & Kundu, 2010). It was reported that defective and large-diameter nanofibers are formed when this distance is kept small, whereas the diameter of the nanofiber decreased as the distance was increased (Baumgarten, 1971; Matabola & Moutloali, 2013; T. Wang & Kumar, 2006). However, some studies reported that there is no effect on the morphology of the nanofiber with a change in the distance between the metallic needle and collector (C. Zhang, Yuan, Wu, Han, & Sheng, 2005).

2.9.2.4 Effects of polymer concentration and solution viscosity

Polymer concentration and solution viscosity is an important parameter in electrospinning. Stretching of solution jet is affected by concentration of polymer solution. It was reported that if the concentration of the polymeric solution is low, the applied electric field and surface tension cause the entangled polymer chains to break into fragments before reaching the collector (Haider et al., 2013). Beaded nanofiber are caused by fragments. Viscosity of polymer solution is increased with concentration of solution which causes increase in chain entanglement among the polymer chains. Chain entanglement of polymer help to produce defect free nanofiber by overcoming the surface tension. The concentration beyond the critical value can hampers the flow of solution which leads to formation of defects in nanofiber. (Haider et al., 2013). The morphologies of the beads depict an interesting shape change from a round droplet-like shape (with low viscosity solutions) to a stretched droplet or ellipse to smooth fibers (with sufficient viscosity) as the solution viscosity changes (Fig. 2.12a–d) (Zargham et al., 2012). Similar phenomenon was reported for electrospinning of PEO varying the solution viscosity (Fig. 2.12e–h) (H Fong, Chun, & Reneker, 1999). In case of poly(D,L-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA), shape of the bead changes were observed with changing in viscosity (Zong et al., 2002). It was reported that optimum viscosity of PEO is 800–4000 cp for defect free nanofiber fabrication (Doshi & Reneker, 1993). In case of polyacrylonitrile (PAN), viscosity of the solution was kept at 1.7–215 cp foe defect free electrospinning. It can be concluded that critical value of concentration or viscosity need to be find out for every polymer for defect free nanofiber (Baumgarten, 1971).

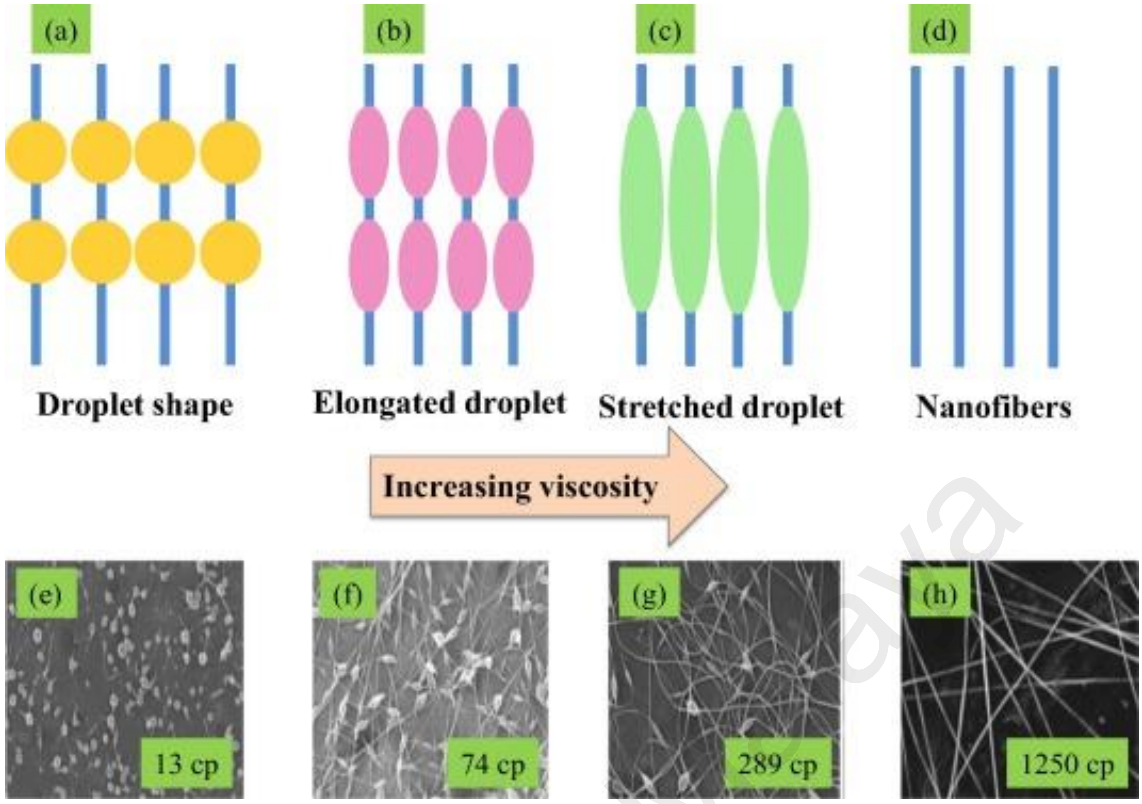


Figure 2.12: (a–d) Variation in morphology of electrospun nanofibers of PEO with viscosity and (e–h) SEM micrographs. Reproduce with permission from the publisher (H Fong et al., 1999; Luzio, Canesi, Bertarelli, & Caironi, 2014; Zander, 2013)

CHAPTER 3: EXPERIMENTAL WORK

3.1 Materials

Chitosan (M_w =8.96×10^5 g/mole, degree of deacetylation = 40 %) was obtained from SE Chemical Co. Ltd and PVA (M_w =60000, degree of hydrolysis = 89%) was a commercial product purchased from Kurray Co Ltd, Tokyo, Japan. NaOH was purchased from System. Acetic acid, $FeCl_3.6H_2O$, $NiCl_2.6H_2O$, Zeolite and $K_2Cr_2O_7$ were purchased from Sigma-Aldrich.

3.2 Hydrolysis of Chitosan with NaOH

The degree of deacetylation (%DDA) of chitosan indicates the extent of the transformation of N-acetyl-D-glucosamine to D-glucosamine (Dimzon & Knepper, 2015). Molecular weight and degree of deacetylation of supplied chitosan was not suitable for electrospinning. It was reported that low molecular weight align more effectively in the electromagnetic field of the electrospinning unit. Hydrolysis of chitosan causes deacetylation of chitosan. It means that it increases the degree of deacetylation concurrently decreases molecular weight (Homayoni, Ravandi, & Valizadeh, 2009). Moreover, a degree of deacetylation greater than 70% is needed for the solubility of chitosan (L. Li & Hsieh, 2006). Molecular weight and degree of deacetylation of supplied chitosan was not suitable for electrospinning. Therefore, hydrolysis was done to increase the degree of deacetylation and decrease the molecular weight of chitosan. At first, 40 g of NaOH was added to 80 g of distilled water. The solution was stirred and temperature was set to 90°C. At this temperature, 2.5 wt.% of chitosan was added to the solution and stirred for 24 hours at elevated temperature (90 °C). After that, the chitosan was filtered and washed several times to remove the NaOH. Finally, chitosan was dried 60 °C for 7 hours. The details of the process is shown in Fig. 3.1

3.2.1 Characterization of Hydrolyzed Chitosan

3.2.1.1 FTIR Analysis

FTIR spectroscopy was used to study the chemical structure of chitosan after hydrolysis. It was also used to determine the degree of deacetylation (DDA) of chitosan before and after hydrolysis process. It was done using Nicolet iS10 FTIR spectrometer from Thermo Scientific. Spectral range is 600-3000 wavenumber with resolution of 4 cm^{-1}.

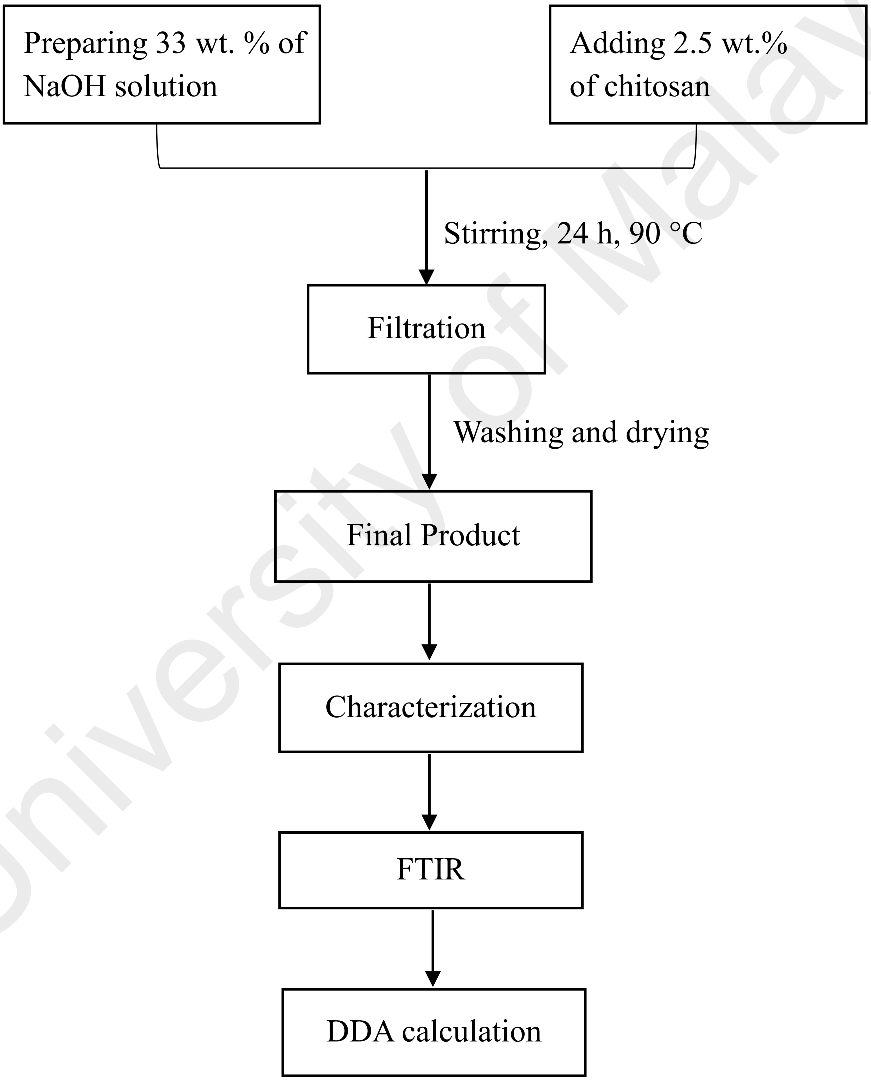


Figure 3.1: **Flowchart of hydrolysis process**

3.3 Fabrication of Chitosan/PVA Electrospun Nanofiber

Electrospinning of chitosan/PVA was completed by several steps. It has been shown in Fig. 3.2. Details of the electrospinning process has been described below.

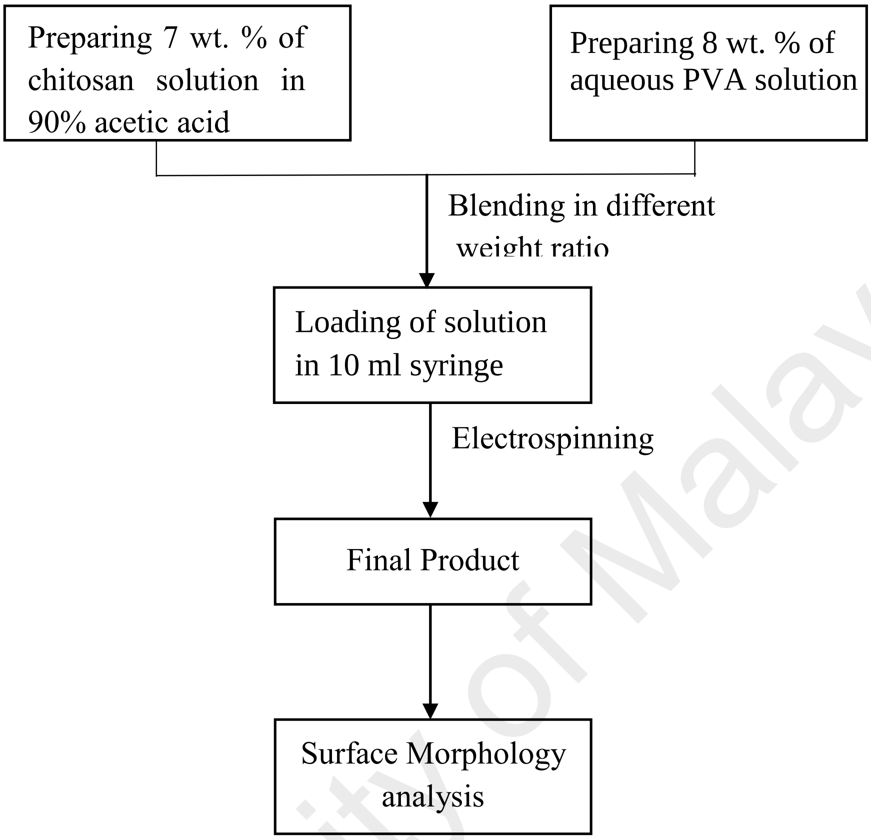


Figure 3.2: **Flowchart of electrospinning of chitosan/PVA nanofiber**

3.3.1 Solution Preparation

At first, 7 wt.% of chitosan solution was made in concentrated acetic acid by stirring for 1 hour . Second, 8 wt.% of aqueous PVA solution was prepared by stirring for 24 hour. Finally, blended solution was prepared with weight ratio of 50:50, 60:40, 70:30, 80:20 and 90:10 of chitosan and PVA, respectively. Blend solution was numbered as A_1, A_2, A_3, A_4 and A_5, respectively. Previous study reported that chitosan/PVA can be electrospun with 30:70 weight ratio (Jia et al., 2007). In this study, first composition of blend solution was chosen to be 50:50 to ensure more biopolymer, which is the chitosan content in the resulting nanofiber.

3.3.2 Electrospinning

Previously prepared solutions A_1, A_2, A_3, A_4 and A_5 were loaded in 10ml syringe for electrospinning process. Electrospinning setup consisted of an high-voltage power supply 25 kV (LD Didactic GmbH, Germany), a laboratory syringe pump NE-300 (New Era Pump Systems, NY, USA) and a stainless steel made stationary collector. Electrospinning was done under the following conditions: 19 gauge needles, 10 cm tip to collector distance, 0·1– 0.4 $mL.h^{-1}$ feed-rate, 7·1-14 kV voltage. Feed rate was needed to decrease with increasing chitosan percentage in the blend solution. On the other hand applied voltage was required to increase as viscosity of the solution became higher with increasing chitosan content (Homayoni et al., 2009). Electrospinning set up of current study has been shown in Fig. 3.3.

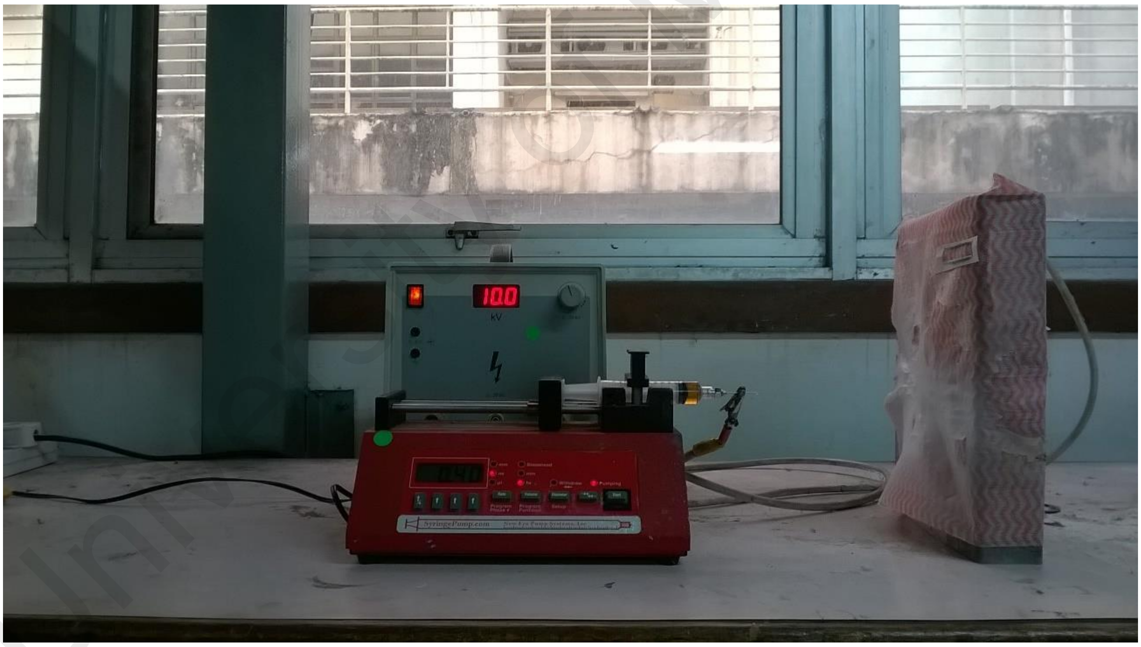


Figure 3.3: Electrospinning set up used in current study

3.3.3 Morphology Observation of Chitosan/PVA Nanofiber

Morphology observation and measurement of fiber diameter was done by field emission scanning electron spectroscopy (ZEISS AURIGA). Mean diameter and size distribution of fiber was determined from 100 fibers.

