Porous Poly(L-lactic acid) Nano Fibres Coated Chitosan and their Applications

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Abstract

This thesis explain methods based on the coating of chitosan on porous poly(L-lactic acid) (PLLA) nanofibrous membrane for the production of high surface area adsorbents for the removal of toxic contaminants from aqueous solution. The surface modification of PLLA membrane by chitosan allowed heavy metals and dyes to attach on the adsorbent by electrostatic interactions. In order to achieve this, the chitosan was coated on porous nanofibrous support by three different methods: a) simple dip coating of pure chitosan porous membrane, b) chitosan grafted on polydopamine modified porous membrane and c) 3-aminopropyltriethoxysilane cross-linked chitosan coated on porous membrane.

The prepared adsorbents in this work were designed to be used in the adsorption of impurities. Results showed that the use of such adsorbents can adsorb the large quantities of pollutants in less time reducing the costs and waste disposal.

The chitosan used in this work was selected based on its biocompatibility, biodegradability, cost and availability from natural resources. Dopamine and 3-aminopropyltriethoxysilane were used to increase the adsorption sites and stability of chitosan in the aqueous solution. All materials were successfully immobilized on the porous support to produce large surface area adsorbent membrane.

PLLA membrane was fabricated by electrospinning process and porosity was induced in the membrane via non solvent induced phase separation process and acetone treatment after electrospinning. This porous PLLA membrane was used as a support due to their high surface area, PLLA can be obtained from low cost renewable resources and it is biodegradable.

The prepared adsorbent materials were tested in the removal of toxic ions and synthetic dyes from water solutions such as copper, methylene blue and rhodamine B. Batch experiments were carried out to determine the adsorption kinetics, equilibrium isotherm and thermodynamic parameters of adsorption copper ions, methylene blue and rhodamine B on prepared adsorbents. The experimental kinetic data were analysed using the pseudo first order, pseudo second order and inter particle diffusion models. The experimental isotherm data were analysed using Langmuir, Freundlich and Temkin isotherm models. Adsorption experiments showed that immobilization of chitosan on large surface area porous membrane improved their uptake efficiency and capacity. Finally, the regeneration of prepared adsorbent membranes was studied for five cycles. It was concluded that adsorbent was effective up to three regeneration cycles.

Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or another institute of learning.

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Last but not the least, my special thanks to my wife Dr. Madeeha Tabassum, whose unconditional love, support and prayers have always been the motivation behind my success.

Dedication

To my grandfather Muhammad Anwar Kamal Butt (Late), my mother Samiya Kamal and my grandmother for their unconditional love, support, guidance and prayers

To my lovely brother's, Fahad Zia and Zil Muarij, my daughter Eileen Qasim and my beloved wife Dr. Madeeha Tabassum, who has always been there to guide me through the difficult times

Rationale for submitting an alternative format thesis

During my PhD project, one review paper and three papers were published in peer-reviewed journals of international standing. These publications made the thesis more suited to an alternative journal format. The thesis is centred on the synthesis of novel adsorbent with the following primary objectives:

Preparation of high surface area porous PLLA nanofibers by electrospinning method to be used as substrates for the adsorption of heavy metal ions and textile dyes from aqueous solutions. To date few studies has been reported on the modification of hydrophobic nanofibers and their usage as suitable adsorbents.

In the first paper, chitosan in different concentrations was simply coated on the porous PLLA membrane. The prepared adsorbent was characterized and tested in various adsorption environments for copper ions. The study showed that maximum adsorption could be reached in ten minutes, it is faster as compared to the previous studies. However, chitosan can lose its stability in water if present for longer hours, which leads to our second study.

In the second study, chitosan was grafted on the dopamine modified porous PLLA membrane to increase the stability of chitosan in aqueous solution. This study showed that higher adsorption capacities for copper ions can be attained within 60 min of the study in the optimum adsorption conditions.

In the third study, chitosan was cross-linked with 3-aminopropyltriethoxysilane to increase the amino functional groups which are responsible for adsorption after the crosslinking of chitosan. Previous studies showed that crosslinking can reduce the number the functional groups on chitosan backbone due to crosslinking reaction. In this study, crosslinking reaction was optimized by varying concentrations of 3-aminopropyltrietoxysilane to achieve the maximum adsorption of textile dyes such as methylene blue and rhodamine B.

Overall structure of the alternative format thesis

Chapter 1 encompasses the general introduction of the research areas used in this thesis. This chapter can be classified into two parts. In the first part, background of water pollution in the world and the current methods to reduce the water contamination were discussed. Furthermore, impact of water pollution in developing countries and the industries responsible for polluting the drinking water were mentioned.

The second part consists of the literature review of the electrospinning, water treatment methods, chitosan and PLLA. Finally the purpose of the published papers and the research objectives were described briefly.

Chapter 2 gives a literature overview about the role of industries involved in water pollution, current advanced water treatment. In latter, a detailed comparison of processes used in various industrial set ups and their annual waste production was provided. Furthermore, techniques used for removing the pollutants from water were described and compared in detail. Also, various commercial adsorbents and factors that affect the adsorption process were reviewed.

It also include our review paper that was published in Journal of fibre bioengineering and informatics in June 2019. This paper aims to review the past and present researches on chitosan for the adsorption of heavy metals from the wastewater. To begin with, mechanism of adsorption of heavy metal ions on chitosan and disadvantages of heavy metal ions were reviewed. Further, a detailed review had been done on the adsorption capacities of cross-linked chitosan, chitosan nanofibers, chitosan nanoparticles, chitosan composites, modified/pure chitosan, and porous chitosan. Lastly, research gaps and future recommendations were given for further development and accurate results of adsorption.

Finally**,** comprises of a brief introduction to electrospinning method and its setup, methods to produce porous nanofibers and properties and applications of PLLA. The electrospinning process parameters and their effect on the morphology of the nanofibers were discussed in detail. Moreover, different strategies that are used to create pores in electrospun fibres and their effect on the pore size, shape and morphology was discussed.

Chapter 3 consists of the manuscript and supporting information for our publication in Carbohydrate Polymers that was published in January 2020. In this work chitosan in different concentrations was coated on porous PLLA nanofibers via simple dip coating method. Whereas, porous PLLA nanofibers were fabricated by electrospinning. Porous fibres provide the high surface area platform for chitosan to increase the adsorption of copper ions. It was observed that copper was rapidly and efficiently adsorb on the 1 % chitosan coated porous nanofibers. The maximum adsorption of copper ions was achieved under optimal conditions of pH 7, contact time of 10 min and temperature of 25 °C. This is an initial study and further work on increasing the adsorption of heavy metal ions by grafting and cross-linking chitosan is also done in the next chapters.

Chapter 4 consists of the manuscript and supporting information for our publication in International Journal of Biological Macromolecules that was published in January 2021. In this work, chitosan was grafted on porous PLLA membrane by using polydopamine as an intermediate layer. It was observed that adsorption of copper ions from aqueous solution increased due to the increase of amine groups and stability of chitosan. The variation in adsorption is due to the change in surface area of porous PLLA membranes with respect to polymerization times of dopamine. Moreover, the adsorbent membrane was efficient for three adsorption cycles.

Chapter 5 consists of the manuscript and supporting information for our publication in Reactive and Functional Polymers that was published in September 2021. This research describe the crosslinking of chitosan with 3-aminopropyltriethoxysilane. Moreover, the cross-linked chitosan was coated on biodegradable porous PLLA nanofibrous membrane for the removal of methylene blue and rhodamine B dyes. The prepared adsorbent was tested under different adsorption parameters such as pH, temperature, time and dye concentration. Non-linear and linear adsorption isotherms and kinetic models were studied. Finally, adsorbent can be reusable up to three adsorption cycles.

Chapter 6 outlined the overall conclusion of the research work presented in this thesis and suggestions for possible future work that can be done in this research area. Finally, the limitations of current studies were also mentioned.

1.Chapter 1

Introduction to porous poly(l-lactic acid) nanofibers coated chitosan and their applications

1.1 Scope

In the new global economy, environmental pollution has become a central health issue for all the living beings. Water pollution is of particular concern, it has caused severe well-being issues and diseases in human beings and marine creatures. Water is fundamental to every living organisms, as humans, we need water because our 70% of the body is made up of it. We need clean water to drink and wash. The evidence **[1]** suggests that more than 1.1 billion of earth population does not have access to clean drinking water because of the expensive treatment for cleaning water, rapid increase in population with lack of resources and various changes in the climate **[2]**. Moreover, the industries use water in their various manufacturing processes. Briefly, life is not possible without water.

The past decade has seen the rapid expansion of chemical, textile, paper printing, publishing, leather mining, metal plating and electronic industries in many developing countries, these modern setups has contributed enormously to the water contamination through continuous ejection of harmful by products into the local water systems **[3-5]**. Heavy metals, dyes, pesticides, volatile organic compounds and oil unregulated and unauthorized spillage in the water bodies from factories and town municipalities is a classic problem of water pollution. Figure 1.1 shows the sources of water pollution. The water contamination due to heavy metals and chemicals is a major area of interest with in the field of environmental pollution, particularly due to their toxicity and major impact on the human health **[6]**.

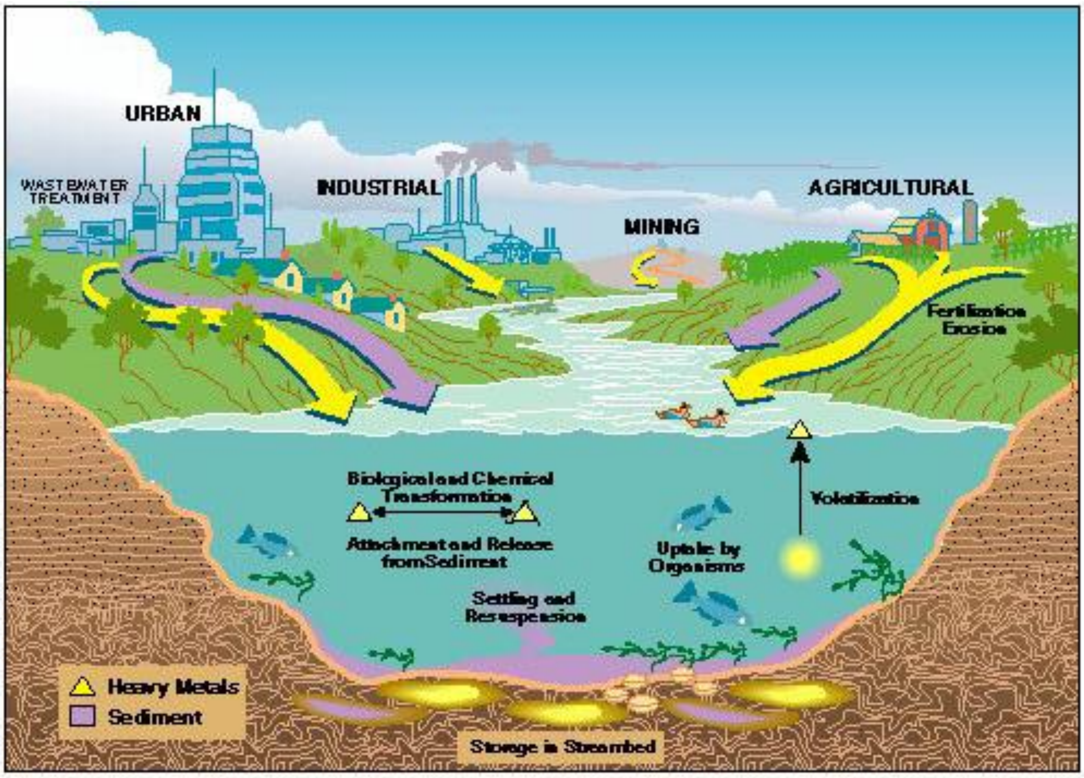

Figure 1. 1 Major sources of toxic pollutants in water [7].

1.2 Background

The term heavy metals refers to those elements in the periodic table, whose specific gravity is five folds higher than water and atomic mass ranging between 63 to 200 g/mol **[8, 9]**, such as, copper (Cu), lead (Pb), chromium (Cr), cobalt (Co), mercury (Hg), iron (Fe), Zinc (Zn) and nickel (Ni). Heavy metals in certain quantities are essential for the normal functioning of human body, however, when present in acute quantities, they are not metabolized by the body and can accumulate in the soft tissues and cause several diseases in human beings (Table 1.1) **[10, 11]**.

According to the anonymous survey by United Nations in 2010, approximately 2 million tons of sewage and industrial waste is discharged into the water globally **[12]**. Mainly, the developing countries are most affected, where more than 90 % of the sewage waste and 70 % of raw industrial wastes are discarded into the water sources. A prime example in the developing countries is Pakistan, where 18.51 % of registered industries are considered to be extremely poisoning the environment **[13]**.

Table 1.1 Standards for maximum permissible limits for heavy metals (mg/L) in drinking water by different agencies (Reprinted by permission of Springer Link from ref [14] Copyright 2021).

Heavy metal	Toxic effects	WHO#1	ICMR#2	USEPA#3	BIS#4
Lead	Fatal brain damaging, kidney, nervous and circulatory system deteriorations; gradual haemoglobin decrease	0.01	0.05	0.15	0.01
Copper	Causes Wilson disease and sleep disorders, affects the liver	1.8	1.5	1.3	1.5
Nickel	Dermatitis, carcinogenic, nausea and chronic asthma, sometimes gastrointestinal distress	0.07	-	-	0.02
Zinc	Lethargy, depression and neurological signs, also thirst increments	5.0	5.0	5.0	15.0
Arsenic	Affects skin, visceral cancers, as well as vascular disease	0.01	0.05	0.05	0.05
Cadmium	Kidney problems, renal disorder, and carcinogenic	0.003	0.003	0.005	0.003
Chromium	Diarrhoea, headache, nausea with occasional vomiting and carcinogenic	0.05	-	0.1	0.05

#1World Health Organization, #2Inidan Council of Medical Research, #3United States Environmental Protection Agency, #4Bureau of Indian Standards

Many industrial units in Pakistan are installed near the big cities such as, textile industries located in Lahore and Faisalabad (2nd and 3rd largest cities of Pakistan), leather and sports units in Sialkot and steel and mining industries in Karachi (biggest city of Pakistan). They get rid of their waste which contains large amount of toxic metals and pollutants in the nearby drains, rivers, ponds and agriculture lands **[15]** (Figure 1.2). For example, Kabul River in the Khyber

Pakhtoonkhwa province gets an estimated 8 × 10^7 L of industrial wastewater every day **[12]**. The same wastewater is used for agriculture as shown in Figure 1.2.

Figure 1. 2 Wastewater in Pakistan is discharged to the nearby river, canal, drain or open land without any prior treatment which ultimately causes pollution of surface and groundwater (a) municipal wastewater is discharged in the drain without any treatment (b) industrial wastewater is drained into a canal without any prior treatment (c) effects of sewage application on soil (d) municipal wastewater is used for agriculture (Reprinted from ref [12] Copyright 2011 with the permission of Elsevier).

1.3 Current literature

Different methods exist in the literature regarding the removal of contaminants from the wastewater such as, precipitation **[16]**, membrane filtration **[17, 18]**, ultrafiltration **[19, 20]**, nano filtration **[21]**, reverse osmosis **[22, 23]**, electro dialysis **[24-26]**, flotation **[27, 28]**, electrochemical method **[29]**, chemical coagulation/flocculation **[30-32]**, and adsorption **[32-34]**. However, much of the current literature on water filtration pays particular attention to adsorption. A possible explanation is that these previous techniques are expensive and their operating conditions are difficult and time consuming (Table 1.2). On contrary, adsorption process gives flexibility in design and operations, it is reversible and provides high quality treated water in reduced time. Nevertheless, this technique can cause secondary pollution due to regeneration of adsorbents, and its removal capacity can be limited by the stability of adsorbent in various environments (Table 1.2). Furthermore, all the mentioned techniques are discussed in detail in the literature review section of thesis.

Several adsorbents currently exist for the removal of impurities form the industrial wastewater, for example, activated carbon **[35]**, natural zeolites **[36]**, graphene **[37]**, and nano particles **[38]**. The morphology of these materials are either granular or powdery. It is a widely held view that granular materials have low surface area and porosity due to which their adsorption capability and removal times are reduced. Furthermore, nano powdery materials have large surface area, therefore, their adsorption capacities and rates are considerable (Table 1.3). However, they are practically difficult to collect from the water and are prone to cause secondary water pollution. By contrast, the nanofibrous materials have potentially greater surface area and highly porous morphology, which enable them for higher adsorption values and rapid adsorption rates. Therefore, nanofibrous membranes can prove to be excellent adsorbents for the sorption of contaminants from the aqueous solutions **[39]**.

Electrospinning is a simple equipment with low cost, easy procedure and higher production of nanofibers. These nanofibers can be stacked as nanofibrous membranes, which makes them easier to handle, operate and recycle without losing their functional properties **[40]**. These membranes are become essential for use in the wide range of technologies such as, energy, medicine and electronics **[41]**. In recent years, there has been increasing amount of literature on electrospun nanofibrous membranes in the area of water pollution **[42]**. A number of hydrophilic polymers containing functional groups like amino, carboxyl, hydroxyl and sulfonate groups were electrospun and used for the removal of heavy metal dyes and other contaminations from the water **[43]**. Moreover, in most recent research, electrospun hydrophobic polymers poly lactic acid, polytetrafluoroethylene, polystyrene and various other were also reported to be useful for the adsorption of heavy metal ions. The hydrophobic electrospun membranes were converted into functionalized membranes by using surface modification techniques or blend electrospinning them with functionalized polymers **[44]**.

Table 1.2 Various techniques for heavy metal remediation (Reprinted by permission of Springer Link from ref [14] Copyright 2021).

Methods	Advantages	Disadvantages
Precipitation method	Convenient, inexpensive	Need of excess amount of chemicals, generation of excessive sludge
Membrane filtration technique	Beneficial for the removal of oils, heavy metals, suspended solids	Low flux consume high operation pressure
Ultrafiltration method	Good range of size selectivity	-
Nano filtration	Reliable, easy to operate, low energy consumption	Expensive
Reverse osmosis	Applicable to variety of industrial effluents	Expensive
Electro dialysis	Ion selective membrane, effective, removes metals from sludge	High capital cost
Flotation	Widely applied for toxic metals, Selective	Expensive running cost
Electrochemical method	Effective removal through redox Reactions	Expensive
Chemical coagulation and flocculation	Simple, sludge treatment with proper settling	Generate large volume of sludge, require additional treatment
Adsorption	High adsorption capacity restorable Wide pH range, economic, convenient	Host materials requirement for Nano sized adsorbents, Secondary pollution caused due to regeneration

Chitosan is widely used polymer for the adsorption of heavy metal ions from the wastewater. The presence of amino and hydroxyl groups present in molecule acts as a functional sites for the adsorption **[45]**. Moreover, chitosan is low cost, biocompatible, non-toxic, and biodegradable which makes it a promising material for the adsorption application **[46, 47]**. However, the large scale application of chitosan in adsorption is limited due to its instability in water and acids, a lower surface area and weak mechanical properties **[48]**. Therefore, the current research needs to focus on to overcome these disadvantages by modifying the chitosan via crosslinking, surface grafting and various other modification techniques.

1.4 Research aim

The purpose of this thesis is to use the electrospinning technique to develop the novel high surface area porous poly l-lactic acid (PPLLA) nanofibers coated with chitosan, grafted chitosan and crosslinked chitosan for the adsorption of heavy metal ions, synthetic dyes from the aqueous solutions. The electrospun PPLLA is intended to be used as large surface area support material to attach the chitosan and modified chitosan on the surface. It is believed that if the chitosan is well dispersed onto the highly porous support, more active area will be available for the adsorbate. Finally, the fabricated adsorbents will be tested for their adsorption capacity against copper metal ions, methylene blue and rhodamine B dyes in various environments.

1.5 Rationale of objectives

Currently, nanofibers produced via electrospinning and chitosan have been suggested as adsorbents for the adsorption of contaminants from wastewater. Additionally, the development of modified PLLA hydrophobic porous nanofibrous membranes with high surface area for the improved adsorption capacities and fast adsorption rates is also promising. Three possible scenarios can be forecasted for the modification of porous membranes with chitosan that are pure chitosan coating on porous nanofibers, chitosan grafting on dopamine modified porous membranes and APTES crosslinked chitosan coating on porous nanofibers. These three adsorbent membranes can be used remove pollutants from wastewater that effects the human health.

As mentioned earlier, recent evidence suggests that chitosan may have a direct role in the adsorption of contaminants from water because of the amino and hydroxyl groups present on its back bone. In light of the findings linking high surface area porous nanofibers and modified chitosan, it is predicted that modifying the chitosan with materials containing free sites for adsorption and coating these on porous nanofibrous membrane can enhance the adsorptive capabilities and rates from the wastewater solutions. This hypothesis will be tested in the current study and are described in the sections which follows.

1.6 Research objectives

The main objectives of this work identified from the literature review in part 2 of this thesis are:

1. To fabricate the porous poly l-lactic acid nanofibers with high surface area by using electrospinning. First, the nanofibers are produced by using solvent/non-solvent to make the PLLA electrospinning solution. After electrospinning the PLLA solution, the nanofibrous membranes are immersed in the acetone to induce the porosity in the membranes. These porous nanofibrous membranes are used as a large surface area support material to immobilize the adsorbents such as chitosan for adsorption applications.
2. To coat the chitosan in various concentrations on the porous PLLA nanofibrous membranes to adsorb the copper ions from the aqueous solutions. The chitosan is coated on the support material by using a simple direct immersion method.

3. To self-polymerize the dopamine on porous PLLA membranes to form a nano layer of polydopamine. Meanwhile, chitosan is grafted on the polydopamine coated support material to provide more active sites such as amine and hydroxyl to enhance the adsorption of copper ions.
4. To chemically crosslink the chitosan with 3-aminopropyltriethoxysilane and immobilize it on porous PLLA support membranes. The crosslinker will provide more stability to chitosan in marine environments without reducing the functional groups on chitosan. These membranes are efficiently used to enhance the adsorption of toxic methylene blue and rhodamine B dyes from the industrial wastewater.
5. To comprehensively characterize the adsorbent morphological and chemical properties by using advanced characterization techniques.
6. To evaluate and compare the adsorption performance of fabricated adsorbents against heavy metal ions and dyes in aqueous environments and varying parameters of adsorption such as, pH, initial concentration, time, temperature and adsorbent concentrations.
7. To successfully develop and study the kinetic models and adsorption isotherms to predict the performance of adsorbent in different conditions.

Table 1.3 Comparison of the advantages and disadvantages of nanofibrous membrane adsorbents for the removal of heavy metals from water with those of nano powdery and granular adsorbents (Reprinted from ref [49] Copyright 2021 with permission from Elsevier).

Adsorbent categories	Advantages	Disadvantages
Nanofibrous materials	(1) Large specific surface area and high porosity; (2)Generally high adsorption capacity and fast adsorption rate; (3) Easy to be separated or recycled; (4) Easy to be prepared and functionalized.	(1) Generally poor mechanical properties; (2) Regeneration and mass production are challenging
Nano powdery materials	(1) High specific surface area; (2) Abundant surface active groups; (3)Generally high adsorption capacity and fast adsorption rate.	(1) Easy to be agglomerated and affected by environment; (2) Difficult to be separated or regenerated; (3) Difficult to be large-scale produced and high cost; (4) High risk of secondary pollution.
Granular materials	(1) Usually easy to be prepared or functionalized; (2) Wide sources of raw materials and low cost; (3) Easy to be separated or regenerated.	(1) Low specific surface area; (2) Generally low adsorption capacity and slow adsorption rate.

1.7 Research methodology

The outline of research methodology is shown briefly as a flow chart in the Figure 1.3.

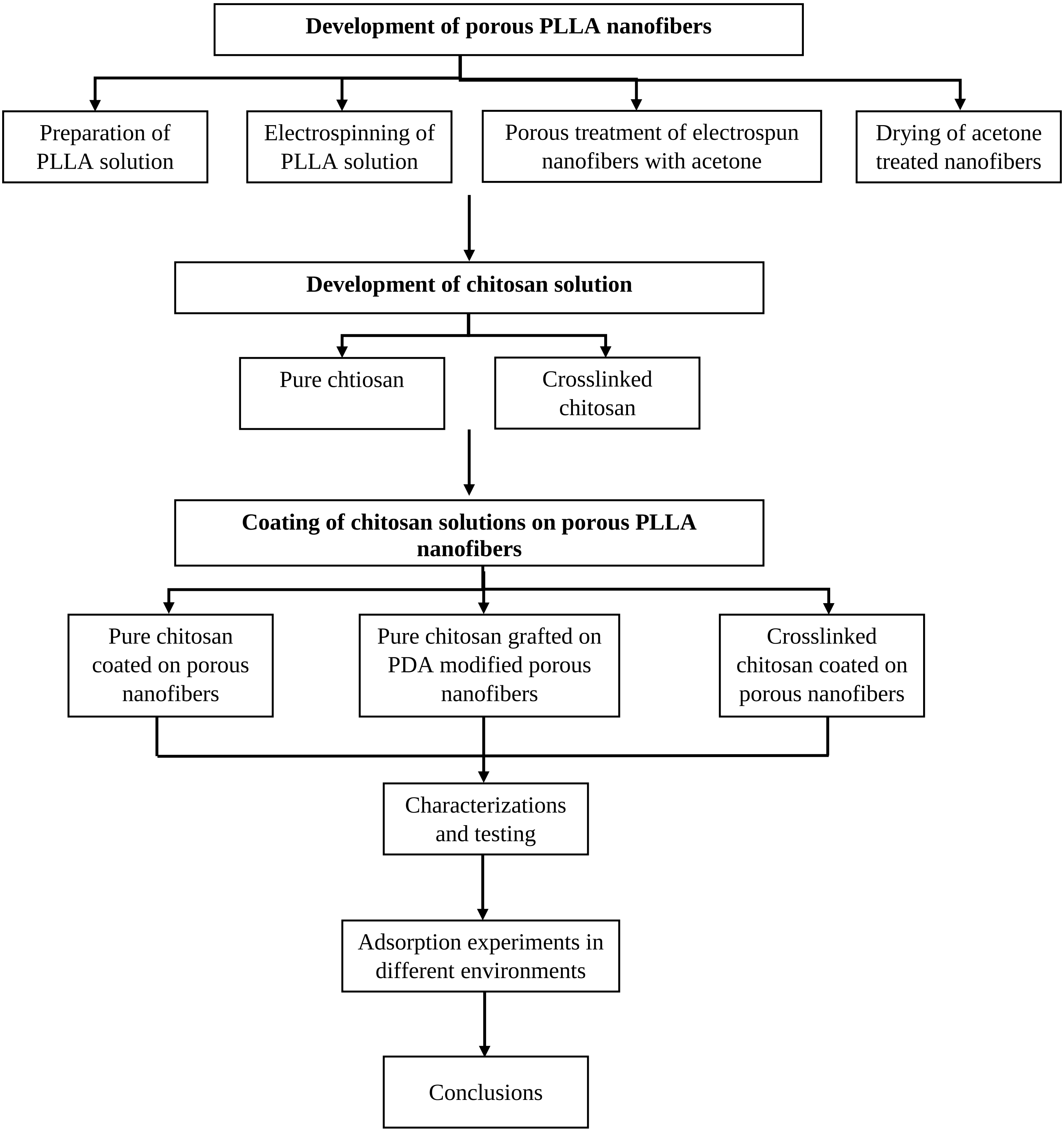

Figure 1. 3 Flow chart of the research methodology

1.8 Thesis outline

The outline of current thesis is described as a brief flow chart in the Figure 1.4.

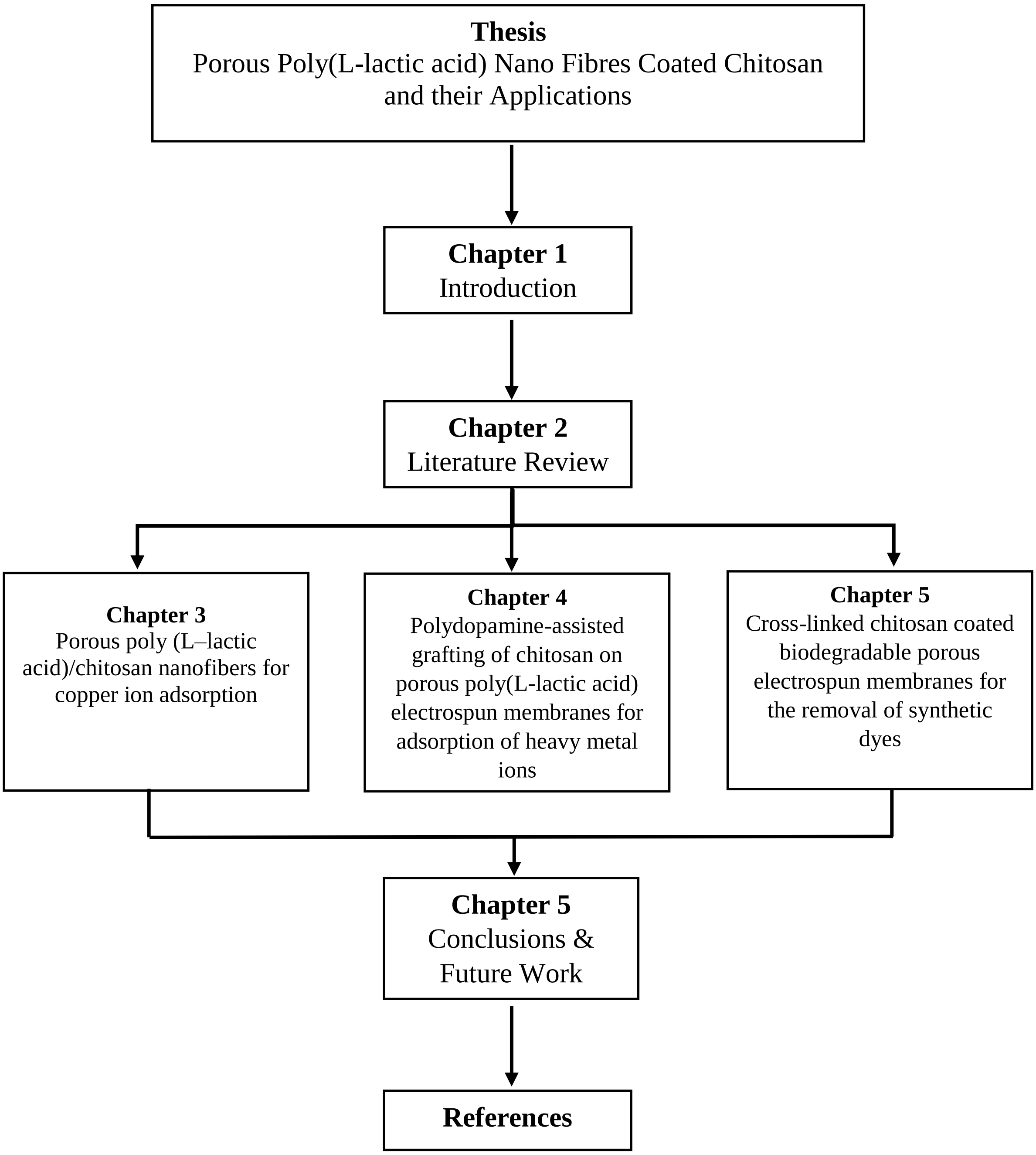

Figure 1. 4 Flow chart of the thesis outline.

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2.Chapter 2

Literature Review

2.1 Role of industries in water pollution and advanced physicochemical wastewater treatment methods

2.1.1 Introduction

Various manmade practices like industrial processes are an important component in the climate change and plays a vital role in polluting the fresh water reservoirs. The industries for releasing the toxic pollutants into waterbodies and creating shortage of clean water are: textile, electroplating, tannery, mining, pulp and paper and distilleries (Figure 2.1) **[1, 2]**. These industries use large amounts of fresh water in various processes and discharge the wastewater without proper filtration into the marine environments. This wastewater includes high level of heavy metals, volatile organic compounds, biological oxygen demand, chemical oxygen demand and various other hazardous pollutants **[3]**. Moreover, when this wastewater is directly discharged into ponds and rivers, it affects all the living organisms including human beings **[4]**.

Inadequate treatment of wastewater is a growing public health concern worldwide. The everyday rising demand of industrial products is creating pressure on the natural resources and environment **[5]**. The debate about contamination in water bodies has gained fresh prominence with many arguing that by 2050, the scarcity of clean water will affect the food production, biodiversity and drinking water for the projected human population of 9 billion **[6]**.

Figure 2.1 Industries responsible for global water pollution (Reprinted by permission of Springer Link from ref [7] Copyright 2020).

2.1.2 Industries involved in water pollution

2.1.2.1 Distillery industry

The distillery industries has contributed to the rise in water and soil pollution **[8]**. One study by Uppal **[9]** examined the increased trend in liquor production of 319 distillery units in India, the study shows that the annual production of alcohol was 3.25×10^9 L with the wastewater release of 40.4×10^{10} L. It is believed that, in production of 1 L alcohol, the amount of wastewater released by the molasses based distillery is projected to be as high as 15 L. Recent research has revealed that distillery wastewater has a detrimental effect on both aquatic and terrestrial ecosystem, in terrestrial regions it affects the soil fertility by reducing the amount of manganese, dissolved oxygen and other important minerals, whereas in aquatic environments it destroys almost all of the animals and living organisms **[10]**. Finally, the colour of wastewater that comes from distilleries is dark brown, it is mainly due to the presence of melanoidins, nitrogen, potassium and phosphates.

2.1.2.2 Leather industry

The tannery wastewater has a significant impact on the environment and living organisms. The processing of leather requires huge amount of chemicals and water and 90 % of these compounds are released in the different water sources **[11]**. In this wastewater, different kind of toxic pollutants are present such as, heavy metals, inorganic and organic pollutants, sodium chloride and sulphates **[12]**. Consequently, these contaminants disturbs the everyday normal life of marine creatures **[13]**. Moreover, the sludge coming out of the leather industries are heavily loaded with chromium salts, which is the major source of chromium heavy metal contamination in the water **[14]**.

2.1.2.3 Paper and pulp industry

Paper industry may have been an important factor in global economy. There is evidence that pollutants coming out of paper and pulp production units are responsible for spreading the pollution in air and water **[3]**. Main contaminants like nitrogen and sulphur gases are toxic to the air, whereas heavy metals, organic and chlorinated compounds are released into the fresh water reservoirs. Moreover, this industry is consuming large quantities of clean water and energy **[15]**. In a study investigating the consumption of water in paper industries, Thompson et al **[16]** reported that water usage is still very high (60 m^3/ton paper) despite of using the best available modern equipment. Finally, kumar et al **[17]** identifies high concentration of heavy metals and organic pollutants in paper industry wastewater as the major causes of severe impacts on aquatic life.