3.4 Preparation of Chitosan/PVA/Zeolite Electrospun Nanofibrous Composite Membrane

In this section, electrospinning process of chitosan/PVA/zeolite will be discussed elaborately. The flowchart of the process is shown in Fig. 3.3

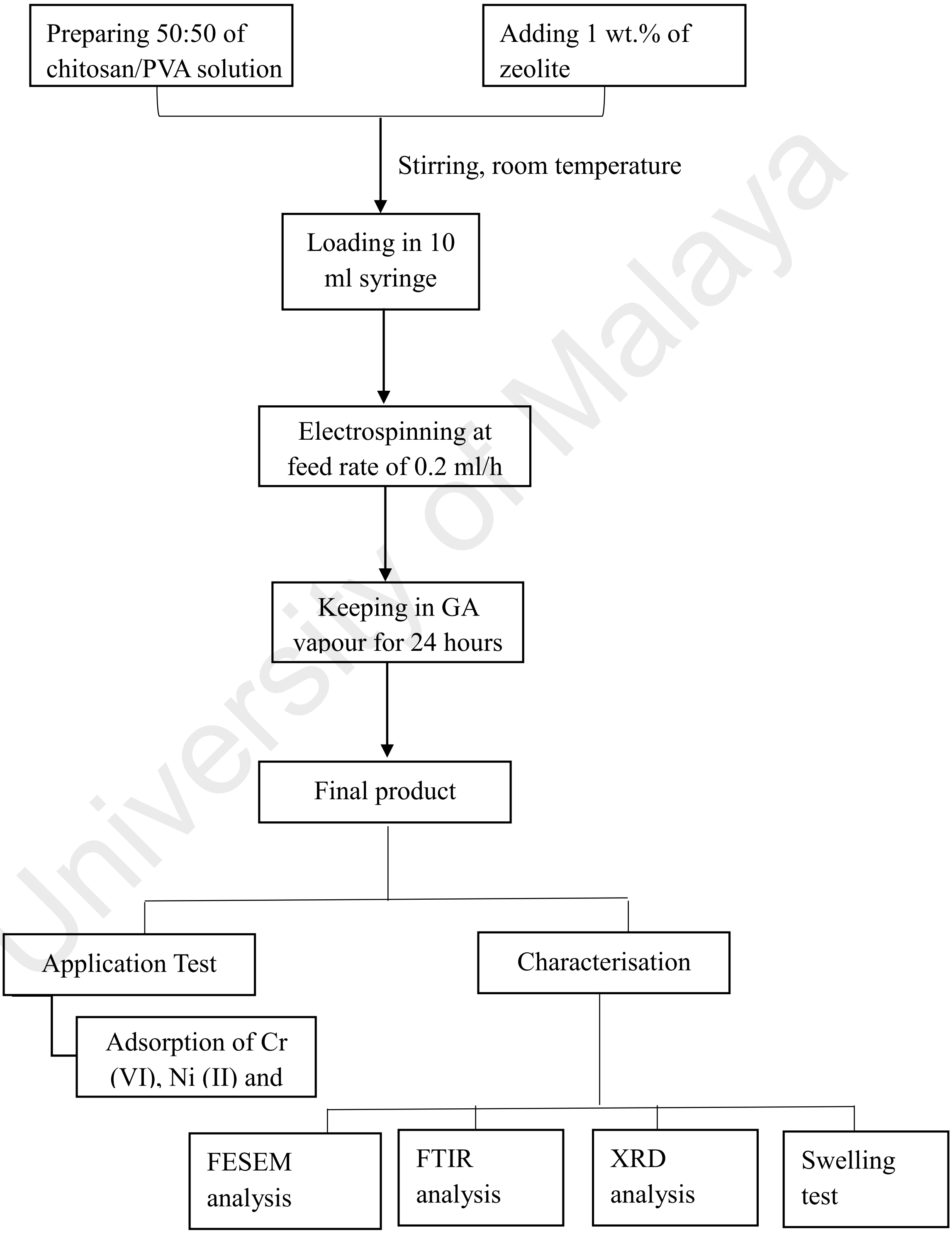


Figure 3.4: **Flowchart of electrospinning of chitosan/PVA/zeolite nanofiber**

3.4.1 Electrospinning

50:50 of chitosan/PVA was chosen for this study and 1 wt. % of zeolite was added and continuously stirred for 15 min. Finally, electrospinning was performed under the following conditions: 19-gauge needle, 10 cm tip to the collector distance, 0.4 mL.h^{-1} feed-rate, and 10 kV applied voltage. The electrospun fibers were kept in desiccator with GA vapor for 24 h.

3.4.2 Characterization of Chitosan/PVA/Zeolite Nanofibrous Composite Membrane

3.4.2.1 Morphological Analysis of Chitosan/PVA/Zeolite Nanofibrous Composite Membrane

The morphology of chitosan/PVA/zeolite nanofibrous composite was studied under a field-emission scanning electron microscope (FE-SEM; High-resolution FEI Quanta 200F;Hitachi; Japan).

3.4.2.2 FTIR Analysis of Chitosan/PVA/Zeolite Nanofiber

In the case of chitosan/PVA/zeolite nanofibrous composite membrane, bonding among membrane materials was analyzed with FTIR. It was also done using Nicolet iS10 FTIR spectrometer from Thermo Scientific. Spectral range is 600-3000 wavenumber with resolution 4 cm^{-1}.

3.4.2.3 XRD Analysis of Chitosan/PVA/Zeolite Nanofibrous Membrane

XRD analysis was done to know the overall crystallinity of the nanofibrous composite membrane. The X-ray diffraction (XRD) patterns of the powder and the composite were obtained by the PAN analytical's Empyrean XRD (USA) with monochromated CuK radiation (λ=1.54056Å), operated at 45 kV, 40 mA, a step size of 0.026 °, and a scanning rate of 0.1 ° s^{-1} over a 2θ range from 5 ° to 100 °.

3.4.2.4 Swelling Experiments

Swelling behavior of resulting nanofiber was necessary to know the durability of the fiber in water. In this study distilled water (pH = 7), acidic medium (pH = 3) and basic medium (pH = 10) was chosen for swelling test. Though chitosan is insoluble but PVA is soluble in distilled water (Çay, Miraftab, & Kumbasar, 2014). Therefore it was necessary to compare the swelling behavior of resulting nanofiber with PVA in distilled water. Chitosan/PVA and chitosan/PVA/zeolite membrane samples were weighted and subsequently immersed in distilled water for 24 h at room temperature. The swollen samples was weighted immediately after excess water was removed. The swelling ratio S_w was estimated using the following equation

$$\mathbf{S_w} = \frac{\mathbf{W_s - W_d}}{\mathbf{W_d}} \qquad 3.1$$

Where, W_d and W_s are the masses before and after dipping in water, respectively.

3.4.2.5 Adsorption Study

In this study, industrial wastewater was not used for treatment as it contains not only heavy metal but also different chemical and elements. Therefore, the capacity of the resulting membrane for heavy metal adsorption will not be well understood and heavy metal containing water was prepared in the laboratory. Adsorption behavior of the resulting nanofibrous membrane was evaluated on Cr (VI), Fe (III) and Ni (II). Sources of these heavy metal ion and health effects have been discussed in literature review, section 2.5. 0.1 g of the chitosan/PVA/zeolite nanofibrous composite membrane was agitated with 10ml of Potassium (VI) dichromate, Nickel (II) Chloride and Iron (III) Chloride solution by magnetic stirrer. Initial concentration of heavy metal ion was varied from 10 to 80 mg/L. Concentration of solution was calculated after different time interval. Stirring was done to ensure the maximum contact of fiber surface with the metal ions present in the solution. Concentration of the solution was measured by using Flame atomic absorption spectrometer (Analyst 400, Perkin Elmer). Sufficient amount of clear part of solution was taken for concentration measurement.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Hydrolysis of Chitosan

4.1.1 FTIR Analysis of Hydrolyzed Chitosan

FTIR spectrum of resulting chitosan is shown in Fig. 4.1. The presence of saccharide group was verified by absorption observed at 894, 1080 and 1150cm^{-1} (Homayoni et al., 2009). Absorption band at 1590 and 1653 cm^{-1} indicated the presence of –NH_2 and C=O-NHR, respectively, where 3363 cm^{-1} indicated N-H stretch (Homayoni et al., 2009). All these conclude the presence of chitosan. Therefore, it can be concluded that the chemical structure of chitosan remained unaffected after 24 hour hydrolysis treatment.

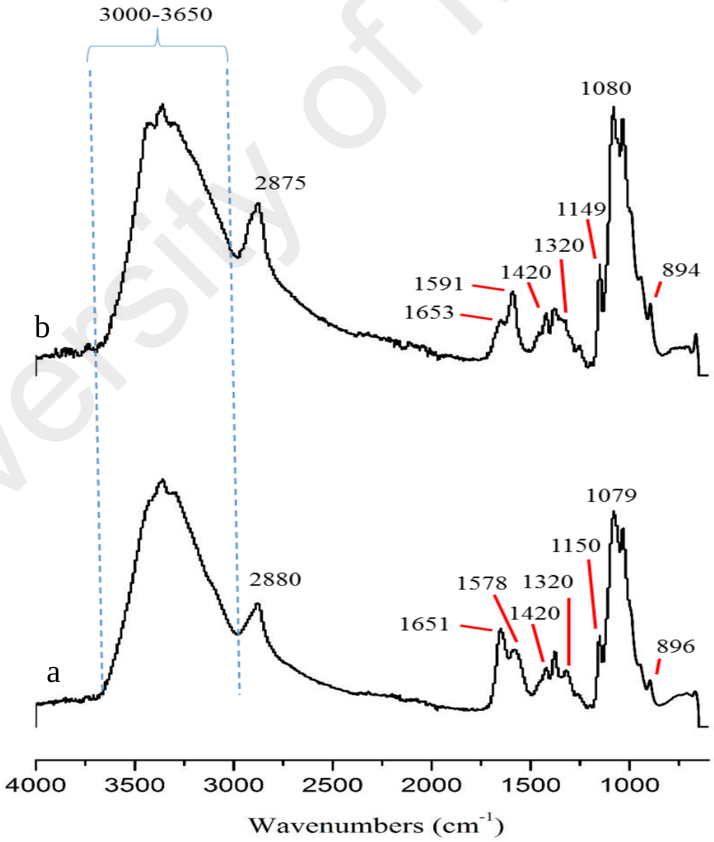


Figure 4.1: **FTIR spectra of (a) crude chitosan and (b) hydrolyzed chitosan**

4.1.2 Calculation of the Degree of Deacetylation (DDA)

Several methods have been already developed to determine the DA. IR spectroscopy is a relatively quick technique for a qualitative evaluation of the DA through the determination of absorption ratios. Several procedures using different absorption ratios have been already proposed for determination of the DA. Several absorption band ratios such as A_{1560}/A_{2875}, A_{1655}/A_{2875}, A_{1655}/A_{3450}, A_{1320}/A_{3450}, A_{1655}/A_{1070}, A_{1655}/A_{1030}, A_{1560}/A_{1160}, A_{1560}/A_{897}, and A_{1320}/A_{1420} have been proposed to determine the DA (Baxter, Dillon, Taylor, & Roberts, 1992; Brugnerotto et al., 2001; Domszy & Roberts, 1985; Dong et al., 2002; Miya, Iwamoto, Yoshikawa, & Mima, 1980; Muzzarelli, Tanfani, Scarpini, & Laterza, 1980; Sannan, Kurita, Ogura, & Iwakura, 1978; Y Shigemasa, Matsuura, Sashiwa, & Saimato, 1996; Yoshihiro Shigemasa, Matsuura, Sashiwa, & Saimoto, 1996).

However, in this study the ratio of A_{1320} and A_{1420} was selected for determination of DA. The degree of deacetylation was calculated using the following equations (Muhd Julkapli et al., 2011).

$$DA = (31.92\frac{A_{1320}}{A_{1420}} - 12.20) \times 100 \quad 4.1$$

$$DD = 1 - DA \quad 4.2$$

Here, DDA = Degree of Deacetylation

DA = Degree of Acetylation

A= Absorption peak

This ratio of A_{1320}/A_{1420} has been chosen for this calculation as it is sensitive to chemical composition of chitin and chitosan (Muhd Julkapli et al., 2011). The absorption band at 1320 cm^{-1} was considered as contribution of amide III (Brugnerotto et al., 2001; C. Qin et al., 2006). It was reported that the DA determined from the ratio of A_{1320}/A_{1420}

of FTIR spectra of chitosan was in agreement with the DA determined from 1H NMR and 13C NMR spectra which was reported by Brugneretto et.al. (2001).This is because the intensities and positions of bands appeared at 1320 and 1420 cm^{-1} did not change with humidity and hydrogen bonds. The degree of deacetylation calculated using the FTIR spectra is 84% for 24 hour hydrolysis. It means that 84% is D-glucosamine units of total chitosan (Czechowska-Biskup, Jarosińska, Rokita, Ulański, & Rosiak, 2012).

4.2 Fabrication of Chitosan/PVA Nanofiber

4.2.1 Electrospinning of Chitosan/PVA Blends

Chitosan did not give any nanofiber structure because of large repelling action between chitosan molecules. This problem can be solved by blending the chitosan solution with PVA. Solutions numbered A_1, A_2, A_3, A_4 and A_5 were tried for electrospinning. From the result, it showed that 70% was the maximum chitosan content in the blend solution for possible electrospinning to give fiber structure. In case of lower compositions of PVA, the interaction was predominantly with the -OH groups of chitosan while, as the composition of PVA increased, the interaction with the NH_2 groups increased. The -OH group of chitosan displays free rotation; hence, it is more available for interaction with the OH groups of PVA. In addition, as the amount of PVA increases with decreasing chitosan content, the availability of -OH groups of chitosan become less. Therefore, -OH groups of PVA begin to interact with the NH_2 groups of chitosan and his formation will help in getting a good distributed nanofiber in electrospinning process.

4.2.2 Morphology Study and Diameter Distribution for Chitosan/PVA Nanofibers

Fig. 4.2 shows FESEM micrographs of nanofibers. From the micrographs, the surface of nanofiber seems to be comparatively smooth. However, some irregular shape and beads were observed in the nanofibrous mat of A_2 and A_3, respectively. Instability of jet, lower molecular weight, higher applied voltage, lower viscosity and higher surface tension are some reasons of beads formation in nanofiber (Homayoni et al., 2009; Muhd Julkapli et al., 2011; Yarin, 1993). Referring to Table 4.1, applied voltage for A_2 and A_3 are higher than A_1. This might be the reason for bead formation with increasing chitosan content in the polymer blend. In case of polymer blend A_4, only few fiber was observed with beads. However, A_5 formed particles only. This may due to the hydrolysis process reduces the molecular weight of chitosan (Homayoni et al., 2009). Therefore, another possible reason for bead formation is lower molecular weight as the chitosan was hydrolyzed for 24 hours. It was reported by other study that hydrolysis decreases the molecular weight of chitosan (Homayoni et al., 2009).

100 fibers were analyzed via Digimizer for every sample and the size distribution histogram was drawn. Fig. 4.2 shows respective fiber diameter distribution of the nanofibers. It was observed that when chitosan content in polymer blend increased the mean diameter and standard deviation increased. In addition, the value of standard deviation is maximum for the polymer blend containing higher amount of chitosan. It may be the result of uneven splaying of jet for higher viscosity of blend solution. On the other hand, applied voltage required for 70:30 weight ratio of chitosan/PVA polymer blend is 9.8 kV which was much higher than 7.1 kV, required for 50:50 weight ratio of chitosan/PVA blend. This is because amino group of chitosan was protonated in the solution which made the solution viscous and higher voltage was required to get the stretched jet (Hao Fong & Reneker, 1999). As reported by Huang et al. (2003), higher voltage results in larger diameter.

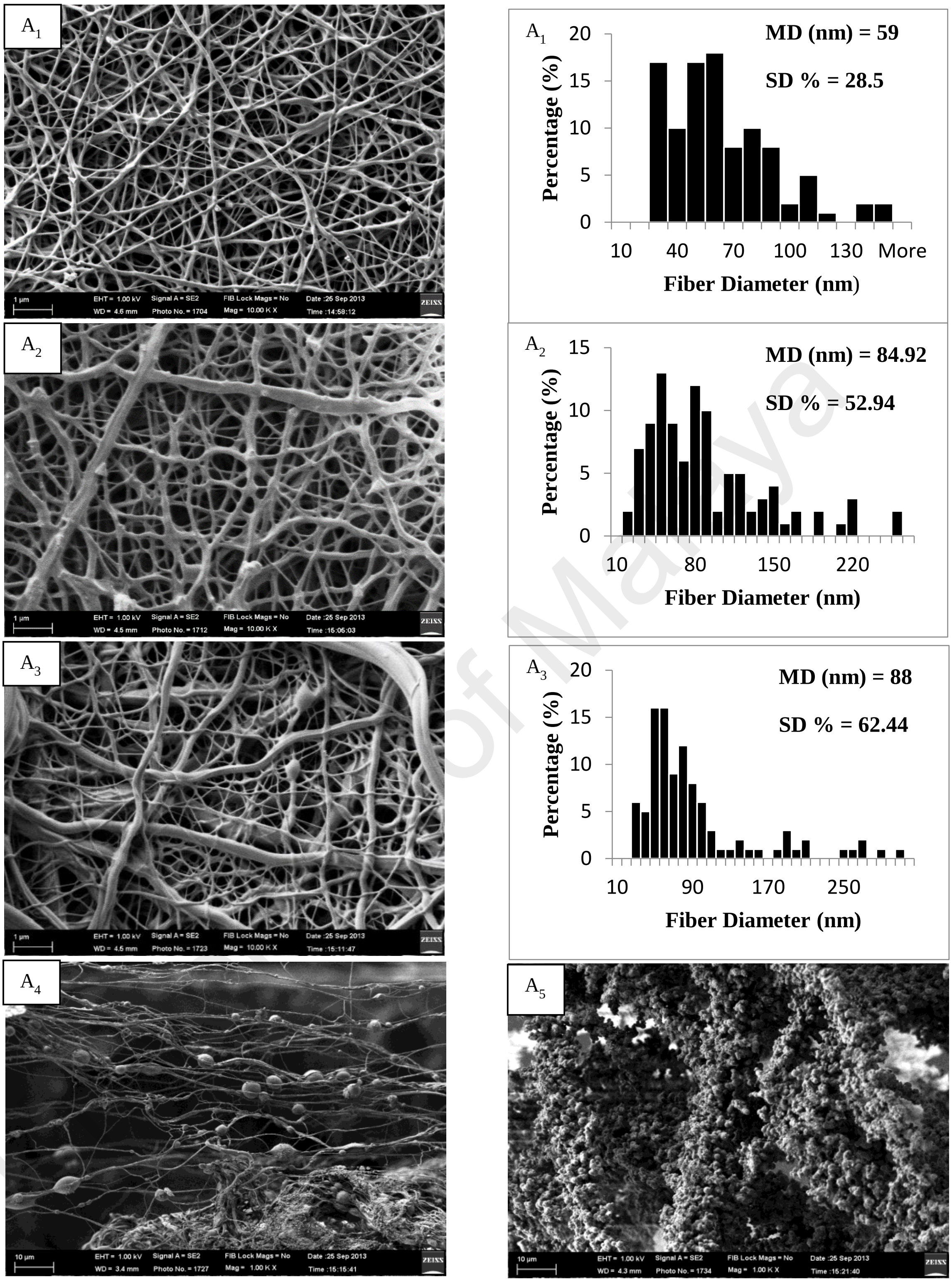


Figure 4.2: FESEM image of nanofiber membrane and fiber diameter distribution of polymer blends

Table 4.1: Applied voltage and Mean diameter of the blend solutions

Sample Name	Chitosan/ PVA	Product type	Voltage(kV)	Feed Rate ($ml.h^{-1}$)	SD %	MD(nm)
A_1	50:50	Fibers	7.1	0.40	28.50	59
A_2	60:40	Fibers	9.1	0.30	52.94	85
A_3	70:30	Fibers	9.8	0.25	62.50	88
A_4	80:20	Mixture of fibers and Particles	12	0.1		
A_5	90:10	Particles	12	0.1		

Therefore, 50:50 of chitosan/PVA is the best in mean diameter and standard deviation. It is believed that larger amount of PVA prevented repelling action between polycationic chitosan molecules and leaded to good fiber diameter distribution.

4.3 Fabrication of Chitosan/PVA/zeolite Nanofibrous Composite Membrane

4.3.1 Electrospinning of Chitosan/PVA/zeolite Nanofibrous Composite Membrane

It was observed that 50:50 weight ratio of chitosan/PVA blend produced better nanofiber comparing to other ratio. Therefore, this weight percentage was selected as polymer matrix for chitosan/PVA/zeolite nanofiber fabrication. Applied voltage required for electrospinning of chitosan/PVA/zeolite blend solution was 10 kV which is higher than required voltage for electrospinning of A_1 solution with the flow rate of 0.2 $ml.h^{-1}$. This is due to the addition of filler material causes incensement in viscosity and viscoelastic force (S. S. Homaeigohar & Elbahri, 2012). Higher viscoelastic force leads to a higher resistance toward electrostatic force stretching the jet. Higher the viscoelastic force is seen at 1 wt.% zeolite which inhibits a continuous jet formation. Hence, to continue electrospinning a higher voltage was needed. A photo of prepared nanofiber has been shown in Fig. 4.3

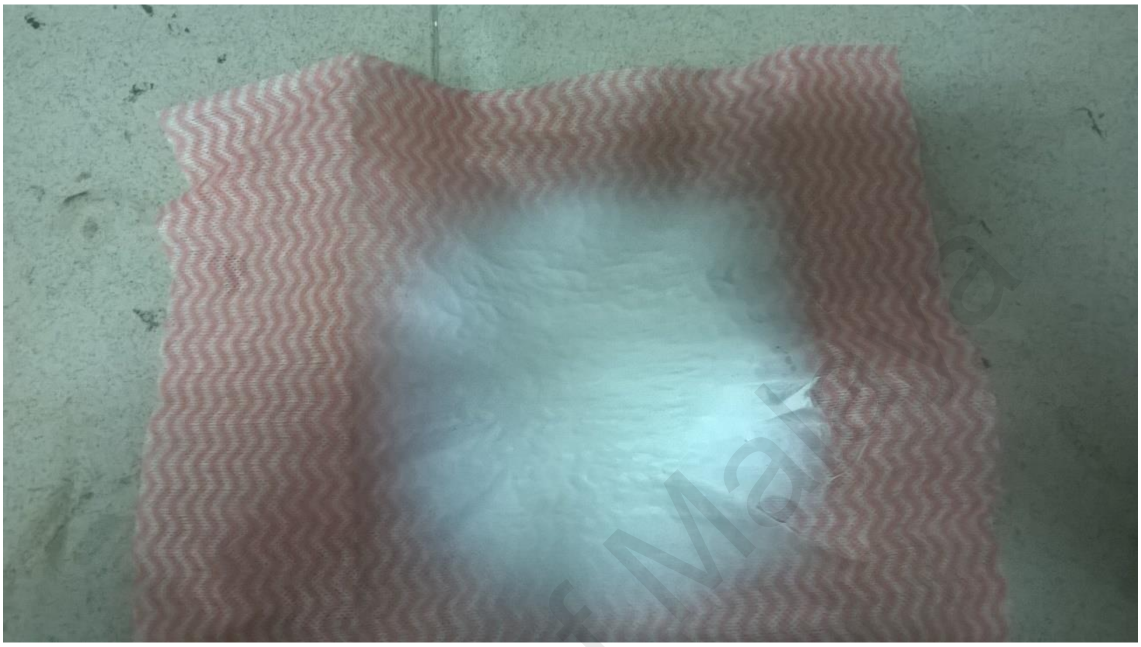


Figure 4.3: Nanofiber of current study

4.3.2 Characterization of Chitosan/PVA/zeolite Nanofibrous Membrane

4.3.2.1 Morphology Study of Chitosan/PVA/Zeolite Nanofiber

Morphological characteristic of electrospun chitosan/PVA/zeolite nanofibrous membrane was studied by Field Emission Scanning Electron Microscope. FESEM image and fiber diameter distribution are shown in Figure 4.4. From the figure, it showed that most of the zeolite particles were embedded into the nanofiber where some articles were uniformly distributed over the surface of nanofiber. Strong interaction of zeolite with functional group of chitosan and PVA considered to be the reason of uniform particle distribution. This behavior also considered to be the reason of formation of rough and porous surface (S. S. Homaeigohar & Elbahri, 2012). In addition, beads were not observed. Increase of the conductivity of electrospun solution is one of the main reason for formation of bead free nanofiber (S. S. Homaeigohar, Mahdavi, & Elbahri, 2012).

Presence of appropriate filler material in solution can be a reason of increased conductivity. Hence it showed that zeolite fulfilled the requirement as a filler material in electrospun solution. While addition of the inorganic filler increases the viscosity and viscoelastic force, it hampers the surface tension of the chitosan solution to be electrospun (S. S. Homaeigohar & Elbahri, 2012). Consequently, formation of structural irregularities such as beads and surface roughness decreases and the fiber diameter distribution becomes more uniform (H Fong et al., 1999). However, higher viscoelastic force leads to a higher resistance toward electrostatic force stretching the jet. This effect magnifies the fiber diameter at the higher filler concentrations. Moreover, FESEM images showed homogeneous distribution of zeolite over the surface of the fiber. From the image, it showed that some of the particles are hold as an individual particle onto the surface and some are dispersed among the fibers. 100 fibers were analyzed with Digimizer and where the size distribution histogram was drawn. Fig. 4.4 shows the respective fiber diameter distribution of the nanofibers. Comparison between nanofiber with and without zeolite was presented too. It was observed that mean diameter was increased from 59 nm to 70 nm. However, standard deviation was decreased from 28.5 to 19%. Though fiber diameter were increased to some extent, but homogeneity of fiber increased after adding zeolite in the chitosan/PVA blend solution. It may be due to very strong interaction of zeolite with chitosan. It will be discussed in FTIR and XRD analysis. One of the active site of chitosan is $–NH_2$ which is susceptible to protonation in acidic medium. Protonation of amino group is one of the obstacles in electrospinning. As zeolite made hydrogen bond with the amino group of chitosan, it decreased the possibility of protonation of amino group. Therefore, zeolite may ensure uniform jet flow rate charge distribution along the jet surface which can help to maintain smaller deviation in fiber diameter. Another reason of smaller standard deviation of fiber diameter distribution was smaller standard deviation of volume of Taylor cone (Yan & Gevelber, 2010). In this study, applied voltage for electrospinning of chitosan/PVA/Zeolite was higher than the voltage required for chitosan/PVA. Usually, higher voltage is helpful to maintain smaller standard deviation of Taylor cone (Yan & Gevelber, 2010).

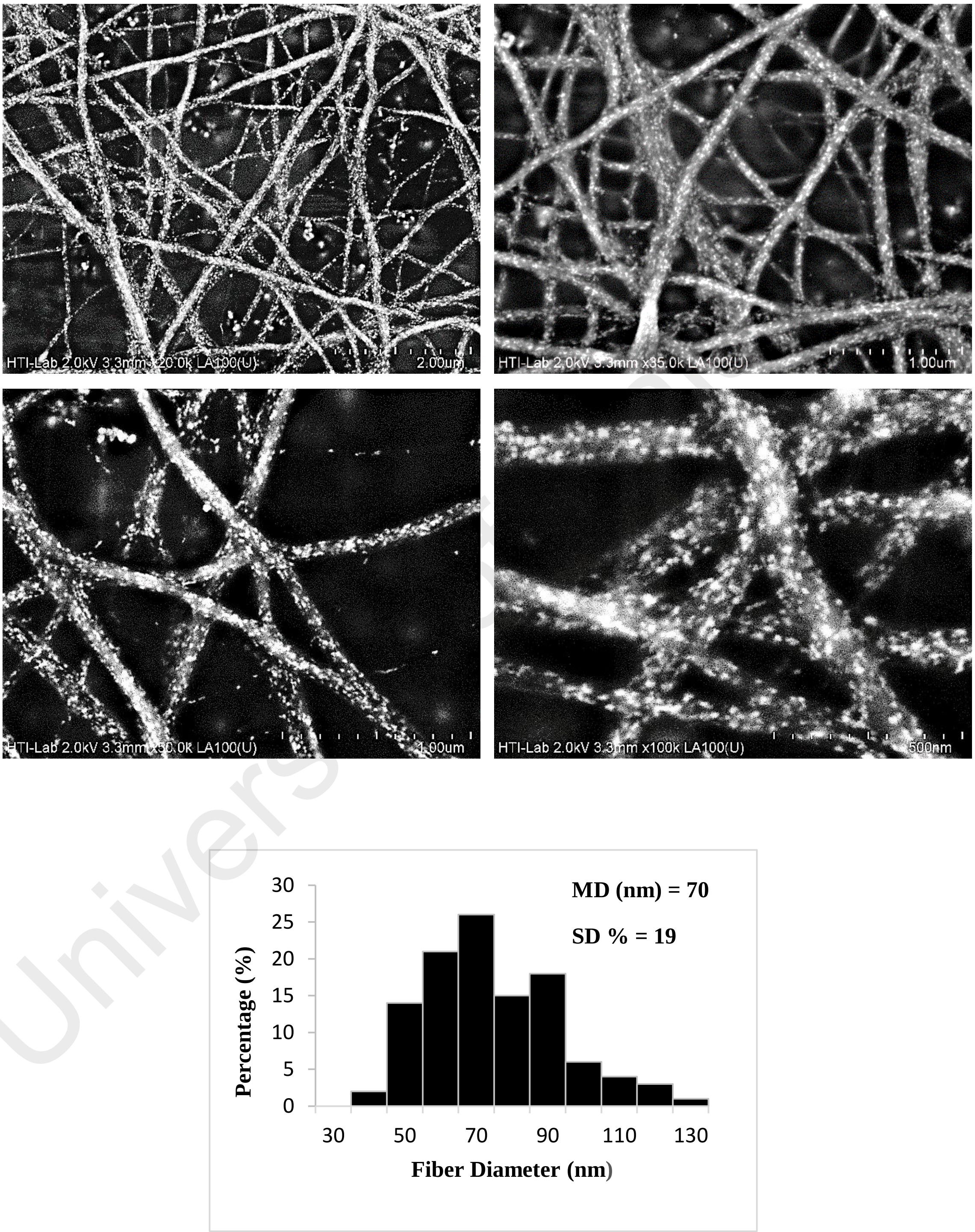
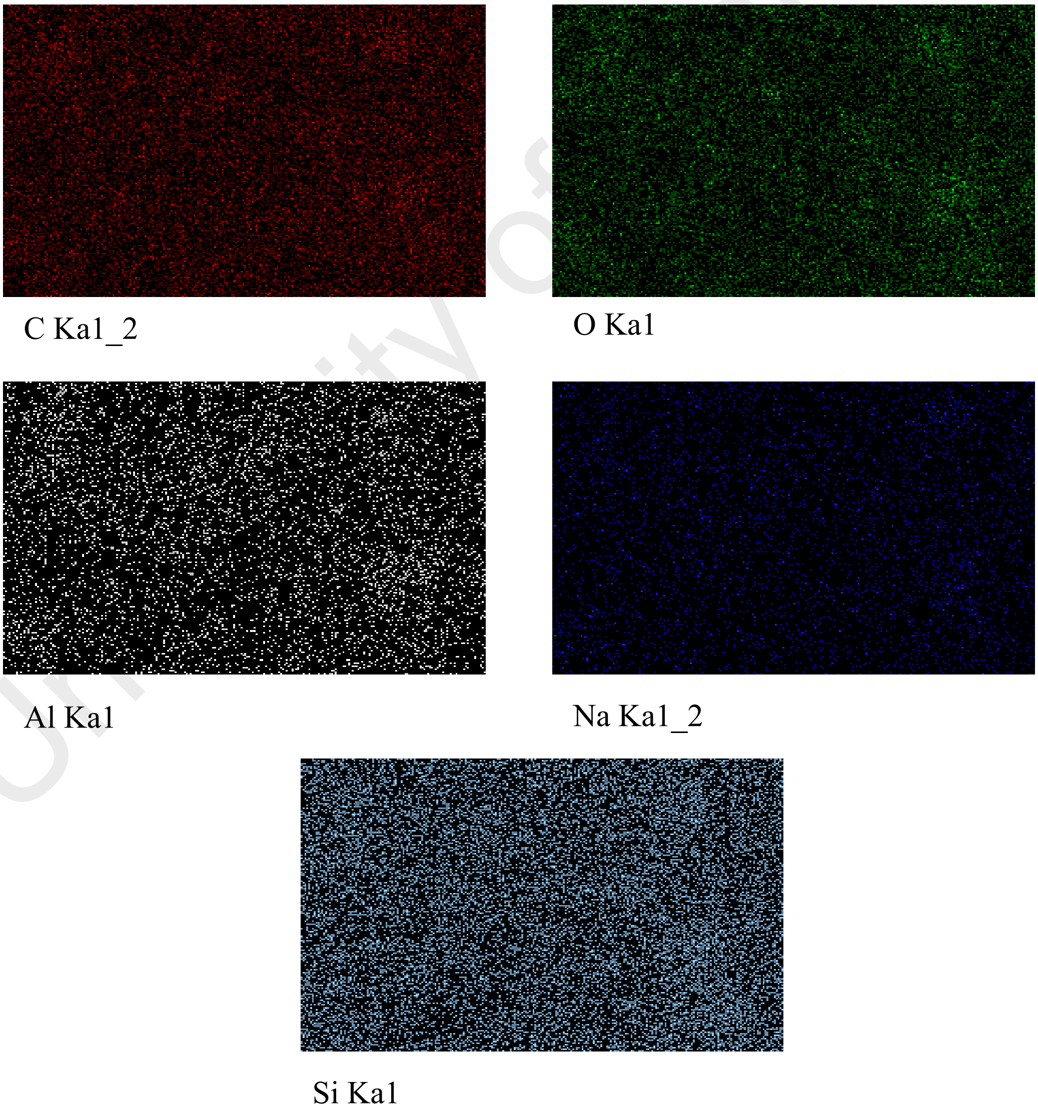


Figure 4.4: FESEM image of chitosan/PVA/zeolite nanofiber and fiber diameter distribution

Fig. 4.5 shows the mapping results of chitosan/PVA/zeolite nanofiber. It revealed the uniform distribution of zeolite particles in the membrane. From this result, it can be hypothesized that zeolite particles were scattered through the fiber interior and outer surface. Particles inside the fiber are responsible for strong interaction between polymer matrix and filler materials. On the other hand, particle in the outer surface can ensure surface roughness which leads to higher hydrophilicity of the membrane (Frohbergh et al., 2012; X. Song, Ling, Ma, Yang, & Chen, 2013). It indicates that the resulting membrane can be useful for water treatment application as hydrophilicity is very important property for any material to be used in water treatment application.



C Ka1_2

O Ka1

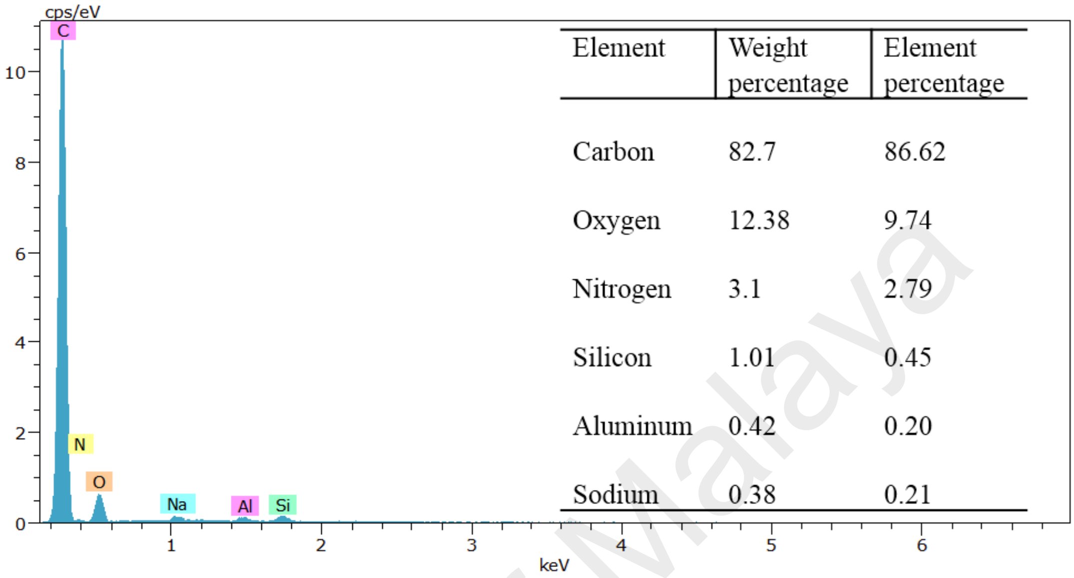
Al Ka1

Na Ka1_2

Si Ka1

Figure 4.5: Mapping Analysis showing the elemental topographical distribution of carbon, oxygen, silicon, sodium and aluminum

The EDX analysis of chitosan/PVA/zeolite nanofiber (Fig. 4.6), confirmed the elemental composition of these materials. It was observed that main component of the fiber were C, O, N, Si, Al and Na as expected.