2.1.2.4 Textile industry

The textile industry is a dominant contributor in the economies of developing as well as developed countries for a long time. This is the oldest sector that is responsible mainly for providing the bread and butter to the farmers and workers involved in various processes of textile production units **[18]**. However, this industry produce extreme volume of wastewater which contains excessively high colour intensities and organic concentrations that severely affects the health of human beings and aquatic creatures **[19]**. According to the World Bank estimation, approximately 20 % of world water pollution comes from the dyeing and finishing processes in textile industries. Moreover, hazardous research substance centre (HSRC) reported that most of the chemicals used in textile dyeing are very hard to eliminate or degrade **[20]** . Since it was reported in 2005 as a major environmental issue, it is now attracting a lot of interest from clothing and textile manufacturers **[21]**. In another study, it is reported that about 40 % of all the colourings agents used in textile industry contains chlorine, which is a known carcinogen. Also, when these toxic chemicals are released in the air, they can cause allergic reaction in the children even before they are born via inhalation and absorption **[22]**.

2.1.2.5 Mining industry

Mining is an important aspect of industrial processes and it is considered as the origin of all metal related activities. It is a well-known fact that for obtaining the raw materials, the first step is the extraction of materials from the earth crust. Moreover, this process is crucial in all the human activities including the construction of building and convenience daily use tools **[23]**. In 2013, tilton **[24]** described mineral resources as one of the important indicator to the economic and political circumstances of a nation. However, it is reported that wastewater coming out as a result of mining activities contains hazardous pollutants such as, heavy metals, metalloids and cyanides. And these wastes have detrimental effect on the soil, surface and ground water **[25]**. Acid mine drainage (AMD) commonly occurs due to the mining processes and is a real threat to environment due to its treatment cost and complexity. Furthermore, the existence of heavy metals and some metalloids makes the treatment process more complicated.

Therefore, due its high prices and complexity, most of the time AMD is left untreated. Consequently, it is damaging our water reservoirs, animals, and plants lives **[26]**.

2.1.2.6 Electroplating industry

Electroplating can be loosely described as movement of metal ions via electric field towards the electrode for surface coating. This process is mainly used to alter the physical, chemical, and mechanical properties of the particular object. However, the wastewater of this process includes hazardous chemical and by products **[23]**. Moreover, the nature of wastewater is highly acidic. Therefore, it is quite difficult to develop technologies to remove these contaminants from the wastewater **[27]**. In a recent study, Huang et al **[28]** showed the potential of removing some of the metals from electroplating wastewater solutions such as copper, chromium, iron, nickel and zinc.

2.1.2.7 Semiconductor industry

The semiconductor refer to a material which has property of electrical conductivity. Semiconductor is a key material in modern devices such as, computers, radios, televisions, solar cells and many other daily use devices **[29]**. The past thirty years have seen increasing rapid advances in the semiconductor industries. Owing to the high growth of this industry, pressure is also increasing annually for its waste management. The production of semiconductor materials involves high levels of chemicals and metals. Therefore, proper waste management plan is needed for these materials to avoid the huge environmental impact in the future **[30]**.

2.1.3 Techniques for wastewater treatment

2.1.3.1 Chemical precipitation

Chemical precipitation is a process, where the impurities dissolved in the wastewater precipitate out as solid particles **[31]**. Chemical precipitation proved an effective and most widely used process in the 90's and early 2000's industries because of its low cost and simple operation (Figure 2.2) **[32]**. It is mainly used to remove metallic cations from the water, however, it also removes other hazardous substances from the water such as, fluoride, cyanide, phosphate, phenols, aromatic amines, detergents and oily emulsions by barium chloride **[33]**. Zinc, copper, chromium and lead has been removed by hydroxide precipitation using calcium oxide as precipitant **[34]**. Moreover, blue et al **[35]** utilized 1, 3-benzenediamidoethanethiolate to eliminate mercury ions in the pH of 4.7 and 6.4. In a similar research, copper, zinc and lead ions were eradicated with the help of hydrogen sulphide at the optimum pH of 3 **[36]**. Nevertheless, the use of chemical precipitation has been restricted due to the use of expensive chemicals and the higher costs to dispose of the precipitated sludge from the wastewater **[37]**.

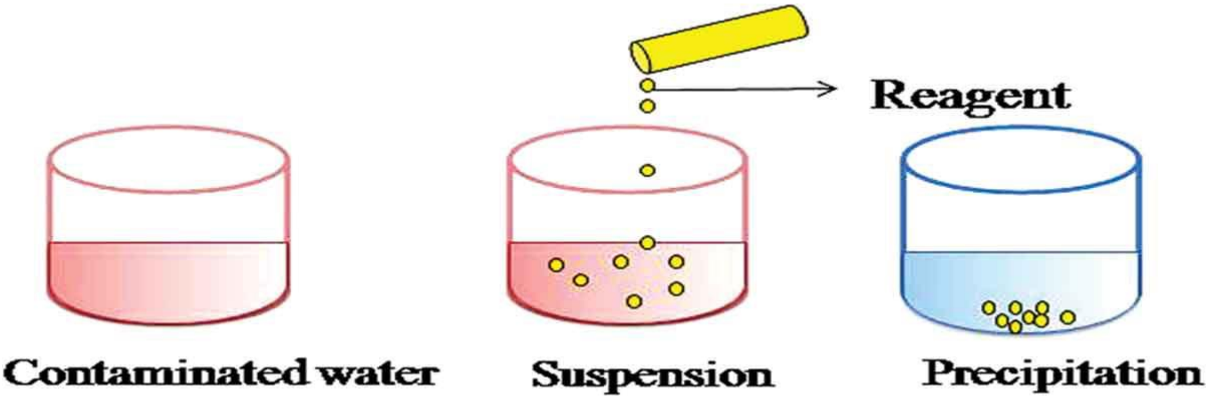


Figure 2.2 Schematic of chemical precipitation method (Reprinted by the permission of Taylor & Francis Group from ref [38] Copyright 2020)

2.1.3.2 Flotation

Flotation has been extensively used in the wastewater treatment plants to remove the industrial pollutants. It uses gas bubbles as a transport medium. These bubbles are allowed to attach to the suspended particles of impurities in the water, developing clusters lighter than the water, initiating the agglomerates to rise and accumulate on the water surface, where they can be eliminated in the form of sludge (Figure 2.3) **[39]**. The process is suitable for removing lighter impurities which are difficult to settle, easy to operate and the maintenance is cheap. However, the generation of micro bubbles and addition of chemicals to improve the process efficiency require higher costs **[40]**. Since 1990's, flotation process is widely used to remove the heavy metal ions from the wastewater **[41, 42]**. In a study, flotation process was used to remove the lead, copper and cadmium ions from the aqueous solution by using plant derived tea saponin adsorbent **[43]**. Moreover, polat and erdogan et al **[44]** applied flotation method to exclude the copper, zinc, chromium and silver metal ions from the wastewater, removal efficiency was reached nearly 74 % at lower pH conditions and 90 % at higher pH values. Similarly, at laboratory scale, medina et al **[45]** reported the removal efficiency as high as 96 % for chromium ions in industrial wastewater. In another study, micro plastics with sizes less than 5 nm were investigated and removed from the four municipal wastewater treatment plants by using flotation and other advanced treatment methods **[46]**.

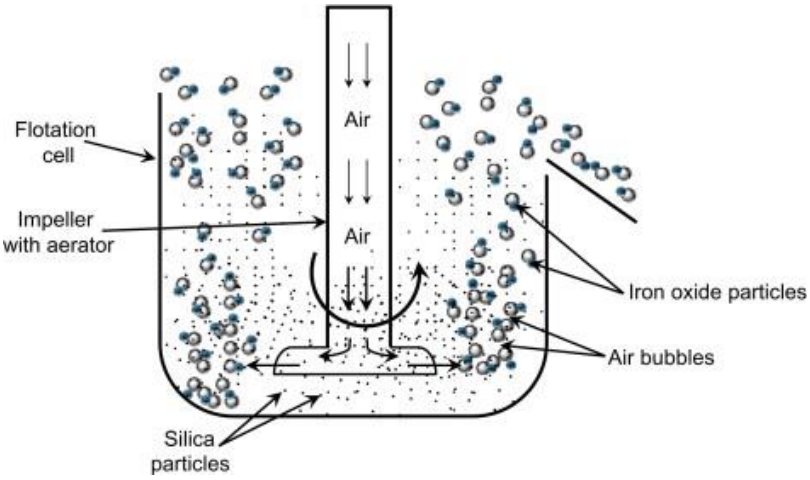


Figure 2.3 Schematic of flotation method (Reprinted from ref [47] Copyright 2014 with the permission of Elsevier).

2.1.3.3 Coagulation and flocculation

Coagulation and flocculation are one of the most significant methods for the wastewater treatment **[48]**. Coagulation and flocculation is done in successive stages. Firstly, coagulation is done by adding the chemical in wastewater to neutralize the charge on the suspended particulates of impurities. Once neutralize, the suspended particles tend to stick together and form micro flocs. Flocculation is the gentle mixing stage to support the coagulants to narrow the gap between particles to form larger agglomerates and settle down. Finally, impurities are removed by the sedimentation process (Figure 2.4) **[49]**. A wide variety of coagulants and flocculants is commercial available such as, aluminium, ferrous sulphate, ferrous chloride, polyferric sulphate and polyacrylamide. El samrani et al **[50]** studied the removal of metal ions by using ferric chloride solution and polyaluminium chloride. Excellent removal efficiency was reported at optimum coagulant concentrations. In 2007, chang and wang **[51]** fabricated novel coagulant made of polyethyleneimine grafted with xanthogenate group to remove the nickel ions from wastewater. The disadvantage of this method is same as of chemical precipitation method, it needs an additional process to remove the agglomerates and excessive sludge, which adds to the additional costs.

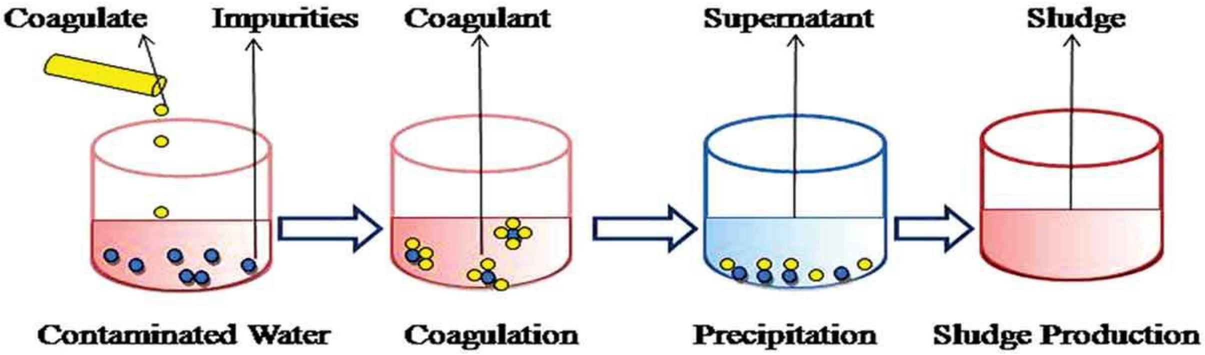


Figure 2.4 Schematic of coagulation/flocculation method (Reprinted by the permission of Taylor & Francis Group from ref [38] Copyright 2020).

2.1.3.4 Membrane filtration

A membrane acts as a barrier, and restricts the transport of impurities present in wastewater. Membrane filtration methods have shown great potential to clean the wastewater by using different types of membrane processes. The most commonly used processes in wastewater treatment are ultrafiltration, nanofiltration and reverse osmosis.

2.1.3.5 Ultrafiltration

Ultrafiltration technology is mostly used to treat the surface waters such as, rivers, lakes and reservoir waters. Now, this method is used for more than ten years by the municipal authorities to clean the drinking water **[52]**. It is an important process because it has the ability to retain the essential components in water and filter the undesirable components. Ultrafiltration membranes have pore sizes in the range of 1 to 100 nm **[53]**. In recent research, scientists studied the possibility to remove the zinc and cadmium ions from wastewater by ultrafiltration membranes made of regenerated cellulose, the membranes were more than 99 % efficient in eliminating the zinc and cadmium heavy metal ions **[54]**. In another study, barakat and schmidt et al **[55]** purified the wastewater from copper, nickel and chromium ions by using polyethersulfone ultrafiltration membranes, they were able to successfully remove the heavy metal ions with the efficiencies of 97.6, 99.1 and 99.5 % for copper, nickel and chromium ions respectively.

2.1.3.6 Nanofiltration

Nanofiltration is referred as a middle process between the ultrafiltration and reverse osmosis. The membranes used in nanofiltration process has large pore sizes than the reverse osmosis as shown in Figure 2.5 **[56]**. This method is widely used to clean the drinking water because it has the ability to retain the divalent ions such as calcium and magnesium, and this can efficiently reduce the hardness of water as compared with the traditional chlorination methods. Moreover, this method is more energy efficient than reverse osmosis **[56]**. In a recent study, researchers have improved the removal efficiency of commercially available nanofiltration membrane i.e. polyamide via chemical modification for the removal of organic micro-pollutants. The efficiency of polyamide membrane was increased from 74 % to greater than 95 % for the bis-phenol A **[57]**. In a different study, soyekwo et al used the combination of polyethyleneimine nanofiltration and ultrafiltration membranes to eliminate the organic dyes and heavy metal ions. The metal ion removal showed excellent efficiency of greater than 98 % and removal efficacies of organic dyes reached the maximum of 99.8 % **[58]**.

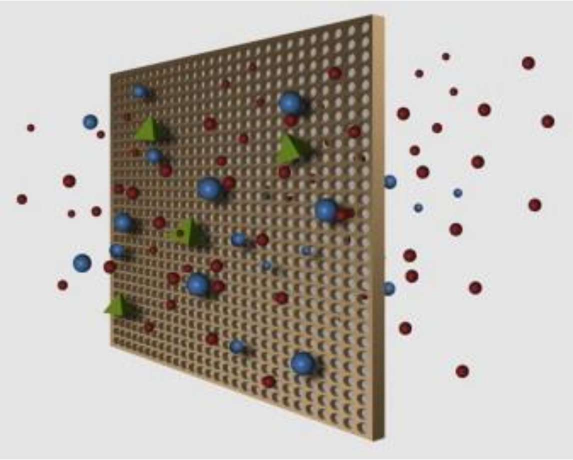


Figure 2.5 Model of basic membrane filtration process (Reprinted from ref [59] Copyright 2014 with the permission of Elsevier).

2.1.3.7 Reverse osmosis

Reverse osmosis technique is widely used to desalinate the sea water and to kill the bacterial, viruses and other germs present in the wastewater **[56]**. The concentrated aqueous solution will flow towards the low concentration solution by the applying the high pressure, the impurities will flow through the semipermeable membrane, while the water is driven through the membrane (Figure 2.6). The reverse osmosis membranes have smallest pore sizes with the diameters ranging from 0.5 to 1.5 nm **[56]**. The major advantage of this method is, it requires limited floor space for high capacity units and its good recovery and rejection rates. However, the large scale application of this process requires high power consumptions for pressure pumps and higher potential of membrane fouling **[56]**. Scientists have investigated reverse osmosis systems for the removal of heavy metal ions, they reported successful removal of copper and nickel ions from the wastewater with the rejection efficiencies of greater than 99.5 % **[60]**. In a recent work, researchers have made a hybrid system by combining reverse and forward osmosis methods to reduce the quantity of phosphorus and ammonia from the water used for irrigation purposes. The removal efficiencies obtained for phosphorus and ammonia were 99 and 97 %, respectively **[61]**.

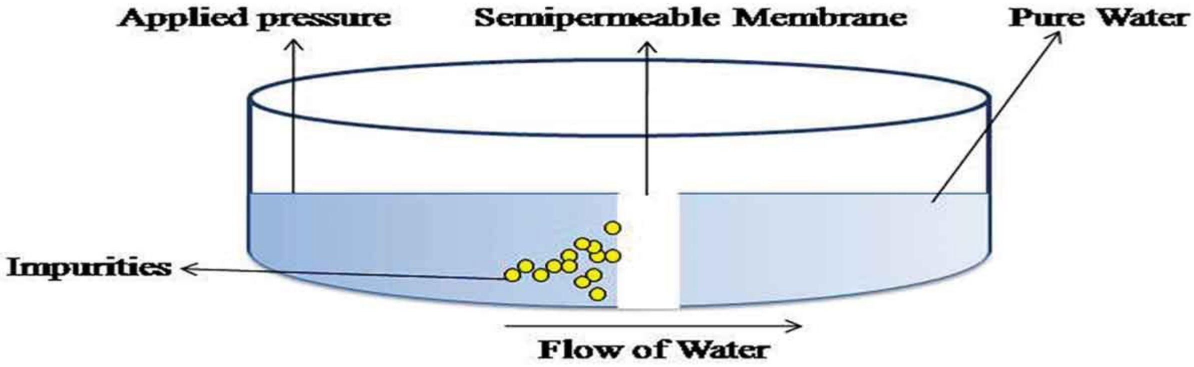


Figure 2.6 Schematic of reverse osmosis process (Reprinted by the permission of Taylor & Francis Group from ref [38] Copyright 2020).

2.1.3.8 Electrochemical methods

Electrochemical treatment is a method of cleaning wastewater by plating out the heavy metal ions on the cathode surface. This method allows to recover the metals in their elemental form. Due to huge amount of electricity consumption involved in electrochemical processes, this method is not widely used **[48]**. Though, recently, with the implantation of strict policies for wastewater discharge, electrochemical methods have gained importance in past three decades **[62]**. The established technologies in electrochemical methods are electrocoagulation, electroflotation and electrodeposition.

2.1.3.9 Electrocoagulation

Electrocoagulation is an electrochemical method, in which coagulants are produced in situ by electrically dissolving the iron or aluminium ions from aluminium and iron electrodes **[48]**. The mechanism of electrocoagulation is described as, the metals ions are produced at the anode and the hydrogen gas is released at the cathode. The hydrogen gas helps the agglomerated metal ions to float at the water surface, finally the metal ions are collected by further processing (Figure 2.7) **[62]**. In previous research, electrocoagulation system was tested for the removal of zinc, copper, nickel, silver and chromium ions by using the aluminium electrode. All the metal ions were successfully hydrolysed, co-precipitated and eliminated at higher concentrations of larger than 5000 mg/L **[63]**. In a recent study by Nigri et al **[64]**, electrocoagulation and adsorption processes were simultaneously used to remove the organic matter, calcium and strontium from the wastewater discharging from petroleum industry. By using multiple techniques at the same time helped to reduce the higher costs associated with using the single method. The scientists also noted the improvement in the removal efficiencies of strontium (72 %), calcium (88 %) and organic matter (52 %) under optimal conditions.

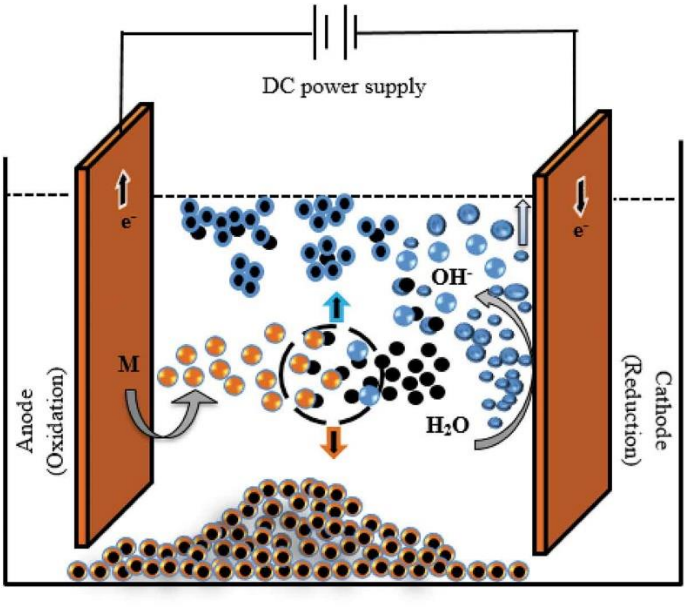


Figure 2.7 Schematic of coagulation process (Reprinted by the permission of Taylor & Francis Group from ref [65] Copyright 2019).

2.1.3.10 Electroflotation

In electroflotation method oxygen and hydrogen bubbles are generated by the electrolysis of water, these tiny bubbles helps the pollutants to float on the surface of water and eventually removed from there **[48]**. The electroflotation system consists of an anode, cathode placed at the bottom of the treatment tank, and the bubbles of oxygen and hydrogen are produced by applying direct current to the water. The operation is simple and electrodes can be modified according the dimensions of the treatment tank (Figure 2.8) **[66]**. Recently, mohtashami **[67]** has designed a continuous flow electroflotation reactor with stainless steel electrode for the removal of automobile industry wastewater. During the painting of the automobiles, the excess paint and rinsing chemicals discharged into the water systems. Under optimum conditions, the researchers were able to remove the suspended impurities by more than 95 % from the wastewater. Belkecam et al **[68]** studied the removal of heavy metal ions such as, iron, nickel, copper, zinc, lead and cadmium with the aluminium electrode. Their work showed that the removal efficiencies of heavy metal ions was greater 99 %.

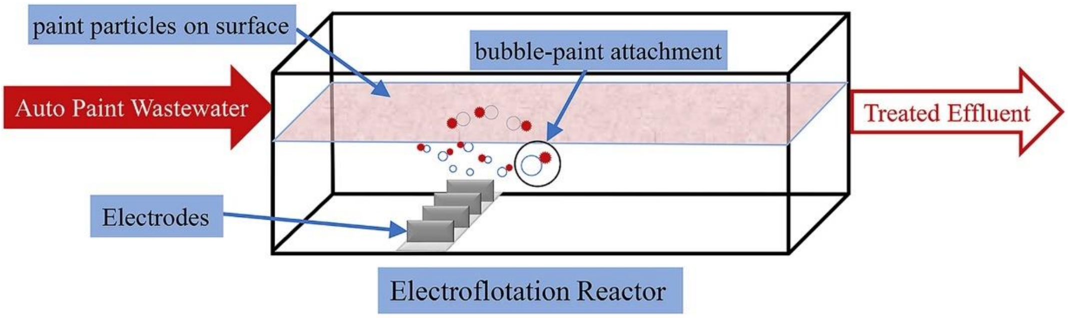


Figure 2.8 Schematic of electroflotation process (Reprinted from ref [67] Copyright 2019 with the permission of Elsevier).

2.1.3.11 Electrodeposition

Electrodeposition is a simple and environmental friendly method to remove the heavy metal ions from wastewater. The electrodeposition system consists of an electrolysis medium, anode and a cathode. Metal ions present in the electrolytic medium reduce at the cathode by the application of electric current provided from the external source and form an atomic layer on the cathode (Figure 2.9) **[69]**. The application of electrodeposition is limited due to the low applied current density, which results in long processing times. In a recent communication, ning et al **[70]** solved this limitation by developing a jet electrodeposition process for the removal of copper ions, which has higher current densities. The scientists reported 97.4 % of copper removal in the short span. In another study, researchers used the pulsed electrodeposition method for the removal of nickel ions from the real jewellery industry electroplating wastewater. The use of fast pulses allow the copper to remove up to 83 % in 115 minutes under optimum environment **[71]**.

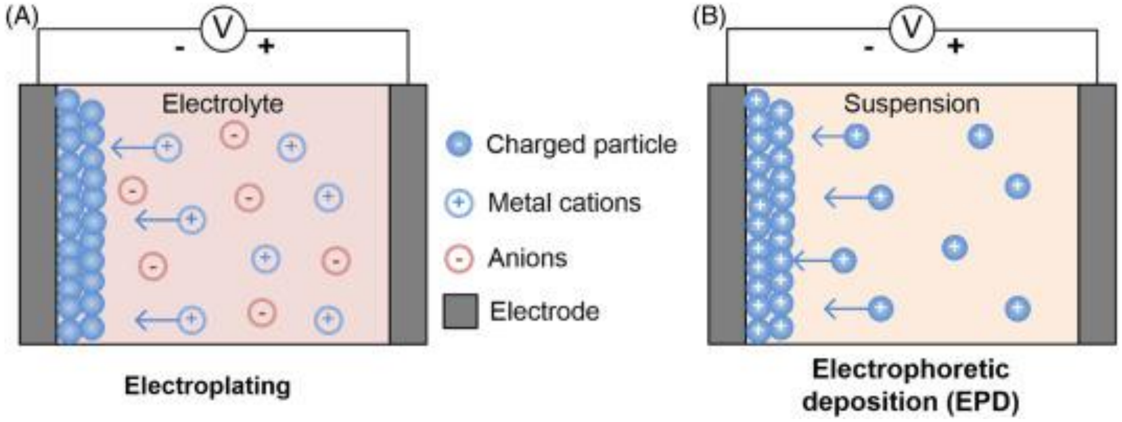


Figure 2.9 Schematics of electrodeposition processes, (A): Electroplating, (B): Electrophoretic deposition (Reprinted from ref [72] Copyright 2018 with the permission of Elsevier).

2.1.4 Adsorption and ion exchange

Adsorption can be broadly defined as a surface phenomenon which includes the transfer of material on the solid surface from its liquid or gaseous environment. It involves capturing of atoms or molecules that collide on the surface. The term adsorbate has come to be used to refer to a substance that is attached onto a surface, and adsorbent refers to the solid onto which the substance is adsorbed (Figure 2.10) **[73]**. It is appropriate to discuss adsorption and ion exchange together because they have similar design configurations. During the removal of water pollutants, combination of physical adsorption, chemical adsorption, ion exchange and precipitation mechanism can occur depending upon the environment of medium such as pH and temperature **[74]**. It is difficult to know which mechanism is happening exclusively during the removal process. Adsorption/ion exchange has been identified as a promising method to remove the contaminants in the wastewater. It is cheap, rapid and simple **[75]**. The major benefits of adsorption is that adsorbents can be reused several time without affecting their removal efficiency and ability to remove contaminants at lower concentrations **[74]**. However, choice of right adsorbent is the key factor, an efficient adsorbent should have a high surface area for high adsorption capacity, easily available, low cost and environment friendly **[76]**. Currently, there are many adsorbents commercially available and are discussed here.

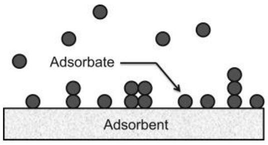


Figure 2.10 Schematic of adsorption (Reprinted from ref [76] **Copyright 2018 with the permission of Elsevier).**

2.1.4.1 Activated carbon

Activated carbon is the most used adsorbent globally for the removal of water pollutants such as, heavy metals, dyes and various other organic impurities **[48]**. The presence of large porosity in activated carbon structure leads to the higher surface area, which makes it an excellent adsorbent for the heavy metals (Figure 2.11). The precursors use to make activated carbon are mainly based on coal which includes lignite, peat and wood **[77]**. The manufacturing process consists of carbonization and activation. In carbonization process, the material is heat at 400-600 °C in the absence of oxygen in order to remove the impurities from the raw material such as tar and other hydrocarbons **[77]**. The activation is providing functional groups on the activated carbon surface for the adsorption by chemical or physical methods. Various chemicals are being used to activate the carbon adsorbents, which includes zinc chloride, phosphoric acid, sulphuric acid and potassium hydroxide **[78]**. These days, numerous scientists are studying the use of activated carbons to remove the heavy metal ions and organic pollutants **[79, 80]**. However, now a days, due to the high prices, the coal based activated carbon increase the cost of the adsorption process.

Now, the research is focused towards finding an alternative source for the activated carbon or modifying the currently available activated carbon with additives or composites. In various studies, additives like alginate **[81]**, tannic acid **[82]**, magnesium **[83]** and surfactants **[84]** are proved to be the effective adsorbents for the removal of heavy metal ions. Moreover, manufacturing activated carbon from the unconventional carbonaceous precursors has been reported actively in the literature. Guo et al **[85]** stated the production of activated carbon from the poultry litter waste for the treatment of metal contaminated wastewater. They reported the higher adsorption capacities of litter based activated carbon as compared to the commercially available activated carbon derived from bituminous coal and coconut shell. Moreover, Dias et al **[86]** reviewed the waste materials for the preparation of activated carbon.

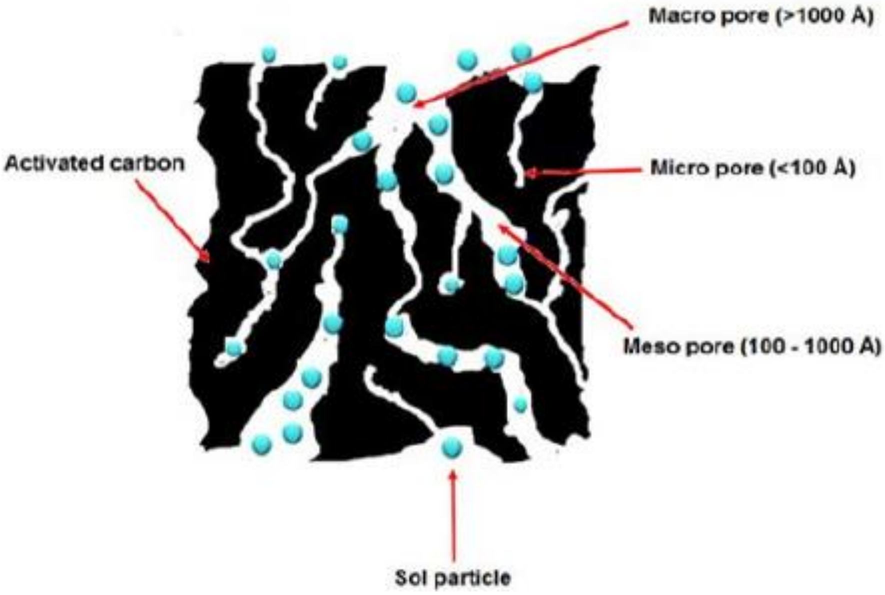


Figure 2.11 Schematic of activated carbon [87].

2.1.4.2 Other low cost adsorbents

Zeolites are good alternate adsorbents for the expensive activated carbon adsorbents, because they are low in cost and easily available worldwide. Zeolites occur naturally as well as can be manufactured commercially. The zeolitic structure is highly porous commonly made of aluminium and silicon **[77]**. The positively charged ions such as, calcium, magnesium and potassium are weakly bound in the porous structure and can be exchanged easily with other ions in the solution, and thus possess the ion exchange abilities (Figure 2.12). Zeolites has many species present in the nature, so far clinoptilolite is widely available and repeatedly studied for the adsorption applications by the scientists **[74]**. Recently, zanin et al **[88]** investigated clinoptilolite zeolite for the adsorption of copper, chromium and iron heavy metal ions from the paint industry wastewater. The removal efficiencies reported at room temperature and pH 4 were 95.4 %, 96.0 % and 85.1 % for the iron, copper and chromium ions, respectively. Moreover adsorption mechanism was best described by the pseudo first order kinetics and Langmuir isotherms. In another study, similar adsorbent was used to remove the amido black 10B and safranine T dyes from the wastewater. The adsorption ability for amido black 10B dye was limited, however, the removal efficiency was good against the safranine T dye in optimum conditions. Both adsorption models best fitted with the Langmuir isotherms **[89]**.

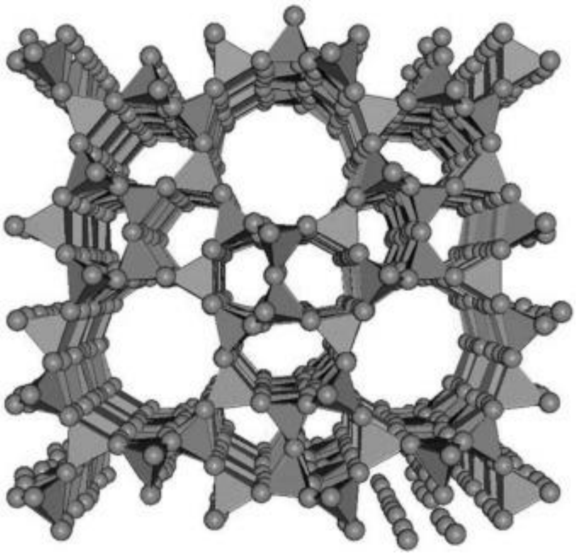
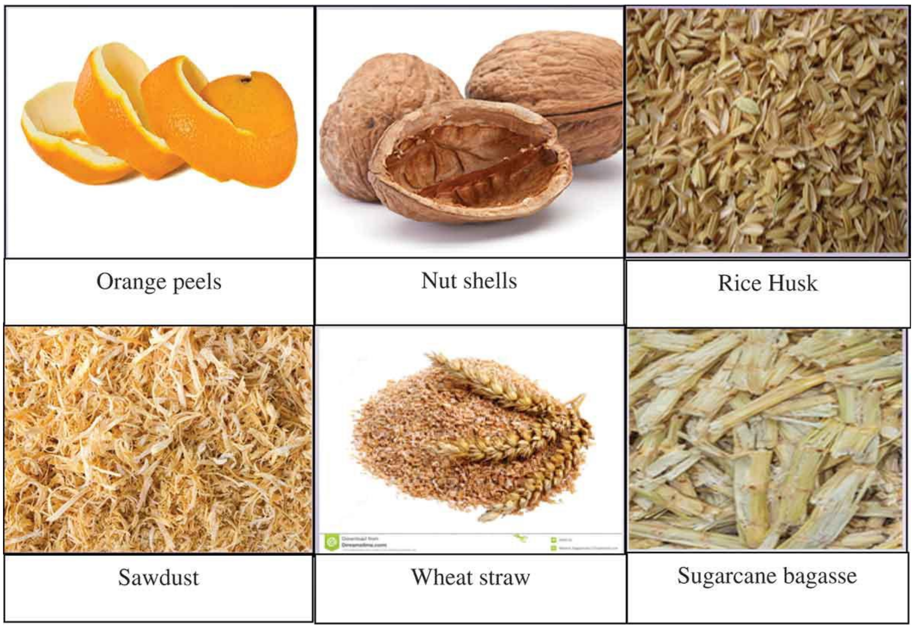


Figure 2.12 Structure of ZSM-5 zeolite (Reprinted from ref [77] Copyright 2006 with the permission of Elsevier).

Chitosan is another excellent bio adsorbent which is most abundant material after cellulose in nature. Moreover, it is hydrophilic, biodegradable and antibacterial **[90]**. It is mainly derived from deacetylation of chitin, also, it can be found naturally in the cell wall of some fungi such as mucorales strain. Previous studies reported that chitosan showed six time higher adsorption capacities for the water pollutants as compared to the chitin **[90]**. This is due to the presence of functional groups on the chitosan backbone such as, amino and hydroxyl groups **[91]**. Chitosan is commercially available at the market price of 15.43 $/kg. Chitosan has wide use in various biomedical applications and has been used as adsorbent for removal of heavy metal ions in various studies **[92, 93]**. Note, a detail review on chitosan for adsorption heavy metal ions is discussed in the further chapters of this thesis.