Element	Weight percentage	Element percentage
Carbon	82.7	86.62
Oxygen	12.38	9.74
Nitrogen	3.1	2.79
Silicon	1.01	0.45
Aluminum	0.42	0.20
Sodium	0.38	0.21

Figure 4.6: EDX analysis of chitosan/PVA/zeolite nanofibrous membrane

4.3.2.2 XRD Analysis of Chitosan/PVA/zeolite Nanofibrous Membrane

Figure 4.7 shows the X-Ray diffraction patterns of PVA, chitosan, Zeolite A and Zeolite filled chitosan/PVA membrane. Pure Zeolite A showed its major crystalline peaks at 7.05°, 10.03°, 12.3°, 15.9°, 21.5°, 23.8°, 25.9°, 26.9°, 29.8°, 30.68°, 34.03°, 44° and 52.4° .All the identical characteristic peaks of zeolite was not observed in the chitosan zeolite membrane. Some peaks of zeolite has been changed after incorporating with chitosan membrane. The reason of limitation in crystallization of zeolite due to strong interaction between chitosan and Zeolite (Xin Chen, Yang, Gu, & Shao, 2001).

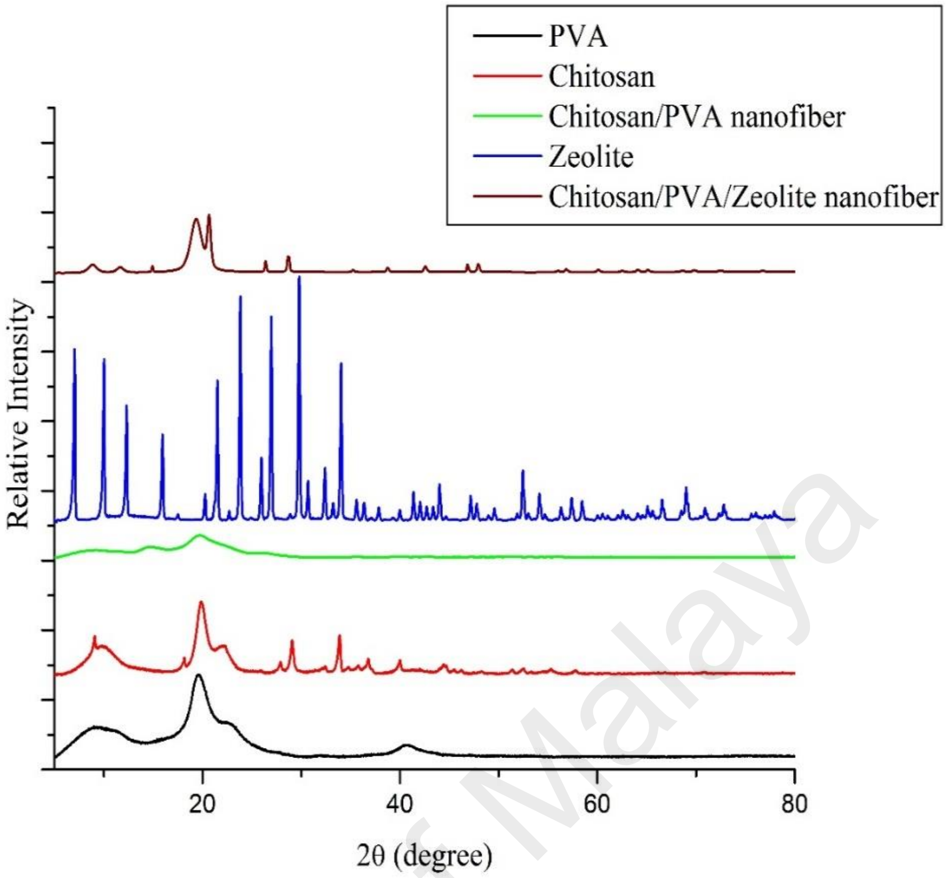


Figure 4.7: XRD spectra of chitosan, PVA, zeolite, chitosan/PVA and chitosan/PVA/zeolite nanofibrous composite membrane

Chitosan has two crystal forms: form I has the major crystalline peaks at 11.2° and 18.0°, while form II has major peaks at 15°, 20.9° and 23.8° (Xin Chen et al., 2001). 11.65°, 14.91°, 19.34° and 20.65° peaks at XRD spectra of the composite nanofibrous composite membrane are expected to be peaks of two crystalline forms of chitosan. 12.3°, 15.9°, 20.3° and 21.5° peaks of pure zeolite also consider to be shifted to lower theta degree position because of bonding between chitosan and zeolite. So 11.65°, 14.91°, 19.34° and 20.65° peaks are also considered as overlapping peaks of zeolite. Peak shifting of zeolite symbolizes that crystallinity of zeolite was affected by chitosan molecule. It has been shown in Table 4.2 that some more peaks of zeolite with respective crystal plane changed due to strong interaction between chitosan and zeolite. The peak intensity of chitosan around 10^0 and 20^0 became weak in the composites representing strong interaction among chitosan, PVA and filler materials and loosing of crystallinity (Yen, Yang, & Mau, 2009).

Table 4.2: Comparison of Characteristic Peak Positions Zeolite and chitosan/PVA/zeolite nanofibrous composite membrane

No.	[h k l]	2θ position (Zeolite)	2θ position (nanofiber membrane)	Change in 2θ position
1	0 0 1	7.05	8.85	1.8
2	1 1 1	12.3	11.65	0.65
3	0 1 2	15.9	14.9	1.0
4	0 2 2	20.3	19.3	1.0
5	0 0 3	21.5	20.65	0.8
6	1 2 3	26.9	26.4	0.5
7	0 1 4	29.8	28.8	1.0
8	2 2 4	35.6	35.2	0.4
9	2 3 4	39.2	38.7	0.5
10	3 3 4	42.7	42.5	0.2
11	3 4 4	47.2	46.8	0.4
12	2 2 6	48.9	47.9	1.0
13	0 3 7	56.3	56	0.3
14	0 4 7	60	60	0
15	3 5 6	62.6	62.5	0.1
16	5 5 5	65	65	0
17	3 3 8	68	68	0
18	5 5 6	70.4	69.8	0.6
19	1 3 9	72	72	0
20	0 10	77	76.7	0.3

4.3.2.3 FTIR Analysis of Chitosan/PVA/zeolite Nanofibrous Membrane

FTIR spectra of nanofibrous membrane is shown in Fig. 4.8. Absorption peak at 1257 cm^{-1} is assigned to O-H band (Zheng et al., 2001) of PVA shifted to 1260 cm^{-1} with lower frequency for chitosan/PVA nanofiber. Broad band at 3335 to 3357 cm^{-1} is attributed to stretching vibration of –OH group which indicated characteristic peak for both chitosan and PVA. 1375 cm^{-1} is the characteristic peak of $–CH_2$ connecting to –OH group which is present in spectra of PVA, chitosan and chitosan/PVA. This peak becomes weaker in the chitosan/PVA/zeolite due to vibration limitation (Sun, Lu, Chen, & Jiang, 2008). It also indicates that interaction of zeolite with chitosan occurred over the O-H groups. Characteristic peak of primary amino of chitosan was observed at 1650 cm^{-1} which becomes weaker in chitosan/PVA and chitosan/PVA/zeolite membrane due to the H-bonds. Some common peaks in the range of 1000 to 1200 cm^{-1} were characteristic peaks of C-O vibration of chitosan and PVA molecule (Kittur, Kulkarni, Aralaguppi, & Kariduraganavar, 2005).These bands overlapped with the band of T-O stretching vibration of zeolite in the resulting membrane (Elaiopoulos, Perraki, & Grigoropoulou, 2010; Jansen, Van der Gaag, & Van Bekkum, 1984). 1432 and 1420 cm^{-1} are characteristic peaks of C–H wagging vibration in PVA and chitosan, respectively (J. Bai et al., 2007). 1591 cm^{-1} was assigned to secondary amino in chitosan molecule (Kittur et al., 2005). Shifting to lower frequency with significant increasing in peak intensity is observed at 1420 and 1592 cm^{-1} in the composite membrane. This is because of increased strength of hydrogen bond due to increased dipoles. FTIR spectra of chitosan/PVA/zeolite contains peaks of chitosan, PVA and zeolite. Some shifting of peaks were observed. No new peaks were introduced. It indicated that chemical reaction was not occurred among chitosan, PVA and zeolite. This FTIR result is in line with the XRD result which showing the occurrence of the interaction among Chitosan, PVA and zeolites.

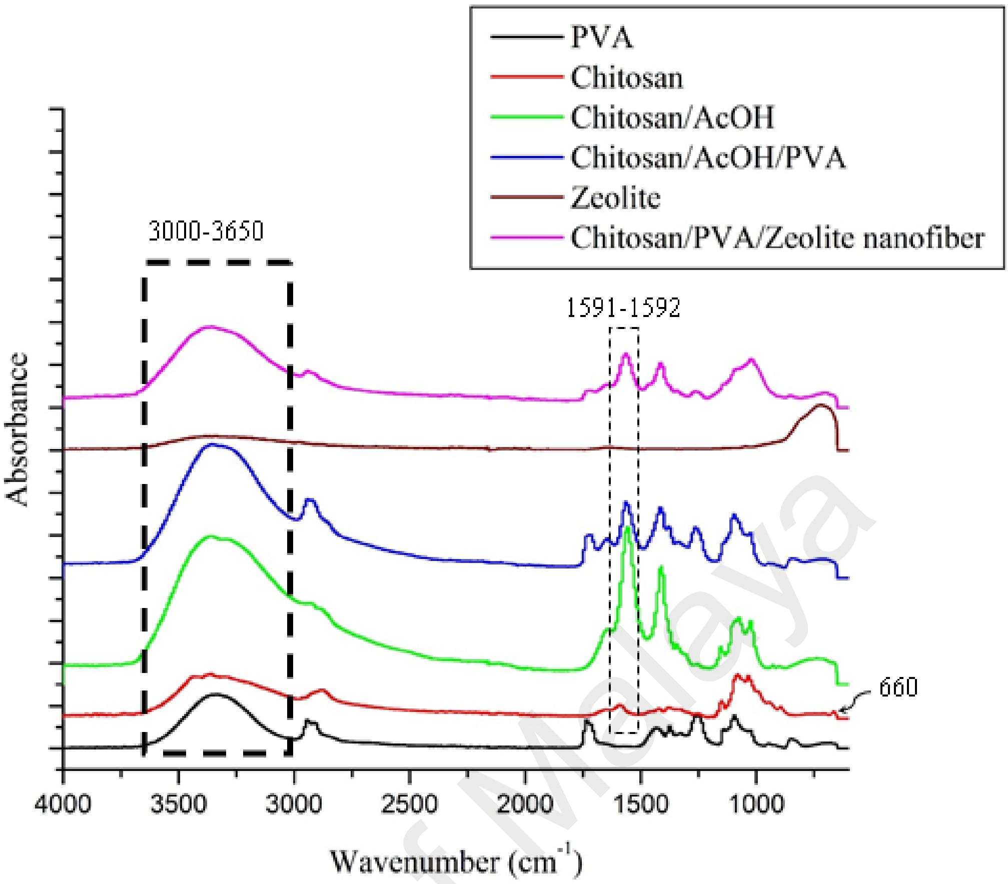


Figure 4.8: FTIR spectra for PVA nanofiber, Chitosan, Chitosan/PVA nanofiber, Chitosan/PVA/Zeolite nanofiber

4.3.2.4 TGA Analysis

Thermal behavior of chitosan/PVA/zeolite nanofibrous membrane was analyzed by thermal gravimetric analysis and results has been shown in Fig. 4.9. Thermal degradation values at different temperature has been listed in Table 4.3. In the case of chitosan, mass loss of 15% occurred in the region of 40-145ºC due to moisture evaporation. It is notable that the temperature 145ºC is higher than in free water (usually 110ºC). Strong hydrogen bonding between water molecule and active groups (-NH_2, -OH) of chitosan can be the probable reason of this high temperature. Pure chitosan powder was decomposed at 296 ºC. Chitosan/PVA and chitosan/PVA/zeolite nanofiber was decomposed at 228ºC and 245ºC, respectively. Decomposition temperature of chitosan/PVA and chitosan/PVA/zeolite nanofiber is lower than respective chitosan.

According to FTIR and XRD result, there is strong interaction between chitosan, zeolite and PVA. Therefore, decomposition temperature of chitosan/PVA and chitosan/PVA/zeolite nanofiber should be increased. Decreased thermal stability may be caused by physical form of the polymer sample (Hatakeyama & Quinn, 1994).

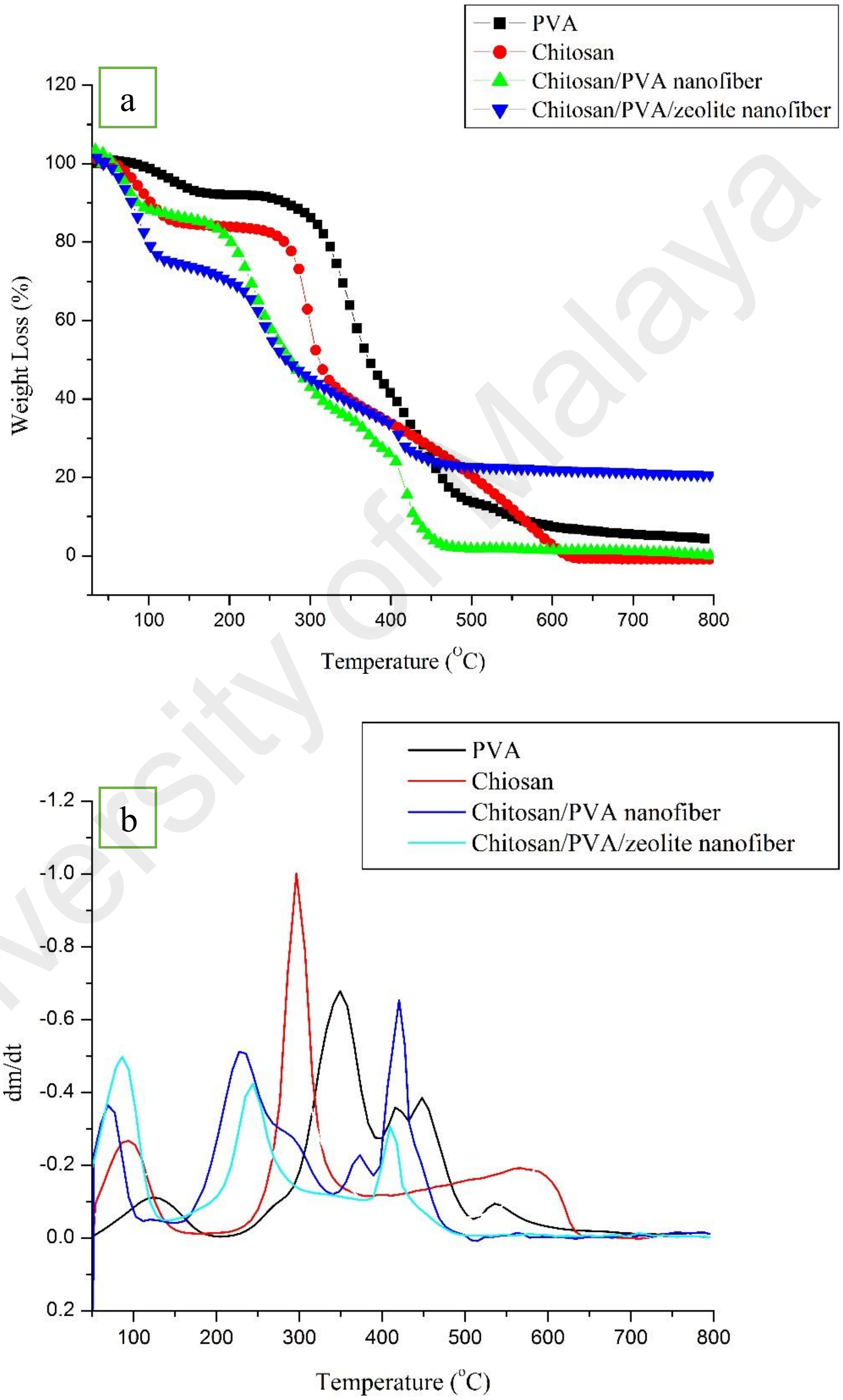


Figure 4.9: (a) TGA and (b) DTG curve of chitosan/PVA/zeolite nanofiber

Table 4.3: Percentage cumulative weight loss obtained in different temperature

Sample	Percentage cumulative weight loss (%)							
	100ºC	200ºC	300ºC	400ºC	500ºC	600ºC	700ºC	800ºC
PVA	1	8	14	58.5	86	92	94	95
Ch powder	9	20	41	66	79.5	97	0	0
Ch/PVA nanofiber	11.8	20	57	75	98.2	98.6	98.8	100
Ch/PVA/zeolite nanofiber	21	30	55	68	77.3	78.1	78.7	80

4.3.2.5 Swelling Test for Chitosan/PVA/zeolite Nanofibrous Membrane

Swelling test of chitosan/zeolite composite nanofiber was carried out for 20 days in distilled water, and also to basic and acidic medium. All medium showing no weight change. Several factors can be responsible for this behavior like insolubility of chitosan fraction (M. N. R. Kumar, 2000), hydrogen bonding interactions among chitosan, PVA and zeolite, lower degree of deacetylation (Çay et al., 2014) and crystallinity of the membrane (Xin Chen et al., 2001). The rigidity and shape of the nanofibrous membrane were unaltered after dipping in distilled water and basic medium. But shrinkage was observed after dipping in acidic medium. The shrinkage of the chitosan/PVA/zeolite nanofibrous membrane may be caused by decreasing in internal pore size (L. Jeong & Park, 2014).The color of the nanofibrous membrane was changed to brown after dipping in acidic and basic medium. Color change may be due to interaction of amino groups of chitosan with H^+/OH^- of acidic and basic medium.