Peat moss is extensively available natural material. It is a complex soil substance which contains cellulose and lignin as major constituents. It structure of peat moss is highly porous and have large surface area. It is also available commercially in the market at relatively cost of 0.023 $/kg **[77]**. In a recent study, scientists used sphagnum peat moss to rapidly purify the real lead contaminated water. They reported that more than 95 % lead was eliminated from the water in 60 seconds under optimum pH, initial concertation and temperature conditions **[94]**. Moreover, peat moss derived from bio char was reported to effectively remove the volatile organic compounds commonly found in ground water of South Korea such as, benzene, toluene, ethylbenzene, p-xylene, trichloroethylene and tetrachloroethylene **[95]**.

Furthermore, various low cost natural adsorbents have been developed from the agricultural waste and industrial by products and applied for the removal of heavy metal ions from the wastewater (Figure. 2.13) **[74]**. For example, rice husk **[96]**, saw dust **[96]**, sugarcane bagasse **[97]** and coconut husk **[98]** are some of the adsorbents, whose simplicity and effectiveness has been proven in several studies to remove the water pollutants.



Orange peels

Nut shells

Rice Husk

Sawdust

Wheat straw

Sugarcane bagasse

Figure 2.13 Other low cost adsorbents (Reprinted by the permission of Taylor & Francis Group from ref [38] Copyright 2020).

2.1.5 Factors affecting the process of adsorption

2.1.5.1 pH

pH is a common variable which has considerable impact on the adsorption of pollutants from the aqueous solutions. The pH of the solution can affect the surface nature of adsorbent and ionization state of the adsorbate. In solid-liquid adsorption process, adsorption occurs by the interaction of adsorbate hydrogen and hydroxide ions with adsorbent surface. Therefore, pH of the solution greatly affects the adsorption process **[99]**. For example, in a recent study the adsorption of copper ions from the water was studied in the pH range from 2 to 7. They reported a drop in adsorption capacity of copper in the pH greater than 7, this is due to the fact that above pH 7 precipitation of copper ions occur and they converted into copper hydroxide **[100]**.

2.1.5.2 Adsorbent dose

The active sites for the removal of pollutants rise with the increase of adsorbent dose in the solution. Nevertheless, with the increase in adsorbent mass the maximum adsorption of the contaminants decreases, which is due to the presence of unsaturated sites during the adsorption process **[99]**. Similar results have been reported in previous studies, for example, scientists examined that with the increase of saw dust dose the removal percentage of chromium ions risen from 20 to 100 %, whereas, the adsorption capacity was decreased from 2.72 to 1.7 mg/g **[101]**.

2.1.5.3 Surface area

As described earlier, adsorption is referred to as surface phenomena, therefore, surface is directly proportional to the adsorption capacity. Surface area can broadly be defined as available space on the adsorbent for the adsorption of pollutants. Smaller adsorbents or adsorbents with high porosity have large surface area while, large adsorbents have smaller area accessible for the adsorption. Recently, various studies have been conducted to prepare high surface area adsorbents for the removal of water contaminants such as, mesoporous large surface area chitosan/PEO membrane for the removal of divalent ions form the wastewater **[102]** and, very high surface area nano porous geo polymer for the adsorption of copper ions **[103]**.

2.1.5.4 Co-existing ions

The industrial wastewater consists of different co-existing ions, which decreases the removal efficiency of adsorbent by giving competition to adsorbate ions to retain the functional sites on the adsorbent **[99]**. The competition between ions depend on their molecular weight of adsorbent, solute quantity and adsorbate relative affinity towards adsorbent. Terangpi et al. **[104]** reported that presence of nitrate and phosphate ions in the wastewater reduces the adsorption capacity of chromium ions on aniline-formaldehyde condensate polymer by 30 %.

2.1.5.5 Temperature

The temperature of batch adsorption process significantly affects the stability of adsorbate ions, properties of adsorbent and interaction between adsorbent and adsorbate. Thermodynamic parameters calculated from the vont hoff's plot gives information about the nature of adsorption phenomena, whether it is exothermic or endothermic, random or spontaneous **[99]**. For example, in a study, scientists showed that with increasing temperature, the adsorption capability of polymeric gels decreases, which shows that adsorption reaction is exothermic in nature for the removal of methylene blue and malachite green **[105]**.

2.2 A review on chitosan for the removal of heavy metals ions

2.2.1 Overview

This chapter was published as a review paper "A review on chitosan for the removal of heavy metal ions" in Journal of Fibre Bioengineering and Informatics (2019). In this review, extensive literature was compared on removal capacities of heavy metal ions from wastewater using chitosan and its derivatives. Moreover, mechanism of chitosan was reviewed to adsorb the heavy metal ions. Finally, future recommendations and conclusion was provided.

2.2.2 Author contributions

I drafted the article and substantially contributed to the conception and design of the article and interpreting the relevant literature and published. Madeeha Tabassum substantially contributed to the conception and design of the article and interpreting the relevant literature. Jaishen Li drafted the article and revised it critically for important intellectual content. Hugh Gong revised it critically for important intellectual content.

2.2.3 Citation

Qasim Zia, Madeeha Tabassum, Hugh Gong, et al. A Review on Chitosan for the Removal of Heavy Metals Ions [J]. Journal of Fibre Bioengineering and Informatics, 2019, 12(3): 103-128.

2.2.4 Review paper: A review on chitosan for the removal of heavy metals ions

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2.2.5 Abstract

There has recently been an increasing interest in water treatment methods as a result of growing concerns over shortages of clean water. This paper aims to review the past and present researches on chitosan for the adsorption of heavy metals from the wastewater. Adsorption is considered to be the most efficient method for the removal of metal impurities from drinking water. Chitosan, a deacetylated derivative of chitin, has many commercial applications due to its biocompatibility, nontoxicity, and biodegradability. Moreover, amine groups are present on the backbone of chitosan. For this reason, chitosan has been used for the adsorption of heavy metals. To begin with, mechanism of adsorption of heavy metal ions on chitosan and disadvantages of heavy metal ions were reviewed. Further, a detailed review had been done on the adsorption capacities of crosslinked chitosan, chitosan nanofibers, chitosan nanoparticles, chitosan composites, modified/pure chitosan, and porous chitosan. Lastly, research gaps and future recommendations were given for further development and accurate results of adsorption.

2.2.6 Introduction

2.2.6.1 The chemical construction of chitosan

Chitosan is linear amino polysaccharide consisting of two basic units, glucose amine and N-acetyl glucosamine, acquired from the deacetylation of chitin in the alkaline environment

[106]. Chitin is a natural polymer discovered 200 years ago. It is mainly extracted from cell walls of fungi as well as from the exoskeleton of crustaceans such as shrimp and crabs **[107-111]**. The structure of chitosan is composed of (1, 4)-linked 2-amino-2-deoxy-β-D-glucan as shown in Figure 2.14, its chemical name is poly [-(1, 4)-2-amino-2-deoxy-D-glucopiranose] **[110, 112, 113]**. The structures of chitosan contain amine (NH_2) groups, and as a result have good medical properties for instance biodegradability, biocompatibility and excellent antibacterial activity. It is the only cationic natural occurring polymer **[90, 114]**. Furthermore, chitosan is extensively used for the adsorption of heavy metal ions due to the presence of amine and hydroxyl groups **[115-117]**.

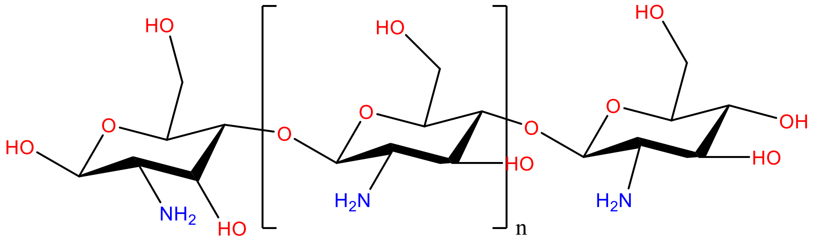

Figure 2. 14 Chemical construction of chitosan.

2.2.6.2 Complex formation of chitosan with heavy metal ions

The ability of chitosan to adsorb metal ions through forming complexes was discovered when researchers expressed interest in it **[118-121]**. Studies show that the complexation ability of chitosan is influenced by its physical state, when it is in the form of powder, gel, fibre, particles or films **[122, 123]**. The degree of acetylation is however considered to be the major factor in the complexation process, proved by Micera **[124]** and Kurita **[125]**.

Potentiometry is considered to be the fundamental method to describe the complex formation of chitosan with metals by studying acid-base reactions and metal-ligand interactions. The acid accepts a pair of the electron (metal) from the base (chitosan) and forms a covalent bond with the metallic ions. The only one free site available in chitosan monomeric unit, amine groups, initiates the covalent bonds with metallic ions. Equations (1), (2) and (3) described the interaction of chitosan with metals **[122]**.

$$\text{Chitosan-NH}_2\text{+H}_3\text{O}^+ \rightleftharpoons \text{Chitosan- NH}_3^+\text{+ H}_2\text{O} \quad \textbf{(1)}$$

$$\text{Chitosan- NH}_2\text{+ M}^{n+} \rightleftharpoons \text{(Complex)}^{n+} \quad \textbf{(2)}$$

$$\text{Chitosan- NH}_3^+\text{+ M}^{n+}\text{+ H}_2\text{O} \rightarrow \text{(Complex)}^{n+}\text{+ H}_3\text{O}^+ \quad \textbf{(3)}$$

M. Rhazi et al **[118]** studied the adsorption process of copper at different pH values. It was discovered that when the pH of a solution is less than 5.30 there was no or very small complex formed between copper Cu (II) ions and chitosan. When pH is greater than 5.30, amino groups made a covalent bond with copper ions and formed $[Cu(-NH_2)]^{2+}$ complex as shown in Figure 2.15 and in the following equation (4) and (5):

$$\text{Cu}^{2+}\text{+-NH}_3^+\text{+H}_2\text{O} \rightleftharpoons \text{[Cu(-NH}_2\text{)]}^{2+}\text{+H}_3\text{O}^+ \quad \textbf{(4)}$$

$$\text{Cu}^{2+}\text{+-NH}_2 \rightleftharpoons \text{[Cu(-NH}_2\text{)]}^{2+} \quad \textbf{(5)}$$

Another type of complex was also investigated when pH goes above 5.80 where another amino group is incorporated $[Cu(-NH_2)_2]^{2+}$as shown in Figure 2.15 and in the equations (6) and (7).

$$\text{[Cu(-NH}_2\text{)]}^{2+}\text{+-NH}_3^+\text{+H}_2\text{O} \rightleftharpoons \text{[Cu(-NH}_2\text{)}_2\text{]}^{2+}\text{+H}_3\text{O}^+ \quad \textbf{(6)}$$

$$\text{[Cu(-NH}_2\text{)]}^{2+}\text{+-NH}_2 \rightleftharpoons \text{[Cu(-NH}_2\text{)}_2\text{]}^{2+} \quad \textbf{(7)}$$

This complex is stable up to pH 7.7; beyond this pH, copper hydroxides will precipitate and the procedure will become difficult to study.

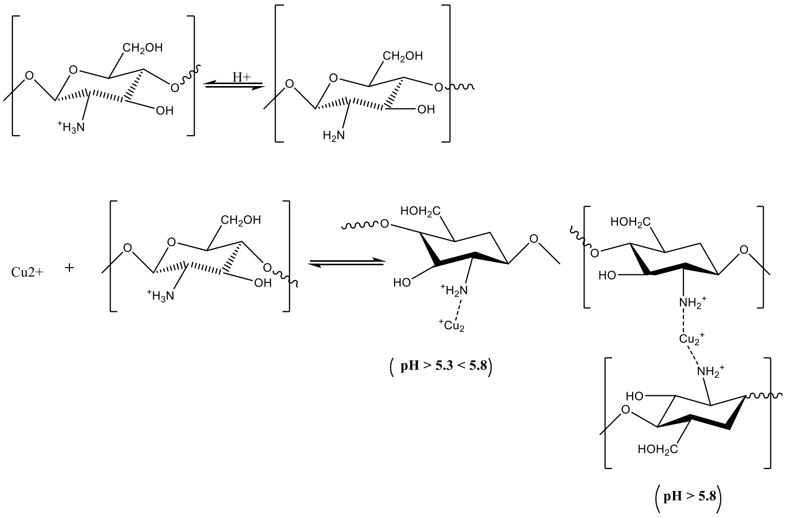

Figure 2.15 Structures of chitosan - copper complexes.

2.2.7 Crosslinked chitosan for the removal of heavy metal ions

In crosslinked chitosan, polymeric chains are interconnected with cross linkers, leading to the formation of a 3D network. Chitosan was crosslinked with diethylenetriaminepentacetic acid when eliminating Cr (VI) ions from aqueous solution **[126]**. In another study, chitosan was crosslinked with trimesic acid for a similar purpose **[127]**. The adsorption coefficient was discovered to be higher with the latter crosslinking acid i.e. 192.3 mg/g and 129.53 mg/g when compared with the former at an optimized pH of 3 and 2. Furthermore, both were discovered to be beneficial for removing Pb (II) and Fe (II) ions from chrome plating effluent. Chitosan (CS)/Polyvinyl Alcohol (PVA) physically crosslinked nanoparticles were developed for the adsorption of manganese Mn (II) ions from an aqueous solution. Mn (II) is a major pollutant, which affects the colour, taste and odour of water. The adsorption capability of Mn (II) ions on CS/PVA nanoparticles was studied as a function of pH, adsorbent dose, contact time and different concentrations of solutions **[128]**. Adsorbent dose had a major effect on the removal of heavy metal ions; this can be attributed to the enhanced surface and more binding sites on

CS/PVA nanoparticles. It was found that 83.5% metals ions were removed for 20 mg/L at 0.8g in 100 mL, which is similar to their earlier studies on the removal of Mn (II) ions from water **[129]**.

In a different study, epichlorohydrin was chosen to crosslink with chitosan for the adsorption of Cu (II), Pb (II) and Zn (II) ions from an aqueous solution. The adsorption capacity for Cu(II) (35.40 mg/g) was found to be highest when compared to Pb (II) (13.05 mg/g) and Zn (II) (10.21 mg/g) **[130]**. However, when compared to pure chitosan, crosslinking has a negative effect on the adsorption of Pb (II) and Zn (II) ions, decreasing their removal efficiencies up to 6.39% and 1.07%. However in the case of Cu (II), it showed an increase in efficiency by more than twofold **[131]**. Similar studies on the adsorption of Cu (II), Pb (II) and Zn (II) by chitosan crosslinked with glutaraldehyde exhibited correlates with the results in **[132]**. Table 2.1 shows the maximum adsorption capacities of crosslinked chitosan.

Table 2. 1 Maximum removal ability for heavy metal ions of crosslinked chitosan.

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption (q_{max}) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan-clay/Epicholorhydrin	Ni (II)	32.36	6.0	**[133]**
		Cd (II)	72.31		
2	Chitosan-PVA/Glutaraldehyde	Cd (II)	142.9	6.0	**[134]**
3	Chitosan/Silica	Cr (VI)	28.88, 23.40	5.0-6.0	**[135]**
4	Chitosan-halomonas/Glutaraldehyde	Pb (II)	24.15	5.0-7.0	**[136]**
		Cd (II)	23.88		
5	Chitosan/ 6,6 - piperazine-1,4-diyldimethylenebis (4-methyl-2-formyl) phenol	Cu (II)	76.88		**[137]**
		Ni (II)	38.15		
		Co (II)	27.11		

		Mn (II)	23.62	6.5-8.5	
		Fe (II)	23.45		
		Cd (II)	58.45		
		Pb (II)	84.94		
6	Chitosan/Epichlorohydrin	Cu (II)	35.46	6.0	**[117]**
		Zn (II)	10.21		
		Pb (II)	34.13		

2.2.8 Chitosan composites for the removal of heavy metal ions

To enhance the removal and adsorption efficiency of hexavalent Cr (VI) ions, chitosan, graphene oxide and 1, 2-cyclohexylenedinitrilotetraacetic acid nanocomposite was synthesized for the first time. Graphene has more free groups available for adsorption i.e. hydroxyl, carboxyl and epoxy, which results in improved adsorption of heavy metals from aqueous solutions. Maximum adsorption of 166.98 mg/g for Cr (VI)ions was achieved in optimized conditions of pH, temperature and time **[138]**. In previously reported studies on the adsorption of Cr (VI) ions by chitosan composites, the highest adsorption capacity of 153.85 mg/g was reported **[139]**. In a further study, chitosan/organoclay composites were developed and the removal efficiency was also found to be less than an above-reported study that is 128.43 mg/g **[140]**. The adsorption capacity of chitosan can be varied by degree of deacetylation **[141]**. Habiba et al. studied the degree of effectiveness for the deacetylation of chitosan in chitosan/PVA/TiO_2nanocomposites. They proved that a degree of deacetylation increased the adsorption efficiency of the composite. This is evident from the presence of NH_2 groups in deacetylated chitosan which functions as essential sites for adsorption **[142]**.

Comparative adsorption of Pb (II), Cu (II) and Cd (II) ions were investigated by chitosan/montmorillonite (Mt) composite **[143]**. Mt was used because of its good cation exchangeability [144]. Composite was reported to have the highest adsorption capacity for Pb

(II).The sequence of the adsorption was Pb (II)> Cu (II)> Cd (II). This is due to the higher electronegativity of Pb (II) (3.29) as compared to Cu (II) (2.98) and Cd (II) (2.71) correspondingly. This is due to the high affinity between two atoms when the electronegativity difference of N or O is smaller **[145-148]**. In another work, chitosan/PVA magnetic composite was prepared by co-precipitation method **[149]** for the adsorption of Cu (II) ions. This composite can adsorb up to 143.0mg/g of Cu (II) ions from wastewater **[150]**.

A novel composite Chitosan/Hydroxyapatite membrane was prepared for removal of Pb (II), Co (II) and Ni (II) ions from aqueous solutions. Composite membrane demonstrated maximum adsorption ability for Pb (II) i.e. 296.7 mg/g as compared to Ni (II) (213.8 mg/g) and Co (II) (180.2 mg/g) **[151]**. In comparison to other studies, chitosan/clinoptilolite composite membrane claimed the highest adsorption of Co (II) (467.9 mg/g) **[152]** and chitosan /silica have enhanced the ability to adsorbed Ni (II) (254.3 mg/g) **[153]**. Further studies showed that chitosan/hydroxyapatite composite was used for removal of Fe (II) ions from drinking water and adsorption capacity of 6.753 mg/g was reported **[154]**.

Table 2.2 Maximum removal ability for heavy metal ions of chitosan composites.

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption (q_{max}) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/CDTA/GO	Cr (VI)	166.98	2.0-3.0	**[138]**
2	Chitosan/Clay	Cu (II)	181.5	7.0	**[155]**
3	Chitosan/Alumina	Cu (II)	86.2	4.0	**[156, 157]**
		Ni (II)	78.1		
		As (III)	56.50		
		As (V)	96.46		
4	Chitosan/Glucosamine	Cr (VI)	153.85	4.0	**[139]**

5	Chitosan/Graphene Oxide	Pb (II)	76.94	5.0	**[158]**
6	Magnetic Chitosan	Cr (VI)	17.29	1.0-3.5 for Cr(VI) 6.0-7.0	**[159, 160]**
		Pb (II)	27.95		
		Hg (II)	23.03		
		Cd (II)	27.83		
		Ni (II)	22.07		
		Cu (II)	216.6		
7	Chitosan/PVA	Cu (II)	143.0, 193.39	6.0	**[150, 161]**
8	Chitosan/Sulfydryl/Graphene Oxide	Cd (II)	177.0	5.0	**[162]**
		Pb (II)	447.0		
		Cu (II)	425.0		
9	Chitosan/Anaerobic Granular Sludge	Pb (II)	97.97	6.0	**[163]**
		Cu (II)	83.65	3.0	
10	Chitosan/PVA/Silk Fibroin	Pb (II)	194.099	6.0	**[164]**
11	Chitosan/Fe-Hydroxyapatite	Pb (II)	1385.0	-	**[165]**
12	Chitosan/Magnetite	Ni (II)	63.33	4.0-6.0	**[166]**
		Pb (II)	52.55		
13	Chitosan/Perlite	Cu (II)	196.07	3.0-4.5	**[167-170]**
		Ni (II)	114.94		
		Cd (II)	178.6		

		Cr (VI)	153.8		
		Cu (II)	104.0		
14	Chitosan/Silica	Ni (II)	254.3	5.0	**[153]**
15	Chitosan/PVC	Cu (II)	87.9	4.0	**[171]**
		Ni (II)	120.5		
16	Chitosan/Sand	Cu (II)	10.87, 8.18	4.2	**[172]**
		Pb (II)	12.32		
17	Chitosan/Montmorillonite	Cr (VI)	41.67	4.0	**[173]**
18	Chitosan/Alginate	Cu (II)	67.66	6.0	**[174]**
19	Chitosan/Calcium Alginate	Ni (II)	222.2	5.0	**[153]**

In a different research, chitosan/clinoptilolite composite claimed to have good adsorption capacity against Uranium (UO_2^{2+}) and Thorium (Th^{4+}) ions from radioactive solutions. The maximum adsorption for Th^{4+} 328.32mg/g and 408.62mg/g for UO_2^{2+} ions were recorded **[175]**. Similar material was also used by incorporating zeolite particles for the removal of Cu(II), Co(II)and Ni(II)ions in further studies and the highest adsorption capacity 11.32 mmol/g, 7.94mmol/g and 4.4209 mmol/g was reported **[152, 176, 177]**. Table 2.2 illustrates the maximum adsorption capacities of chitosan composite.

2.2.9 Chitosan nanofibers for the removal of heavy metal ions

Polyethylene oxide (PEO)/CS nanofibers were tested for their capacity to adsorb Ni (II), Cu (II), Pb (II) and Cd (II) heavy metals from water. Under optimal conditions of pH, temperature and time, results showed the adsorption potential of nanofibers in increasing order, Ni (II) > Cu (II) > Cd (II) > Pb (II). This is due to smaller ionic radius of ions, as radius decreases charge density will increase and number of available sites for adsorption would be enhanced. Therefore, adsorption efficiencies were obtained 89%, 82%, 72% and 68% for Ni (II), Cu (II), Cd (II) and Pb (II) **[178]**. Similar nanofibers were also used for adsorption of Cu (II) ions from water used in paper making industry. They found to be highly efficient adsorbent for copper ions with 94.7% removal efficiency by using only 75mg of nanofibers **[179]**.

In previous studies slow adsorption rate of chitosan/PVA nanofibers was reported **[180]**. To improve rate of adsorption, zeolite nanoparticles were incorporated in nanofibers, These nanofibers proved to adsorb chromium, nickel and iron ions rapidly with maximum removal efficiencies of about 100% **[181]**. Ionic radius of these metals in decreasing order are Cr (VI) < Fe (III) < Ni (II) **[182]**. Adsorption was also reported in the similar sequence. Moreover, researchers also studied the effect of degree of deacetylation (DD) of chitosan/PVA nanofibers for adsorption of chromium and iron metal ions. They found that as DD is increased adsorption efficiency was improved for chromium due to increase in amino groups. On the contrary, adsorption efficiency was reduced for iron **[183]**. This was explained by low molecular weight of chitosan at higher DD due to which a polymer chain may be released from chitosan structure which creates steric hindrance with large Fe ions. Therefore, affecting the adsorption capacity **[184]**.

Furthermore, pure chitosan nanofibers were also synthesized for adsorption of copper and lead ions. Adsorption capacity for copper and lead was 263.15mg/g and 485.44 mg/g respectively **[185]**. For copper this value is 6 to 11 times higher than the capacities reported in different studies of chitosan **[186-189]**.

Table 2.3 Maximum removal ability for heavy metal ions of chitosan nanofibers.

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption (q_{max}) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/PEO	Ni (II)	175.1	5.5	**[178]** **[179]**
		Cd (II)	143.8		
		Pb (II)	135.4		
		Cu (II)	163.7, 106.38		
		Cr (VI)	136.0		
2	Chitosan/PVA	Fe (III)	136	-	**[183]**
		Cu (II)	485.44		
3	Chitosan	Pb (II)	263.15	2.0-3.0	**[185]** **[190]**
		Cr (VI)	68.3		
4	Chitosan/ Graphene oxide	Cu (II)	423.8	3.0 & 6.0	**[191]**
		Pb (II)	461.3		
		Cr (VI)	310.4		
5	Chitosan/ Hydroxyapatite	Pb (II)	296.7	-	**[151]**
		Ni (II)	213.8		
		Co (II)	180.2		
6	Chitosan/TiO_2	Cu (II)	710.3, 579.1	6.0	**[192]**
		Pb (II)	526.5, 475.5		
7	Chitosan/polymethylmethcrylate	Cr (VI)	92.5	3.0	**[193]**

2.2.10 Chitosan nano particles for the removal of heavy metal ions

Nanocomposites of chitosan/clay with silver (Ag) and gold (Au) nanoparticles were made to achieve maximum adsorption of Cu (II) from aqueous solution. They used the surface properties of clay to give additional active sites for adsorption including cations exchange and large surface area. Researchers claimed that there is 100% efficiency of chitosan/clay/Ag nanocomposite for the removal of copper with maximum adsorption capacity of 181.5 mg/g **[155]**. This capacity is higher than the previously reported highest value for the adsorption of copper ions which was 153.9 mg/g when semi-IPN based hydrogel is used based on chitosan and gelatine **[194]**. Furthermore, chitosan and alginate nanocomposites were prepared by ion crosslinking method for the adsorption of chromium ions from wastewater **[195]**. Chitosan was also crosslinked with polyacrylamide to develop nanocomposite with copper; adsorption of lead ions from aquatic solutions in environmental conditions was investigated. The maximum adsorption capacity was found to be 38.93 mg/g **[196]**. A novel biodegradable and non-toxic nano sorbent based on chitosan-alginate nanoparticles was developed for the removal of mercury (Hg) ions from water. As chitosan is cationic and alginate is anionic in nature, the nano sorbent is efficient in adsorbing both negatively and positively charged heavy metal ions. Researchers claimed that it is the highest adsorption capability of this sorbent as compared to the values reported in the previous literature, where it was recorded as 217.39 mg/g at 30 °C **[197]**. Similarly, alginate coated chitosan nanoparticles were investigated for the removal of nickel ions from industrial effluents. It was found that 94.48% of nickel was adsorbed at a pH 3 **[198]**. In another work, quaternized chitosan microspheres (QCMS) were synthesized for removal of Cr (VI) ions from wastewater. It was discovered that 97.34% of chromium was detached under the optimal condition of pH 5 **[199]**.

Table 2.4 Maximum removal ability for heavy metal ions of chitosan nano/micro particles.

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption (q_{max}) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan-Fe_3O_4	Cu (II)	21.5	5.5	**[200]**
		Co (II)	27.5		**[201]**
2	α–ketoglutaric acid-Chitosan	Cu (II)	96.2	6.0	**[202]**
3	Ethylenediamine-Chitosan	Pt (IV)	171.0	2.0	**[203]**
		Pb (II)	138.0		
4	Chitosan-Magnetite	Ni (II)	833.3	5.5	**[204]**
		Co (II)	588.2		
5	Chitosan	Pb (II)	398.0	5.5	**[205]**
6	Chitosan – Poly acrylic acid	Ni (II)	435.0	4.0	**[206]**
		Cu (II)	174.0		
7	Chitosan-Alginate	Hg (II)	217.39	5.0	**[197]**
		Ni (II)	20.09		**[198]**
8	Chitosan-Co Fe_2O_4	Pb (II)	228.31	6.0	**[207]**
		Cu (II)	168.06		
9	Chitosan-MAA	Pb (II)	11.30	5.0	**[208]**
		Cd (II)	1.84		
		Ni (II)	0.87		
10	Chitosan - $MnFe_2O_4$	Cu (II)	22.6	6.3	**[209]**
		Cr (II)	15.4		

Further investigations were also made on magnetic chitosan/Fe_3O_4 nanoparticles synthesized by using gravity precipitation method. These particles were used as adsorbents for lead and cadmium ions from aqueous solutions and the maximum removal capacity was found to be 79.24 mg/g for lead and 36.42 mg/g for cadmium ions **[210]**. These nanoparticles proved to be most efficient for the adsorption of lead and cadmium than any other reported studies on Fe_3O_4nanoparticles with different materials **[159, 211-215]**. Table 2.4 shows the maximum adsorption capacities of chitosan nano/micro particles.

2.2.11 Chemically modified chitosan for the removal of heavy metal ions

Badawi et.al. modified the chitosan with tannic acid for the adsorption of Pb and aluminium (Al) ions from water **[216]**. Tannic acid was previously used for the removal of metal ions because of its ability to form metal complexes **[217]**. This research reported tannic acid with chitosan for the first time. Results concluded that maximum adsorption was achieved at pH 6 by increasing metal ion concentration and temperature **[216]**. In another study **[218]** chitosan was modified with thiosemicarbazide (TSCS) through a condensation reaction for the removal of Cu (II) ions. TSCS has both sulphur and amino groups as compared to chitosan which has only an amino group. As a result, TSCS have more adsorption sites which leads to the increased removal of heavy metals. The adsorption rate however only increased up till 1.5 g/L of TSCS concentration, beyond this point, the adsorption rate remained constant due to the limitation of free sites. In another work **[219]** a group of researchers studied the kinetics and adsorption isotherms for the adsorption of Cu (II) ions on chitin as well as pure and modified chitosan. Chitosan was chemically modified with ethylenediamine tetra-acetic acid (CS-EDTA) to eliminate copper ions from wastewater and its adsorption was compared with pure chitosan and chitin. 110mg/g was found to be the highest adsorption with CS-EDTA as compared to 58 and 67 mg/g for chitin and pure chitosan at pH 7 **[220]**.

In a study, chitosan was also found to be a suitable biopolymer for the adsorption of reactive dyes from water bodies. This is due to the presence of amine and hydroxyl groups on chitosan; dyes have a strong tendency to be adsorbed at primary hydroxyl adsorption sites **[221]**. The temperature was found to be a major factor for the maximum adsorption of dye on chitosan; this is explained by the swelling behaviour of chitosan in previous studies. As temperature increases the internal structure of chitosan, it will swell enabling dye molecules to penetrate further **[222]**.

In another research, the scientist made chitosan/$CoFe_2O_4$ magnetic particles modified with tetraethylenepentamine (TEPA) to have maximum adsorption and magnetic properties at the same time. These particles were used for the separate adsorption of copper and lead and also with solutions that have both ions. The maximum adsorption capacity in single solutions was found to be 168 and 228 mg/g for copper and lead, while in bi-component solutions, these values were decreased to 139 and 160 mg/g with a magnetization value of 63.83 emu/g **[207]**. This application was lacking in preceding studies of chitosan magnetic particles where it was not possible to maintain maximum adsorption and magnetic property **[158, 166, 206, 223]**. However, magnetic nanoparticles are chemically active and can be easily oxidised in the air which may result in the loss of magnetism.

They also cause secondary pollution in the environment due to their small dimensions [224, 225]. In order to eliminate these disadvantages, magnetic chitosan composite with macro particles was developed by adding porous activated carbon for the removal of copper ions and it showed successful results with a maximum capacity for adsorption at 216.6 mg/g with 95% efficiency **[160]**. Elwakeel et al. modified magnetic chitosan with TEPA for the adsorption of uranium ions and the maximum adsorption capacity reached to 1.8mmol/g **[226]**.

Table 2.5 Maximum removal ability for heavy metal ions of chemically modified chitosan.

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption (q_{max}) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/Xanthate	Pb (II)	76.9	5.0	**[227]**
		Cu (II)	34.5		
		Zn (II)	20.8		
2	Chitosan/Thiourea	Cu (II)	60.6	5.5	**[228]**
3	Chitosan/EGTA	Cd (II)	83.18	4.0	**[229]**
		Pb (II)	103.5		
4	Chitosan/Activated Carbon	Cd (II)	52.63	6.0	**[230]**
5	Chitosan/Glycine	Cu (II)	234.9	7.0-9.0	**[231]**
		Co (II)	281.28		
6	Chitosan/Polystyrene	Cu (II)	99.8	6.0	**[232]**
7	Chitosan/Diethylenetriamine	U (VI)	177.93	3.61	**[233]**

In another study, chitosan was demonstrated as an efficient material for the removal of heavy metals from gold mining effluent. Equilibrium adsorption studies on mercury, copper, lead and zinc showed the maximum removal of these ions at higher pH values between 4 and 6 **[234]**. A. Ghee et al. comparatively studied chitosan dense and porous membranes for filtration by increasing polymer concentration and silica ratios. They found that the adsorption increased when polymer concentration is increased; this is due to the increase of amino groups. In a similar fashion, the ratio of silica increased when porosity and roughness is increased **[235,**

236], leading to higher surface area and more exposure to amino groups for the adsorption of copper **[237]**. These macroporous chitosan membranes were also used to compare adsorption of copper and nickel ion and it was found that copper ion adsorption was 19.87 mg/g which is higher than nickel (5.21 mg/g) **[238]**.

Scientists proved that chitosan is a suitable bio sorbent for household purposes. In one study, molybdate ions were successfully removed from common household contaminated groundwater. Maximum adsorption was found to be 265 mg/g, which is far below bio sorbent values reported in the earlier literature **[239]**. (Wu et al.) and (Bertoni et al.) achieved adsorption up to 1280 mg/g by using magnetic chitosan resin and green seaweed **[240, 241]**. Table 2.5 shows maximum adsorption capacities of modified chitosan.

2.2.12 Coated/porous chitosan for the removal of heavy metal ions

Indium (III) ions were adsorbed by using chitosan coated with bentonite beads. Research showed that using chitosan alone for the removal of heavy metals has disadvantages such as high cost and low chemical stability. So, several studies investigated to reduce above mentioned drawbacks by coating of chitosan with sand **[242]**, calcium alginate beads **[153]**, alumina **[171]**, PVC beads **[139]** and bentonite beads. And in present study bentonite was found to be most efficient coating material for chitosan **[243]**. Bentonite coated chitosan displayed maximum removal percentage of indium from aqueous solution that is 99.6%. Similarly it was also used in different research for adsorption of Cr (VI) and azo dye AB10B. Adsorption capacity for chromium (66.6 mg/g) and for AB10B (847.5 mg/g) respectively was reported **[244]**.

In other application of adsorption, chitosan was coated on commercially available cotton gauze by UV radiation to remove copper and chromium ions from water solutions. Main advantages of using cotton are: it helps to limit pressure drop during continuous filament due to its open structure and it is also low cost and easily available. Research showed the optimum values for adsorption of chromium and copper at pH 3 and 5 **[245]**.

Porous foam of chitosan imprinted with Ni^{2+} was developed to improve selective adsorption of nickel from liquid solutions. This structure can provide good mechanical properties and high adsorption rate. In this research adsorption capacity was found to be 69.93 mg/g **[246]**. Recently many similar studies of chitosan porous foams have been done. Particularly chitosan/polyvinyl alcohol foam was prepared for adsorption of copper ions, which also proves to be efficient adsorbent having capacity of 193.38 mg/g for copper **[161]**.

Another porous chitosan/graphene oxide (PGOC) was developed by unidirectional freeze drying method **[247]**. Graphene also has good adsorption ability and high surface area **[248, 249]**. Reported material showed better adsorption capability for lead ions with 31% increase due to better interaction between carboxyl groups of graphene and lead ions **[250]**.

Table 2.6 Maximum removal ability for heavy metal ions of coated/porous chitosan.

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption (q_{max}) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/Bentonite	In (III)	17.89	4.0	**[243]**
2	Chitosan/Cotton Gauze	Cu (II)	4.09	5.0 & 3.0	**[245]**
		Cr (VI)	1.47		
3	Chitosan/Resin	Fe (II)	0.075	-	**[251]**
		Cr (VI)	0.038		
		Pb (II)	0.185		
4	Chitosan/Diatomaceous Earth	Zn (II)	127.4	6.0	**[252]**
5		Ni (II)	406.6		**[253]**

	Chitosan/Calcium Silicate	Zn (II)	400.0	4.0-8.0	
		Pb (II)	796.0		
		Cu (II)	578.0		
		Cd (II)	425.0		

2.2.13 Conclusion

In summary, chitosan is a natural low-cost polymer with amine groups on its backbone. It is proved to be the most efficient and effective for the removal of metal pollution by the adsorption method. According to the mechanism of adsorption of heavy metals on chitosan, the pH of a solution is the important factor to successfully adsorb the metal ions from wastewater. However, there are other factors which significantly affect the adsorption of metal ions i.e. contact time, adsorbent dosage, temperature, concentration etc. are not covered in this review. Moreover, this literature comprehensively reported and compared the adsorption capacities of cross-linked chitosan, chitosan composites, chitosan nanofibers, chitosan nanoparticles, coated chitosan and porous chitosan. Finally, the world is facing a critical issue of heavy metal pollution in wastewater, which is dangerous for both the environment and humans. Water cleaning technologies can be better understand and improved by simulating the purification processes in the future.

2.3 Introduction to electrospinning, electrospinning process and its parameters

2.3.1 Introduction

Electrospinning has emerged as a powerful platform for the fabrication of fibres due to its versatility and simplicity. It is the most effective and broadly used technology for the formation of continuous fibres with diameters ranging from few nano meters to several micro meters

[254]. Moreover, the electro spun nanofibers have numerous advantages including, very high surface area to volume ratio, controlled porosity, malleability and ability to regulate the composition of nanofibers to achieve the desired properties and functionalities for various applications. Furthermore, different structures of fibres such as, porous, core shell, hollow, and helical fibres can be made by using electrospinning technique **[254]**. Due to these benefits, the nanofibers have find their way in the wide range of applications such as, filtration, tissue engineering, optics, defence, security and environmental engineering.

Since the beginning of the 20th century, scientists have been investigating the electrospinning process. However, for many years, this process was neglected and much less attention was given to the development of advanced electrospinning processes. Only in the last two decades have seen a growing research and commercial trend towards the synthesis of electro spun fibres using natural and synthetic polymer, metals and ceramics. More work has been reported by the researchers to fabricate nanofibrous membranes for various applications such as, poly lactic acid, polyurethanes, silk fibrion, collagen, chitosan and hyaluronic acid **[255]**. Additionally, many commercial companies namely, Nano Technics, eSpin Technologies, Elmarco Limited and Kato Tech have shown active involvement in electrospinning process. Some companies like Freudenberg and Donaldson have been earning major profits by using the electro spun nanofibers in different applications **[256]**. Overall, the electrospinning is a robust and simple technique to produce functional nanofibers from the wide variety of materials.

2.3.2 Electrospinning equipment and process

Electrospinning process is generally classified into three parts: a DC high current power supply, a needle as a spinneret, and an electrically grounded collector for the collection of nanofibers, as shown in Figure 2.16 **[257].** To begin the electrospinning process, a high voltage is applied to the polymer solution droplet at the needle, which distort into a cone shape (Taylor cone) due to the presence of electrostatic forces. These strong electrostatic forces are responsible to start the electrospinning process. Once the process is started, voltage is increased gradually to produce a strong electrostatic forces on the droplet, due to which polymer solution droplet at the tip needle change its size to maintain the balance of electrostatic force. As the current is increased, shear stresses are produced due to the repulsion of charges on the surface of drop. These repulsive forces are opposite to the surface tension of the polymer solution, and are responsible for the formation of Taylor cone. When the applied voltage reaches the critical voltage, the repulsive forces overcomes the surface tension of the polymer solution. Finally, an unstable charged jet from the solution drop is emitted between the Taylor cone and the collector, which gives time for the solvent to evaporate and only the pure polymer is collected on the grounded collector. Thus, electrospinning is a simple method to produce nanofibers **[257]**.

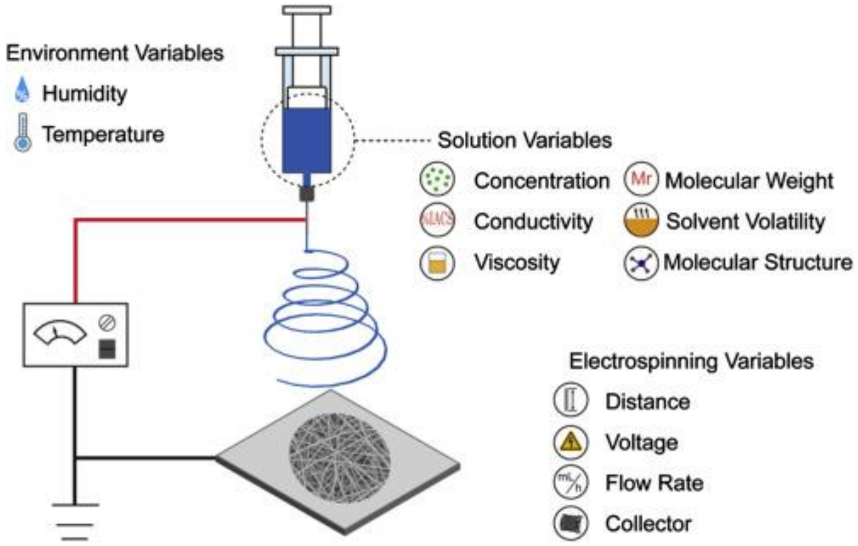

Figure 2. 16 Schematic of electrospinning setup and its process variables (Reprinted from ref [257] Copyright 2019 with the permission of Elsevier).

2.3.3 Factors affecting the electrospinning process

As discussed in previous section, electrospinning is a simple machine. However, there are some important electrospinning parameters that greatly affects the production of nanofibers, their structure and morphologies. Figure 2.16 shows the operating and process conditions of electrospinning. It is extremely vital to optimize the process parameters of electrospinning for the production of defect free and stable ultrathin electro spun nanofibers. We have discussed some important parameters of electrospinning in the below sections.

2.3.3.1 Applied voltage

Voltage applied in the electrospinning process plays a critical role in the production of nanofibers. It is commonly believe among the scientists that increasing the electrospinning voltage will increase the jet formations and leads to drawing more solution from tip to needle, which results in fading of Taylor cone and ultimately decrease the diameter of nanofibers (Figure 2.17). In other studies, scientists reported that by increasing the applied voltage, the stretching of solution was increased, which results in the formation of thin nanofibers **[258]**. Moreover, in another similar study, it was discussed that low viscosity electrospinning solutions are responsible for the creation of secondary jets, due to which smaller nanofibers were synthesized. However, there were exceptional studies reported by the researchers, they investigated that by increasing the voltage the diameter of nanofibers first reduced and then rise after a certain voltage **[259]**. In a different work, inverse behaviour of above research was reported. It was studied that diameter of electro spun nanofibers was first decreased with increase in voltage, before the trend reversed beyond the critical voltage **[260]**.

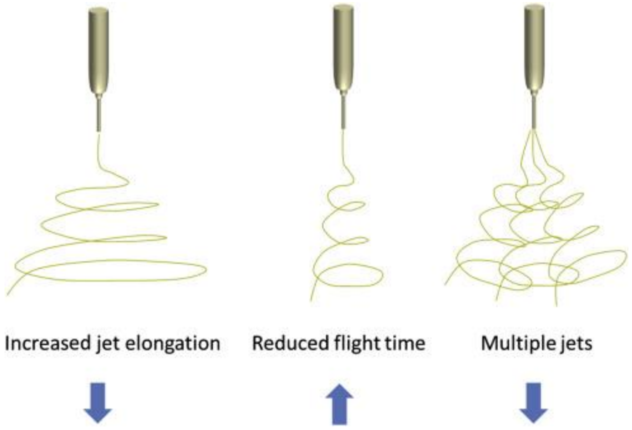

Figure 2.17 Effect of voltage on electrospinning process and diameter of fibres (Reprinted from ref [257] Copyright 2019 with the permission of Elsevier).

2.3.3.2 Tip to collector distance

The distance from tip to collector effects the solution jet travelling path from before settling on the collector. In a classic electrospinning setup, the distance from tip to collector is 10 to 15 cm. This allows enough time for the solvent to evaporate and the let the dry polymer nanofibers to deposit on the collector. Increasing the distance will result in small diameter nanofibers due to the large stretching of solution jet. However, with further increase in the distance the diameter of fibres will rise, this is due to the fact that electric strength will decrease by increasing the tip to collector distance (Figure 2.18) **[261]**.

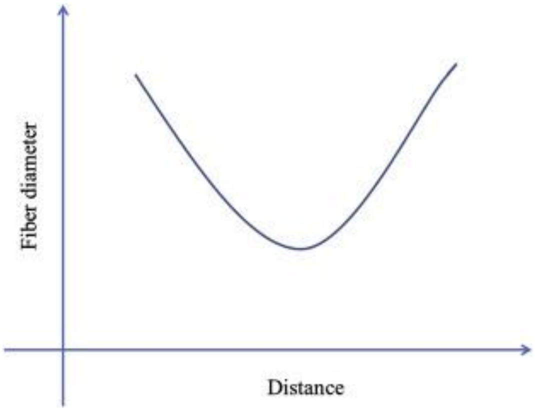

Figure 2.18 Relationship between tip to collector distance and fibre diameter (Reprinted from ref [257] Copyright 2019 with the permission of Elsevier).

2.3.3.3 Flow rate

The solution feed rate is generally not considered a significant parameter that effects the electro spun nanofibers. However, an optimum flow rate is necessary for the production of smooth nanofibers. A high flow rate will cause excessive dripping of solution and results in beaded nanofibers. Several studies have also reported the increased diameter and ribbon morphology due the high flow rate **[262]**.

2.3.3.4 Solution conductivity

The conductivity of the electrospinning solution depends on the type of polymer, solvent used to dissolve the polymer and the salts added in the polymer solution **[263]**. Higher conductivities of electrospinning solution tend to reduce the beads in nanofibers and produce thin diameter fibres. Additionally, conductivities of the solutions can be modified by the addition of ionic salts or organic acid solvents. In a previous study, researchers fabricated ultrathin 3 nm nylon nanofibers by using formic acid as a solvent. Moreover, pyridine was added to increase the conductivity of nylon and formic acid solution, which eliminates the beads from the nanofibers **[264]**.

2.3.3.5 Solution viscosity

The viscosity of the electrospinning solution is considered critical for the synthesis of continuous bead free nanofibers. It is described in various studies that, very high viscosity of the solution is difficult due to the absence of sufficient charges to stretch the polymer solution **[265]**. Moreover, for very low viscosity solutions, surface tension dominates and the beaded fibres are obtained **[257]**. It is evident that an optimum viscosity of polymer solution is required to produce continuous and bead free nanofibers via electrospinning. Viscosity can be adjusted by varying the polymer concentration or using different molecular weight of the polymer. Various studies have studied the effect of solution viscosities on the morphology of nanofibers **[266, 267].**

2.3.3.6 Temperature and humidity

Ambient conditions such as, temperature and humidity can also effect the diameter and morphology of nanofibers. Higher temperatures will increase the solvent evaporation rate and reduce the solution viscosity, which result in thinner fibres **[268]**. Mituppatham et al. **[269]** has described the similar relation between temperature and fibre diameter in their research. They showed that thinner fibres of polyamide-6 were obtained via electrospinning at higher temperature. Also, at lower humidity, solvent dries quickly and increase the solvent evaporation rate, which produces small diameter fibres. However, at higher humidity levels, stretching of solution at needle is reduced, which leads to the formation of thick fibres. In a previous study, scientists have studied the effect of humidity on the morphology and diameter of nanofibers **[270]**.

2.4 Strategies to fabricate porous nanofibers via electrospinning

2.4.1 Introduction to porous fibres

The fibres made via electrospinning have high porosity, due to which they stand out in many applications as compared to fibres synthesized by different methods. The term porosity is generally understood to mean gap between the fibres interconnected in a web. It is the nature of the nonwoven and may be it is due to the residual charge on the fibres. Hence, all the electro spun membranes can be called as porous fibrous membranes **[271]**. However, in this thesis, the focus is on the porous fibres, which have pores present externally on the surface of fibres or internally into the fibre structure. The fibres which have porosity on their surface have much greater surface area to volume ratio as compared to the porous electro spun membranes. Figure 2.19 shows the comparison between porous membranes and porous fibres.

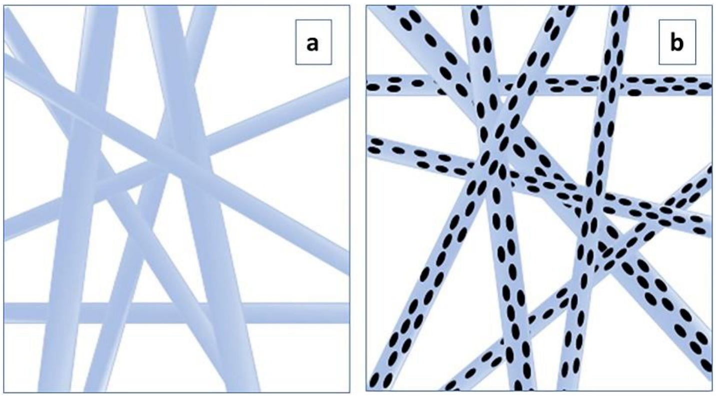

Figure 2. 19 Schematic comparison of (a): porous electro spun membranes and, (b): electro spun porous fibres [271].

2.4.2 Mechanisms for pore development in electro spun fibres

2.4.2.1 Phase separation

It is only since the work of Bognitzki and co-workers (2001) **[272]** that the creation of porous nanofibers have gained momentum. They were the first to report the synthesis of porous nanofibers via single step electrospinning process. In their research, they electro spun poly lactic acid, amorphous polycarbonate and polyvinylcarbazole solutions in highly volatile dichloromethane and found porosity in all three polymer nanofibers. The scientists described that porosity was generated due to the rapid evaporation of the solvent initiating the phase separation between polymer and solvent during electrospinning. The phase separation leads to the formation of solvent rich regions, which are responsible for porous structure after evaporation. However, different studies have reported contradicting results for the generation of porous fibres by phase separation method. For example, Tan el al. **[273]** did not report porosity in the electrospinning of poly lactic acid and dichloromethane solution, while, Casasola et al. **[274]** developed porous poly lactic acid fibres by using dichloromethane and chloroform as solvents.

Hence, it is proved that simple phase separation mechanism is not sufficient to explain the creation of porosity in electro spun fibres. So that to induce porosity, choice of suitable polymer-solvent system as well as environmental factors (temperature and humidity) should be considered.

On the basis of above discussion, phase separation can be divided into three methods:

- Thermally induced phase separation (TIPS)
- Vapour induced phase separation (VIPS)
- Non-solvent induced phase separation (NIPS)

2.4.2.2 Thermally induced phase separation

This type of phase separation occur, when fibres go through a large decrease or increase in the temperature during electrospinning. Temperature difference between the fibres and collector is the major cause for phase separation. Thus, rapid evaporation of solvent from the electro spun fibres can facilitate the formation of porosity on fibres.

McCann and Yu et al. **[275, 276]** described that porous structure in fibres can be achieved by electrospinning the polymer solution in liquid nitrogen bath and increasing the temperature of the electrospinning. Latter showed that, when fibres immersed into liquid nitrogen bath (-200 °C), the fibres undergo rapid quenching and promoted the phase separation. Former researcher made an electrospinning set up that reached the temperature up to 300 °C, during electrospinning the fibres experienced a high temperature initially and drop in temperature when collected on the rotating drum. This temperature difference triggered the phase separation process in just 0.35 second and porous structure was formed on the electro spun fibres. The main disadvantage of this process is uncontrollable morphology and distribution of pores on the fibre. Overall, TIPS is considered as simple and effective method to generate pores on electro spun fibres.

2.4.2.3 Vapour induced phase separation

The phase separation in electro spun fibres due to the surrounding vapours generally involves the water vapours. Therefore, this mechanism requires relatively high humidity (≈ 40 % RH). Solvents used in this mechanism must have a low volatility and good miscibility with water. A known example of a good solvent is dimethylformamide (DMF).

The solvent evaporates slowly during the electrospinning and drying of fibres, which give water vapours a good chance to penetrate into the fibres. As the water penetration increases into the fibres, it start interacting with the solvent and create liquid-liquid phase separation, which leads to the generation of porous structures inside the fibres as shown in Figure 2.20.

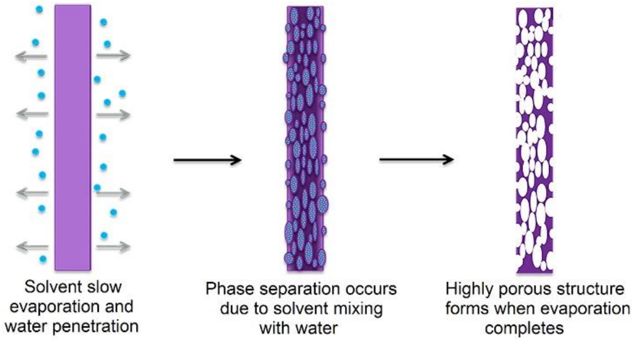

Figure 2.20 Schematic if internal pores induced by VIPS mechanism [271].

Lu et al. **[277]** demonstrated in their work that water vapour are critical in forming porous structure internally in the fibres. They compared the morphology of electro spun poly styrene/DMF fibres at 2 % and 62 % RH. In their study, they showed that fibres were smooth on the surface and solid internally, whereas, fibres prepared at 62 % RH have highly porous structure internally and nano wrinkles on the surface of fibres. This is due to the condensation of water vapours on the fibre surface and interaction with the solvent. Moreover, some researchers have also reported in the rise of specific surface area of PS fibres after formation of pores. Demir and Lin et al. **[278, 279]** showed that the surface area of fibres with the presence of internal pores was increased 6 and 14 times as compared to the fibres that has pores present on the surface only. The fabrication of internal porous structure in poly lactic acid and polymethylmethacrylate (PMMA) fibres in DMF was also reported in the previous studies.

2.4.2.4 Non-solvent induced phase separation

To generate the porous structure in the electro spun fibres, a non-solvent is added into the polymer/solvent system. This is termed as NIPS. It is essential to select a correct solvent and non-solvent for the electrospinning of polymer. A good solvent should have a higher volatility, while the non-solvent with low volatile rate is vital. In this case, solvent rapidly evaporate leaving behind the polymer rich phases, which results in large porous structure after complete evaporation. Many researchers have reported formation of porous structure in polycaprolactone (PCL) **[280]**, polyvinyldineflouride (PVDF) **[281]** and poly lactic acid (PLA) **[282]** electro spun fibres NIPS mechanism. They used combination of various solvent/non-solvent system like, dichloromethane (DCM)/hexane, dimethylformamide (DMF)/chloroform (CHL) and DMF/water.

2.4.2.5 Breath figure mechanism

Another interesting mechanism for the creation of porosity on electro spun fibres is breath figure, it involves the condensation of water vapours on the fibres in form of droplets. The porosity by breath figure mechanism can only occur if these two conditions satisfy, that is, relatively high humidity and low temperatures during electrospinning. In order to reduce the temperature in electrospinning, volatile solvents are used such as, DCM and CHL **[271]**.

Due to the decrease in temperature, surrounding water vapours start condensing on the surface of electro spun fibres and act as a template for the pores, the porous structure formed after the complete evaporation of water and the solvent as shown in Figure 2.21. The shape of pores formed via breath figure mechanism is circular. Moreover, the pores are present only on the surface of fibres, which shows that porous structure is generated after the electrospinning of fibres.

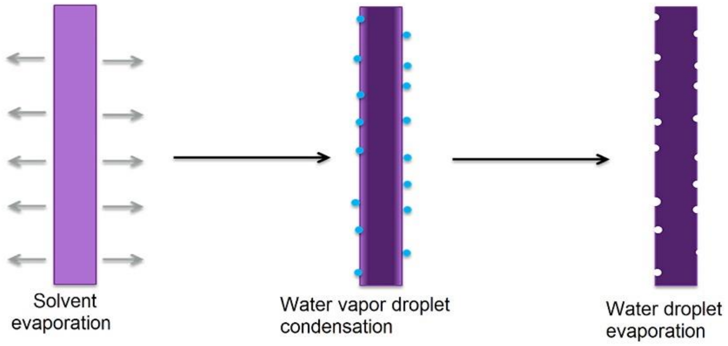

Figure 2.21 Schematic of breath figure mechanism [271].

The main weakness with this mechanism is that, pores can only be formed on the hydrophobic polymers/water immiscible solvent system. This is due to the fact that in hydrophilic polymers water does not stabilize on the surface and mix with the solvent to disrupt the process of pore generation. In a study investigating breath figure mechanism for making porous structure in electro spun fibres, Megelski et al. reported the surface porosity in the hydrophobic PMMA/CHL fibres, whereas, they reported a wrinkled surface on the hydrophilic polyethyleneoxide (PEO) fibres **[283]**.

2.4.2.6 Selective removal method

As discussed above, phase separation and breath figure mechanisms are mostly used for the generation of pores in the electro spun fibres, an alternative method called selective removal of components from the polymer matrix is also used for the preparation of porous structure in hydrophobic and hydrophilic polymers **[271]**. It is a two-step method which includes electrospinning and post-treatment of fibres. The post-treatment is carefully controlled to remove the sacrificial components while retaining the polymer matrix. Commonly used sacrificial materials can be either inorganic salts, silica or polymers. They can be removed by immersing the fibres in the appropriate solvent or treating the fibres at elevated temperatures. Scientists reported the addition of sodium chloride (NaCl) particles in the production of porous PCL fibres, NaCl can be easily removed by immersing the PCL fibres in deionized water **[284]**. Moreover, Silica was used to synthesize porous polyacrylonitrile (PAN) fibres **[285]**. In different studies, scientists have used PEO as a sacrificial polymer frequently for the fabrication of porous electro spin fibres such as, PCL, PVDF and PAN fibres **[271]**. PEO can be easily removed in the presence of water or at high temperature, which supports in the formation of porous structure. However, an optimum ratio of PEO is required because higher quantities can be retained in the fibres affecting their properties. Also, the fibre surface become irregular because of the large dispersed spheres and phases of PEO retained in the fibres **[286]**.

2.4.2.7 Porous anodic aluminium oxide template method

In addition to the selective removal method, chen et al. **[287]** developed a novel method to produce porous nanofibers with the help of porous anodic aluminium oxide (AAO) templates. Porous fibres can produce either by direct electrospinning on the porous template or by collecting the fibres on the substrate, put them on the AAO porous sheet and apply thermal treatment. In latter approach, solvents with high evaporation rates are required, while in former method temperatures above glass transition points are used. This method does not create porous structure on the whole fibre, however, it is useful when controlled pore sizes, shapes and grains are required. To date, PMMA and PS porous fibres are reported by using porous AAO template method **[287]**.

2.5 Critical analysis on literature

In this literature, the involvement of industries towards polluting the drinking water was discussed in detail. The industrial processes, chemicals used and their waste disposal methods were proved to be the main sources of water pollution. Moreover, various water treatment methods were explored such as, adsorption, ion exchange, flocculation/coagulation, membrane filtration, chemical precipitation, flotation and electrochemical processes. Adsorption was found to be the most reliable method to remove the pollutants from water because of its higher efficiencies, inexpensiveness, versatility and ability to regenerate. Furthermore, a detailed literature review on the ability of chitosan to be used as an adsorbent for the removal of toxic metals from wastewater was done. Also, the importance of electrospinning in producing nanofibers by using wide range of polymers was discussed and the introduction, applications and properties of PLLA was provided in this section.

2.6 Research gaps identified from literature

Finally, it was concluded that, there is a lack of literature on the use of hydrophobic nanofibrous membranes as adsorbents for the removal of toxic pollutants from the water. Moreover, a high surface area adsorbent could be an interesting candidate to study the adsorption process. The generation of porous structure inside and outside the nanofibers is one option to produce large surface area adsorbents for faster and efficient removal of toxic pollutants from aqueous solutions. However, lack of functional groups on the hydrophobic polymers can cause a problem in the usage of these membranes as a suitable adsorbents. Chitosan is considered as an appropriate material to modify the hydrophobic porous nanofibrous membranes. This is due to the fact that, chitosan is abundant on nature, it is cheap, biodegradable, biocompatible and non-toxic. In the current study, a novel method is devised in order to fabricate the higher surface area porous PLLA nanofibers via electrospinning and non-solvent induced phase separation method. Finally, the surface of porous PLLA membrane was modified with chitosan in order to make them suitable adsorbent for the removal of pollutants from wastewater.

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3.CHAPTER 3

Porous poly(L-lactic acid)/chitosan nanofibers for copper ion adsorption

3.1 Introduction

This part is available as research article “*Porous poly (L-lactic acid)/chitosan nanofibers for copper ion adsorption*” in journal of Carbohydrate Polymers (2020). In this work chitosan in different concentrations was coated on porous PLLA nanofibers via simple dip coating method. Whereas, porous PLLA nanofibers were fabricated by electrospinning. Porous fibres provide the high surface area platform for chitosan to increase the adsorption of copper ions. It was observed that copper was rapidly and efficiently adsorb on the 1 % chitosan coated porous nanofibers. The maximum adsorption of copper ions was achieved under optimal conditions of pH 7, contact time of 10 min and temperature of 25 °C. In addition, mechanism of copper ion adsorption shows that amino groups on the backbone of chitosan are mainly responsible for adsorption. Moreover, the kinetics, isotherm and thermodynamic studies shows that, adsorption process is exothermic and spontaneous, while adsorption data fitted well with the pseudo second order kinetics and Langmuir isotherms. Finally, this study gives a simple, versatile and efficient method to remove the copper ions from wastewater.

3.2 Author contributions

I performed the experimental work on porous PLLA nanofibers electrospinning, chitosan coatings, characterization of adsorbents and mathematical modelling. Madeeha Tabassum did scanning electron microscopy analysis and mathematical modelling. Muhammad Tauseef Khawar and Jun Song contributed to useful discussions in the project. Zihan Lu and Zhi Li proof read and provided useful insights in the manuscript. Jiashen Li and Hugh Gong provided supervision during the project.

3.3 Citation

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3.4 Relationship with objectives

In the current study, the first two objectives of this these are satisfied that are fabrication of PLLA porous nanofibrous membrane and coating it with various concentrations of chitosan. Moreover, these membranes are successfully characterized and evaluated in various adsorption environments. Finally, these adsorbents were successfully tested for adsorption of copper ions from wastewater solutions.

3.5 Manuscript 1: Porous poly (L–lactic acid)/chitosan nanofibers for copper ion adsorption

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3.6 Abstract

Porous poly(L-lactic acid) (PLLA) nanofibrous membrane with the high surface area was developed by electrospinning and post acetone treatment and used as a substrate for deposition of chitosan. Chitosan was coated onto porous nanofibrous membrane via direct immersion coating method. The porous PLLA/chitosan structure provided chitosan a high surface framework to fully and effectively adsorb heavy metal ions from water and showed higher and faster ion adsorption. The composite membrane was used to eliminate copper ions from aqueous solutions. Chitosan acts as an adsorbent due to the presence of aminic and hydroxide groups which are operating sites for the capture of copper ions. The maximum adsorption capacity of copper ions reached 111.66 ± 3.22 mg/g at pH (7), interaction time (10 min) and temperature (25 °C). The adsorption kinetics of copper ions was established and was well agreed with the second-order model and Langmuir isotherm. Finally, the thermodynamic parameters were studied.

Keywords: Chitosan, Porous PLLA nanofibres, Adsorption, Langmuir model

3.7 Introduction

The ground and industrial wastewater contain several contaminations including heavy metal ions, for instance, Cu, Pb, Ni, As, Cr, Hg, and Cd. The rise in the amount of heavy metal in the groundwater is due to contamination by many industries including paper, battery, refineries, metallurgy, leather and textile **[1]**. The European Commission Science for Environment Policy (SEP) **[2]** has stated heavy metals as most common contaminants (31%) in the groundwater second to the mineral oil (22%). It is important to remove these elements as their presence acts as a severe threat to human well-being and ecosystem because of their toxic effects **[3-6]**. Among heavy metals, copper (Cu) is one of the most commonly used elements in the production industries such as electrical, antifouling and paint industries. It has many toxic effects on human health including cancer, liver damage, Wilson disease, and insomnia **[7, 8]**. The protection agency for the environment (USA) has fixed the highest contamination limit of copper ions in the water to 0.25 mg/L. Beyond this value, it causes severe effects on health including cancer, organ damage, nervous system damage and in extreme cases death **[7, 9]**. Multiple techniques are in practice with varying efficiencies to remove the Cu ions from water, including chemical precipitation, membrane filtration, adsorption, photocatalysis, ion exchange and reverse osmosis **[10, 11]**. However, each of these techniques has certain limitations. For example, chemical precipitation generates a large amount of sludge **[9]**. Membrane filtration and reverse osmosis require high operational costs **[9]**, while photocatalysis is a relatively slow process **[12]**. Out of these methods, ion adsorption is one of the most practical methods for water filtration due to its cost-effectiveness, high binding capacities, and facile operation **[13]**. Nanoporous glass, sand, palm oil, chitosan and ceramic alumina are used for the adsorption of heavy metals from the water **[3, 14-17]**.

Chitosan is another suitable material for the removal of heavy metals as it contains active amino and hydroxyl groups on its surface. These groups act as anchors to capture and fix metal ions from water. The higher density of active sites chitosan has, the more and faster it adsorbs ions. Moreover, it is easily available, biodegradable, non-toxic and biocompatible. The Figure S 7.1 displays the chemical structure of chitosan **[18-22]**.

The large scale application of chitosan in adsorption of heavy metals ions is limited by its low mechanical strength, pH sensitivity, swelling, and low surface area **[23-25]**. The properties of chitosan can be improved by crosslinking or immobilizing it on a support material. Previously the chitosan has been crosslinked with glutaraldehyde **[26]**, epichlorohydrin **[27]**, and diethylenetriaminepentacetic acid **[28]** to raise the mechanical strength and chemical balance. Whilst crosslinking improves the mechanical properties, it reduces the density of active sites which weakens the capacity of chitosan to purify water **[4]**. Coating of chitosan on a support material is another viable approach to improve its properties while keeping most of the functional groups on the exterior of chitosan **[29]**. Recently, Yaolin et al. **[30]** reported the removal of Cu(II), Pb(II) and Zn(II) ions by chitosan coated polyethylene terephthalate (PET) adsorbent. Franco et al. **[31]** examined the adsorption of Cu(II) and Cr(VI) ions from water on chitosan-coated cotton gauze. Qu et al. **[4, 32, 33]** coated chitosan onto cotton fibre for the removal of Au(III), Hg(II), Cd(II), Cu(II) and Ni(II) ions from wastewater. It was observed in these studies that the substrate plays an important role in providing chitosan a stable framework for adsorption from water.

In the present study, we have used highly porous poly(L-lactic acid) (PLLA) nanoporous fibrous membrane as supporting material for chitosan. PLLA is a kind of biocompatible, biodegradable, eco-friendly and cost-effective material. These properties make it a suitable host material for water purification **[34, 35].** PLLA fibres can be produced by electrospinning which is a straightforward, versatile and cost-effective technique and allows the control of fibre diameter from nanometer to micrometer **[36, 37]**. The electrospun nanofibres are considered to be the next generation material for water filtration because of large porosity, tunable orifice size and high surface area to volume ratio **[18, 38]**. The large surface area provided by electrospun fibres can enhance the ion adsorption capacity of composite material. To utilize these properties, chitosan was coated on porous PLLA fibrous membrane by immersion method for preparation of a composite for water filtration (CHPLLA). Without further crosslinking, chitosan could keep most of its active sites for metal ion adsorption. The adsorption performance of CHPLLA for Cu (II) heavy metal from water was examined. The adsorption parameters, including effects of pH, initial metal concentration, temperature and chitosan quantity on the adsorption capability of CHPLLA for Cu (II) ions, the kinetics of adsorption, and isotherm models were explored and procedure for the adsorption of copper ions was discussed. To the best of our information, this is the first study of porous PLLA nanofibres as supportive materials for removal of Cu (II) ions from water.

3.8 Experimental

3.8.1 Materials

Chitosan with low molecular weight (M_w = 50,000-190,000 Da), 75-85 % deacetylated was purchased from Sigma Aldrich. Poly(L-lactic acid) (PLLA) ($MW=1.43\times10^6$) was supplied by PURAC biochem, Holland. Dichloromethane (DCM, 99.99%) was purchased from Sigma Aldrich. Dimethylformamide (DMF, 99.8%), was purchased from Fisher Scientific Ltd. Ethanol (EtOH, 99.97%) and acetone (99.70%) were purchased from VWR Science Company., Limited. Deionized water was acquired from USF-ELGA water filter in the laboratory. Copper sulfate pentahydrate ($CuSO_4.5H_2O$) was purchased from Fisher Scientific Ltd.

3.8.2 Preparation of Porous PLLA nanofibers

The porous PLLA nanofibres were prepared by electrospinning technique and subsequent solvent treatment. First, 1.8 wt % PLLA was dissolved in DCM and DMF with a 19:1 w/w by stirring and heating at 50 °C in the closed container to avoid the evaporation of solvents until the solution becomes transparent and PLLA was completely dissolved. The mixture was filled in a 30 ml syringe with a metal needle (19G) and fixed on an electrospinning setup. The distance between the needle tip and the metal collector (roller) was maintained to be 30 cm and 23 kV power source was used to charge the mixture. The mixture was released towards the revolving grounded roller (200 rpm) to collect nanofibrous membranes. The collected membranes were allowed to dry overnight. The produced fibrous membrane was immersed in acetone for 5 minutes at room temperature and then dried in the fume cupboard to get porous nanofibrous mats.

3.8.3 Coating of chitosan

The coating of chitosan onto porous PLLA nanofibres was achieved by a direct immersion coating method. For this, aqueous solutions of chitosan (0.5, 1, 2 and 3 wt%) with pH 3 were prepared by dissolving chitosan (0.1, 0.2, 0.4, 0.6 g) in 20 ml of 0.5 % (v/v) acetic acid solution by magnetically mixing at room temperature. Electrospun porous PLLA nanofibrous membranes were immersed in chitosan mixture for 10 mins, withdrawn from the solution, blotted carefully and dried to a constant mass.