4.3.3 Adsorption Study

4.3.3.1 Adsorption Isotherm Studies

Adsorption isotherm studies are used to predict the interaction between the adsorbate such as dye molecule or heavy metal ions and the adsorbent materials. Several adsorption isotherm can be used to determine the adsorption process. In this study, the standard isotherm such as Langmuir isotherms has been used. The mathematical expression of the Langmuir isotherm equation (M. Kumar, Tamilarasan, & Sivakumar, 2013) is given as

$$q_{e}=\frac{q_m k_a C_e}{1+K_a C_e} \qquad 4.3$$

Linear form of equation 4.3 is written below

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \qquad 4.4$$

Where, q_e (mg.g^{-1}) is the amounts of heavy metal ions adsorbed per unit mass of adsorbent, C_e (mg.L^{-1}) is the concentration of remained heavy metal ions in solution at equilibrium, q_m is the maximum amount of heavy metal ions adsorbed per unit mass of adsorbent and K_a (L.mg^{-1}) is a constant related to the affinity of the binding sites.

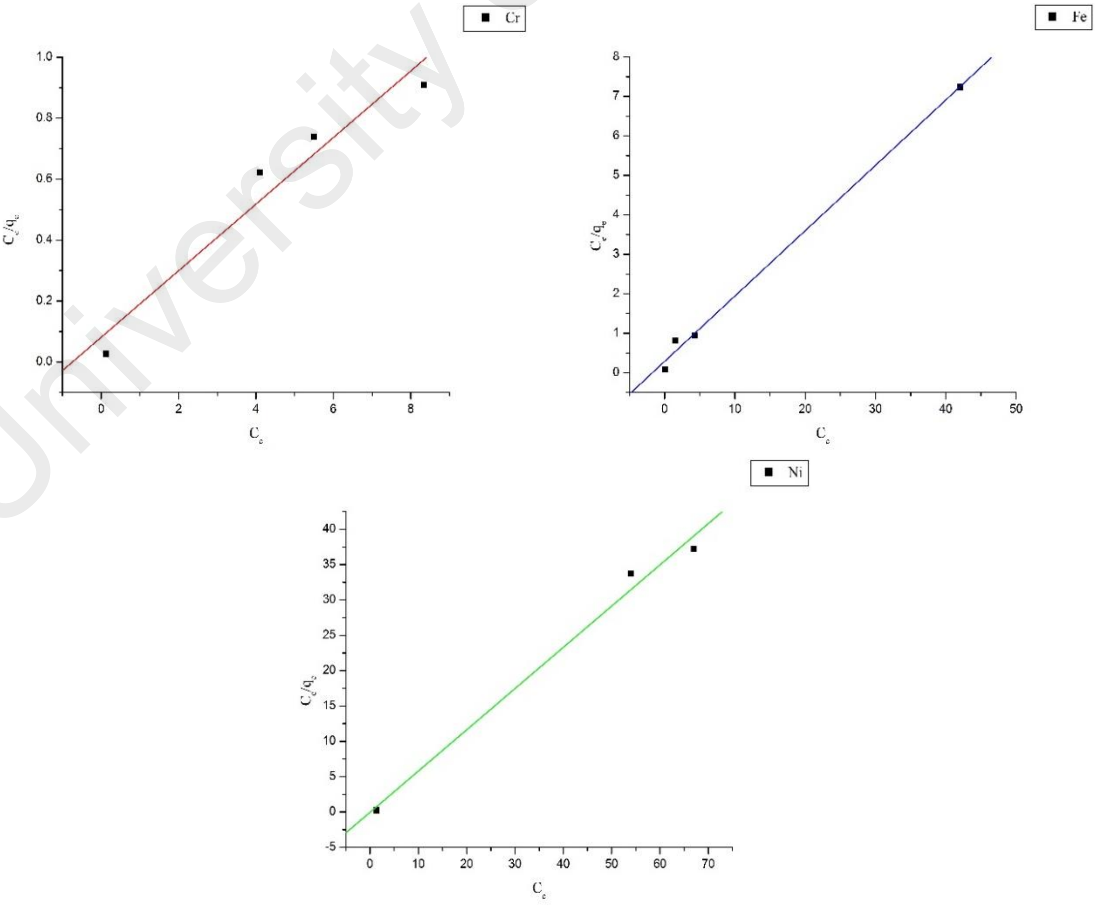


Figure 4.10: Langmuir plot for adsorption of Cr (VI), Fe (III) and Ni (II)

Langmuir isotherm parameters obtained by using linear method has tabulated in Table 4.4. The Langmuir isotherm of chitosan/PVA/zeolite nanofibrous membrane for adsorption of Cr (VI), Fe (III) and Ni (II) has been shown in Fig. 4.10. From the results, a closer proximity to unity of the correlation coefficients for adsorption of Cr (VI), Fe (III) and Ni (II) were observed. This indicates that the Langmuir isotherm was the best fit for the absorption of Cr (VI), Fe (III) and Ni (II) onto chitosan/PVA/zeolite nanofibrous membrane. The results of the data confirms that the monolayer adsorption process of the Cr (VI), Fe (III) and Ni (II) onto the resulting membrane (H. Zhang et al., 2011).

Table 4.4: Langmuir isotherm parameters obtained by using linear method

Heavy Metal	q_m (mg.g^{-1})	K_a (L.mg^{-1})	R^2
Cr (VI)	9.17	1.34	0.97
Fe (III)	6	0.57	0.99
Ni (II)	1.7	14.57	0.99

4.3.3.2 Effect of Initial Concentration of Heavy Metal

The present study was done to know the effect of initial concentration of heavy metal ions to the adsorption capacity of the chitosan/PVA/zeolite nanofibrous membrane. The concentration of Cr (VI) were varied from 10 to 80 mg.L^{-1}. Fig. 4.11 shows the relationship between initial and final concentrations of heavy metal ions. It was observed that the final concentration of heavy metals was almost zero at an initial concentration of 10 mg.L^{-1}.The final concentration of heavy metal in the solution increases with increasing initial concentration. These results indicate that energetically less favorable sites became involved in increasing metal concentrations in the aqueous solution.

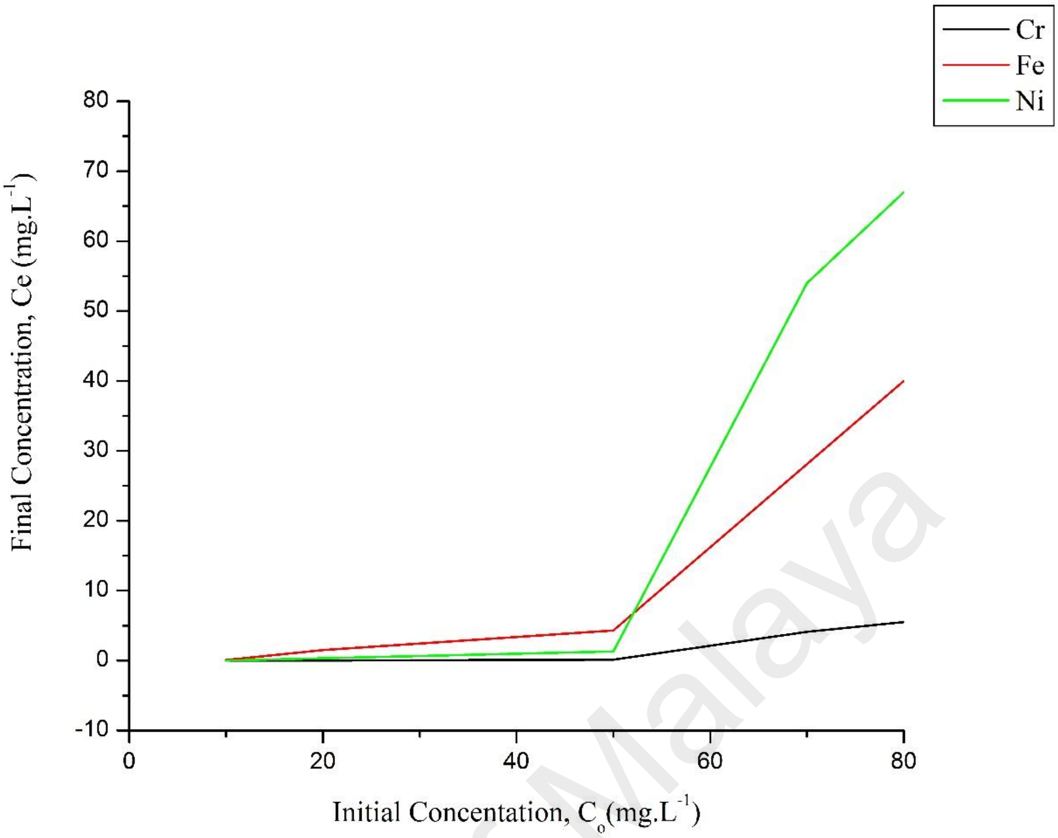


Figure 4.11: Relation between initial and final concentration of heavy metal

The removal percentage of heavy metal at different initial concentration was determined by the following expression (Mahanta, Manna, Madras, & Patil, 2010)

$$\eta = \frac{C_o - C_t}{C_o} \times 100\% \qquad 4.5$$

Where,η, C_o and C_t are removal percentage, initial concentration and final concentration of heavy metal, respectively.

Fig. 4.12 shows the effect of initial concentration of heavy metal on adsorption capacity of chitosan/PVA/zeolite nanofibrous membrane. The removal percentage of heavy metal ions decrease with the increase in the initial concentration of heavy metal ions. This is because the adsorption sites on the chitosan/PVA/zeolite nanofiber were decreased at higher concentration of heavy metal (M. Kumar et al., 2013). The maximum removal of Cr (VI) was 100% at concentration of 20 mg.L^{-1} and the lowest was 91.66%

at 100 mg.L^{-1}. It indicated the highly favorable active sites were involved in the removal process of Cr (VI). The removal process can be attributed to both ion exchange process and direct adsorption on the surface (Erdem et al., 2004). This behavior implies that Cr has strong affinity to the surface of chitosan/PVA/zeolite nanofiber (Jing et al., 2011). The maximum removal of Fe (III) was 99% at the concentration of 10 mg.L^{-1} and lowest was 50% at 80 mg.L^{-1}. From the graph, it was observed that the adsorption efficiency start to drop after reaching 60 mg L^{-1}. This showed the limit of this nanofibrous membrane in term of adsorption capability. In the case of Ni (II), the maximum removal rate was 100% at concentration of 10 mg.L^{-1} and the lowest was 21% at 80 mg.L^{-1}. Same phenomena was observed, a sudden drop after 60 mg.L^{-1}. This might be the limit of this nanofibrous membrane. Results showed that the adsorption capacity of different metal ions decreased in order of Cr (VI) >Fe (III) >Ni (II). The ionic radius range for these heavy metal ions are in order of Cr (VI) <Fe (III) < Ni (II) (R. t. Shannon, 1976). As ionic radius increases due to charge density decreases, the availability of active sites to react with nanofibrous membranes for adsorption process decreases; which resulted in decreasing the adsorption capacity of different metal ions by increasing the ionic radius (Aliabadi, Irani, Ismaeili, Piri, & Parnian, 2013).

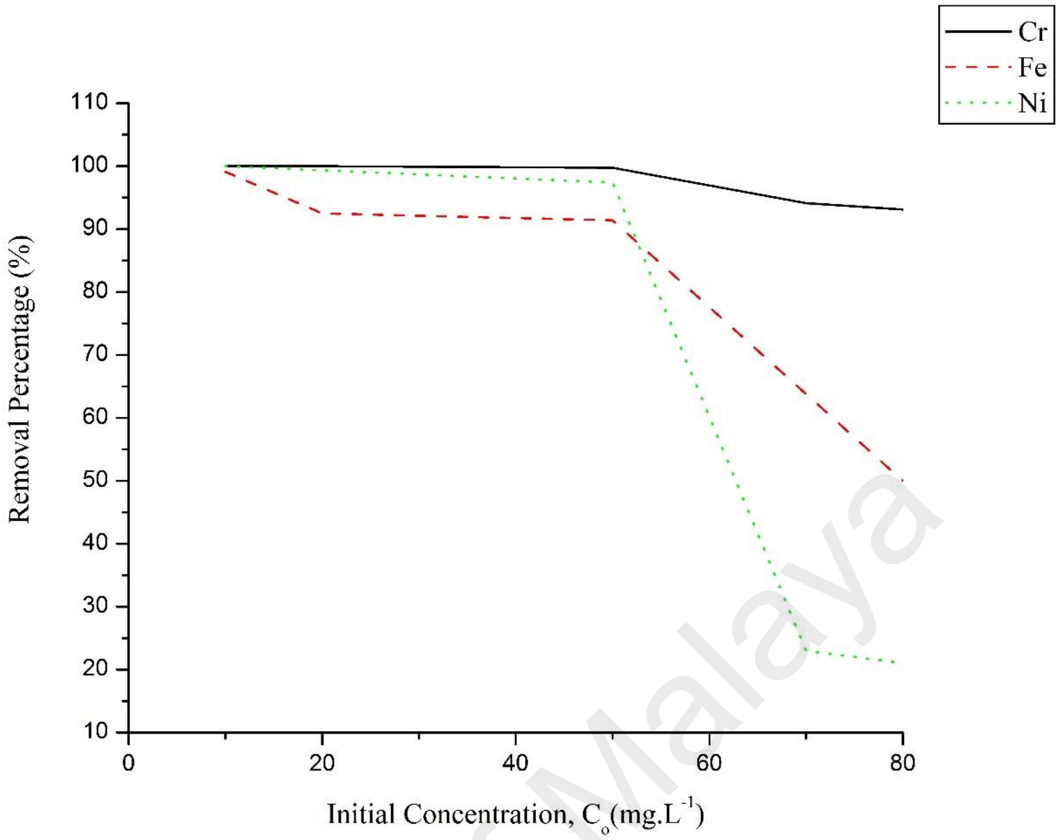


Figure 4.12: Effect of initial concentration of heavy metal on removal percentage

4.3.3.3 The Reusability of Chitosan/PVA/zeolite Nanofibrous Membrane

In any adsorption process, one common difficulty is regeneration of adsorbent. Normally, chemical, ultrasonic and thermal methods are used for regeneration of adsorbent (Breitbach & Bathen, 2001; Rege, Yang, & Cain, 1998). However, several limitations such as the necessity of high temperature, unreasonable burnout of the adsorbent, pollution of the adsorbent by inorganic chemicals or organic solvents (Breitbach & Bathen, 2001) are happening. In view of practical application, the adsorbent should be chemically stable after several repeated adsorption treatments. Therefore, the adsorption experiment was repeated five times to investigate the reusability of chitosan/PVA/zeolite. For each run, the adsorbent dosage and initial heavy metal ion concentration were 0.05g and 50 mg.L^{-1}, respectively. pH of solutions were 6.5, 6.5 and 5 for Cr, Fe and Ni, respectively. After every adsorption test, the chitosan/PVA/zeolite nanofibrous membrane were washed with distilled water. It has been shown in Fig. 4.13 that after five cycle adsorption experiment, chitosan/PVA/zeolite nanofibrous membrane did not show deterioration in adsorption efficiency. From these results, it can be hypothesized that chitosan/PVA/zeolite membrane is stable under the experimental process. It owned an impressive reusability which is a key factor in practical application.

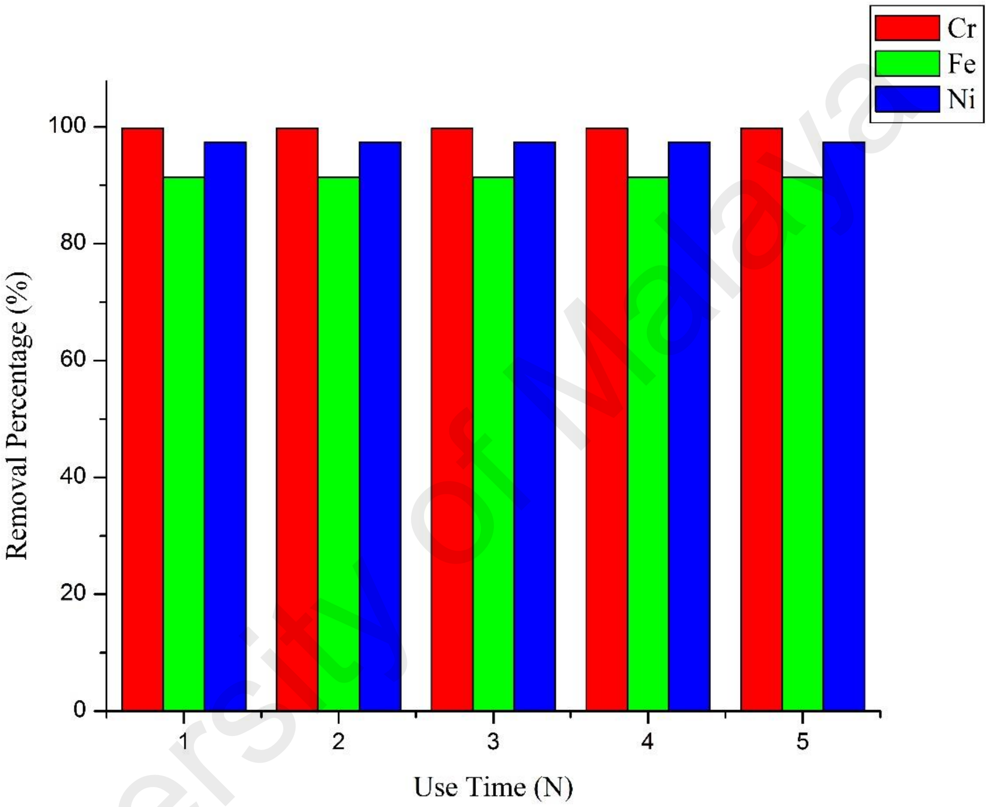


Figure 4.13: Cycling runs of heavy metal ion adsorption by chitosan/PVA/zeolite nanofibrous membrane.

CHAPTER 5: CONCLUSION

In this study, chitosan/PVA/zeolite electrospun nanofibrous composite membrane was fabricated. At first, crude chitosan was hydrolyzed for 24 hour at 90 °C. Intrinsic Viscosity and molecular weight of hydrolyzed chitosan was calculated. Then, 50:50, 60:40, 70:30, 80:20 and 90:10 weight ratio of chitosan/PVA nanofiber was electrospun. It was found that nanofiber with 50:50 weight ratio of chitosan/PVA was finer, defect free and comparatively homogeneous in diameter. Therefore, 50:50 weight ratio of chitosan/PVA blend solution was selected for polymer matrix of zeolite. Then, 1 wt % of zeolite was added to blend solution and electrospinning was done. The composite nanofibrous membrane was characterized with field emission scanning electron microscopy, X-Ray Diffraction, Fourier Transform Infrared spectroscopy, swelling test and adsorption test. Adsorption capacity of the composite nanofiber was studied over Cr (VI), Fe (III) and Ni (II) ions.

Several points can be concluded from this study:

1. Hydrolysis of chitosan increased the degree of deacetylation of chitosan. This will ease the electrospinning process.
2. Defect free nanofiber was fabricated with 50:50 weight ration of chitosan/PVA. Higher chitosan content in the blend solution lead to poor nanofiber.
3. Chitosan/PVA/zeolite nanofibrous composite membrane was successfully produced via electrospinning process. Finer, bead free nanofiber with homogeneous nanofiber was electrospun.
4. Fourier Transform Infrared spectroscopy test showed, strong bond between chitosan and zeolite.
5. X-Ray diffraction spectra also showed strong interaction of chitosan and zeolite. Zeolite loses its crystallinity due to strong bonding with chitosan molecules.

6. Swelling test showed no change in weight after immersing in water, acidic and basic medium for 20 days.
7. The isotherm models showed that the Langmuir model best described the equilibrium data of Cr (VI), Fe (III) and Ni (II) adsorption mechanism.
8. Adsorption capacity of the nanofiber was unaltered after 5 runs. This phenomenon ensures the reusability of the membrane.

Future Work

In spite of the fact that chitosan/PVA/zeolite nanofiber fabricated in this study showed superior adsorption capacity on Cr (VI), Fe (III) and Ni (II) but there is still room for more research on other heavy metals, organic dyes and microbial. In this study, adsorption study was done on distilled water at room temperature. Therefore more research can be done on adsorption by varying the solution pH and temperature. Magnetic stirrer was used for agitating the solution during adsorption test. Water bath shaker can be used during adsorption.

REFERENCES

Aguado, J., Arsuaga, J. M., Arencibia, A., Lindo, M., & Gascón, V. (2009). *Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica.* (163). (1)

Ahmed, N. K., & El-Arabi, A. G. M. (2005). Natural radioactivity in farm soil and phosphate fertilizer and its environmental implications in Qena governorate, Upper Egypt. *Journal of Environmental Radioactivity, 84*(1), 51-64.

Aiba, S.-i. (1991). Studies on chitosan: 3. Evidence for the presence of random and block copolymer structures in partially N-acetylated chitosans. *International Journal of Biological Macromolecules, 13*(1), 40-44.

Aliabadi, M., Irani, M., Ismaeili, J., Piri, H., & Parnian, M. J. (2013). Electrospun nanofiber membrane of PEO/Chitosan for the adsorption of nickel, cadmium, lead and copper ions from aqueous solution. *Chemical Engineering Journal, 220,* 237-243.

Alluri, H. K., Ronda, S. R., Settalluri, V. S., Bondili, J. S., Suryanarayana, V., & Venkateshwar, P. (2007). Biosorption: An eco-friendly alternative for heavy metal removal. *African Journal of Biotechnology, 6*(25).

Alpat, S. K., Özbayrak, Ö., Alpat, Ş., & Akçay, H. (2008). The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite. *Journal of Hazardous Materials, 151*(1), 213-220.

Anderson, A., Meyer, D., & Mayer, F. (1973). Heavy metal toxicities: levels of nickel, cobalt and chromium in the soil and plants associated with visual symptoms and variation in growth of an oat crop. *Crop and Pasture Science, 24*(4), 557-571.

Annadurai, G., Ling, L. Y., & Lee, J.-F. (2008). Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. *Journal of Hazardous Materials, 152*(1), 337-346.

Argun, M. E., & Dursun, S. (2008). A new approach to modification of natural adsorbent for heavy metal adsorption. *Bioresource Technology, 99*(7), 2516-2527.

Auffan, M., Rose, J., Bottero, J.Y., Lowry, G. V., Jolivet, J. P., & Wiesner, M. R. (2009). *Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective.* 4(10),634-641.

Auffan, M., Rose, J., Proux, O., Borschneck, D., Masion, A., Chaurand, P.,Wiesner, M. R. (2008). Enhanced adsorption of arsenic onto maghemites nanoparticles: As (III) as a probe of the surface structure and heterogeneity. *Langmuir*, *24*(7), 3215-3222.

Aussawasathien, D., Teerawattananon, C., & Vongachariya, A. (2008). Separation of micron to sub-micron particles from water: electrospun nylon-6 nanofibrous membranes as pre-filters. *Journal of Membrane Science, 315*(1), 11-19.

Austero, M. S., Donius, A. E., Wegst, U. G., & Schauer, C. L. (2012). New crosslinkers for electrospun chitosan fibre mats. I. Chemical analysis. *Journal of The Royal Society Interface*, rsif20120241.

Bae, T. H., & Tak, T. M. (2005). Effect of TiO 2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. *Journal of Membrane Science*, *249*(1), 1-8.

Bai, J., Li, Y., Yang, S., Du, J., Wang, S., Zheng, J., Jing, X. (2007). A simple and effective route for the preparation of poly (vinylalcohol)(PVA) nanofibers containing gold nanoparticles by electrospinning method. *Solid State Communications, 141*(5), 292-295.

Bai, R. S., & Abraham, T. E. (2003). Studies on chromium (VI) adsorption–desorption using immobilized fungal biomass. *Bioresource Technology, 87*(1), 17-26.

Baker, B. M., Gee, A. O., Metter, R. B., Nathan, A. S., Marklein, R. A., Burdick, J. A., & Mauck, R. L. (2008). The potential to improve cell infiltration in composite fiber-aligned electrospun scaffolds by the selective removal of sacrificial fibers. *Biomaterials*, *29*(15), 2348-2358.

Balmat, J. (1957). Biochemical oxidation of various particulate fractions of sewage. *Sewage and Industrial Wastes*, 757-761.

Barceloux, D. G., & Barceloux, D. (1999). Chromium. *Journal of Toxicology: Clinical Toxicology, 37*(2), 173-194. doi:10.1081/CLT-100102418

Baumgarten, P. K. (1971). Electrostatic spinning of acrylic microfibers. *Journal of colloid and interface science, 36*(1), 71-79.

Baxter, A., Dillon, M., Taylor, K. A., & Roberts, G. A. (1992). Improved method for ir determination of the degree of N-acetylation of chitosan. *International Journal of Biological Macromolecules*, *14*(3), 166-169.

Benavente, M., Moreno, L., & Martinez, J. (2011). Sorption of heavy metals from gold mining wastewater using chitosan. *Journal of the Taiwan Institute of Chemical Engineers, 42*(6), 976-988.

Bhardwaj, N., & Kundu, S. C. (2010). Electrospinning: a fascinating fiber fabrication technique. *Biotechnology advances, 28*(3), 325-347.

Bhattarai, N., Edmondson, D., Veiseh, O., Matsen, F. A., & Zhang, M. (2005). Electrospun chitosan-based nanofibers and their cellular compatibility. *Biomaterials*, *26*(31), 6176-6184.

Blocki, S. W. (1993). Hydrophobic zeolite adsorbent: a proven advancement in solvent separation technology. *Environmental Progress, 12*(3), 226-230.

Bognitzki, M., Czado, W., Frese, T., Schaper, A., Hellwig, M., Steinhart, M., Wendorff, J. H. (2001). Nanostructured fibers via electrospinning. *Advanced Materials*(13), 70.

Borchard, G. (2001). Chitosans for gene delivery. *Advanced drug delivery reviews, 52*(2), 145-150.

Bottino, A., Capannelli, G., D'asti, V., & Piaggio, P. (2001). Preparation and properties of novel organic–inorganic porous membranes. *Separation and purification Technology, 22*, 269-275.

Breitbach, M., & Bathen, D. (2001). Influence of ultrasound on adsorption processes. *Ultrasonics sonochemistry, 8*(3), 277-283.

Brugnerotto, J., Lizardi, J., Goycoolea, F., Argüelles-Monal, W., Desbrieres, J., & Rinaudo, M. (2001). An infrared investigation in relation with chitin and chitosan characterization. *Polymer, 42*(8), 3569-3580.

Burger, C., Hsiao, B. S., & Chu, B. (2006). Nanofibrous materials and their applications. *Annu. Rev. Mater. Res., 36*, 333-368.

Butin, R., Harding, J., & Keller, J. (1974). Non-woven mats by melt blowing: Google Patents.

Butterfield, C., Purdy, W., & Theriault, E. (1931). Experimental Studies of Natural Purification in Polluted Waters: IV. The Influence of the Plankton on the

Biochemical Oxidation of Organic Matter. *Public Health Reports (1896-1970)*, 393-426.

Butterfield, C., Ruchhoft, C., & McNamee, P. (1937). Studies of Sewage Purification: VI. Biochemical Oxidation by Sludges Developed by Pure Cultures of Bacteria Isolated from Activated Sludge. *Public Health Reports (1896-1970)*, 387-412.

Cancer, I. A. f. R. o., & Organization, W. H. (1990). Chromium, nickel and welding. *IARC monographs on the evaluation of carcinogenic risks to humans, 49*.

Carmen, Z., & Daniela, S. (2012). *Textile organic dyes–characteristics, polluting effects and separation/elimination procedures from industrial effluents–a critical overview*. Paper presented at the Organic Pollutants Ten Years After the Stockholm Convention-Environmental and Analytical Update.

Cartier, N., Domard, A., & Chanzy, H. (1990). Single crystals of chitosan. *International Journal of Biological Macromolecules, 12*(5), 289-294.

Cauchie, H. M. (2002). Chitin production by arthropods in the hydrosphere. *Hydrobiologia*, *470*(1-3), 63-95.

Çay, A., Miraftab, M., & Kumbasar, E. P. A. (2014). Characterization and swelling performance of physically stabilized electrospun poly (vinyl alcohol)/chitosan nanofibres. *European Polymer Journal, 61*, 253-262.

Celik, E., Park, H., Choi, H., & Choi, H. (2011). Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment. *Water Research, 45*(1), 274-282.

Chakinala, A. G., Gogate, P. R., Burgess, A. E., & Bremner, D. H. (2008). Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process. *Ultrasonics sonochemistry, 15*(1), 49-54.

Chen, W., Duan, L., & Zhu, D. (2007). Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. *Environmental Science & Technology, 41*(24), 8295-8300.

Chen, X., Hou, J., Yang, H., & Xu, Z.-L. (2016). Facile preparation of NPs based on Ag–AgCl immobilized in porous PVA sphere with high visible light photoactivity and good photostability under Cl− condition. *Journal of Environmental Chemical Engineering, 4*(1), 1068-1075.

Chen, X., Yang, H., Gu, Z., & Shao, Z. (2001). Preparation and characterization of HY zeolite-filled chitosan membranes for pervaporation separation. *Journal of applied polymer science, 79*(6), 1144-1149.

Chiou, M., & Li, H. (2003). Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere, 50*(8), 1095-1105.

Clark, J. R. (1969). Thermal pollution and aquatic life. *Scientific American, 220*, 18-27.

Cloete, T. E. (2010). *Nanotechnology in water treatment applications*: Horizon Scientific Press.

Colella, C. (2007). Recent advances in natural zeolite applications based on external surface interaction with cations and molecules. *Studies in Surface Science and Catalysis, 170*, 2063-2073.

Cooper, A., Oldinski, R., Ma, H., Bryers, J. D., & Zhang, M. (2013). Chitosan-based nanofibrous membranes for antibacterial filter applications. *Carbohydrate polymers, 92*(1), 254-259.

Crooks, R. M., Zhao, M., Sun, L., Chechik, V., & Yeung, L. K. (2001). Dendrimer-encapsulated metal nanoparticles: synthesis, characterization, and applications to catalysis. *Accounts of Chemical Research, 34*(3), 181-190.

Cutting, R. S., Coker, V. S., Telling, N. D., Kimber, R. L., Pearce, C. I., Ellis, B. L., Vaughan, D. J. (2010). Optimizing Cr (VI) and Tc (VII) remediation through nanoscale biomineral engineering. *Environmental science & technology, 44*(7), 2577-2584.

Czechowska-Biskup, R., Jarosińska, D., Rokita, B., Ulański, P., & Rosiak, J. M. (2012). Determination of degree of deacetylation of chitosan-comparision of methods. *Prog. Chem. Appl. Chitin Its Deriv, 17*, 5-20.

Dahe, G. J., Teotia, R. S., & Bellare, J. R. (2012). The role of zeolite nanoparticles additive on morphology, mechanical properties and performance of polysulfone hollow fiber membranes. *Chemical Engineering Journal, 197*, 398-406.

Dantas, T. D. C., Neto, A. D., & Moura, M. D. A. (2001). Removal of chromium from aqueous solutions by diatomite treated with microemulsion. *Water Research, 35*(9), 2219-2224.

Daus, B., Wennrich, R., & Weiss, H. (2004). Sorption materials for arsenic removal from water:: a comparative study. *Water Research, 38*(12), 2948-2954.

Davis, J. R. (2000). ASM specialty handbook: nickel, cobalt, and their alloys. *ASM International, Member/Customer Service Center, Materials Park, OH 44073-0002, USA, 2000. 442*.

Deitzel, J., Kleinmeyer, J., Harris, D., & Tan, N. B. (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer, 42*(1), 261-272.

Deitzel, J., Kleinmeyer, J., Hirvonen, J., & Tan, N. B. (2001). Controlled deposition of electrospun poly (ethylene oxide) fibers. *Polymer, 42*(19), 8163-8170.

Deliyanni, E., Bakoyannakis, D., Zouboulis, A., & Matis, K. (2003). Sorption of As (V) ions by akaganeite-type nanocrystals. *Chemosphere, 50*(1), 155-163.

Demirbas, E., Kobya, M., Senturk, E., & Ozkan, T. (2004). Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water Sa, 30*(4), p. 533-539.

Desai, K., Kit, K., Li, J., Davidson, P. M., Zivanovic, S., & Meyer, H. (2009). Nanofibrous chitosan non-wovens for filtration applications. *Polymer, 50*(15), 3661-3669.

Diallo, M. S., Christie, S., Swaminathan, P., Johnson, J. H., & Goddard, W. A. (2005). Dendrimer enhanced ultrafiltration. 1. Recovery of Cu (II) from aqueous solutions using PAMAM dendrimers with ethylene diamine core and terminal NH2 groups. *Environmental Science & Technology, 39*(5), 1366-1377.

Dimzon, I. K. D., & Knepper, T. P. (2015). Degree of deacetylation of chitosan by infrared spectroscopy and partial least squares. *International Journal of Biological Macromolecules, 72,* 939-945.

Domszy, J. G., & Roberts, G. A. (1985). Evaluation of infrared spectroscopic techniques for analysing chitosan. *Die Makromolekulare Chemie, 186*(8), 1671-1677.

Dong, Y., Xu, C., Wang, J., Wu, Y., Wang, M., & Ruan, Y. (2002). Influence of degree of deacetylation on critical concentration of chitosan/dichloroacetic acid liquid-crystalline solution. *Journal of applied polymer science, 83*(6), 1204-1208.

Doshi, J., & Reneker, D. H. (1993). *Electrospinning process and applications of electrospun fibers.* Paper presented at the Industry Applications Society Annual Meeting, 1993., Conference Record of the 1993 IEEE.

Duarte, M., Ferreira, M., Marvao, M., & Rocha, J. (2002). An optimised method to determine the degree of acetylation of chitin and chitosan by FTIR spectroscopy. *International Journal of Biological Macromolecules, 31*(1), 1-8.

Dupont, L., & Guillon, E. (2003). Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. *Environmental science & technology, 37*(18), 4235-4241.

Ebert, K., Fritsch, D., Koll, J., & Tjahjawiguna, C. (2004). Influence of inorganic fillers on the compaction behaviour of porous polymer based membranes. *Journal of Membrane Science, 233*(1), 71-78.

El Harbawi, M., Sabidi, A., Kamarudin, E., Hamid, A., Harun, S. B., Nazlan, A. B., & Yi, C. (2010). Design of a portable dual purposes water filter system. *Journal of Engineering Science and Technology, 5*(2), 165-175.

Elaiopoulos, K., Perraki, T., & Grigoropoulou, E. (2010). Monitoring the effect of hydrothermal treatments on the structure of a natural zeolite through a combined XRD, FTIR, XRF, SEM and N 2-porosimetry analysis. *Microporous and Mesoporous Materials, 134*(1), 29-43.

Ellison, C. J., Phatak, A., Giles, D. W., Macosko, C. W., & Bates, F. S. (2007). Melt blown nanofibers: fiber diameter distributions and onset of fiber breakup. *Polymer, 48*(11), 3306-3316.

Erdem, E., Karapinar, N., & Donat, R. (2004). The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science, 280*(2), 309-314.

Fávaro, D. (2005). Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil. *Journal of Radioanalytical and Nuclear Chemistry, 264*(2), 445-448.

Feng, L., Li, S., Li, H., Zhai, J., Song, Y., Jiang, L., & Zhu, D. (2002). Super-hydrophobic surface of aligned polyacrylonitrile nanofibers. *Angewandte Chemie, 114*(7), 1269-1271.

Fong, H., Chun, I., & Reneker, D. (1999). Beaded nanofibers formed during electrospinning. *Polymer, 40*(16), 4585-4592.

Fong, H., & Reneker, D. H. (1999). Elastomeric nanofibers of styrene-butadiene-styrene triblock copolymer. *Journal of Polymer Science Part B Polymer Physics, 37*(24), 3488-3493.

Frenot, A., & Chronakis, I. S. (2003). Polymer nanofibers assembled by electrospinning. *Current opinion in colloid & interface science, 8*(1), 64-75.