3.8.4 Characterizations

The morphology of nanofibrous membranes was characterized by Quanta 250 FEG electron microscope (FE-SEM), USA. Elemental analysis was conducted using Energy Dispersive Spectrophotometer (EDS) by Oxford Instruments. Fourier transform infrared spectra (FTIR) was recorded on NICOLET 5700 spectrophotometer. X-Ray Diffraction (XRD) was performed using PANalytical X'pert PRO USA. The quantification of heavy metals was done using Inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

3.8.5 Adsorption experiments

The adsorption of copper ions on the chitosan modified porous PLLA nanofibres (CHPLLA) was observed with varying parameters of chitosan concentration (0.5-3 wt%), pH (3-10), interaction period (1-30 min), original Cu (II) ions quantity (50-200 mg/L) and temperature (25-50 °C) in a group structure. The amount of the porous PLLA nanofibres was changed in order to provide the same amount of adsorbent after coating with different chitosan concentrations (0.6 mg/20 mL). The original pH of the copper ion solutions was modified with HNO_3 (0.1 M) and NaOH (0.1 M). The adsorption ability (q_e) of copper ions was computed by following mathematical expression (1):

$$\mathbf{q_e = \frac{(C_i - C_e)V}{M}} \tag{1}$$

3.8.6 Swelling test of chitosan-coated PLLA nanofibers

The swelling behaviour of CHPLLA nanofibres was studied by adding 0.2 g of chitosan and 1 wt % CHPLLA nanofibres in each of distilled water, dilute acidic and alkaline solutions at room temperature for 12 hours. Chitosan and CHPLLA nanofibres were tested to compare the swelling behaviour in different environments. The percentage of swelling was calculated by using the following equation:

$$\textbf{Percentage of swelling} = \mathbf{\frac{W_s - W_d}{W_D} \times 100}\ \% \tag{2}$$

Where W_d and W_s is the weight of dry and swollen chitosan-coated PLLA nanofibres, respectively.

3.9 Results and Discussions

3.9.1 Characterization of chitosan-coated porous PLLA nanofibres

The FTIR spectra of CHPLLA nanofibres, chitosan, and porous PLLA nanofibres are demonstrated in Figure 3.1 (a, b and c). The spectrum shows bands at 2919 and 3000 cm^{-1} for porous PLLA, 3000 cm^{-1} for CHPLLA and 2936, 2857 cm^{-1} for chitosan. These bands belong to C-H stretch from CH_3. The bands at 1741 cm^{-1} for both PLLA and CHPLLA corresponds to C═O extending of ester. C-O-C extending vibration was observed at 1082 and 1185 cm^{-1} in both PLLA and CHPLLA. In CHPLLA spectrum, bands at 1541 and 1511 cm^{-1} are assigned to N-H pattern of the chitosan as shown in Figure 3.1 (b) **[39]**. The presence of these bands suggests that chitosan was successfully coated on porous PLLA nanofibres.

Figure 3.2 shows the FESEM images of porous PLLA nanofibres. The surface of the nanofibres is rough and the uniform porous network is observed on nanofibres. After electrospun PLLA fibres were treated by acetone, the fibres were changed to porous ones which provide chitosan a substrate with a very high surface area.

Figure 3.3 (a, b, c and d) exhibits FE-SEM images of porous CHPLLA nanofibres. The exterior of the nanofibres after chitosan coating is comparatively smooth. For 0.5 and 1 % of chitosan concentration, the formation of thin chitosan coating is observed on nanofibres while the porous structure is still visible. The coating becomes thicker and covers the porous structure of nanofibres for 2 and 3 % of chitosan. Moreover, it is observed that the chitosan is physically coated uniformly on the porous nanofibrous membranes.

XRD patterns of porous PLLA nanofibres, chitosan film, and CHPLLA nanofibres are displayed in Figure S 7.2. Diffraction peaks of porous PLLA nanofibres at $2\theta = 14.7°$, $16.6°$, and

19.01° are derived from 104, 200 and 203 phases of α phase **[40]**. The results indicate that

PLLA was crystallized as α phase after treatment with acetone. The diffractogram of chitosan consisted of two major peaks at 2θ = 10.9° and 20.7° **[41]**. Compared with chitosan and porous PLLA nanofibres, the diffractogram of chitosan modified porous PLLA nanofibres exhibited some changes in peak width and peak position. The peak at 14.7° shifted to the left and its width was decreased, while the peak at 16.6° shows a decrease in width. Such stronger and narrow peaks indicated a more crystalline phase of the CHPLLA. In addition, the peak at 10.9° of chitosan disappeared and a new crystalline peak of PLLA appeared at 12.3°, which was confirmed from ICDD card no. 00-064-1624. It implies that the CHPLLA was considerably more crystalline than porous PLLA nanofibres. Chitosan acted as a nucleating agent and caused the fast crystallization of PLLA as stated in previous studies **[42, 43]**.

3.9.2 Adsorption of Cu ions on chitosan-coated porous PLLA nanofibres

Porous PLLA nanofibrous membrane is prepared, coated with chitosan and copper ions are adsorbed as exhibits in Figure 3.4. The presence of Cu ions was displayed by a clear blue colour of the CHPLLA nanofibres after the adsorption process Figure 3.5. Furthermore, the EDS spectra presented in Figure S 3.3 (a) and (b) reveal the existence of Cu peaks in chitosan-coated porous PLLA nanofibres as compared to the uncoated porous PLLA nanofibres. Therefore, the results suggest that the chitosan active sites are capable to act as active sites for adsorption of copper ions.

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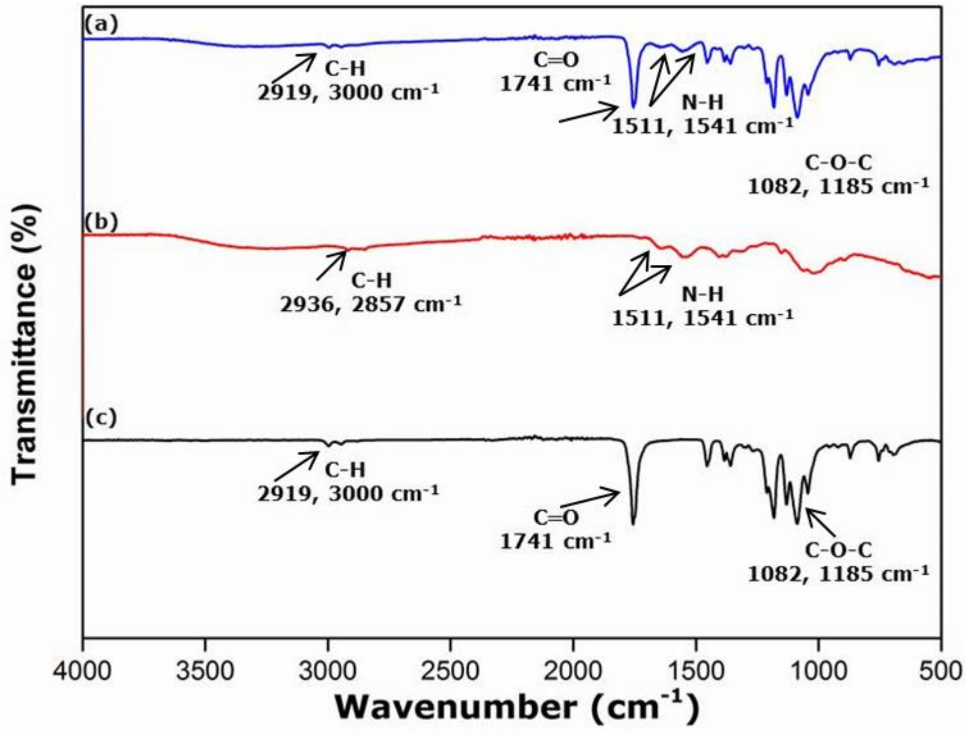


Figure 3. 1 FTIR of (a): chitosan coated porous PLLA nanofibres (b): pure chitosan (c): porous PLLA nanofibers.

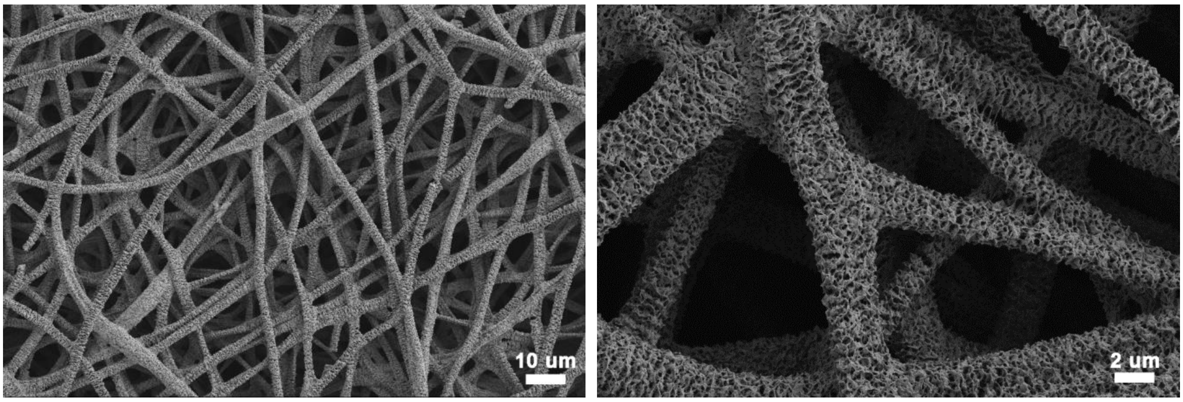


Figure 3.2 SEM of porous PLLA nanofibres with different magnifications.

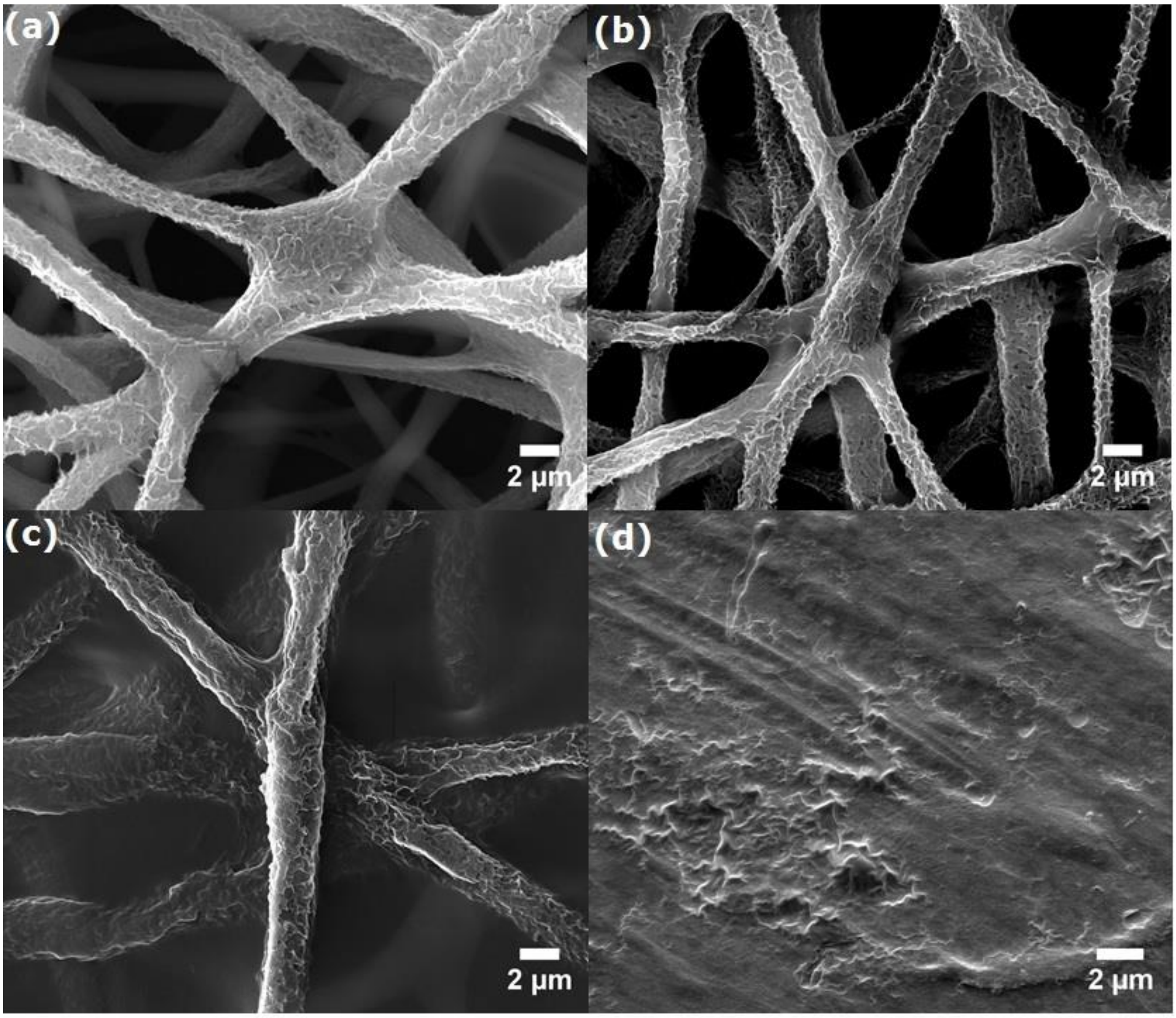
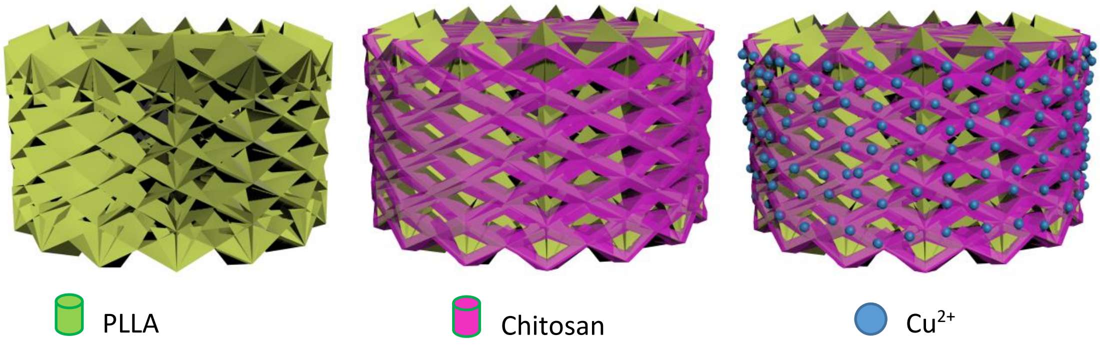


Figure 3.3 SEM of chitosan-coated porous PLLA nanofibres (a): 0.5% chitosan, (b): 1% chitosan (c): 2% chitosan & (d): 3% chitosan.



(a) (b) (c)

Figure 3.4 Schematic of experimental methodology: (a) porous PLLA fiber; (b) porous PLLA fiber with chitosan coating; (c) copper ions are adsorbed by chitosan.

Figure 3.5 The contrast between hue of chitosan-coated porous PLLA nanofibres without and with adsorption of Cu (II) ions.

3.9.3 Stability studies of chitosan-coated porous PLLA nanofibres

The swelling behaviour of chitosan and chitosan-coated porous PLLA nanofibres is shown in Table S 3.1. It is known that chitosan is soluble in dilute acidic environments due to the protonation of amino groups in acidic media. The suitable evidence of chitosan coating on porous PLLA nanofibres is the less swelling of chitosan in dilute acetic acid, distilled water, and NaOH solution. This can be attributed to the strong adhesion of chitosan on porous PLLA nanofibers due to the presence of weak Vander Waal forces between chitosan and ethanol.

3.9.4 Impact of chitosan concentration on the adsorption capacity

To observe the impact of chitosan concentration on the exclusion of copper ions, the CHPLLA nanofibrous sorbents with varying concentrations (0.5, 1, 2 and 3 wt.%) were prepared. The performance of nanofibre adsorbents was evaluated at a copper initial quantity of 100 mg/L with a pH of 7, adsorbent mass of 0.6 mg/20 mL, the interaction time of 30 mins and a temperature of 25 °C. The results are displayed in Figure 3.6 (a). It is observed that Cu (II) adsorption increases by increasing the concentration of chitosan up to 1 %. It is expected that the thin film of chitosan formed up to 1 % concentration increases the active sites such as –NH_2 for the adsorption procedure. With an increase in the amount of chitosan beyond this point, the adsorption capability of copper ions decreased. This behavior could be credited to accumulation and thickening of chitosan at a higher concentration which decreased the surface area of nanofibres and reduced the available functional sites for copper ions adsorption. Therefore, the concentration of 1 % is considered as an optimal value for the coating of porous PLLA nanofibres with chitosan.

3.9.5 Impact of pH on adsorption capacity

The effect of solution pH on the surface reaction was studied by maintaining the number of copper ions to 100 mg/L, adsorbent amount to 0.6 mg/20 mL and contact time of 30 mins. The measurements were executed at room temperature in pH between 3-10. The findings are displayed in Figure 3.6 (b). An increasing trend of adsorption capacity is observed with increasing pH value and the maximum value is found at 7. After this limit, the adsorption capacity starts to decrease and this trend continues until 10. This behaviour can be explicated by the existence of the surplus amount of hydrogen ion at low pH which restricts the reaction of ions with $-NH_2$ working groups of chitosan. Moreover, chitosan is susceptible to dissolution in an acidic environment. Therefore, a maximum adsorption value was found in neutral conditions. At higher pH values, Cu (II) ions form hydroxide complexes ($Cu(OH)_2$) which caused a decrease in adsorption capacities of CHPLLA adsorbent. Based on these findings, pH 7 is designated as an optimal value for more adsorption studies.

3.9.6 Impact of temperature on adsorption capacity

The adsorption process of Cu (II) ions using fabricated CHPLLA nanofibrous adsorbent was conducted at temperatures of 25, 30, 40 and 50 °C, the concentration of 100 mg/L for copper ions, the adsorbent dosage of 0.6 mg/20 mL and the interaction time of 30 mins. The glass transition temperature of PLLA is reported at 65 °C in the previous literature **[44]**. Therefore, temperatures up to 50 °C will not affect the mechanical integrity of the porous PLLA membrane. Figure 3.6 (c) shows the impact of temperature on the adsorption strength of copper ions. It is observed that adsorption capability decreases with increasing temperature. At high temperature, the thickness of the surface layer decreases as copper ions start to leave the adsorbent surface and go into the solution. This led to the decline in adsorption of copper (II) ions at elevated temperature **[45]**. The decrease in adsorption capability with rising temperature suggests weak adsorption synergy between the adsorbent surface and the metal ion, which refers to physisorption. Therefore, 25 °C is considered as the ideal temperature for more studies of adsorption.

3.9.7 Kinetics of adsorption

Figure 3. 6 (d) illustrates the adsorption ability as a function of time from 1-30 mins CHPLLA porous adsorbent in 20 mL of individual changed copper concentration. Initially, the rate of copper removal was fast due to a large amount of available active sites on the adsorbent surface and became constant after that. This is due to the reason that all the adsorption positions were occupied by adsorbed metals **[46]**. It is notable that within only 10 minutes of interaction time maximum elimination of copper ions was attained. The Figure 3.6 (d) also illustrates that the adsorption rate of copper ions was reliant on the primary quantity of copper ions as witnessed in a previous study **[47]**. As presented, the adsorption capability of CHPLLA adsorbent was increased for larger copper ions initial quantity. This observation can be credited to the fact that the transfer of mass effect and driving force of concentration gradient are directly proportional to the initial quantity of metal ions **[3]**.

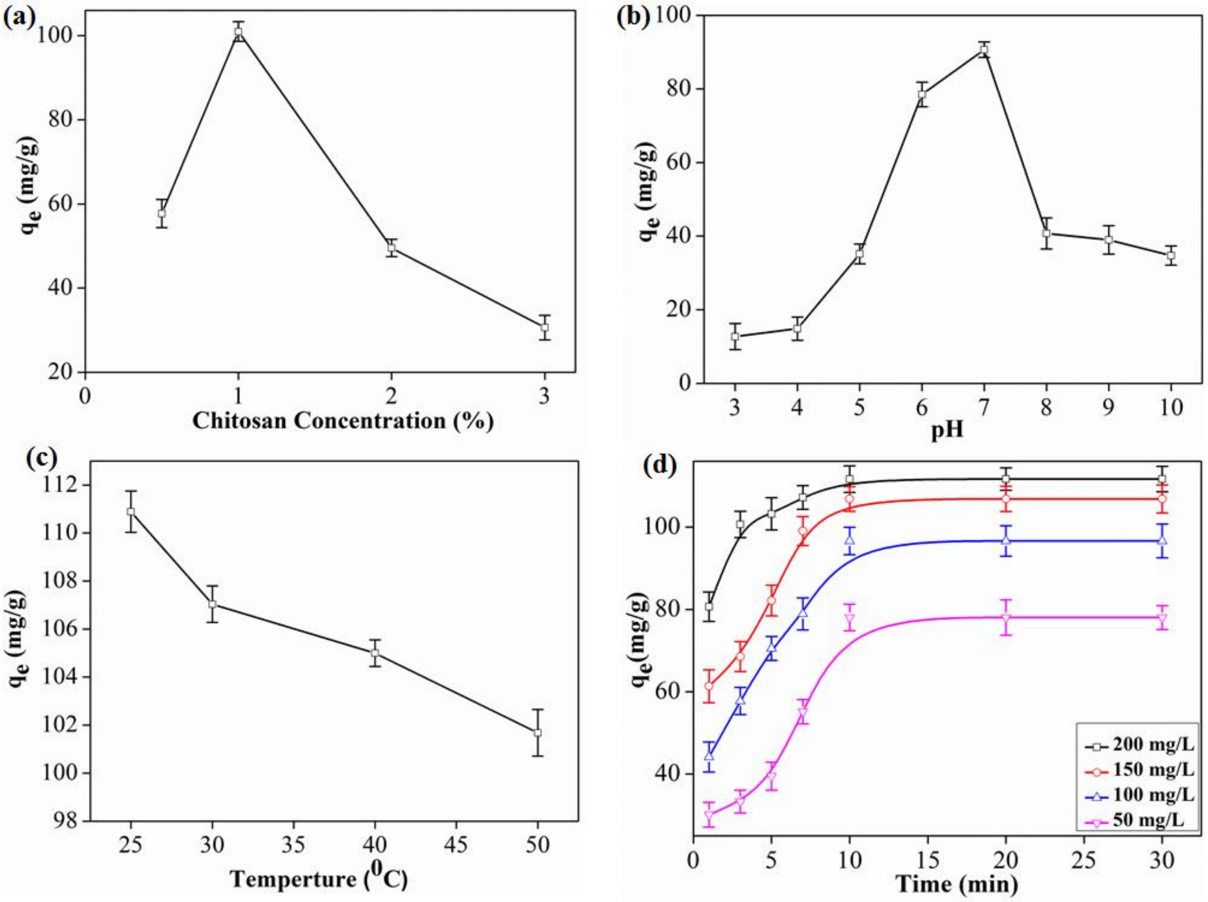


Figure 3.6 Experimental conditions of adsorption (a): effect of chitosan concentration, (b): effect of pH, (c): effect of temperature, (d): adsorption kinetics.

3.10 Mathematical modelling of adsorption kinetics

To study the time of adsorption as well as the time defining the stage of the adsorption process, first-order and second-order kinetic models were studied to simulate the adsorption experimental numbers. Widely used first-order kinetic model for absorption in the solid/liquid complex is indicated as **[48]**:

$$\log(q_{equ} - q_{time}) = \log(q_{equ}) - \frac{k_1}{2.303}t \tag{3}$$

Pseudo-second order model is expressed as follows:

$$\frac{t}{q_{time}} = \frac{1}{k_2 q_{equ}^2} + \frac{1}{q_{equ}}t \tag{4}$$

Where q_{time} (mg/g) and q_{equ} (mg/g) are the quantities of metals adsorbed at the time (t) and at equilibrium respectively. While k_1 (min^{-1}) and k_2 (mg/g min^{-1}) are the constants of first and second-order reaction models.

Figure 3.7 (a) and Table 3.1 indicates that the first-order model did not apt the adsorption investigated statistics well. The correlation coefficients R^2 for the theoretical values of equilibrium adsorption capacity (q_e) is very low because first order is only appropriate for explaining the numbers that are near to the equilibrium adsorption **[49]**. As shown in Figure 3.7 (b) and Table 3.1, pseudo-second-order model describes the adsorption system well since the experimental adsorption values are close to the calculated ones, and the R^2 values are greater than 0.999, demonstrating that the adsorption procedure is administered by the surface reaction **[50]**.

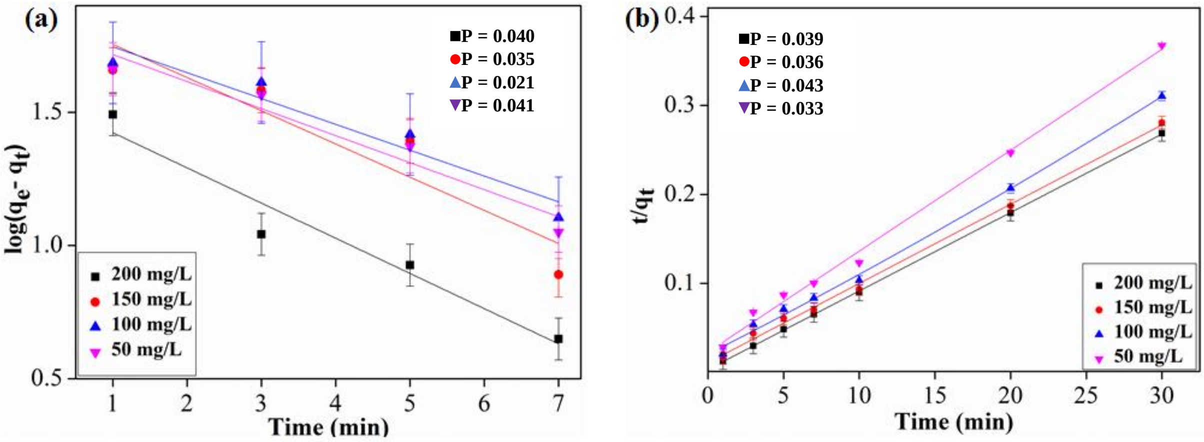


Figure 3.7 (a): pseudo-first-order reaction kinetics, (b): pseudo-second reaction kinetics.

Table 3. 1 Parameters of Pseudo first and second-order reaction kinetics.

Concentration (mg/L)	First-order kinetics			Second-order kinetics				
	k_1 (min^{-1})	R^2	SD	k_2 (g mg^{-1} min^{-1})	$q_{equ, exp}$ (mg g^{-1})	$q_{equ, cal}$ (mg g^{-1})	SD	R^2
50	0.0440	0.94	±0.079	0.00568	81.04	88.10	±0.0089	0.99
100	0.0420	0.92	±0.084	0.00577	96.64	103.30	±0.0071	0.99
150	0.0540	0.86	±0.153	0.00735	106.84	112.23	±0.0052	0.99
200	0.0573	0.94	±0.099	0.0237	111.66	113.37	±0.001	0.99

3.10.1 Modelling of adsorption isotherms

Isotherm models are studied to make a model of adsorption capability of adsorbents against the amount of adsorbate at equilibrium conditions. In this study, we have used the Langmuir model and the Freundlich model to study the adsorption process.

The Langmuir model considered that there are a constant amount of adsorption locations present on the adsorbent surface, active sites are of equal size and shape on a solid surface and each vacant site can bind only one adsorbate molecule to make a homogenous monolayer on the adsorbent. The linear equation of Langmuir isotherm is expressed as **[51]**:

$$\frac{C_{equ}}{q_{equ}} = \frac{1}{k_l q_{max}} + \frac{C_{equ}}{q_{max}} \quad (5)$$

Where q_{equ} (mg/g) and C_{equ} (mg/g) represent the adsorption at equilibrium and adsorbate concentration respectively, q_{max} (mg/g) is the highest adsorption capability, while k_l (L mg/g) is the energy of adsorption. Figure 3.8 (a) and Table 3.2 show that Langmuir isotherm relates significantly better with the experimental values of adsorption for Cu (II) ions.

In contrast, Freundlich isotherm states that there are unlimited adsorption sites available and a heterogeneous layer of adsorbate will form on the adsorbent with non-uniform distribution of adsorption heat. The Freundlich equation can be written as **[52]**:

$$q_{equ} = k_f C_{equ}^{\frac{1}{n}} \tag{6}$$

Where q_{equ} (mg/g) and C_{equ} (mg/g) are the adsorptions at equilibrium and adsorbate concentration respectively, while k_f (L mg^{-1}) is a unit capability coefficient and n shows the degree of heterogeneity in the adsorption system. The greater the value of n, the more heterogeneous system is **[15]**. In Table 3.2, n values greater than 1 designates heterogeneous adsorption. As shown in Figure 3.8 (b) and Table 3.2 the Freundlich model did not fit well with the experimental data of Cu (II) ions adsorption with lower R^2 values as compared to the Langmuir model. The result confirms CHPLLA nanofibres structure and composition.

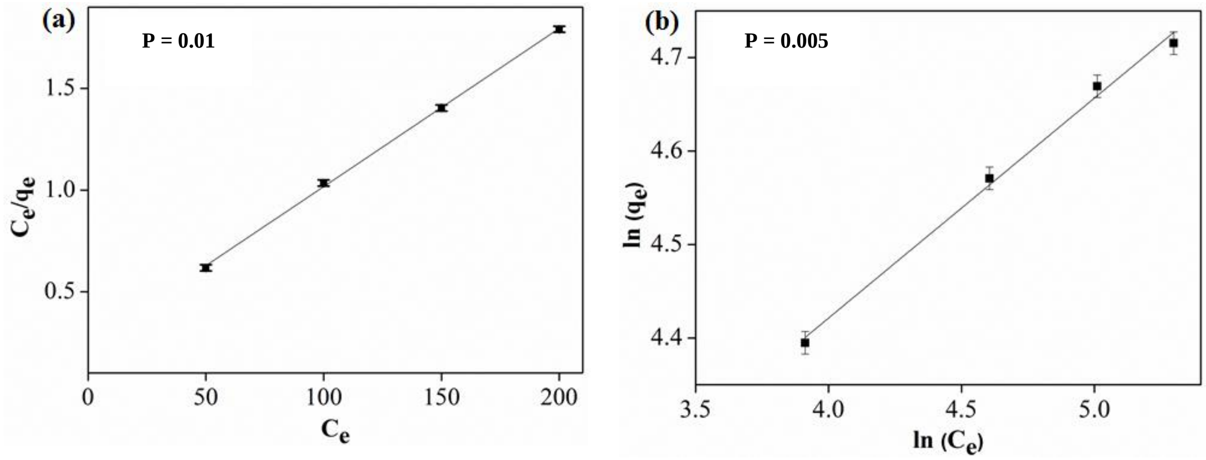


Figure 3.8 (a): Langmuir adsorption isotherm, (b): Freundlich adsorption isotherm.

Table 3.2 Parameters of Langmuir and Freundlich isotherm.

Metal ion	Freundlich constants				Langmuir constants			
	k_f (L mg^{-1})	n	R^2	SD	k_1 (L mg^{-1})	q_{max} (mg g^{-1})	SD	R^2
Cu (II)	3.47	4.24	0.994	±0.012	1.72	128.53	±0.015	> 0.999

3.10.2 Thermodynamic parameters

The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated by thermodynamic equations (7), (8) and (9) **[53]**:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$$k_l = \frac{q_{equ}}{C_{equ}} \quad (8)$$

$$\ln k_l = \frac{\Delta S^\circ}{G} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Where k_l is a constant, q_{equ} is the adsorption capacity (mg/g) at equilibrium, C_{equ} is the metal ion concentration at equilibrium, G is the ideal gas constant (8.314 J/mol/k) and T is the absolute temperature (K). Values of ΔH and ΔS were calculated from the slope and intercept by the linear plot of $\ln k_l$ and the inverse of temperature (1/T) as illustrated in Figure S 3.4.

The obtained thermodynamic factors are displayed in Table S 3.3. The negative values of ΔH and ΔS indicated a decrease in randomness and exothermic nature of the adsorption process. Therefore, increasing the solution temperature will decrease the binding potential at equilibrium. The negative values of ΔG indicate that the adsorption process was spontaneous in the temperature range studied **[53]**.

3.11 Mechanism of chitosan for the removal of Cu ions

Potentiometry is considered to be the fundamental method to describe the complex formation of chitosan with metals by studying acid-base reactions and metal-ligand interactions. The acid accepts a pair of the electron (metal) from the base (chitosan) and forms a covalent bond with the metallic ions. There is only one site available in chitosan monomeric unit (amine groups) which initiates the covalent bonds with metallic ions **[54]**.

During the adsorption process of Cu (II) ions by chitosan, pH of solution plays a notable role **[55]**. When the pH of a solution is less than 5.30 there is no or very small complex formed between copper Cu (II) ions and chitosan. When pH is greater than 5.30, amino groups made a covalent bond with copper ions and formed $[Cu(-NH_2)]^{2+}$ complex as shown in Figure S 3.5 and in the equation (10) and (11):

$$\mathrm{Cu\ (II)+\text{-}NH_3^+ + H_2O \rightleftharpoons [Cu(\text{-}NH_2)]^{2+} + H_3O^+} \tag{10}$$

$$\mathrm{Cu\ (II)+\text{-}NH_2 \rightleftharpoons [Cu(\text{-}NH_2)]^{2+}} \tag{11}$$

Another type of complex was also investigated when pH goes above 5.80 where another amino group is incorporated $[Cu\ (\text{-}NH_2)_2]^{2+}$as shown in Figure S 7.5 and in the equations (12) and (13):

$$\mathrm{[Cu(\text{-}NH_2)]^{2+} + \text{-}NH_3^+ + H_2O \rightleftharpoons [Cu(\text{-}NH_2)_2]^{2+} + H_3O^+} \tag{12}$$

$$\mathrm{[Cu(\text{-}NH_2)]^{2+} + \text{-}NH_2 \rightleftharpoons [Cu(\text{-}NH_2)_2]^{2+}} \tag{13}$$

This complex is stable up to pH 7.7; beyond this pH, copper hydroxides will precipitate and the procedure will become difficult to study.

3.12 Conclusion

Chitosan modified porous PLLA nanofibers were fabricated and used as an adsorbent for the elimination of Cu (II) ions from aqueous solution. The adsorption efficiency of this membrane was assessed by varying chitosan concentration, pH, initial metal ion concentration, contact time and temperature. The adsorption capability for copper elevated with increasing contact time and reached equilibrium after 10 minutes. The kinetic studies show that Cu (II) ions adsorption adheres to the second-order kinetics. The highest adsorption ability (128.53 mg/g) was obtained at pH 7 and experimental data of adsorption process suited to a greater degree with Langmuir adsorption isotherm. The adsorption efficiency raised at larger copper ion amounts while at elevated temperature the adsorption capacity of the adsorbent was decreased. Thermodynamic analysis proved that the adsorption system was exoergic and automatic naturally with negative figures of enthalpy of reaction (ΔH°) and Gibbs free energy (ΔG°). Furthermore, the highest adsorption capability obtained for Cu (II) ions was greater than the figures recorded in previous researches on chitosan-coated adsorbents endorsing that porous supporting material provide more surface area to increase the opportunity of aminic and hydroxide groups of chitosan to bind copper ions. Thus, chitosan modified porous PLLA nanofibrous membrane can be expressed as a green adsorbent for purification of aqueous solutions containing metal ions such as copper.