Frohbergh, M. E., Katsman, A., Botta, G. P., Lazarovici, P., Schauer, C. L., Wegst, U. G., & Lelkes, P. I. (2012). Electrospun hydroxyapatite-containing chitosan nanofibers crosslinked with genipin for bone tissue engineering. *Biomaterials, 33*(36), 9167-9178.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management, 92*(3), 407-418.

Gibson, P., Schreuder Gibson, H., & Rivin, D. (2001). Transport properties of porous membranes based on electrospun nanofibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 187*, 469-481.

Gibson, P., Schreuder-Gibson, H., & Rivin, D. (1999). Electrospun fiber mats: transport properties. *AIChE journal, 45*(1), 190-195.

Golob, V., Vinder, A., & Simonič, M. (2005). Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. *Dyes and pigments, 67*(2), 93-97.

Gopal, R., Kaur, S., Ma, Z., Chan, C., Ramakrishna, S., & Matsuura, T. (2006). Electrospun nanofibrous filtration membrane. *Journal of Membrane Science, 281*(1), 581-586.

Grubb, D. T., & Kearney, F. R. (1990). Modification of gel-drawn poly (vinyl alcohol) fibers with formaldehyde. *Journal of Applied Polymer Science, 39*(3), 695-705.

Hahne, H., & Kroontje, W. (1973). Significance of pH and chloride concentration on behavior of heavy metal pollutants: mercury (II), cadmium (II), zinc (II), and lead (II). *Journal of Environmental Quality, 2*(4), 444-450.

Haider, S., Al Zeghayer, Y., Ali, F. A. A., Haider, A., Mahmood, A., Al-Masry, W. A., Aijaz, M. O. (2013). Highly aligned narrow diameter chitosan electrospun nanofibers. *Journal of Polymer Research*, *20*(4), 1-11.

Hallensleben, M. L. (2000). Polyvinyl compounds, others. *Ullmann's Encyclopedia of Industrial Chemistry*.

Hatakeyama, T., & Quinn, F. (1994). Fundamentals and applications to polymer science. *Thermal Analysis*.

Helander, I., Nurmiaho-Lassila, E. L., Ahvenainen, R., Rhoades, J., & Roller, S. (2001). Chitosan disrupts the barrier properties of the outer membrane of Gram-negative bacteria. *International journal of food microbiology, 71*(2), 235-244.

Homaeigohar, S., Koll, J., Lilleodden, E. T., & Elbahri, M. (2012). The solvent induced interfiber adhesion and its influence on the mechanical and filtration properties of polyethersulfone electrospun nanofibrous microfiltration membranes. *Separation and purification Technology, 98*, 456-463.

Homaeigohar, S. S., & Elbahri, M. (2012). Novel compaction resistant and ductile nanocomposite nanofibrous microfiltration membranes. *Journal of Colloid and Interface Science, 372*(1), 6-15.

Homaeigohar, S. S., Mahdavi, H., & Elbahri, M. (2012). Extraordinarily water permeable sol–gel formed nanocomposite nanofibrous membranes. *Journal of Colloid and Interface Science, 366*(1), 51-56.

Homayoni, H., Ravandi, S. A. H., & Valizadeh, M. (2009). Electrospinning of chitosan nanofibers: Processing optimization. *Carbohydrate polymers*, *77*(3), 656-661.

Hristovski, K. D., Nguyen, H., & Westerhoff, P. K. (2009). Removal of arsenate and 17α-ethinyl estradiol (EE2) by iron (hydr)oxide modified activated carbon fibers. *Journal of Environmental Science and Health, Part A, 44*(4), 354-361.

Hristovski, K. D., Westerhoff, P. K., Möller, T., & Sylvester, P. (2009). Effect of synthesis conditions on nano-iron (hydr)oxide impregnated granulated activated carbon. *Chemical Engineering Journal, 146*(2), 237-243.

Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites science and technology, 63*(15), 2223-2253.

Hunter, P. (2003). Climate change and waterborne and vector-borne disease. *Journal of applied microbiology, 94*(s1), 37-46.

Jameela, S., & Jayakrishnan, A. (1995). Glutaraldehyde cross-linked chitosan microspheres as a long acting biodegradable drug delivery vehicle: studies on the in vitro release of mitoxantrone and in vivo degradation of microspheres in rat muscle. *Biomaterials, 16*(10), 769-775.

Jansen, J., Van der Gaag, F., & Van Bekkum, H. (1984). Identification of ZSM-type and other 5-ring containing zeolites by ir spectroscopy. *Zeolites, 4*(4), 369-372.

Jayakumar, R., Prabaharan, M., Nair, S., & Tamura, H. (2010). Novel chitin and chitosan nanofibers in biomedical applications. *Biotechnology advances, 28*(1), 142-150.

Jeong, B. H., Hoek, E. M., Yan, Y., Subramani, A., Huang, X., Hurwitz, G.,Jawor, A. (2007). Interfacial polymerization of thin film nanocomposites: a new concept for reverse osmosis membranes. *Journal of Membrane Science, 294*(1), 1-7.

Jeong, L., & Park, W. H. (2014). Preparation and characterization of gelatin nanofibers containing silver nanoparticles. *International journal of molecular sciences, 15*(4), 6857-6879.

Ji, L., Chen, W., Duan, L., & Zhu, D. (2009). Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. *Environmental Science & Technology, 43*(7), 2322-2327.

Jia, Y.-T., Gong, J., Gu, X.-H., Kim, H.-Y., Dong, J., & Shen, X.-Y. (2007). Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method. *Carbohydrate Polymers, 67*(3), 403-409.

Jin, J., Wu, G., Zhang, Z., & Guan, Y. (2014). Effect of extracellular polymeric substances on corrosion of cast iron in the reclaimed wastewater. *Bioresource Technology, 165*, 162-165.

Jing, G., Zhou, Z., Song, L., & Dong, M. (2011). Ultrasound enhanced adsorption and desorption of chromium (VI) on activated carbon and polymeric resin. *Desalination, 279*(1), 423-427.

Joachim, C. (1998). Drawing a single nanofibre over hundreds of microns. *EPL (Europhysics Letters), 42*(2), 215.

Juang, R. S., & Shiau, R. C. (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. *Journal of Membrane Science, 165*(2), 159-167.

Kalló, D. (2001). Applications of natural zeolites in water and wastewater treatment. *Reviews in mineralogy and geochemistry, 45*(1), 519-550.

Kanamoto, T., Kiyooka, S., Tovmasyan, Y., Sano, H., & Narukawa, H. (1990). Effect of molecular weight on drawing poly (vinyl alcohol) from solution-grown crystal mats. *Polymer, 31*(11), 2039-2046.

Karadag, D., Akgul, E., Tok, S., Erturk, F., Kaya, M. A., & Turan, M. (2007). Basic and reactive dye removal using natural and modified zeolites. *Journal of Chemical & Engineering Data*, *52*(6), 2436-2441.

Karadag, D., Turan, M., Akgul, E., Tok, S., & Faki, A. (2007). Adsorption equilibrium and kinetics of reactive black 5 and reactive red 239 in aqueous solution onto surfactant-modified zeolite. *Journal of Chemical & Engineering Data*, *52*(5), 1615-1620.

Karn, B., Kuiken, T., & Otto, M. (2009). Nanotechnology and in situ remediation: a review of the benefits and potential risks. *Environmental health perspectives*, 1823-1831.

Kasprzak, K. S., Sunderman, F. W., & Salnikow, K. (2003). Nickel carcinogenesis. *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis, 533*(1), 67-97.

Kesraoui-Ouki, S., Cheeseman, C. R., & Perry, R. (1994). Natural zeolite utilisation in pollution control: A review of applications to metals' effluents. *Journal of Chemical Technology and Biotechnology*, *59*(2), 121-126.

Khor, E., & Lim, L. Y. (2003). Implantable applications of chitin and chitosan. *Biomaterials, 24*(13), 2339-2349.

Kim, J., & Van der Bruggen, B. (2010). The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment. *Environmental Pollution*, *158*(7), 2335-2349.

Kim, J. H., Kim, J. Y., Lee, Y. M., & Kim, K. Y. (1992). Properties and swelling characteristics of cross-linked poly (vinyl alcohol)/chitosan blend membrane. *Journal of applied polymer science, 45*(10), 1711-1717.

Kittur, A., Kulkarni, S., Aralaguppi, M., & Kariduraganavar, M. (2005). Preparation and characterization of novel pervaporation membranes for the separation of water–

isopropanol mixtures using chitosan and NaY zeolite. *Journal of Membrane Science, 247*(1), 75-86.

Koeppenkastrop, D., & De Carlo, E. H. (1993). Uptake of rare earth elements from solution by metal oxides. *Environmental Science & Technology, 27*(9), 1796-1802.

Koski, A., Yim, K., & Shivkumar, S. (2004). Effect of molecular weight on fibrous PVA produced by electrospinning. *Materials Letters, 58*(3), 493-497.

Kubota, N., & Eguchi, Y. (1997). Facile preparation of water-soluble N-acetylated chitosan and molecular weight dependence of its water-solubility. *Polymer journal, 29*(2), 123-127.

Kula, I., Uğurlu, M., Karaoğlu, H., & Celik, A. (2008). Adsorption of Cd (II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl 2 activation. *Bioresource Technology, 99*(3), 492-501.

Kumar, M., Tamilarasan, R., & Sivakumar, V. (2013). Adsorption of Victoria blue by carbon/Ba/alginate beads: Kinetics, thermodynamics and isotherm studies. *Carbohydrate Polymers, 98*(1), 505-513.

Kumar, M. N. R. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers, 46*(1), 1-27.

Kumazawa, K. (2002). Nitrogen fertilization and nitrate pollution in groundwater in Japan: Present status and measures for sustainable agriculture. *Nutrient Cycling in Agroecosystems, 63*(2-3), 129-137.

Kunugi, T., Kawasumi, T., & Ito, T. (1990). Preparation of ultra-high modulus polyvinyl alcohol fibers by the zone-drawing method. *Journal of Applied Polymer Science, 40*(11-12), 2101-2112.

Laudenslager, M. J., & Sigmund, W. M. (2012). Electrospinning *Encyclopedia of Nanotechnology* (pp. 769-775): Springer.

Li, D., Ouyang, G., McCann, J. T., & Xia, Y. (2005). Collecting electrospun nanofibers with patterned electrodes. *Nano Letters, 5*(5), 913-916.

Li, D., & Xia, Y. (2004). Electrospinning of nanofibers: reinventing the wheel? *Advanced Materials*, *16*(14), 1151-1170.

Li, L., & Hsieh, Y. L. (2006). Chitosan bicomponent nanofibers and nanoporous fibers. *Carbohydrate research, 341*(3), 374-381.

Li, Q., Dunn, E., Grandmaison, E., & Goosen, M. (1992). Applications and properties of chitosan. *Journal of Bioactive and Compatible Polymers, 7*(4), 370-397.

Li, W. J., Laurencin, C. T., Caterson, E. J., Tuan, R. S., & Ko, F. K. (2002). Electrospun nanofibrous structure: a novel scaffold for tissue engineering. *Journal of biomedical materials research, 60*(4), 613-621.

Li, Y. H., Ding, J., Luan, Z., Di, Z., Zhu, Y., Xu, C.,Wei, B. (2003). Competitive adsorption of Pb 2+, Cu 2+ and Cd 2+ ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon, 41*(14), 2787-2792.

Li, Z., & Wang, C. (2013). Effects of working parameters on electrospinning *One-Dimensional Nanostructures* (pp. 15-28): Springer.

Lim, S. H., & Hudson, S. M. (2003). Review of chitosan and its derivatives as antimicrobial agents and their uses as textile chemicals. *Journal of Macromolecular Science, Part C: Polymer Reviews, 43*(2), 223-269.

Lin, C. F., Wu, C. H., & Lai, H. T. (2008). Dissolved organic matter and arsenic removal with coupled chitosan/UF operation. *Separation and purification Technology, 60*(3), 292-298.

Lin, D., & Xing, B. (2008). Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups. *Environmental Science & Technology, 42*(19), 7254-7259.

Lin, S. H., & Chen, M. L. (1997). Treatment of textile wastewater by chemical methods for reuse. *Water Research, 31*(4), 868-876.

Lind, M. L., Eumine Suk, D., Nguyen, T. V., & Hoek, E. M. (2010). Tailoring the structure of thin film nanocomposite membranes to achieve seawater RO membrane performance. *Environmental Science & Technology, 44*(21), 8230-8235.

Lind, M. L., Ghosh, A. K., Jawor, A., Huang, X., Hou, W., Yang, Y., & Hoek, E. M. (2009). Influence of zeolite crystal size on zeolite-polyamide thin film nanocomposite membranes. *Langmuir, 25*(17), 10139-10145.

Linden, K. G., & Mohseni, M. (2014). 2.8 Advanced Oxidation Processes: Applications in Drinking Water Treatment. In S. Ahuja (Ed.), *Comprehensive Water Quality and Purification* (pp. 148-172). Waltham: Elsevier.

Liu, G., Ding, J., Qiao, L., Guo, A., Dymov, B. P., Gleeson, J. T.,Saijo, K. (1999). Polystyrene-block-poly (2-cinnamoylethyl methacrylate) Nanofibers—Preparation, Characterization, and Liquid Crystalline Properties. *Chemistry-A European Journal, 5*(9), 2740-2749.

Lokhande, R. S., Singare, P. U., & Pimple, D. S. (2011). Toxicity study of heavy metals pollutants in waste water effluent samples collected from Taloja Industrial Estate of Mumbai, India. *Resources and Environment, 1*(1), 13-19.

Lu, C., Chiu, H., & Liu, C. (2006). Removal of zinc (II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. *Industrial & engineering chemistry research, 45*(8), 2850-2855.

Luzio, A., Canesi, E. V., Bertarelli, C., & Caironi, M. (2014). Electrospun polymer fibers for electronic applications. *Materials, 7*(2), 906-947.

Lv, X., Xu, J., Jiang, G., Tang, J., & Xu, X. (2012). Highly active nanoscale zero-valent iron (nZVI)–Fe 3 O 4 nanocomposites for the removal of chromium (VI) from aqueous solutions. *Journal of colloid and interface science, 369*(1), 460-469.

Lyoo, W. S., Blackwell, J., & Ghim, H. D. (1998). Structure of Poly (vinyl alcohol) Microfibrils Produced by Saponification of Copoly (vinyl pivalate/vinyl acetate). *Macromolecules, 31*(13), 4253-4259.

Mahanta, D., Manna, U., Madras, G., & Patil, S. (2010). Multilayer self-assembly of TiO2 nanoparticles and polyaniline-grafted-chitosan copolymer (CPANI) for photocatalysis. *ACS applied materials & interfaces, 3*(1), 84-92.

Malm, O. (1998). Gold mining as a source of mercury exposure in the Brazilian Amazon. *Environmental Research, 77*(2), 73-78.

Manesh, K., Santhosh, P., Gopalan, A., & Lee, K. P. (2007). Electrospun poly (vinylidene fluoride)/poly (aminophenylboronic acid) composite nanofibrous membrane as a novel glucose sensor. *Analytical biochemistry, 360*(2), 189-195.

Mapanda, F., Mangwayana, E., Nyamangara, J., & Giller, K. (2005). The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. *Agriculture, Ecosystems & Environment, 107*(2), 151-165.

Martin, C. R. (1996). Membrane-based synthesis of nanomaterials. *Chemistry of Materials, 8*(8), 1739-1746.

Martinová, L., & Lubasová, D. (2008). Electrospun chitosan based nanofibers. *Research Journal of Textile and Apparel, 12*(2), 72-79.

Matabola, K., & Moutloali, R. (2013). The influence of electrospinning parameters on the morphology and diameter of poly (vinyledene fluoride) nanofibers-effect of sodium chloride. *Journal of Materials Science, 48*(16), 5475-5482.

Mathialagan, T., & Viraraghavan, T. (2002). Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazardous Materials, 94*(3), 291-303.

Maximous, N., Nakhla, G., Wan, W., & Wong, K. (2010). Effect of the metal oxide particle distributions on modified PES membranes characteristics and performance. *Journal of Membrane Science, 361*(1), 213-222.

Maximous, N., Nakhla, G., Wong, K., & Wan, W. (2010). Optimization of Al 2 O 3/PES membranes for wastewater filtration. *Separation and purification Technology, 73*(2), 294-301.

Mayo, J., Yavuz, C., Yean, S., Cong, L., Shipley, H., Yu, W., Colvin, V. (2007). The effect of nanocrystalline magnetite size on arsenic removal. *Science and Technology of Advanced Materials, 8*(1), 71-75.

Md. ashikur, R., & Rabia , N. (2014). Treatment of electroplating industry wastewater using iron nanoparticle doped spent tea waste charcoal. *Journal of Biodiversity and Environmental Science, 5*(6), 7-17.

Medeiros, E. S., Glenn, G. M., Klamczynski, A. P., Orts, W. J., & Mattoso, L. H. (2009). Solution blow spinning: A new method to produce micro-and nanofibers from polymer solutions. *Journal of applied polymer science, 113*(4), 2322-2330.

Megelski, S., Stephens, J. S., Chase, D. B., & Rabolt, J. F. (2002). Micro-and nanostructured surface morphology on electrospun polymer fibers. *Macromolecules, 35*(22), 8456-8466.

Metcalf, E. (1991). Wastewater Engineering: Treatment. *Disposal, and Reuse, 3*.

Mi, F. L., Tan, Y. C., Liang, H. C., Huang, R.-N., & Sung, H. W. (2001). In vitro evaluation of a chitosan membrane cross-linked with genipin. *Journal of Biomaterials Science, Polymer Edition, 12*(8), 835-850.

Mima, S., Miya, M., Iwamoto, R., & Yoshikawa, S. (1983). Highly deacetylated chitosan and its properties. *Journal of applied polymer science, 28*(6), 1909-1917.

Misaelides, P. (2011). Application of natural zeolites in environmental remediation: A short review. *Microporous and Mesoporous Materials, 144*(1), 15-18.

Miya, M., Iwamoto, R., Yoshikawa, S., & Mima, S. (1980). IR spectroscopic determination of CONH content in highly deacylated chitosan. *International Journal of Biological Macromolecules*, *2*(5), 323-324.

Muhd Julkapli, N., Akil, H. M., & Ahmad, Z. (2011). Preparation, properties and applications of chitosan-based biocomposites/blend materials: a review. *Composite Interfaces, 18*(6), 449-507.

Muzzarelli, R. A., Tanfani, F., Scarpini, G., & Laterza, G. (1980). The degree of acetylation of chitins by gas chromatography and infrared spectroscopy. *Journal of biochemical and biophysical methods, 2*(5), 299-306.

Ngah, W. W., Endud, C., & Mayanar, R. (2002). Removal of copper (II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. *Reactive and Functional Polymers, 50*(2), 181-190.

Nies, D. H. (1999). Microbial heavy metal resistance. *Applied microbiology and biotechnology, 51*(6), 730-750.

Ogawa, K. (1991). Effect of heating an aqueous suspension of chitosan on the crystallinity and polymorphs. *Agricultural and biological chemistry, 55*(9), 2375-2379.

Ogawa, K., Yui, T., & Miya, M. (1992). Dependence on the preparation procedure of the polymorphism and crystallinity of chitosan membranes. *Bioscience, biotechnology, and biochemistry, 56*(6), 858-862.

Ohkawa, K., Minato, K. I., Kumagai, G., Hayashi, S., & Yamamoto, H. (2006). Chitosan nanofiber. *Biomacromolecules, 7*(11), 3291-3294.

Oliveira, J. E., Moraes, E. A., Costa, R. G., Afonso, A. S., Mattoso, L. H., Orts, W. J., & Medeiros, E. S. (2011). Nano and submicrometric fibers of poly (D, L-lactide) obtained by solution blow spinning: Process and solution variables. *Journal of applied polymer science, 122*(5), 3396-3405.

Oller, I., Malato, S., & Sánchez-Pérez, J. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. *Science of the Total Environment, 409*(20), 4141-4166.

Ong, W. y., & Halliwell, B. (2004). Iron, Atherosclerosis, and Neurodegeneration: A Key Role for Cholesterol in Promoting Iron-Dependent Oxidative Damage? *Annals of the New York Academy of Sciences, 1012*(1), 51-64.

Organization, W. H. (1988). *Requirements of Vitamin A, Iron, Folate, and Vitamin B12: Report of a joint FAO/WHO Expert Consultation*: Food & Agriculture Org.

Organization, W. H. (2004). *Guidelines for drinking-water quality: recommendations* (Vol. 1): World Health Organization.

Pan, B., Lin, D., Mashayekhi, H., & Xing, B. (2008). Adsorption and hysteresis of bisphenol A and 17alpha-ethinyl estradiol on carbon nanomaterials. *Environ Sci Technol, 42*(15), 5480-5485.

Pan, B., & Xing, B. (2008). Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environmental Science & Technology, 42*(24), 9005-9013.

Park, W. H., Jeong, L., Yoo, D. I., & Hudson, S. (2004). Effect of chitosan on morphology and conformation of electrospun silk fibroin nanofibers. *Polymer, 45*(21), 7151-7157.

Pawlak, A., & Mucha, M. (2003). Thermogravimetric and FTIR studies of chitosan blends. *Thermochimica acta, 396*(1), 153-166.

Pendergast, M. T. M., Nygaard, J. M., Ghosh, A. K., & Hoek, E. M. (2010). Using nanocomposite materials technology to understand and control reverse osmosis membrane compaction. *Desalination, 261*(3), 255-263.

Perez, V. P., Martins de Lima, M. N., da Silva, R. S., Dornelles, A. S., Vedana, G., Bogo, M. R.,Schroder, N. (2010). Iron leads to memory impairment that is associated with a decrease in acetylcholinesterase pathways. *Current neurovascular research, 7*(1), 15-22.

Perminova, I. V., Hatfield, K., & Hertkorn, N. (2005). *Use of humic substances to remediate polluted environments: from theory to practice*: Springer.

Peter, M. G. (1995). Applications and environmental aspects of chitin and chitosan. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 32*(4), 629-640.

Pitcher, S., Slade, R., & Ward, N. (2004). Heavy metal removal from motorway stormwater using zeolites. *Science of the Total Environment, 334*, 161-166.

Pradeep, T. (2009). Noble metal nanoparticles for water purification: a critical review. *Thin solid films, 517*(24), 6441-6478.

Q. Li, L. H., H. Li and S. H. Fang. (2010). Preparation of chitosan/polyvinyl alcohol composite scaffold at different mass ratio. Comparison of structure and characteristics. *Journal of Clinical Rehabilitative Tissue Engineering Research, 14*, 5.

Qi, B., Yu, A., Zhu, S., Chen, B., & Li, Y. (2010). The preparation and cytocompatibility of injectable thermosensitive chitosan/poly (vinyl alcohol) hydrogel. *Journal of Huazhong University of Science and Technology [Medical Sciences], 30*, 89-93.

Qin, C., Li, H., Xiao, Q., Liu, Y., Zhu, J., & Du, Y. (2006). Water-solubility of chitosan and its antimicrobial activity. *Carbohydrate polymers, 63*(3), 367-374.

Qin, X. H., & Wang, S. Y. (2006). Filtration properties of electrospinning nanofibers. *Journal of applied polymer science, 102*(2), 1285-1290.

Qu, X., Alvarez, P. J., & Li, Q. (2013). Applications of nanotechnology in water and wastewater treatment. *Water Research, 47*(12), 3931-3946.

Qu, X., Brame, J., Li, Q., & Alvarez, P. J. (2012). Nanotechnology for a safe and sustainable water supply: enabling integrated water treatment and reuse. *Accounts of Chemical Research, 46*(3), 834-843.

Ramakrishna, S., Fujihara, K., Teo, W. E., Yong, T., Ma, Z., & Ramaseshan, R. (2006). Electrospun nanofibers: solving global issues. *Materials today, 9*(3), 40-50.

Ramakrishna, S., Jose, R., Archana, P., Nair, A., Balamurugan, R., Venugopal, J., & Teo, W. (2010). Science and engineering of electrospun nanofibers for advances in clean energy, water filtration, and regenerative medicine. *Journal of materials science, 45*(23), 6283-6312.

Rao, G. P., Lu, C., & Su, F. (2007). Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review. *Separation and purification Technology, 58*(1), 224-231.

Rege, S. U., Yang, R. T., & Cain, C. A. (1998). Desorption by ultrasound: phenol on activated carbon and polymeric resin.

Reneker, D., Kataphinan, W., Theron, A., Zussman, E., & Yarin, A. (2002). Nanofiber garlands of polycaprolactone by electrospinning. *Polymer, 43*(25), 6785-6794.

Ribeiro, A. R., Nunes, O. C., Pereira, M. F. R., & Silva, A. M. T. (2015). An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environment International, 75*(0), 33-51.

Rinaudc, M., Pavlov, G., & Desbrieres, J. (1999). Solubilization of chitosan in strong acid medium. *International Journal of Polymer Analysis and Characterization, 5*(3), 267-276.

Rinaudo, M. (2006). Chitin and chitosan: properties and applications. *Progress in polymer science, 31*(7), 603-632.

Rinaudo, M., Pavlov, G., & Desbrieres, J. (1999). Influence of acetic acid concentration on the solubilization of chitosan. *Polymer, 40*(25), 7029-7032.

Roberts, G. A. (1992). Structure of chitin and chitosan. *Chitin chemistry*, 1-100.

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology, 77*(3), 247-255.

Rogers, H. R. (1996). Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Science of the Total Environment, 185*(1), 3-26.

Sahlström, L., Aspan, A., Bagge, E., Danielsson-Tham, M. L., & Albihn, A. (2004). Bacterial pathogen incidences in sludge from Swedish sewage treatment plants. *Water research, 38*(8), 1989-1994.

Sannan, T., Kurita, K., Ogura, K., & Iwakura, Y. (1978). Studies on chitin: 7. IR spectroscopic determination of degree of deacetylation. *Polymer, 19*(4), 458-459.

Savage, N., & Diallo, M. S. (2005). Nanomaterials and water purification: opportunities and challenges. *Journal of Nanoparticle Research, 7*(4-5), 331-342.

Sawada, I., Fachrul, R., Ito, T., Ohmukai, Y., Maruyama, T., & Matsuyama, H. (2012). Development of a hydrophilic polymer membrane containing silver nanoparticles with both organic antifouling and antibacterial properties. *Journal of Membrane Science, 387*, 1-6.

Schiffman, J. D., & Schauer, C. L. (2007a). Cross-linking chitosan nanofibers. *Biomacromolecules, 8*(2), 594-601.

Schiffman, J. D., & Schauer, C. L. (2007b). One-step electrospinning of cross-linked chitosan fibers. *Biomacromolecules, 8*(9), 2665-2667.

Seif, H. A., Joshi, S., & Gupta, S. (1992). Effect of organic load and reactor height on the performance of anaerobic mesophilic and thermophilic fixed film reactors in the treatment of pharmaceutical wastewater. *Environmental technology, 13*(12), 1161-1168.

Selvi, K., Pattabhi, S., & Kadirvelu, K. (2001). Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon. *Bioresource Technology, 80*(1), 87-89.

Şenel, S., & McClure, S. J. (2004). Potential applications of chitosan in veterinary medicine. *Advanced drug delivery reviews, 56*(10), 1467-1480.

Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Mariñas, B. J., & Mayes, A. M. (2008). Science and technology for water purification in the coming decades. *Nature, 452*(7185), 301-310.

Shannon, R. t. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography, 32*(5), 751-767.

Sharma, Y., Srivastava, V., Singh, V., Kaul, S., & Weng, C. (2009). Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environmental technology, 30*(6), 583-609.

Shauer, C. L., & Schiffman, J. D. (2008). Fibrous mats containing chitosan nanofibers: Google Patents.

Shigemasa, Y., Matsuura, H., Sashiwa, H., & Saimato, H. (1996). An improved IR spectroscopic determination of degree of deacetylation of chitin. *Advances in chitin science, 1,* 204-209.

Shigemasa, Y., Matsuura, H., Sashiwa, H., & Saimoto, H. (1996). Evaluation of different absorbance ratios from infrared spectroscopy for analyzing the degree of deacetylation in chitin. *International Journal of Biological Macromolecules, 18*(3), 237-242.

Sieliechi, J.-M., Kayem, G. J., & Sandu, I. (2010). Effect of water treatment residuals (aluminum and iron ions) on human health and drinking water distribution systems. *International Journal of Conservation Science, 1*(3), 175-182.

Sill, T. J., & von Recum, H. A. (2008). Electrospinning: applications in drug delivery and tissue engineering. *Biomaterials, 29*(13), 1989-2006.

Silver, S., & Phung, L. T. (1996). Bacterial heavy metal resistance: new surprises. *Annual Reviews in Microbiology, 50*(1), 753-789.

Snoeyink, V. L. (1990). Adsorption of organic compounds. *MCGRAW-HILL, INC.,(USA). 1194*, 1990.

Song, M. Y., Kim, D. K., Ihn, K. J., Jo, S. M., & Kim, D. Y. (2004). Electrospun TiO2 electrodes for dye-sensitized solar cells. *Nanotechnology, 15*(12), 1861.

Song, X., Ling, F., Ma, L., Yang, C., & Chen, X. (2013). Electrospun hydroxyapatite grafted poly (L-lactide)/poly (lactic-co-glycolic acid) nanofibers for guided bone regeneration membrane. *Composites science and technology, 79,* 8-14.

Sorlier, P., Denuziere, A., Viton, C., & Domard, A. (2001). Relation between the degree of acetylation and the electrostatic properties of chitin and chitosan. *Biomacromolecules, 2*(3), 765-772.

Subbiah, T., Bhat, G., Tock, R., Parameswaran, S., & Ramkumar, S. (2005). Electrospinning of nanofibers. *Journal of applied polymer science, 96*(2), 557-569.

Sultan, S., & Hasnain, S. (2005). Chromate reduction capability of a gram positive bacterium isolated from effluent of dying industry. *Bulletin of environmental contamination and toxicology, 75*(4), 699-706.

Sun, H., Lu, L., Chen, X., & Jiang, Z. (2008). Surface-modified zeolite-filled chitosan membranes for pervaporation dehydration of ethanol. *Applied Surface Science, 254*(17), 5367-5374.

Tabatabaee, M., & Abolfazl Mirrahimi, S. (2011). Photodegradation of dye pollutant on Ag/ZnO Nanocatalyst under UV-irradiation. *Oriental Journal of Chemistry, 27*(1), 65.

Tadros, T. F. (1974). The interaction of cetyltrimethylammonium bromide and sodium dodecylbenzene sulfonate with polyvinyl alcohol. adsorption of the polymer—surfactant complexes on silica. *Journal of Colloid and Interface Science, 46*(3), 528-540.

Tadros, T. F. (1978). Adsorption of polyvinyl alcohol on silica at various pH values and its effect on the flocculation of the dispersion. *Journal of Colloid and Interface Science, 64*(1), 36-47.

Tan, S. C., Khor, E., Tan, T. K., & Wong, S. M. (1998). The degree of deacetylation of chitosan: advocating the first derivative UV-spectrophotometry method of determination. *Talanta, 45*(4), 713-719.

Thacker, U., Parikh, R., Shouche, Y., & Madamwar, D. (2006). Hexavalent chromium reduction by Providencia sp. *Process Biochemistry, 41*(6), 1332-1337.

Trivedi, P., & Axe, L. (2000). Modeling Cd and Zn sorption to hydrous metal oxides. *Environmental Science & Technology, 34*(11), 2215-2223.

Wang, S., & Ariyanto, E. (2007). Competitive adsorption of malachite green and Pb ions on natural zeolite. *Journal of Colloid and Interface Science, 314*(1), 25-31.

Wang, S., Boyjoo, Y., Choueib, A., & Zhu, Z. (2005). Removal of dyes from aqueous solution using fly ash and red mud. *Water Research, 39*(1), 129-138.

Wang, S., & Peng, Y. (2010). Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal, 156*(1), 11-24.

Wang, S., & Zhu, Z. (2006). Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution. *Journal of Hazardous Materials, 136*(3), 946-952.

Wang, T., & Kumar, S. (2006). Electrospinning of polyacrylonitrile nanofibers. *Journal of Applied Polymer Science, 102*(2), 1023-1029.

Wang, Y., & Hsieh, Y. L. (2008). Immobilization of lipase enzyme in polyvinyl alcohol (PVA) nanofibrous membranes. *Journal of Membrane Science, 309*(1), 73-81.

Wang, Z., Ma, W., Chen, C., & Zhao, J. (2008). Photochemical coupling reactions between Fe (III)/Fe (II), Cr (VI)/Cr (III), and polycarboxylates: inhibitory effect of Cr species. *Environmental science & technology, 42*(19), 7260-7266.

Weber, W. J. (1972). *Physicochemical processes for water quality control*: Wiley interscience.

Whanger, P. (1992). Selenium in the treatment of heavy metal poisoning and chemical carcinogenesis. *Journal of trace elements and electrolytes in health and disease, 6*(4), 209-221.

Wu, T., Zivanovic, S., Draughon, F. A., & Sams, C. E. (2004). Chitin and chitosan value-added products from mushroom waste. *Journal of agricultural and food chemistry, 52*(26), 7905-7910.

Yan, X., & Gevelber, M. (2010). Investigation of electrospun fiber diameter distribution and process variations. *Journal of Electrostatics, 68*(5), 458-464.

Yang, K., Wu, W., Jing, Q., & Zhu, L. (2008). Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes. *Environmental Science & Technology, 42*(21), 7931-7936.

Yang, K., & Xing, B. (2010). Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. *Chemical reviews, 110*(10), 5989-6008.

Yarin, A. L. (1993). Free liquid jets and films. *Hydrodynamics and Rheology*.

Yean, S., Cong, L., Yavuz, C., Mayo, J., Yu, W., Kan, A.,Tomson, M. (2005). Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate. *Journal of Materials Research, 20*(12), 3255-3264.

Yen, M. T., Yang, J.-H., & Mau, J.-L. (2009). Physicochemical characterization of chitin and chitosan from crab shells. *Carbohydrate Polymers*, *75*(1), 15-21.

Zamzow, M., & Murphy, J. (1992). Removal of metal cations from water using zeolites. *Separation Science and Technology, 27*(14), 1969-1984.

Zander, N. E. (2013). Hierarchically structured electrospun fibers. *Polymers*, *5*(1), 19-44.

Zargham, S., Bazgir, S., Tavakoli, A., Rashidi, A. S., & Damerchely, R. (2012). The effect of flow rate on morphology and deposition area of electrospun nylon 6 nanofiber. *J Eng Fibers Fabr, 7*(4), 42-49.

Zeleny, J. (1935). The role of surface instability in electrical discharges from drops of alcohol and water in air at atmospheric pressure. *Journal of the Franklin Institute, 219*(6), 659-675.

Zhang, C., Yuan, X., Wu, L., Han, Y., & Sheng, J. (2005). Study on morphology of electrospun poly (vinyl alcohol) mats. *European Polymer Journal, 41*(3), 423-432.

Zhang, H., Gao, X., Guo, T., Li, Q., Liu, H., Ye, X., Wu, Z. (2011). Adsorption of iodide ions on a calcium alginate–silver chloride composite adsorbent. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 386*(1), 166-171.

Zheng, H., Du, Y., Yu, J., Huang, R., & Zhang, L. (2001). Preparation and characterization of chitosan/poly (vinyl alcohol) blend fibers. *Journal of applied polymer science, 80*(13), 2558-2565.

Zong, X., Kim, K., Fang, D., Ran, S., Hsiao, B. S., & Chu, B. (2002). Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*, *43*(16), 4403-4412.

Zuane, J. D. (1990). Drinking water quality standards and controls.

LIST OF PUBLICATIONS AND PAPER PRESENTED

JOURNAL PUBLICATION

1. Umma Habiba, Amalina M. Afifi, Bee Chin Ang, Sepehr Talebian, Influence of hydrolysis on electrospinnability of Chitosan/Polyvinyl Alcohol blends solution and fiber diameter distribution, Sains Malaysiana, 45(1): 29–34. January 2016.

PAPER PRESENTED

1. Umma Habiba, Amalina M. Afifi, Bee Chin Ang, Effect of polymer binder and degree of deacetylation in electrospinnability of chitosan, International Conference on plastic, rubber and composite 2014.