3.13 Acknowledgements

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3.14 Novelty statement

According to author's knowledge, little work has been carried out to coat the chitosan on the hydrophobic nanofibrous membranes and previous studies have not comprehensively considered these membranes for the adsorption of heavy metal ions from the aqueous solution. In this research, we have developed porous PLLA membranes with very high specific surface to support the adsorbents and assist them to adsorb metal ions in very high quantities as compared to previous studies.

3.15 Supporting Information: Porous poly (L–lactic acid)/chitosan nanofibers for copper ion adsorption

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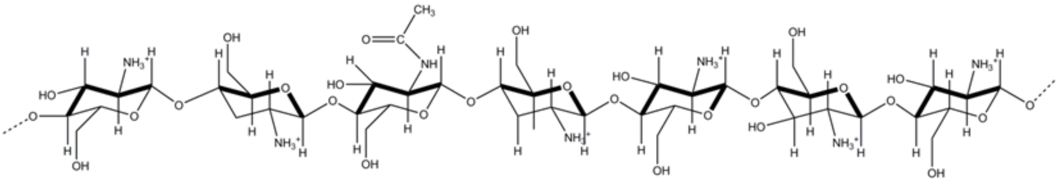

Figure S 3. 1 Chemical construction of chitosan.

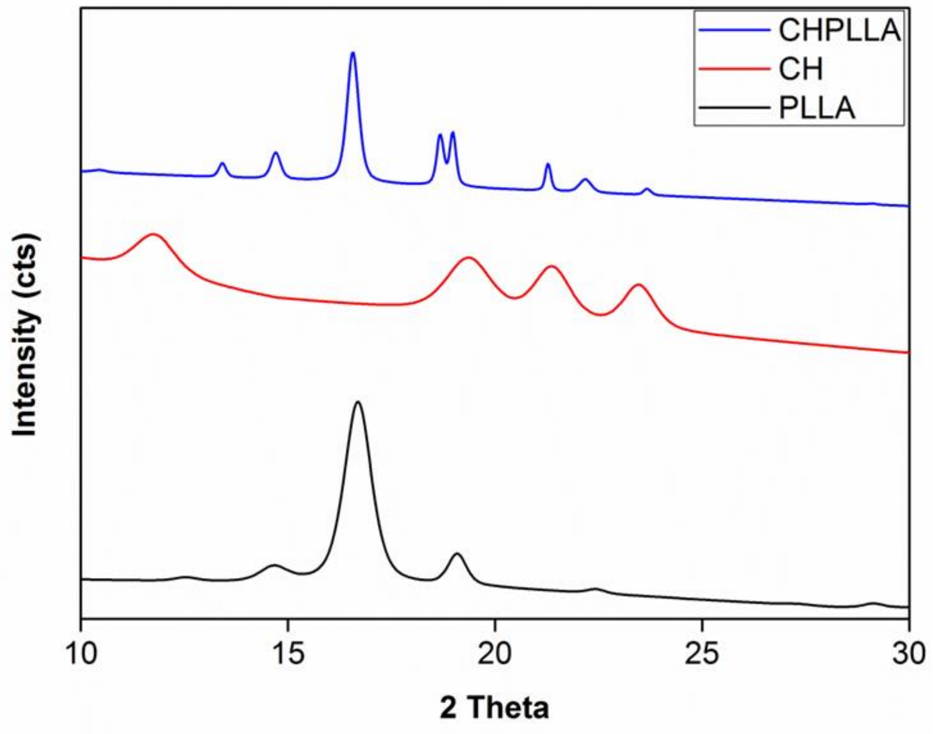

Figure S 3.2 Comparison between XRD patterns of porous PLLA nanofibres, chitosan and chitosan coated porous PLLA nanofibres.

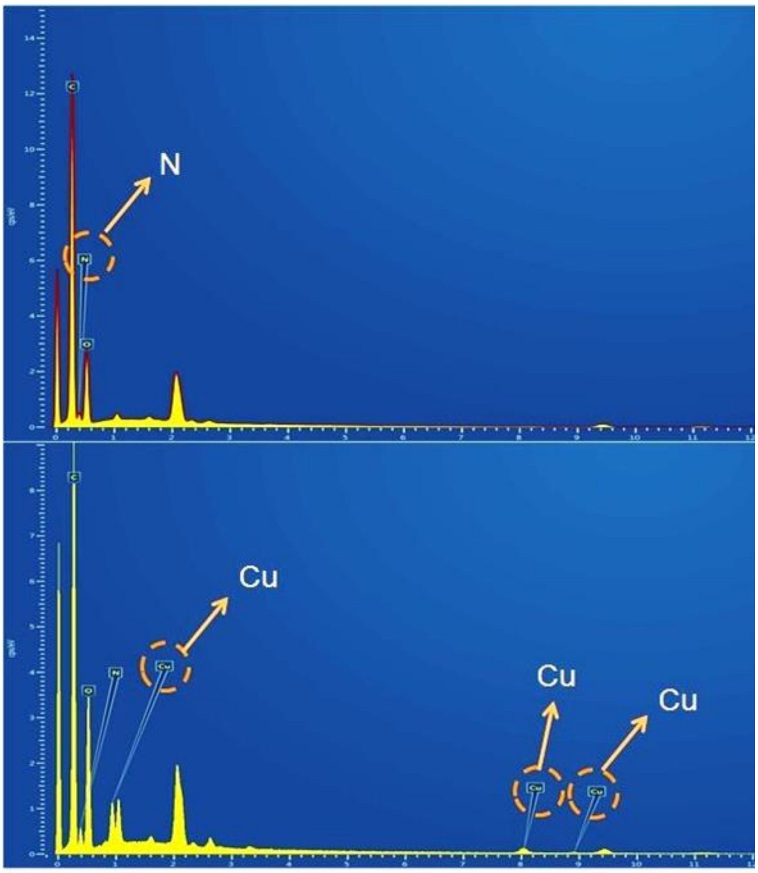

Figure S 3.3 Contrast between EDS spectra of chitosan coated porous PLLA nanofibers (a): before adsorption of Cu (II) ions & (b) after adsorption of Cu (II) ions.

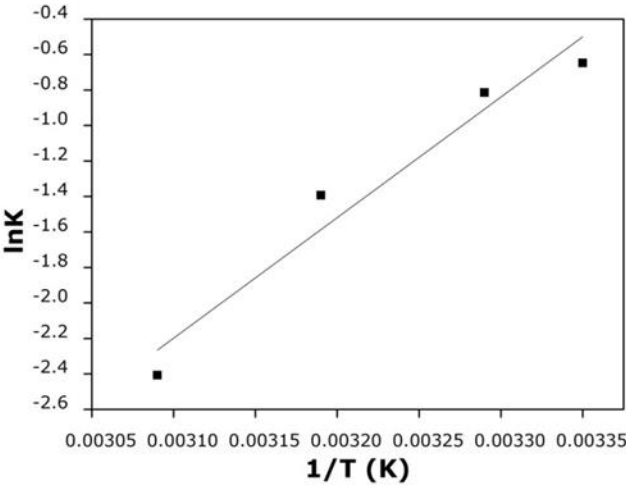

Figure S 3.4 Vont Hoff's plot.

Table S 3. 1 Swelling behaviour of chitosan-coated porous PLLA nanofibers.

Adsorbent	Swelling (%)		
	5 % (v/v) Acetic acid	Distilled water	0.10 M NaOH
Chitosan	Soluble	51.7	40.1
Chitosan-coated PLLA nanofibres	46.9	32.1	28.5

Table S 3.2 Comparison of maximum adsorption capability (mg/g) of Cu (II) ions on different chitosan-coated membranes.

Chitosan-coated membrane	Adsorption capability (mg/g)	Refs
Chitosan-coated cotton gauze	14.1	**[31]**
Chitosan-coated polyethylene terephthalate (PET)	23.70	**[30]**
Chitosan-coated sand	8.18	**[3]**
Chitosan-coated porous PLLA nanofibres	128.53	**Present work**

Table S 3.3 Thermodynamic parameters.

Metal ion	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	Temperature ($^{\circ}$C)	ΔG° (kJ mol^{-1})
Cu (II)	-6.792	-23.25	25	-6.208
			30	-6.091
			40	-5.858
			50	-5.620

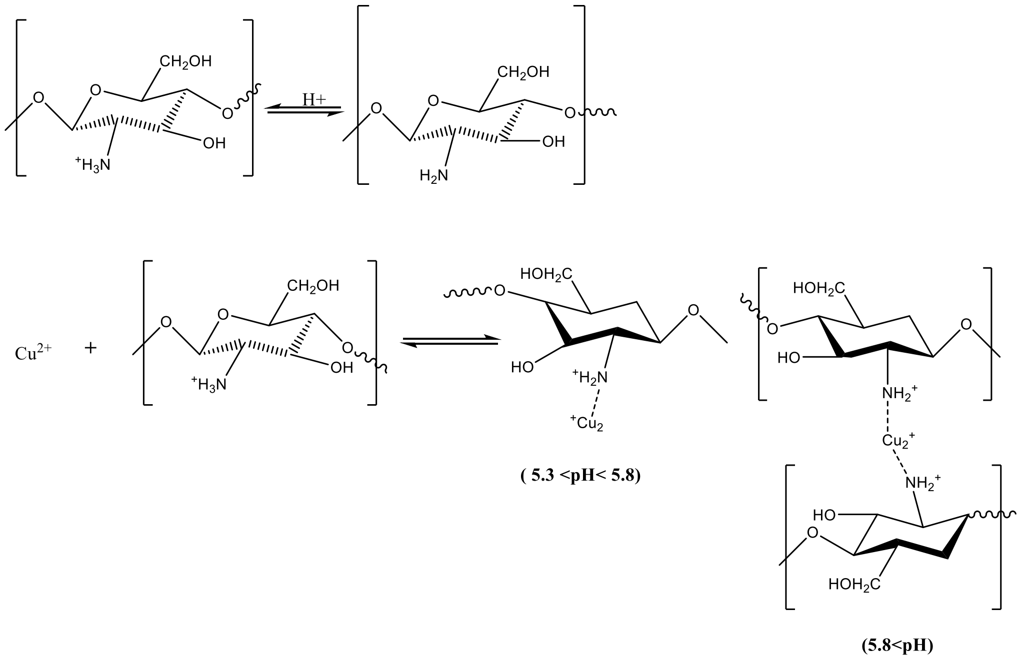

Figure S 3.5 Mechanism of chitosan adsorption for Cu (II) ions.

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4.Chapter 4

Polydopamine-assisted grafting of chitosan on porous poly(L-lactic acid) electrospun membranes for adsorption of heavy metal ions

4.1 Introduction

This chapter was published as the article “Polydopamine-assisted grafting of chitosan on porous poly(L-lactic acid) electrospun membranes for adsorption of heavy metal ions” in International Journal of Biological Macromolecules (2021). In this work, chitosan was grafted on porous PLLA membrane by using polydopamine as an intermediate layer. It was observed that adsorption of copper ions from aqueous solution increased due to the increase of amine groups and stability of chitosan. The variation in adsorption is due to the change in surface area of porous PLLA membranes with respect to polymerization times of dopamine. Moreover, the adsorbent membrane was efficient for three adsorption cycles. Finally, this work provides a simple and facile method to increase the amino groups and surface area for the adsorption of heavy metal ions.

4.2 Author contributions

I performed the experimental work on porous PLLA nanofibers electrospinning, PDA coating and chitosan grafting, characterization of adsorbents and mathematical modelling. Madeeha Tabassum did x-ray photoelectron spectroscopy analysis and x-ray diffraction. Jinmin Meng and Zhiying Xin contributed to useful discussions in the project. Jiashen Li and Hugh Gong provided supervision during the project.

4.3 Citation

Qasim Zia, Madeeha Tabassum, Jinmin Meng, Zhiying Xin, Hugh Gong, Jiashen Li, Polydopamine-assisted grafting of chitosan on porous poly(L-lactic acid) electrospun membranes for adsorption of heavy metal ions, International Journal of Biological Macromolecules, Volume 167, 2021, Pages 1479-1490, ISSN 0141-8130.

4.4 Relationship with objectives

In the current study, the objectives of this thesis are satisfied that are fabrication of PLLA porous nanofibrous membrane dopamine polymerization on porous membranes and grafting of chitosan on dopamine modified membranes with various concentrations. Moreover, these membranes are successfully characterized and evaluated in various adsorption environments. Finally, these adsorbents were successfully tested for adsorption of copper ions from wastewater solutions.

4.5 Manuscript 2: Polydopamine-assisted grafting of chitosan on porous poly(L-lactic acid) electrospun membranes for adsorption of heavy metal ions

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4.6 Abstract

In this study, a versatile method for the manufacturing of chitosan-grafted porous poly(L-lactic acid) (P-PLLA) nanofibrous membrane by using polydopamine (PDA) as an intermediate layer has been developed. P-PLLA fibres were electrospun and collected as nano/micro fibrous membranes. Highly porous fibres could serve as a substrate for chitosan to adsorb heavy metal ions. Moreover, PDA was used to modify P-PLLA surface to increase the coating uniformity and stability of chitosan. Due to the very high surface area of P-PLLA membranes and abundant amine groups of both PDA and chitosan, the fabricated membranes were utilized as adsorbent for removal of copper (Cu^{2+}) ions from the wastewater. The adsorption capability of Cu^{2+} ions was examined with respect to the PDA polymerization times, pH, initial metal ion concentration and time. Finally, the equilibrium adsorption data of chitosan-grafted membranes fitted well with the Langmuir isotherm with the maximum adsorption capacity of 270.27 mg/g.

Keywords: Polydopamine, Chitosan, PLLA, Electrospinning, Grafting

4.7 Introduction

Water pollution by heavy metal ions is a serious concern globally, as they are posturing a bigger threat to the environment and human health **[1]**. These metals are toxic, carcinogenic and non-biodegradable in nature and present worldwide. The heavy metal ions can be broadly defined as metals with relative density more than 5 g/cm^3 and atomic mass ranging between 63 and 200 g/mol. **[2]**. Various heavy metals such as copper, cobalt, iron, zinc and manganese are necessary for living beings in lower quantities, but their presence in higher concentrations are toxic **[3]**. Nowadays, due to the fast-growing modern industrial setups of electronics, metal-plating, mining, textile and various other manufacturing units, heavy metals waste in the water is increasing enormously, particularly in the developing countries **[4]**. Therefore, it becomes an ever more exigent demand to improve methods and processes for effective removal of heavy metal ions from wastewater **[5, 6]**. According to literature, researchers have adopted numerous methods to remove toxic metals from water. These techniques include ion exchange **[7]**, adsorption **[8]**, reverse osmosis **[9]**, chemical precipitation **[10]**, nano filtration **[11]**, and electrochemical filtration **[12]**. Many scholars hold the view that, adsorption is the most economical and effective among the mentioned techniques **[13-15]**. A likely explanation is that adsorption is often reversible, is flexible in design and operation and also produces high quality treated effluents. Nevertheless, this technique depends upon material characteristics for better efficiency, selectivity, equilibrium time, stability and regeneration **[16].**

Electrospun porous nanofibrous membranes have emerged as a powerful platform for wastewater treatment due to their unique highly porous interconnected structure, submicron pore size and a large surface area to volume ratio **[17]**. Extensive research shown that, most studies have only focused on polymer nano fibrous membranes containing hydrophilic groups like cellulose acetate **[18]**, poly acrylonitrile **[19]**, polyvinyl alcohol **[20]**, and chitosan **[21]** for heavy metal removal. However, hydrophilic fibres can be adversely affected under certain conditions, for example, in aqueous environments, these fibres have the tendency to be plasticized. In addition, swelling of these polymers in the water could lead to decreasing in their membrane performances and mechanical strength **[22]**. There is little published data on polymers like poly(L-lactic acid) (PLLA), polytetrafluoroethylene and polyvinyl chloride due to their hydrophobic nature, no functional groups to adsorb heavy metal ions or reactive sites to immobilize heavy metal binding agents **[8, 23]**. Therefore, researchers are applying hydrophobic nano fibrous membranes in water treatment processes by increasing their surface area, hydrophilicity and by immobilizing binders onto their surface with functional groups of $-NH_2$, -SH, $-SO_3H$, respectively. The higher surface area and more capturing agent molecules could notably enhance the removal efficiency of hydrophobic nanofibres **[24, 25]**.

Chitosan can play an important role in addressing the above-mentioned issues. A key aspect of chitosan is that it contains a large number of amino and hydroxyl functional groups, which serve as adsorption sites for heavy metal ions. Another significant characteristic of chitosan is that it is the most abundant natural occurring polysaccharide, low cost, biocompatible, biodegradable and hydrophilic in nature, which brings appealing charm in the field of adsorption **[26-28]**. However, the main obstacles to use chitosan as adsorbent for heavy metal ions are its swelling in water, degradation in acidic media, the low surface area and weak mechanical strength **[8]**. A number of researchers have attempted to overcome these problems via crosslinking **[29, 30]**, surface grafting **[31]**, and coating **[32-34]** the chitosan on the surface of substrates. A much-debated question is whether these solutions are viable? To date, there has been agreement between scientists that crosslinking and the surface modification of chitosan can effectively increase its stability in acids and reduce the swelling in the aqueous mediums **[35, 36]**. Such approaches, however, have greatly decreased the adsorption capacity of chitosan. An implication of this is that the amino and hydroxyl groups of chitosan are likely to react with crosslinking agents, which are main adsorption sites for metal ions **[37, 38]**. Thus, the chemical modification of chitosan with agents having functional groups like amine, hydroxyl and thiol can solve the existing problem.

Surface grafting is another simple and effective technique to immobilize the capturing agents on the surface of electrospun substrates for the longer time. However, for most of hydrophobic electrospun substrates, they have no sufficient reactive sites for direct chitosan grafting. Therefore, it is necessary to modify the surface of hydrophobic substrates with some versatile materials, such as polydopamine (PDA), to graft chitosan and to maintain its extended stability. Dopamine (DA) is fast becoming a key material to modify various adsorbents, because of the presence of a large number of amine and catechol groups on its backbone **[37]**. DA has the ability to self-polymerize in aqueous solution, under oxidative and alkaline conditions to form a stable PDA coating on virtually any kind of materials **[39]**. Several previous studies have reported PDA as an interface for grafting different polymers on electrospun membranes for wastewater applications. For instance, Wu et al **[23]** used PDA as an interlayer between polyvinyl chloride nanofibres and polyethylene imine for adsorption of copper (Cu^{2+}) ions from water. In another study, scientists attached β-cyclodextrin on PDA-functionalized polystyrene porous fibres to remove phenolphthalein from aqueous solution **[40]**. In contrast, recently, only one study has attempted PDA as an intermediate film for grafting chitosan on the polypropylene surface for the prevention of intra-peritoneal adhesion formation **[41]**. Compared to above mentioned literature, our work is focused on providing extremely high surface area, increased functionalized groups and stability of adsorbent to adsorb greater amount of metal ions from the aqueous solution.

Thus, due to the lack of literature and inspired by the PDA and chitosan unique properties, we have made an effective method using electrospun membranes and PDA to develop chitosan-grafted porous PLLA (P-PLLA) nano fibrous membrane for the extraction heavy metal ions. A highly porous nanofibrous PLLA membranes with a large surface area were firstly fabricated via electrospinning and post treatment method. Then, by immersion in dopamine solution their surface was modified. Finally, a layer of chitosan was grafted on the PDA-coated P-PLLA membrane surface. Copper Cu (II) was selected as the target heavy metal ion to assess the adsorption performance of PDA coated P-PLLA and chitosan-grafted P-PLLA nanofibrous membranes. Furthermore, factors affecting the adsorption of heavy metals, including PDA reaction time, pH, initial metal ion concentration, temperature, kinetic and isotherm adsorption models were studied. Finally, the regeneration capability of adsorption membranes was also evaluated.

4.8 Experimental

4.8.1 Materials

PLLA (PL 65) was obtained from PURAC biochem, The Netherlands. Low molecular weight chitosan (M_w = 50,000-190,000 Da), with 75-85% degree of deacetylation, dopamine hydrochloride, TRIS HCl buffer solution (1 M, pH = 8.5), dichloromethane (DCM, 99.99%), Polyethyleneimine (PEI), sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) were procured from Sigma Aldrich. Glacial acetic acid (≥ 98%), ethanol and acetone (99.97%) were purchased from the VWR scientific company limited. Dimethylformamide (DMF, 99.80%) and copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) were acquired from Fischer scientific limited. Distilled water was obtained from the USF-ELGA filter in the University of Manchester laboratory.

4.8.2 Preparation of sample

The sample was prepared according to the steps illustrated in Figure 4.1. P-PLLA nanofibres were electrospun with a trinal system of solvent/non-solvent and polymer. To begin this process, PLLA (1.8 wt %) was dispersed by overnight stirring and heating at 50 °C in the mixture of DCM (solvent) and DMF (non-solvent) with a 19:1 w/w in a tightly closed glass container until PLLA was completely dissolved. The PLLA/DCM/DMF solution was then electrospun to be PLLA fibrous membrane. The electrospinning was carried out at 25 ℃, a humidity of 40%, a voltage of 23 kV, a collecting distance of 30 cm, and the feed rate of 3 mL/min. After collection, the nano fibrous mat was immersed in acetone for five minutes to produce P-PLLA membrane with pores inside and outside the fibres **[42]**. Following this procedure, a piece of P-PLLA membrane (10×10 cm^2) was soaked in ethanol and then washed completely by distilled water. For PDA modification, the wet membrane was dipped into 500 mL of DA solution (2 mg/mL) with 10 mM TRIS (pH 8.5) at 25 ℃ for different time lengths (1, 6, 12, 18 & 24 h). They are denoted as P-PLLA/PDA-1, P-PLLA/PDA-6, P-PLLA/PDA-12, P-PLLA/PDA-18 and P-PLLA/PDA-24. Subsequently, the membranes were washed three times with distilled water to remove any unreacted DA and dried overnight at room temperature.

It is now well established from a variety of studies that polymers containing $–NH_2$ groups can be easily and strongly adhered on the PDA reactive layer **[43-45]**. To chemically graft the chitosan on P-PLLA/PDA membranes, each P-PLLA/PDA membrane was immersed into the 1% chitosan solution (1% v/v, acetic acid) at 25 ℃ for 12 h. After this reaction, samples were washed with ultrapure water three times in order to wipe out physically adsorbed chitosan. Finally, all samples were dried at room temperature for 24 h.

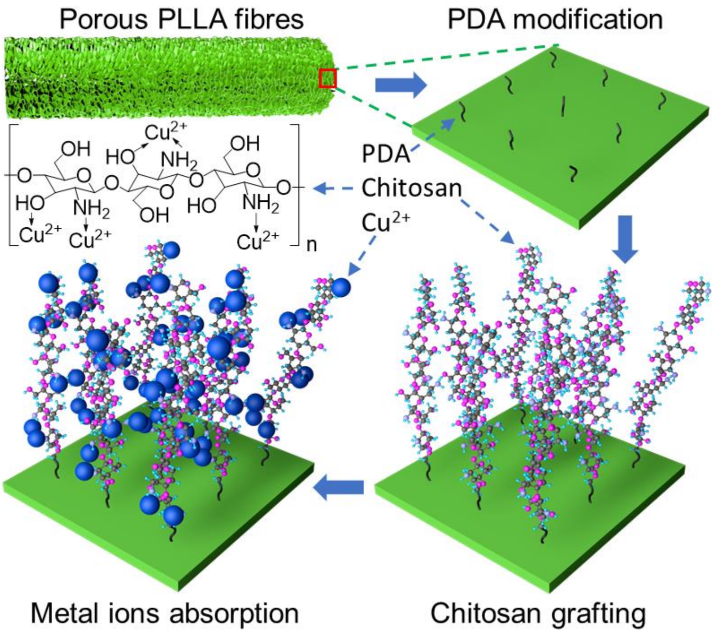


Figure 4. 1 Schematic representation showing the membrane sample preparation and metal ion absorption.

4.8.3 Surface chemistry and morphologies

A NICOLET 500 FTIR spectrophotometer was used to characterize the change in the functional group of chemical structure of P-PLLA, P-PLLA/PDA and P-PLLA/PDA/chitosan membranes. The characterization was carried out in the range of 4000 to 500 cm^{-1} to analyse the chemical composition of the membranes. X-ray photoelectron spectroscopy (XPS) Fisher Scientific with Al-Kα micro-focused monochromator (variable spot size) as radiation source was used.

The surface morphologies of P-PLLA membranes were characterized before and after modification by the scanning electron microscope (SEM, FEI Quanta 250 FEG). Before SEM analysis, for the better resolution of images coating of all the samples was done with platinum for 2 min under the vacuum.

4.8.4 X-ray diffraction (XRD)

A wide-angle X-ray diffraction (WAXD), PANalytical (X'pert pro diffractometer, Netherland) Cu-Kα (1.5406 Å) with nickel filter, was used to analyse the crystalline nature of P-PLLA membranes after the modification with PDA and chitosan. The scanning range of 10 - 25° was used during all the measurements.

4.8.5 Measurement of water contact angle (WCA)

Static water contact angle test was used to estimate the hydrophilicity of P-PLLA/PDA (1, 6, 12, 18 & 24 h) membranes on KRUSS FTA 100, Germany. All the measurements were conducted with deionized water and under room temperature. For every sample, the process was repeated three times and the average reading was reported.

4.8.6 Porosity and surface area of P-PLLA/PDA nanofibrous membranes

A simple weighing method was used to estimate the porosity (P_k) of P-PLLA membranes after PDA modification. The membrane samples were first weighed cautiously, and after weighing the samples were drenched into ethanol for 1 h, once the membranes were taken out the excess ethanol on the surface of membranes was removed by using filter paper and finally the wet membranes were weighed again. The membrane porosity was then calculated by using equation (1):

$$\boldsymbol{P_k = \frac{(w_0 - w)\varrho}{\varrho w_0 - (\rho - \varrho) w} \times 100\%} \tag{1}$$

Where w and w_0 are the initial and immersed weight of membranes, and ρ (0.8 g/cm^3) and ϱ (1.24 g/cm^3) are the densities of ethanol and PLLA, respectively.

The surface area of the P-PLLA/PDA membranes was measured by the Brunauer- Emmett-Teller (BET) method by using Gemini 2360 BET surface area analyser.

4.8.7 Batch adsorption tests

The copper ions adsorptions on P-PLLA/PDA and P-PLLA/PDA/chitosan membrane from aqueous solution were investigated with different conditions of PDA self-polymerization time (1, 6, 12, 18 & 24 h), pH (3-10), copper ion concentration (50-200 mg/L), time (1-60 min) at room temperature in batch technique. A piece of PDA-modified or PDA/chitosan-modified P-PLLA membrane (10 × 10 mm^2) was used in 5 mL of copper ion solution for all the adsorption experiments. The mass of adsorbents was measured on highly sensitive weighing balance with a weight accuracy to 0.1 mg. 0.1 M NaOH and 0.1 M HCl was added dropwise in the copper ions solutions to adjust their pH in the range of 3-10. The absorbability of P-PLLA/PDA and P-PLLA/PDA/chitosan membrane was calculated by the equation (2):

$$\boldsymbol{q_e = \frac{(C_o - C_e)V}{IA}} \qquad \textbf{(2)}$$

Where q_e (mg/g) is the equilibrium adsorption, C_o and C_e (mg/L) are the original and end copper ions concentration in the water, respectively, V (mL) is the volume of solution containing copper ions and IA (mg) is the immobilization amount of adsorbent on the P-PLLA membrane.

4.8.8 UV-visible spectrophotometer

After the adsorption, the final concentration of copper ions was determined via Agilent technologies (United Kingdom) cary-60 UV-vis spectrophotometer in the wavelength range of 800-200 nm. It is quite difficult to calculate the final concentration of copper ions by using UV-vis spectrophotometer, it is due to the broad absorption band of copper (II) near long wavelengths. In this study, we have used a simpler and more rapid test method developed recently by Ting et al **[46]**. In this test, we used polyethyleneimine (PEI) as a cationic polymer to detect the copper ions in aqueous solutions. PEI itself does not show any absorption in the range of 1000-200 nm. After adsorption, PEI was added into the copper solution, unabsorbed copper ions reacted with amine groups of PEI and formed a dark blue cuprammonium compound, which showed the absorption in UV-vis spectrophotometer at 630 nm.

4.9 Results and discussion

4.9.1 Morphologies of P-PLLA and P-PLLA/PDA/chitosan fibres

Electrospun PLLA nanofibres were immersed in acetone to obtain the highly porous fibres with a very high surface area. SEM pictures of P-PLLA nanofibres are shown in Figure 4.2. Different from general electrospun solid polymer fibres, P-PLLA fibres contain uniform interpenetrating nano porous network throughout and a coarser surface. The formation of these pores can be explained by the acetone-induced re-crystallization of PLLA **[42]**. The larger surface area of these fibres provides much more anchor points to immobilize the greater number of PDA and chitosan groups.

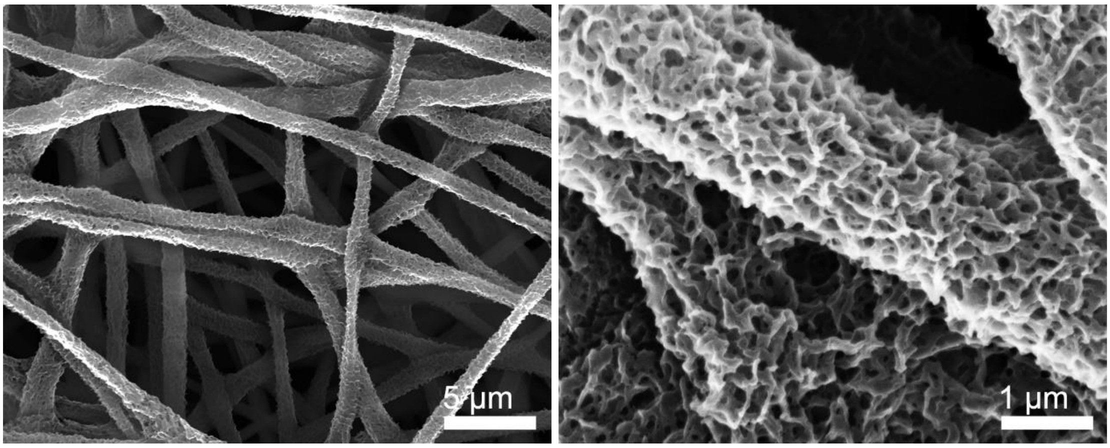


Figure 4.2 SEM of P-PLLA nanofibrous membranes with different magnifications.

During the PDA coating on P-PLLA fibres, it is possible that DA first penetrates into the pores of fibres. With longer durations of coating, PDA layer may cover the surface of membrane, and also the inner porous network of fibres, as evident from the previous study of coating PDA on the porous polystyrene fibres **[40]**. However, a very short coating time leads to only part PDA coating on the fibre surface, which decreases the following chitosan binding. Whereas a very thick PDA coating can block the pores and severely reduce the porosity and surface area of P-PLLA nanofibrous membrane. Figure 4.3 (a-e) compare the surface morphologies of PDA-coated P-PLLA nanofibres for 1 to 24 h. As shown in Figure 4.3 (a), after 1 h of PDA coating, there are still uncovered areas in the fibres. However, it is evident from the Figure 4.3 (b) that a very thin layer of PDA has been formed on all the fibres after 6 h of PDA coating, which also induces the increase in fibre diameter from 1 to 1.2 µm and decrease in porosity to around 85% as shown in Figure 8.4 (a and b). Different from the thin layer on P-PLLA/PDA-6 membrane, the P-PLLA/PDA membranes obtained with relatively longer PDA polymerization time, for example P-PLLA/PDA-24 sample, exhibit thicker PDA layer on the fibres. Moreover, PDA is also polymerized in the space between the fibres, which unavoidably raised the diameter and reduced the overall porosity to 1.8 µm and 55%, respectively. Furthermore, Figure 4.3 (f) shows that, after putting the P-PLLA/PDA-6 membrane in chitosan solution for 12 hours, chitosan is successfully immobilized and made a homogenous layer on surface of each fibre. However, it is interesting to note that from Figure 4.4 (a and b), after coating the chitosan, the porosity is still higher than 80%, which indicates that P-PLLA/PDA-6/chitosan membrane sample has a well intact pore network inside the PDA layer.

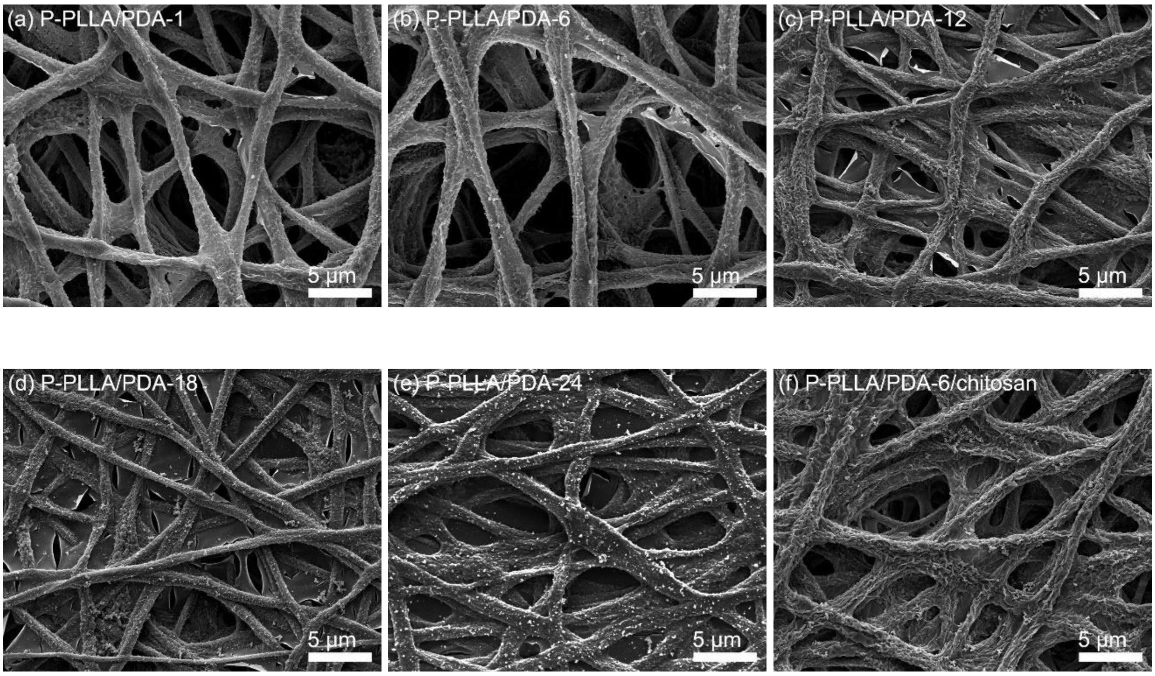


Figure 4.3 SEM of (a-e) P-PLLA/PDA with different coating time (hours); (f) P-PLLA/PDA-6/chitosan.

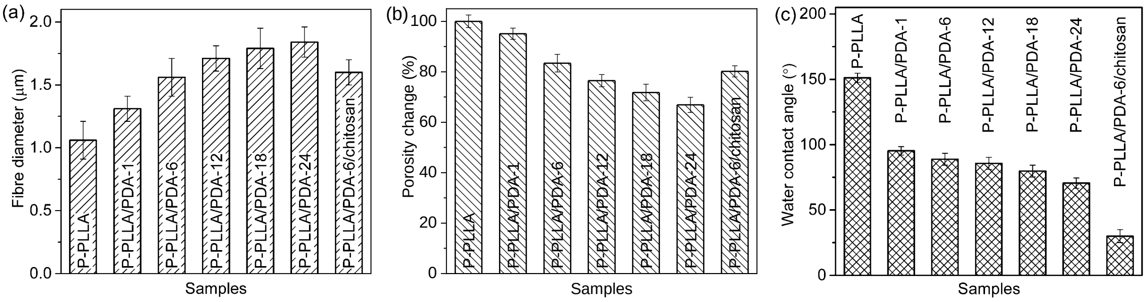


Figure 4.4 (a): Fibre diameter, (b): porosity change of PDA coated and chitosan grafted P-PLLA membranes and (c): Water contact angle of P-PLLA/PDA membranes.

4.9.2 Hydrophilicity of P-PLLA/PDA membranes

Hydrophilicity of nanofibrous membranes is another criterion to evaluate their potential application in the removal of heavy metal ions from the wastewater. An adsorbent must be hydrophilic in nature to ensure its good contact with the metal ions in the aqueous solution. In this study, by using the static WCA on the surface of membrane hydrophilicity of P-PLLA/PDA membranes is determined, as shown in Figure 4.4 (c). Before polymerizing DA on the membrane surface, P-PLLA membrane showed a higher degree of hydrophobicity with a WCA of 151.2°. In another study, Li et al reported the WCA on electrospun PLLA membrane was 120.4° **[47]**. The difference between current study and the reported work is possibly due to the intrinsic and extrinsic porous structure which increased the surface roughness of P-PLLA membranes. After treating the P-PLLA membrane with DA, good hydrophilicity of the P-PLLA/PDA membrane is achieved as expected. P-PLLA/PDA-6 membrane exhibits the WCA of 85°. Further increase in polymerization time of PDA leads to greater hydrophilcity of P-PLLA/PDA membranes. As shown, the WCA can decrease up to 70.6° after the 24 h of PDA polymerization on the membrane surface. However, treatment times larger than 6 h unavoidably decreased the overall surface area and demolished the inner porous structure of P-PLLA membranes which leads to the decrease in performance of P-PLLA/PDA membranes in wastewater treatment. With chitosan grafting, the WCA of P-PLLA/PDA-6/chitosan is further decreased to 30° (wettable surfaces)

4.9.3 Surface group analysis

FTIR spectra, as shown in Figure 4.5 (a), provide the surface groups on P-PLLA, P-PLLA/PDA, P-PLLA/PDA/chitosan nanofibrous membranes and pure chitosan. As compared to the spectrum of pure P-PLLA membrane, two new peaks at 3350 and 1630 cm^{-1} are noted in P-PLLA/PDA, P-PLLA/PDA/chitosan membranes and chitosan spectra, which are assigned to O─H stretching vibrations, N─H bending vibrations and superimposed C═C vibrations of the aromatic ring in PDA, respectively. It can be seen in Figure 4.5 (a) that N─H groups appeared on the hydrophobic P-PLLA membranes after PDA polymerization on the P-PLLA membrane. After immobilizing the chitosan on P-PLLA/PDA membrane, the intensity of the O─H peak at 3350 cm^{-1} increases and becomes broader as compared to the P-PLLA/PDA substrates, which is likely to be related to the high amount of overlaying O─H groups. Furthermore, a new peak at 1550 cm^{-1} shows up, which is likely due to the presence of secondary amine in chitosan. These results suggest that PDA and chitosan are successfully coated on the P-PLLA membranes.

4.9.4 Crystallinity of P-PLLA/PDA and P-PLLA/PDA/chitosan membranes

By using XRD, the crystalline structures of P-PLLA/PDA and P-PLLA/PDA/chitosan membranes were also characterized as shown in Figure 4.5 (b). The XRD profiles of P-PLLA and P-PLLA/PDA membranes display strong peak at 16.7° which belongs to the diffraction of (200) plane of α phase in P-PLLA as described in previous studies **[48]**. This also proves that polymerized PDA does not affect the crystal structure of these P-PLLA membranes. The XRD of anhydrous chitosan film consists of three major peaks at 13.8°, 15.9° and 17.8°, these peaks are referred to anhydrous crystalline forms of chitosan **[49]**. Also, the crystallinity of this chitosan is very poor which is due to the partial rearrangement of chains in the crystal of chitosan during the construction of thin film **[50]**. In comparison, after coating chitosan on P-PLLA/PDA membrane, XRD of P-PLLA/PDA/chitosan membrane exhibits variations in peak intensity and width. The peak at 17.8° of chitosan was shifted to right, the crystallinity of chitosan was also increased. This is possibly due to the formation of hydrogen bonding between chitosan and PDA after chitosan reacting with PDA **[50]**, which also ultimately leads to the increased stability of chitosan thin film on P-PLLA membranes **[43-45]**.

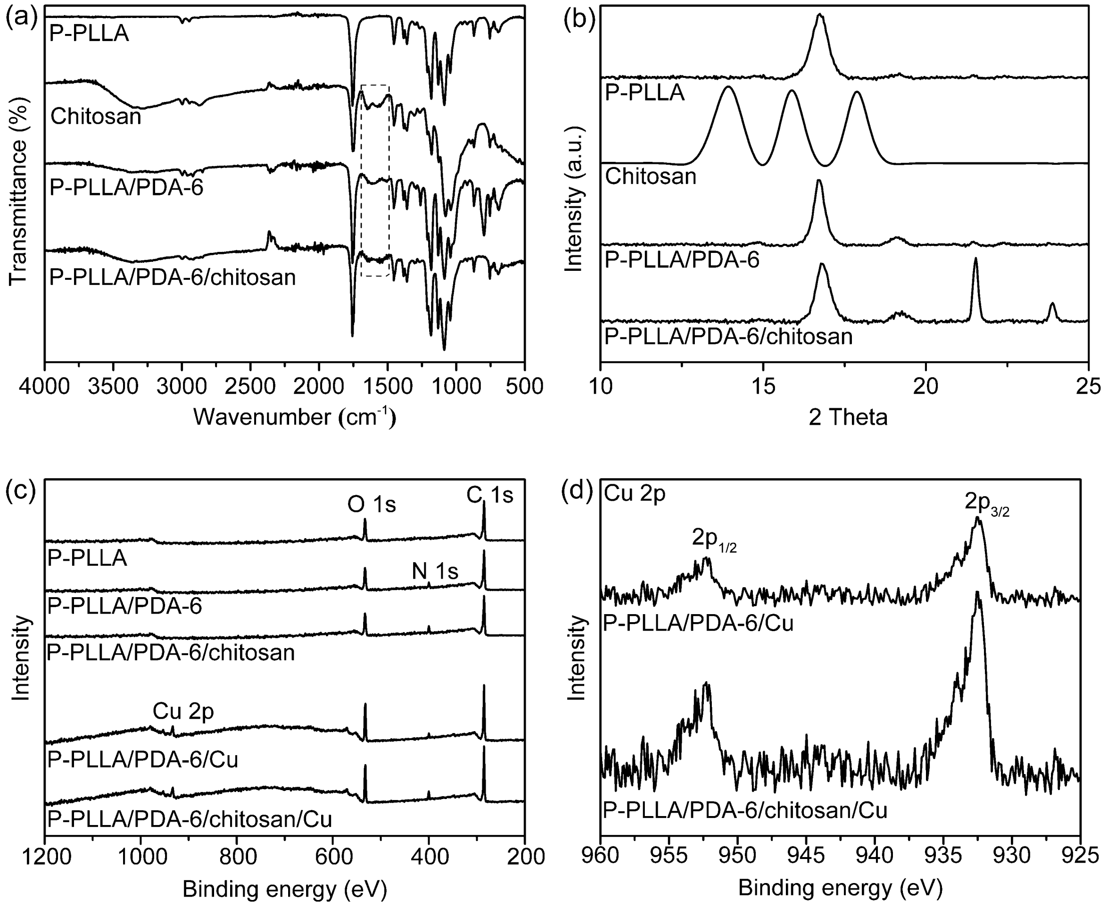


Figure 4.5 (a): FTIR of P-PLLA, chitosan, P-PLLA/PDA and P-PLLA/PDA/chitosan membranes, (b): X-ray diffraction of P-PLLA, P-PLLA/PDA, Chitosan and P-PLLA/PDA/Chitosan membranes, (c): XPS survey spectrums of P-PLLA, P-PLLA/PDA-6, P-PLLA/PDA/chitosan, P-PLLA/PDA-6/Cu and P-PLLA/PDA-6/chitosan/Cu membranes and (d): High resolution copper XPS spectra of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membrane.

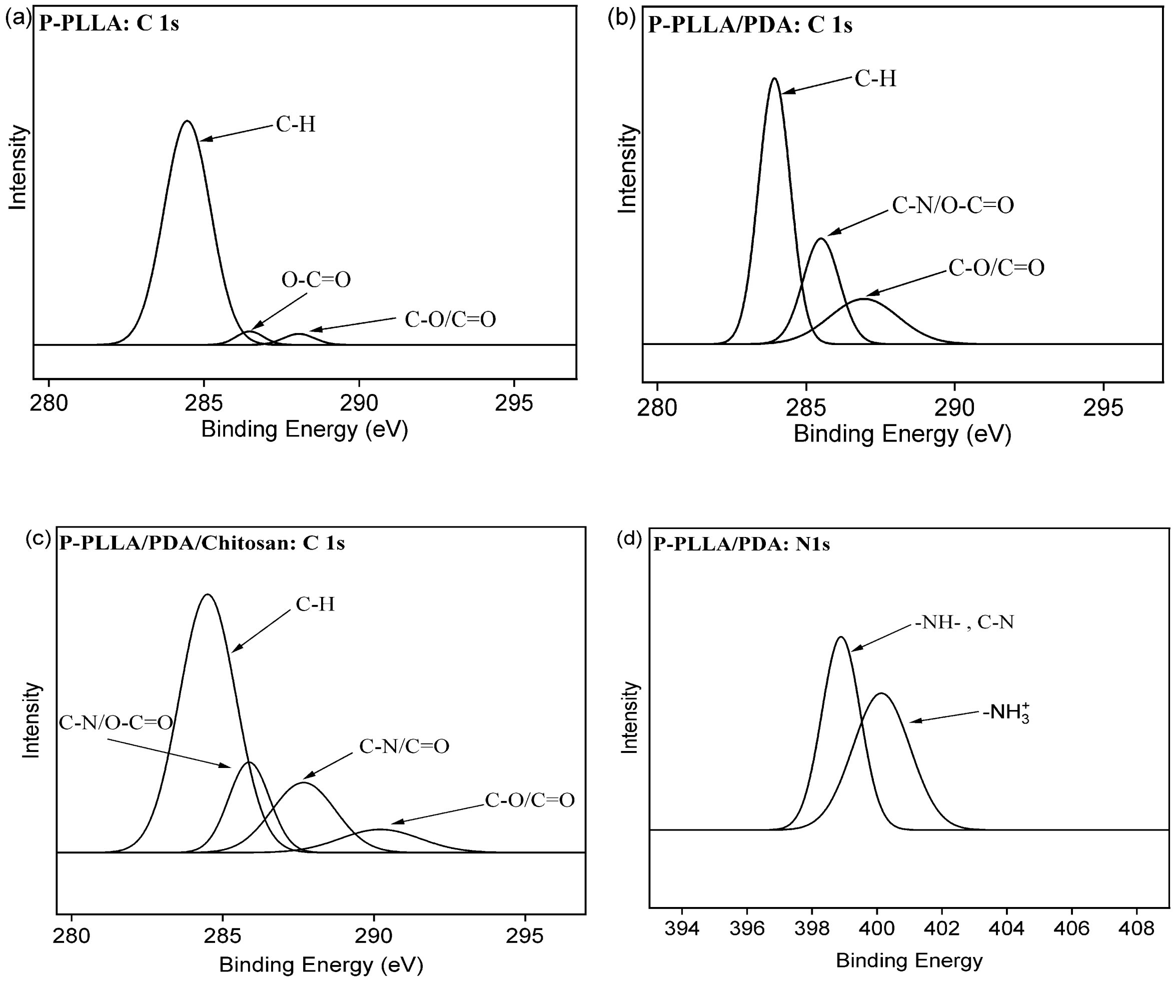
4.9.5 X-ray photoelectron spectroscopy of nanofibrous adsorbents

XPS examination was utilized to identify the change in chemical composition on the surface of electrospun nanofibrous membranes after the modification with PDA and chitosan. It can be seen from XPS surveys in Figure 4.5 (c), the new N 1s peaks appeared at 399.8 eV in the spectra of P-PLLA/PDA and P-PLLA/PDA/Chitosan membranes in contrast with P-PLLA membranes due to the polymerization of PDA and grafting of chitosan **[23]**. Moreover, after the adsorption of Cu^{2+} ions on P-PLLA/PDA and P-PLLA/PDA/Chitosan membranes, a new peak of Cu 2p was emerged. Figure 4.5 (d) shows the high-resolution spectra of copper for both membranes. As shown, two new peaks were identified at 933 and 952 eV. These binding energies corresponds to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks **[51]**. Additionally, a much stronger Cu $2p_{3/2}$ peak after the adsorption of copper was observed on P-PLLA/PDA/Chitosan membrane. This shows the increased interaction of Cu^{2+} ions with P-PLLA/PDA/Chitosan membrane compared to the P-PLLA/PDA membrane. Finally, these results confirm that the PDA and chitosan were successfully immobilized and grafted on P-PLLA membranes and copper was efficiently adsorbed on the surface of P-PLLA/PDA and P-PLLA/PDA/chitosan adsorbents.

Deconvulated C 1s narrow scan spectra of P-PLLA, P-PLLA/PDA and P-PLLA/PDA/Chitosan are presented in Figure 4.6 (a-c). In P-PLLA, peaks appear at about 284.5, 286.4 and 288.1 eV can be attributed to C─H, C═O and O-C═O, respectively. Moreover, after dopamine self-polymerization on P-P-PLLA surface, the intensity of the peak at approximately 286 eV increased as shown in Figure 4.6 (b). Furthermore, after immobilizing the chitosan on the intermediate PDA layer a new peak arise at 285.7 eV (Figure 8.6 (c)), this peak can be assigned to the binding energy of C─N component.

Figure 4.6 (d and e) exhibit the N 1s narrow spectra of P-PLLA/PDA and P-PLLA/PDA/Chitosan membranes, which were deconvulated into two peaks with binding energies at 398.85 and 400.5 eV, which corresponds to –NH and NH_3^+ groups, respectively. In addition, in contrast with P-PLLA/PDA membrane, it was also observed that the intensity of the peak at 400.5 eV was greater than P-PLLA/PDA/Chitosan membrane. The possible explanation of this phenomena is the covalent bonding between the catechol and amino groups in PDA and chitosan.

Briefly, based on the analysis of C 1s and N 1s spectra, it is logical to think that dopamine self-polymerized on the surface of P-PLLA membrane and the chitosan was grafted on the PDA intermediate layer successfully via covalent bonding.



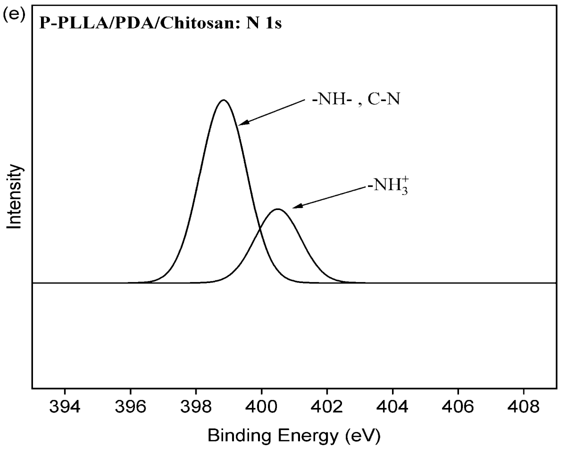


Figure 4.6 (a-c): C 1s high resolution spectra of P-PLLA, P-PLLA/PDA and P-PLLA/PDA/Chitosan, (d and e): N 1s high resolution spectra of P-PLLA/PDA and P-PLLA/PDA/Chitosan membrane.

4.9.6 Mechanism of dopamine polymerization and chitosan grafting

There is little knowledge about the self-polymerization mechanism of dopamine in alkaline environments on hydrophobic substrates like PLLA **[52]**. Many researchers tried to explain the deposition mechanism of PDA on hydrophobic surfaces **[53-55]**. The most common mechanism is the reverse disproportionation reaction. As shown in Figure 4.7, dopamine first oxidizes at pH 8.5 in TRIS buffer solution to form quinones, which further made a compound in an intermediate oxidation state via dismutation reaction and initiate crosslinking. During the reverse reaction and oxidation process, the covalent and π-π interactions between the substrate and dopamine are built up, and make a firmly adhered polydopamine film on the surface of substrate. Moreover, there are some catechol groups available on the polymerized layer of dopamine. These groups can make covalent bond with active amine (-NH) groups in chitosan molecular chains. So, chitosan is strongly immobilized on the porous PLLA membrane surface by polydopamine active layer.

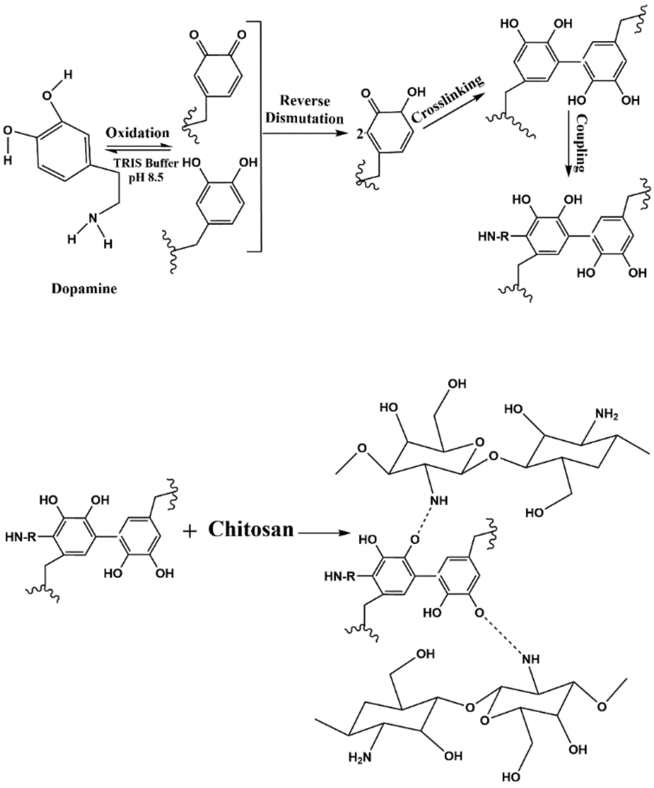


Figure 4.7 Schematic representation of chitosan grafting mechanism on P-PLLA/PDA membrane.

4.9.7 Effect of DA polymerization time on adsorption capability of membranes

Polymerization time of DA on the P-PLLA membranes plays a vital role in the adsorption process of metal ions. Figure 4.8 (a) compares the adsorption of Cu^{2+} ion between P-PLLA/PDA and P-PLLA/PDA/chitosan membranes with respect to the DA polymerization time (1, 6, 12, 18, 24 h). All these experiments were conducted at room temperature and other adsorption parameters were kept constant such as pH of 6, contact time of 60 min, and Cu^{2+} ion concentration of 100 mg/L. In Figure 4.8 (a), it is clear that adsorption was increased for first 1 to 6 h and then started decreasing from 12 to 24 h of DA polymerization time in both P-PLLA/PDA and P-PLLA/PDA/chitosan membranes. A possible explanation of this might be that overall porosity is reduced significantly after 6 h of PDA treatment which leads to decrease in the surface area of the P-PLLA membrane. It is also observed in the Figure 4.8 (a) that after immobilizing the chitosan on the P-PLLA/PDA membranes, the adsorption capacity for Cu^{2+} is enhanced. This outcome is expected because chitosan will reinforce the –NH$_2$ groups present in the P-PLLA/PDA membranes, so there will be more functional groups available for the adsorption process. Therefore, P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes were used as optimal membranes for the remaining trials.

4.9.8 Effect of pH on adsorption capability of membranes

pH is a key parameter for the sorption capacity of adsorbents. The adsorption of Cu^{2+} ions depends to the large extent on the original pH value of the stock solutions because it changes the acid and basic nature of liquids rapidly. In this study, the experiments were carried out in the pH range from 3 to 10, time of 60 min, the initial metal ion concentration of 100 mg/L and at room temperature. As can be seen from Figure 4.8 (b), both P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes share the same trend. The adsorption of metal ions increases as pH of solutions tends to neutrality from acidity, and then falls as pH moves towards basicity. Extremely low adsorption capabilities were shown for both membranes at lower pH. These results may be explained by the fact that more protonated $-NH_3^+$ groups at lower pH repel the metal ions. These positively charged groups decreased as pH of solution rise, which would lower the static repulsion between metal ions and adsorbent surface groups, thus improving the adsorption. At higher pH values, lower adsorption capacities were observed, this is due to the precipitation of the metal ions at the bottom of liquid as hydroxides. Compared with the maximum adsorption capacity of P-PLLA/PDA-6 membrane at pH 5, P-PLLA/PDA-6/chitosan membrane showed the highest adsorption at pH 6. Therefore, pH 5 for P-PLLA/PDA-6 and pH 6 for P-PLLA/PDA-6/chitosan membrane were used respectively throughout this study.

4.9.9 Effect of initial metal ion concentration on adsorption capability of membranes

The effect of Cu^{2+} ions concentration on the adsorbent ability was investigated by varying the initial metal ion concentration in the range of 10-200 mg/L at pH 5 and 6 with 60 min of contact time. From the Figure 4.8 (c), we can see that the adsorption capacity was increased rapidly between 10 to 100 mg/L. The graph also shows that there has been a slight increase in adsorption after 100 mg/L till 200 mg/L. A plausible interpretation of this might be that, at the lower concentration of metal ions more active sites are present on the adsorbent surface. As the concentration increases, the adsorption increases until all the active sites on the surface are used. Then the adsorption may rise a little due to the diffusion of ions in the pores of fibrous membranes.

4.9.10 Kinetics of adsorption process

Another key aspect in the adsorption is the adsorbent contact time with the adsorbate, because it gives the information about adsorption equilibrium. The contact time of adsorbent was studied in the range from 1 to 70 min to examine the effect of time on the adsorption ability of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes. All trials were carried out at optimal parameters of pH 5 and 6 and the initial metal ion concentration of 200 mg/L. The adsorption capacity of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes as a function of time is illustrated in Figure 4.8 (d). As seen, there has been a sharp rise in the adsorption capacity up till 40 min. This trend can be explained by the presence of the large amount of active adsorption sites during the beginning. After 40 min, the adsorption of both membranes remains steady up to 70 min, indicating that the equilibrium adsorption was achieved and metal ions started accumulating on the surface of adsorbent and all the available sites becomes saturated.

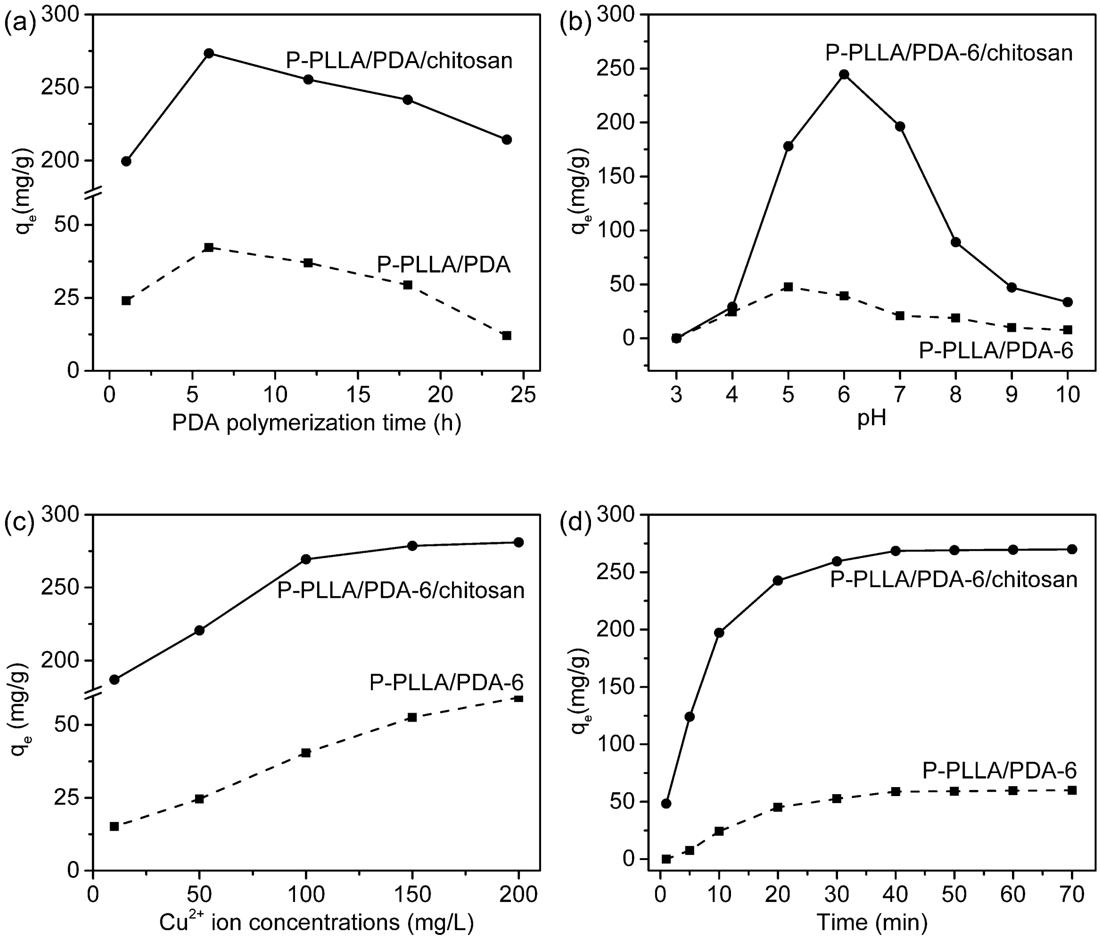


Figure 4.8 Experimental parameters of adsorption; (a) effect of PDA polymerization time, (b) effect of pH, (c) effect of initial metal ion concentration, (d) effect of time.

4.9.11 Linear statistical modelling of adsorption kinetics process

In this study, by using our experimental data, pseudo first order and pseudo second order kinetic models were statistically modelled to simulate and examine the mechanism of adsorption process of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes towards Cu^{2+} ions. According to the previous studies **[56]**, it is assumed that, physical adsorption process relates to the first order model and chemical adsorption is associated with the pseudo second order model.

The linear forms of lagergren pseudo first order **(3)** and pseudo second order **(4)** are as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \textbf{(3)}$$

$$\frac{t}{q_t} = \frac{1}{q_e^2} + \frac{t}{q_e} \tag{4}$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium period and at time (t), respectively. k_1 (min^{-1}) and k_2 (mg/g min^{-1}) are the rate constants of pseudo first and second order adsorption. The linear fitting curves for pseudo first and second order adsorption for both P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes are shown in Figure 4.9 (a) and (b). As shown, the rate constant k_1 and equilibrium adsorption values were calculated from linear plot between $\ln(q_e - q_t)$ and t for pseudo first order adsorption. Similarly, for pseudo second order, the k_2 and q_e values were determined from linear plot between t/q_t and t. Table S 4.1 compares the summary statistics of kinetic parameters and correlation co-efficient (R^2) related to above models for P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes. As it is clearly seen from the Figure 4.9 (a) and (b) and Table S 4.1, P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan differ with each other with respect to their degree of linearity, R^2 values and equilibrium adsorption values with both models. P-PLLA/PDA-6 membranes tend to show better linear response and R^2 (0.97487) value with the pseudo first order model. In contrast to P-PLLA/PDA-6 membranes, linearity degree of the fitted curves and R^2 (0.99813) value of P-PLLA/PDA-6/chitosan membranes were better explained with the pseudo second order equations. Furthermore, $q_{e\ exp}$ values of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes were near to the $q_{e\ cal}$ values of pseudo first order and pseudo second order models, respectively.

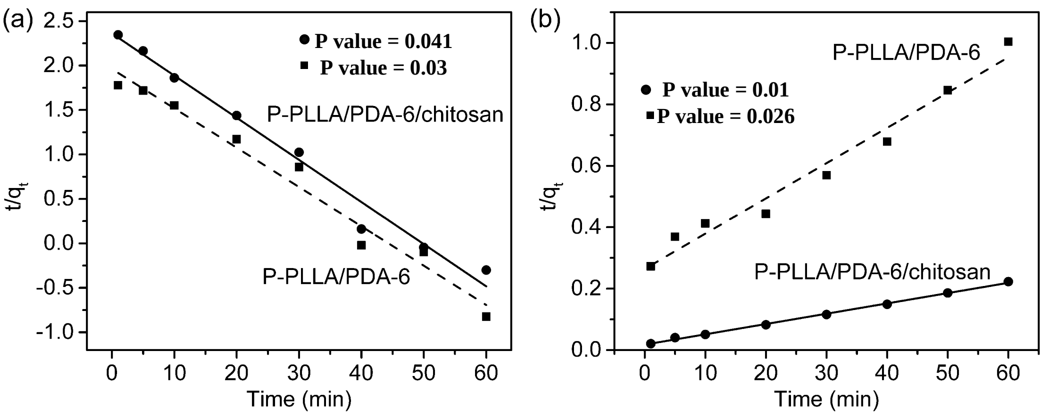


Figure 4.9 (a) Pseudo first order kinetics, (b) Pseudo second order kinetics.

4.9.12 Isotherm study of adsorption process

The isotherm study of adsorption process is important, because it gives the information about interaction between adsorbate and the adsorbent. Most commonly used isotherm models are Langmuir and Freundlich. In this study, these two models have been used to simulate the experimental data for the removal of copper ions from the aqueous solution. The linear equations of Langmuir **(5)** and Freundlich model **(6)** are as follows:

$$\frac{C_{equ}}{q_{equ}} = \frac{1}{k_l q_{max}} + \frac{C_{equ}}{q_{max}} \qquad \textbf{(5)}$$

$$q_{equ} = k_f C_{equ}^{\frac{1}{n}} \qquad \textbf{(6)}$$

Where, q_{max} and q_{equ} (mg/g) are the maximum and equilibrium adsorption capacities of Cu^{2+}, respectively. C_{equ} (mg/L) is the concentration at equilibrium. K_f (L/g) and k_l (L/mg) are the constants of freundlich and langmuir models, respectively. Whereas, n is the degree of heterogeneity in the adsorption system. In the literature, it is assumed that in Langmuir model, the adsorption occurs as a monolayer on the adsorbent surface and the adsorption sites are equal to the number of metal ions. On the contrary, freundlich model predicts that adsorption occurs as a multilayer on the surface of adsorbent and its surface is heterogeneous **[56]**.

The linear fitted plots of the Langmuir and freundlich models are shown in Figure 4.10 (a) and (b) and the summary of isotherm parameters are presented in Table S 4.2. As shown in Table S 4.2, the adsorption process in both P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes for Cu^{2+} ions are better compatible with Langmuir adsorption isotherm. This can be explained by the greater R^2 of both P-PLLA/PDA-6 (0.999) and P-PLLA/PDA-6/chitosan (0.999) membranes with Langmuir model. This validates that, adsorption of copper ions on both membranes is due to the monolayer adsorption mechanism.

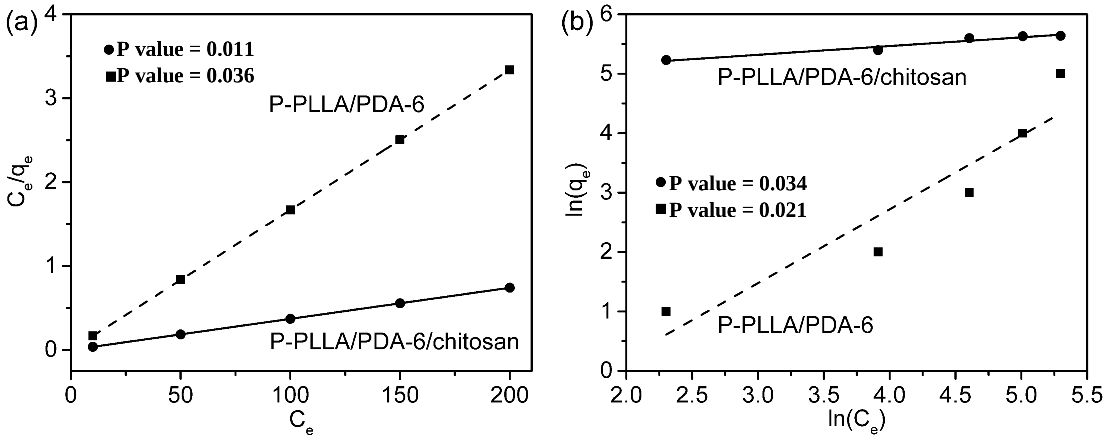


Figure 4.10 (a) Langmuir isotherms, (b) Freundlich isotherms.

The existence of abundant amine and hydroxyl groups and large surface area of P-PLLA membranes, which increases the adsorption of metal ions in chitosan and polydopamine enhances the sorption capability of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan adsorbent. This can be proved by comparing the adsorption capacities with other chitosan and dopamine related adsorbents used to adsorb copper ions in Table S 4.3. As seen, the adsorption capacity of prepared adsorbents in this study is greater than that of previous adsorbents.

4.9.13 Reusability of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes

After adsorption of copper ions on P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes, both saturated membranes were treated with 0.1 M EDTA (desorption solvent) for one hour to remove the copper ions. Subsequently, when copper ions are desorbed from the surface of P-

PLLA/PDA-6 and P-PLLA/PDA-6/chitosan nanofibrous membranes, the membranes were washed with deionized water and used again for next cycles of copper adsorption. The sorption and desorption tests were carried out for three cycles. After adsorption desorption cycle's adsorption capacity of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membrane still remained 90% and 80% of the first cycle, respectively as shown in Figure S 4.2. The minor loss in adsorption capacity is inevitable because of the degradation of adsorbent during the recycling process. The P-PLLA/PDA-6/chitosan membrane sorption capability fall more than that of P-PLLA/PDA-6 membrane, because of the faster degradation of chitosan in deionized water. Even so, after three cycles the adsorption of both membranes was still 80% or higher. Hence, P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes can be used as an efficient and economical adsorbent for the removal of copper ions from aqueous solutions.

4.10 Conclusions

For the first time, chitosan-grafted PLLA nanofibrous membranes were synthesized using PDA as an interlayer. These membranes were utilized to eliminate the copper ions from aqueous solutions. Diameter, porosities and contact angles of nanofibrous membranes suggested that the optimized coating time of PDA and chitosan concentration are 6 hour and 1%, respectively. The effect of various static adsorption parameters, such as polymerization time, pH, initial metal concentration and time, were studied by comparing the adsorption capacities of PDA-coated and chitosan-grafted membranes. The results showed that both membranes were well fitted with Langmuir adsorption isotherm and with the maximum adsorption capability of 59.91 mg/g and 270.27 mg/g, respectively. Finally, the adsorption capacity of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes for Cu^{2+} ions kept about 90% and 80% after two and three regeneration cycles. Therefore, this technique of PDA-mediated chitosan grafting on electrospun fibres can be easily used to synthesize the broad range of high-performance membranes for various special applications.

4.11 Conflicts of interest

There are no conflicts to declare.

4.12 Acknowledgements

The authors acknowledge the support of the Electron Microscopy Center and XRD suite in The University of Manchester.

4.13 Novelty statement

According to author's knowledge, little work has been carried out to graft the chitosan on the hydrophobic nanofibrous membranes using dopamine and previous studies have not comprehensively considered these membranes for the adsorption of heavy metal ions from the aqueous solution. In this research, we have developed porous PLLA membranes with very high specific surface to support the adsorbents and assist them to adsorb metal ions in very high quantities as compared to previous studies.

4.14 Supporting Information Polydopamine-assisted grafting of chitosan on porous poly(L-lactic acid) electrospun membranes for adsorption of heavy metal ions

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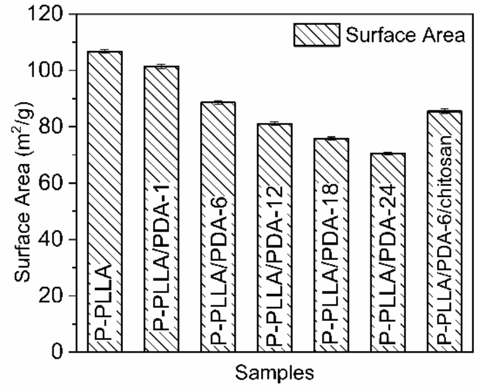

Figure S 4. 1 Surface area of PPLLA nanofibrous membranes before and after coating with PDA and chitosan.

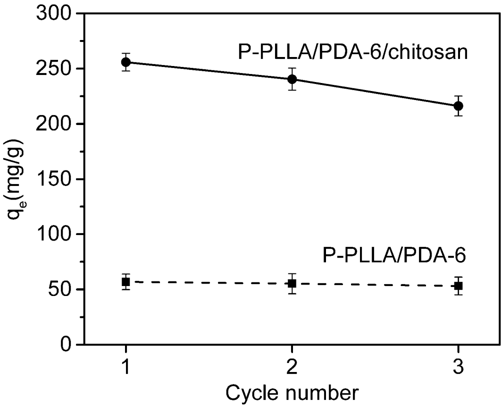

Figure S 4.2 Reusability of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan nanofibrous membranes.

Table S 4. 1 Parameters of pseudo first and second order kinetics.

		P-PLLA/PDA-6	P-PLLA/PDA-6/chitosan
Experimental	q_e (mg/g)	58.95	268.55
Pseudo first order	q_e (mg/g)	71.22	310.9
	k_1 (L/min)	0.1018	0.1091
	R^2	0.97	0.98
Pseudo second order	q_e (mg/g)	87.1	298.5
	k_2 (g/(mg min))	0.000498	0.000626
	R^2	0.96	0.99

Table S 4.2 Parameters of Langmuir and Freundlich isotherms.

		P-PLLA/PDA-6	P-PLLA/PDA-6/chitosan
Langmuir	q_m (mg/g)	59.91	270.27
	k_1 (L/min)	0.0093×10^{-15}	0.0016×10^{-16}
	R^2	0.99	0.99
Freundlich	1/n	1.24	0.14
	k_f (L/mg)	0.1952	140.93
	R^2	0.88	0.95

Table S 4.3 Adsorption capacities comparison of PDA and chitosan-based adsorbents.

Adsorbent	q_m (mg/g)	Reference
PVDF/PDA membrane	26.7	[57]
PEI/PDA/GO	38	[58]
PVC/PDA membrane	21.94	[23]
PVC/PDA/PEI membrane	33.59	[23]
Chitosan-PLLA	128.53	[8]
Chitosan/Perlite	196.1	[59]
P-PLLA/PDA-6	59.91	Present work
P-PLLA/PDA-6/chitosan	270.27	Present work

$$(IA) = W_{ch} - W_{pda} \qquad \textbf{Equ. (S1)}$$

Where, IA represents the immobilization amount of chitosan, and W_{ch} is the weight of nanofibrous membrane after chitosan grafting and W_{pda} is the weight after PDA coating on the PPLLA nanofibrous membrane.

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5.Chapter 5

Cross-linked chitosan coated biodegradable porous electrospun membranes for the removal of synthetic dyes

5.1 Introduction

This work was published as article “Cross-linked chitosan coated biodegradable porous electrospun membranes for the removal of synthetic dyes” in the journal of reactive and functional polymers (2021). This research describe the crosslinking of chitosan with 3-aminopropyltriethoxysilane. Moreover, the cross-linked chitosan was coated on biodegradable porous PLLA nanofibrous membrane for the removal of methylene blue and rhodamine B dyes. The prepared adsorbent was tested under different adsorption parameters such as pH, temperature, time and dye concentration. Non-linear and linear adsorption isotherms and kinetic models were studied. Finally, adsorbent can be reusable up to three adsorption cycles.

5.2 Author Contributions

I performed the experimental work on porous PLLA nanofibers electrospinning, chitosan crosslinking, characterization of adsorbents and mathematical modelling. Madeeha Tabassum helped me in characterizations and mathematical modelling. Muhammad Umar and Hifza Nawaz contributed to useful discussions in the project. Jiashen Li and Hugh Gong provided supervision during the project.

5.3 Citation

Qasim Zia, Madeeha Tabassum, Muhammad Umar, Hifza Nawaz, Hugh Gong, Jiashen Li, Cross-linked chitosan coated biodegradable porous electrospun membranes for the removal of synthetic dyes, Reactive and Functional Polymers, 2021, 104995, ISSN 1381-5148.

5.4 Relationship with objectives

In the current study, the two objectives of this thesis are satisfied that are fabrication of PLLA porous nanofibrous membrane and coating it with APTES crosslinked chitosan with various concentrations. Moreover, these membranes are successfully characterized and evaluated in various adsorption environments. Finally, these adsorbents were successfully tested for adsorption of rhodamine B and methylene blue dyes from wastewater solutions.

5.5 Manuscript 3: Cross-linked chitosan coated biodegradable porous electrospun membranes for the removal of synthetic dyes

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5.6 Abstract

Chitosan crosslinked with 3-aminopropyltriethoxysilane was coated on porous poly(L-lactic acid) nanofibrous membrane to remove dyes from wastewater in the present study. The adsorption capacity of the composite membrane for the removal of methylene blue and rhodamine B was comprehensively studied. Large porous framework provided a high surface area to effectively immobilize the cross-linked chitosan on nanofibrous membranes. Batch trials were performed to evaluate the adsorption behaviour of membranes with variable crosslinking ratio, pH, initial concentration, temperature and time. Moreover, the adsorbent membranes before and after adsorption were characterized using scanning electron microscopy, x-ray energy dispersive analysis, and Fourier transform infrared spectrophotometer. Under optimum parameters, the adsorbent showed the removal capacity of 86.43 and 82.37 mg/g for rhodamine B and methylene blue, respectively. Isothermal and kinetic experiments showed that Langmuir isotherm and pseudo second order kinetics correlated best with adsorption data. Finally, the mechanism of adsorption and reusability of membrane for five cycles was studied.

Key words: Chitosan, 3-aminopropyltriethoxysilane, porous poly (l-lactic acid), electrospinning, adsorption, methylene blue and rhodamine B

5.7 Introduction

In the new global industrialization, water contamination has become a central issue for human health and environment. Major contributors to contamination of water include heavy metals, dyes, pesticides and several other industrial wastes **[1, 2]**. Synthetic dyes such as methylene blue (MB) and rhodamine B (RB) are extensively used in many industries, for example, paper, textiles, printing, leather tanning and dye manufacturing **[3-5]**. Evidences suggest that dyes are among the most important factors that are affecting the water worldwide **[6, 7]**. Data from recent report show that the textile industry alone consumes more than 10,000 tonnes of dye per year and almost 100 tonnes of dyes are discharged into water bodies **[6, 7]**. Although, release of the small amount of dyes in water does not pose a threat to the environment as compared to the azo or reactive dyes. However, exposure to MB and RB (> 0.2 mg/L) dyes in acute quantities has been shown to be related to adverse effects in human health **[8]**. Previous research has established that MB can cause heart related disease, nausea, death of body tissue, paralysis to neck, arms and legs and a damage to liver **[9, 10]**. Whereas, RB is carcinogenic, neurotoxic and can cause irritation of eyes, skin and respiratory tract **[9, 10]**.

In recent years, researchers have investigated the variety of approaches to remove the dyes from wastewater such as membrane filtration **[11]**, reverse osmosis **[12]**, photo-degradation **[13]** and flocculation **[14]**. Up to now, several studies have suggested that adsorption is the most useful technique to clean the water from synthetic dyes **[15-17]**. However, adsorption by using conventional carbon based materials like activated carbon is too expensive (£1,350 / 100 g fine activated carbon) **[15-17]**. Considering this, many scientists are experimenting to find an economical, nontoxic and biodegradable alternative to existing adsorbents **[18, 19]**. Chitosan (CS) is one such material which has an incredible ability to remove the dyes from the water due to the presence of amino and hydroxyl groups on its surface. Furthermore, it is cheap, biocompatible, hydrophilic and easily available. Nevertheless, chitosan alone is not an excellent adsorbent for the basic dyes. A major disadvantage of chitosan is that it is instable in water and has a low surface area for faster water treatment **[20, 21]**. Therefore, it becomes ever more important to modify the chitosan to enhance its adsorption ability and stability.

It is well established from the variety of studies that stability of chitosan can be improved by various crosslinking agents, surface grafting, and immobilizing it on support material **[22]**. Thus far, previous studies have used epichlorohydrin **[23]**, glutaraldehyde **[24]** and trimesic acid **[25]** as crosslinking agents. However, these alternatives cannot enhance the surface area of chitosan. Moreover, carboxylic, epoxide and aldehyde groups present on their backbone reduce the adsorption capability of chitosan by reacting with the amino groups on the chitosan surface **[26]**. These studies would have been more interesting if it had used crosslinking agents with amine groups on their backbone or groups which are less likely to react with the amine groups of chitosan. In addition, it is important to immobilize the cross-linked chitosan on the support surface to provide higher surface area and improve the exposure of active sites for rapid removal of dyes from wastewater. Recently researchers have made attempts to immobilize the chitosan on various substrates such as polyethylene terephthalate **[27]**, cotton gauze **[28]** and cotton fibre **[29]** to remove the contaminants from wastewater. Previous studies recognised the critical role played by the various substrates in providing stable framework to chitosan for better adsorption. However, far too little attention has been paid towards the surface area of these substrates.

- The present research explores, for the first time, the effect of 3-aminopropyltriethoxysilane (APTES) cross-linked chitosan immobilized on a very high surface area and biodegradable porous poly(L-lactic acid) (PPLLA) electrospun membranes for the removal of MB and RB dyes.

- Non-porous PLLA membranes were fabricated via electrospinning and dipped into acetone to develop the porous framework by the solvent induced crystallization method **[30]**.
- The large surface area of membranes can enhance the adsorption ability of chitosan.
- Moreover, APTES is a silane coupling agent with amine and three ethoxysilane groups present on its backbone, it can prove to be an efficient crosslinking agent for improving chitosan stability in water without reducing its capability for dye removal **[31]**.

The different parameters of adsorption, including, pH, crosslinking quantity, temperature and time were thoroughly studied. Furthermore, the kinetics of the adsorption process was studied using various kinetic models. Adsorption was also tested for three isotherm models comprising Langmuir, Freundlich and Temkin. Finally, the reusability of chitosan membranes was studied for MB and RB dyes.

5.8 Experimental

5.8.1 Materials

Low molecular weight chitosan (M_w = 50,000 – 190,000 Da), with 75-85 % degree of deacetylation, methylene blue (M_w = 373.9 g/mol), rhodamine B (M_w = 479.01 g/mol), 3-aminopropyltriethoxysilane (M_w = 221.37 g/mol), sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) were purchased from Sigma Aldrich. PLLA (PL65) was bought from PURAC biochem. Ethanol, acetone (99.99%) and acetic acid (≥ 98%) were procured from the VWR scientific company limited. Dichloromethane (DCM, 99.99%) and dimethylformamide (DMF, 99.80%) were obtained from Fischer scientific limited. Distilled water was acquired from the USF-ELGA filter in The University of Manchester laboratory.

5.8.2 Preparation of PPLLA membrane

PPLLA electrospun membrane was prepared according to the procedure used by Zia et al **[20]**. The first step in this process was to prepare the PLLA solution (1.8 wt. %) by dispersing the polymer in the mixture of DCM and DMF (19:1 w/w). The mixture was heated and stirred on 50 °C in the tightly closed beaker until the polymer was entirely dissolved. The PLLA/DCM/DMF mixture was then carefully transferred into a 30 ml syringe and brought to the tip of the needle by using the syringe pump to begin the electrospinning. This process was executed at 25 °C with the fixed humidity of 40 %, a voltage of 23 KV, a tip to collector distance of 30 cm, a solution transfer rate of 5 ml/min and the revolving collector at the speed of 200 rpm to collect the nanofibers. Finally, the collected nanofibers was immersed into acetone for 5 min and then dried in the fume hood to obtain the porous PLLA nanofibrous membrane.

5.8.3 Preparation of 3-aminopropyltriethoxysilane cross-linked chitosan

A 0.5 g of CS solid granules were dissolved in a 50 mL aqueous solution of 1 % acetic acid w/w to form a 1 % w/w solution of CS. The CS solution was stirred for 3 h at room temperature to make it a homogenous solution. Following this, 1 mL of HCL (2 M) and a certain amount of the APTES was added in the CS mixture to initiate the cross-linking reaction as discussed in section (4.10). Lastly, this mixture was allowed to stir continuously for 12 h at 50 °C. The proportion of APTES and CS was varied as 0, 0.05, 0.1, 0.2 and 0.3.

5.8.4 Immobilization of cross-linked chitosan

The cross-linked CS (CLCH) was successfully immobilized onto PPLLA membrane via simple dip coating method. For this, a piece of 2.5 x 2.5 cm^2 PPLLA membrane was immersed vertically into APTES CLCH solutions present in the beakers for 10 min, taken out from the solutions, blotted carefully to remove the excess CLCH and dried to a constant mass at room temperature. These samples were designated as PPLLA/CLCH – 0, PPLLA/CLCH – 0.05, PPLLA/CLCH – 0.1, PPLLA/CLCH – 0.2 and PPLLA/CLCH – 0.3, respectively.

5.8.5 Membrane surface characterization

The surface morphology of the adsorbent coated membrane before and after the removal of dyes was carefully investigated by using scanning electron microscopy (SEM, Quanta 250-FEG). Energy dispersive spectroscopy analysis (Oxford Instruments Inc.) was done to confirm the adsorption of dye on the PPLLA/APTESCS membranes. For this, all the samples were gold sputtered to increase their conductivity. To study the interactions between the CS and APTES, Fourier transform infrared spectroscopy (FTIR) was performed on NICOLET 5700 spectrometer in the range of 4000 – 600 cm^{-1}.

5.8.6 Dye adsorption study

The removal capacity of PPLLA/CLCH adsorbent membrane was studied with respect to variable cross-linking agent quantity, pH of the dye solution, time, and temperature of the solution. Batch adsorption method was used throughout this study. Initial experiments were carried out initially on 2.5 x 2.5 cm^2 adsorbent, constant pH 6, dye concentration 300 mg/L, time 1 h, at room temperature, volume of 20 mL and varying cross-linker quantity. After this, ultraviolet visible (UV) spectrophotometer (Perkin Elmer, Lambda 900) was used to determine the absorbance of dyes in the aqueous solution. The λ_{max} values of MB and RB were determined at the wavelengths 665 and 554.5 nm, respectively as shown in Figure 5.1 (a, b, c and d). The final concentration of dyes in the solution was measured by using the calibration curves between maximum absorbance and initial concentration of dyes. All the samples were studied five times and the average values are reported in this study. Finally, the adsorption was calculated by following Eq. (1).

$$q_t = \frac{(C_i - C_e)V}{M} \tag{1}$$

Where, q_t is the quantity of dye removed for one unit weight of the adsorbent membrane (mg/g). M is the total mass of the membrane (g). V is the total volume of dye aqueous solution (L). C_i and C_e are the initial and final concentrations of dyes in the aqueous solution (mg/L). All the experiments were performed five times and average values of adsorption were considered throughout this study.

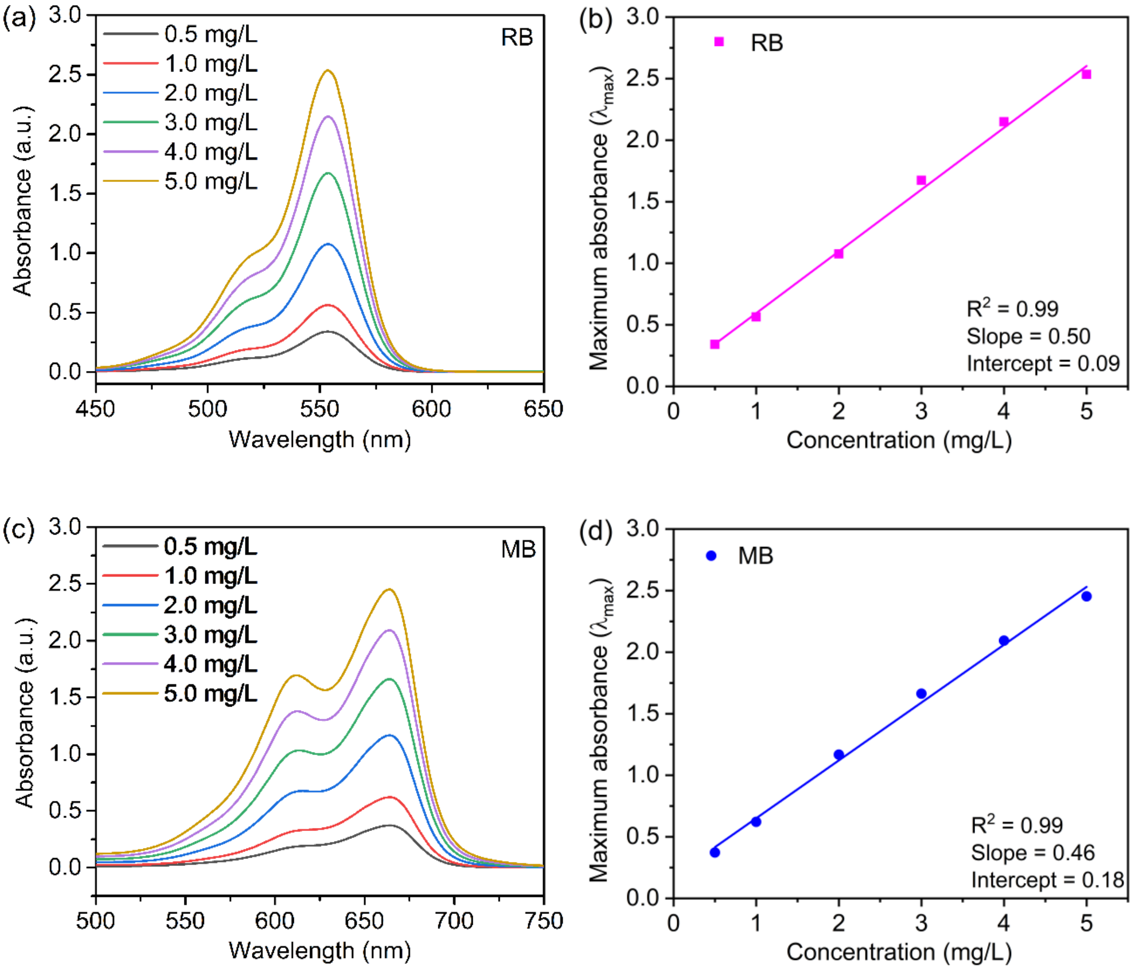


Figure 5. 1 (a & c): UV-visible absorption spectra of RB and MB dyes, (b & d): calibration curves of RB and MB dyes.

5.8.7 Reusability of the adsorbent membrane

The recycling capacity of adsorbent membrane was investigated by performing desorption study. For this experiment, membrane used for the adsorption of dyes was added to 10 mL solution of 0.1 M HCL for 1 h. Subsequently, the membrane was washed with distilled water and dried at room temperature. Finally, the dried the membrane was used again for the adsorption of dyes. This adsorption-desorption was repeated five times to study the reusability of PPLLA/CLCH membranes.

5.9 Mathematical modelling

5.9.1 Adsorption isotherms

Adsorption isotherms give information about adsorption capability of adsorbent in equilibrium conditions. The RB and MB adsorption onto the PPLLA/CLCH membrane was investigated by fitting the data in Origin 2019 against three isotherm models, that is, Langmuir, Freundlich and Temkin equations.

5.9.2 Langmuir isotherm

The Langmuir isotherm assumes that, there are fix number of functional sites on the surface of adsorbent, the adsorbate molecule can occupy only one available active site on the adsorbent to make a homogenous single layer on its surface. Langmuir linear and non-linear expression is given in Eq. (2) and (3).

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{k_l q_{max}} + \frac{C_{eq}}{q_{max}} \tag{2}$$

$$q_e = \frac{K_l C_e}{1+a_l C_e} \tag{3}$$

Where, q_{eq} (mg/g) and C_{eq} (mg/L) are adsorption and concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity of the adsorbent and k_l and a_l (L mg/g) are Langmuir constant.

5.9.3 Freundlich isotherm

The Freundlich isotherm encompasses the non-uniform distribution of the adsorbate on adsorbent, the dye molecules can be adsorbed on un-limited functional sites and can make a heterogeneous layer. The Freundlich linear and non-linear equation is expressed in Eq. (4) and (5).

$$logq_e = b_f logC_e + logk_f \tag{4}$$

$$q_{eq} = k_f C_{eq}^{\frac{1}{n}} \tag{5}$$

Where, q_{eq} (mg/g) and C_{eq} (mg/L) represents the equilibrium adsorption and concentration of dyes, k_f (L/mg) and b_f are freundlich constant, and n is the heterogeneity in the adsorption system.

5.9.4 Temkin isotherm

The temkin isotherm refers to heat of the adsorption process, while ignoring very high and low adsorbate concentrations and considering the interactions between adsorbate and adsorbent. The linear form of temkin isotherm is given in Eq. (6).

$$q_{eq} = BlnA + BlnC_{eq} \tag{6}$$

And,

$$B = \frac{RT}{b} \tag{7}$$

Where, q_{eq} (mg/g) and C_{eq} (mg/L) are equilibrium adsorption and concentration, B and b (J/mol) are temkin constant, A (L/mg) corresponds to maximum binding energy constant at equilibrium binding, R is gas constant (8.314 J/mol K) and T is temperature (K).

5.9.5 Kinetic of dye adsorption process

Kinetic studies of adsorption depend on the effect of time and are essential to design the processes related to adsorption in industries. The kinetic modelling of adsorption process was performed by fitting the adsorption data using pseudo first order, pseudo second order, Elovich and inter particle diffusion models.

5.9.6 Pseudo first and second order kinetic model

The pseudo first and second order linear and non-linear models are expressed in Eqs. (8, 9, 10 and 11)

$$\log(q_{eq} - q_t) = log q_{eq} - k_1 t \tag{8}$$

$$q_t = (q_e - e^{k_1 t}) \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{10}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{11}$$

Where, q_t (mg/g) and q_e (mg/g) are adsorption at equilibrium and at given time, k_1 (min^{-1}) is pseudo first order rate constant, k_2 (mg/g min^{-1}) is pseudo second order reaction constant and t is time (min).

5.9.7 Elovich kinetic model

The linear and non-linear form of Elovich model is given in Eq. (12) and (13).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \tag{12}$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \tag{13}$$

Where, q_t (mg/g) is adsorption of dyes at given time, α is an Elovich constant corresponds to chemisorption and β is constant which shows the degree of surface coverage. These constants can be calculated from slope and intercept of the plot between *lnt* and q_t.

5.9.8 Inter particle diffusion kinetic model

The inter particle model is given in Eq (14).

$$q_t = k_{diff} t^{\frac{1}{2}} + C \tag{14}$$

Where, q_t (mg/g) is the rate of adsorption at given time, k_{diff} is inter particle diffusion constant (mg/g min$^{-1/2}$) and C gives the insight into the boundary layer thickness, greater intercept of the plot suggests larger boundary layer effect.

5.9.9 Thermodynamic studies

The thermodynamic parameters that explain nature (ΔH°), randomness (ΔS°) and spontaneity (ΔG°) of the adsorption reaction with respect to the change in temperature were calculated by using the Eq. (15 and 16).

$$lnk = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{15}$$

$$\Delta G° = -RTnk \tag{16}$$

Where, T is the temperature (K), R is the natural gas constant (8.314 J/mol K), lnk can be calculated from q_e/C_e. $\Delta H°$ and $\Delta S°$ can be obtained from the slope and intercept of vont hoff's plot.

5.10 Results and discussion

5.10.1 Surface group analysis of cross-linked chitosan coated on PPLLA membrane

The surface groups on PPLLA/CLCH membrane were investigated with FTIR. Figure 5.2 (a and b) show the FTIR spectra of un-crosslinked PPLLA/CLCH – 0 and crosslinked PPLLA/CLCH (0.05, 0.1, 0.2 and 0.3) membranes. A broad peak at approximately 3300 cm^{-1} appeared in the PPLLA/CLCH – 0 membrane, which corresponds to the stretching vibrations of hydroxyl O–H and amine N–H groups in CH. Furthermore, the absorbance band at 1638 cm^{-1} corresponds to bending vibrations of amine N–H groups in chitosan. APTES contains both O–H and N–H groups in its backbone, therefore, crosslinking the chitosan leads to the increased intensity of N–H and O–H groups at 3300 and 1638 cm^{-1} bands in PPLLA/CLCH (0.05 and 0.1) adsorbent membranes. Also, the absorption intensity around 1000 cm^{-1} was increased in the similar membranes, this indicates that esterification reaction was occurred between hydroxyl groups in CH and silanol groups in APTES and C–O–Si bonds were formed. However, as the ratio of APTES was increased in the CH to 0.2 and 0.3, there was no significant increase detected in the intensity of amine or hydroxyl groups compared to the PPLLA/CLCH (0.05 and 0.1) membranes. A possible explanation for this might be that the hydrogen bonds were formed between the amine groups in silanol and dissociative hydroxyl groups in CH, which also ultimately decrease the crystallinity of CH **[31, 32]**.

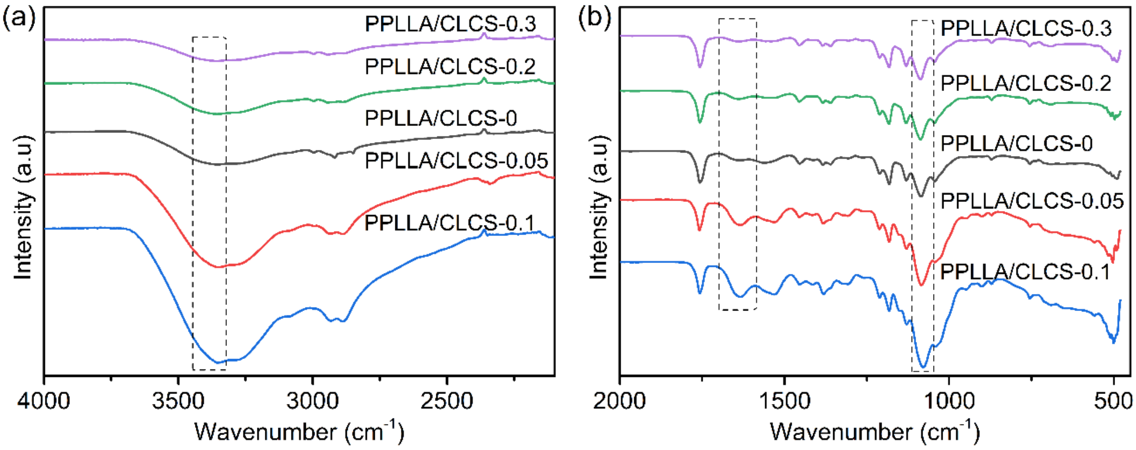


Figure 5.2 (a & b) FTIR of un-crosslinked and crosslinked CH coated PPLLA nanofibrous membrane.

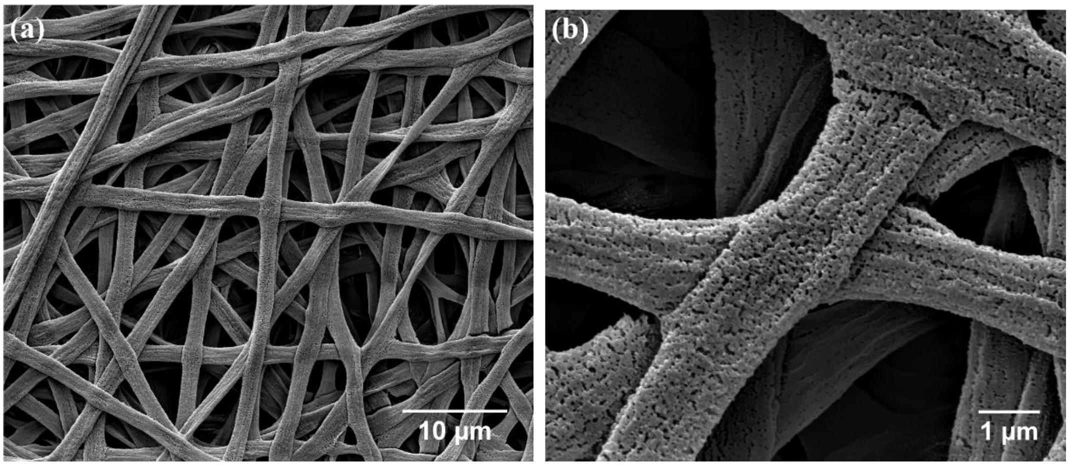
5.10.2 Morphology study of PPLLA/CLCH membranes

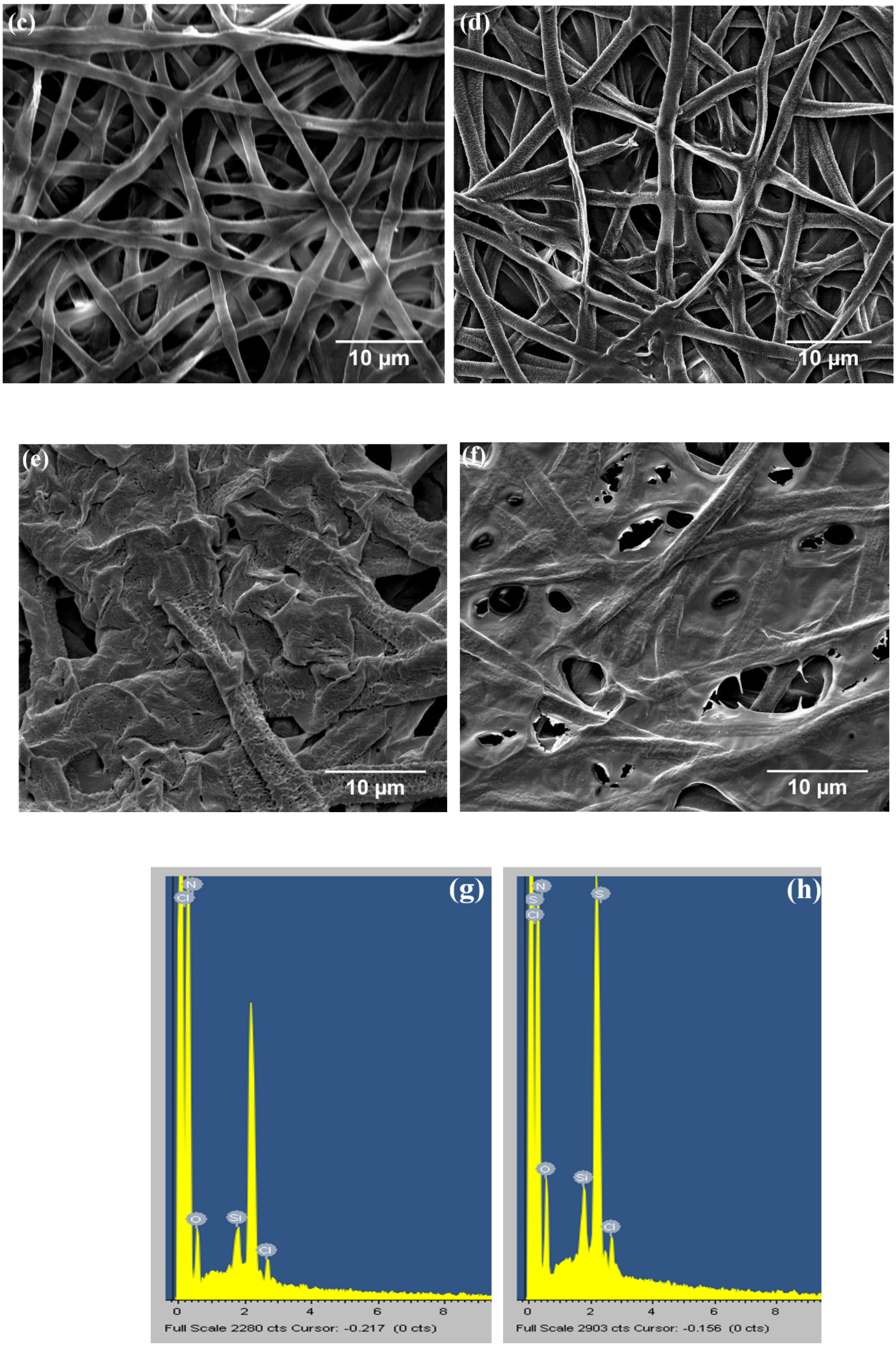
SEM pictures of PPLLA adsorbent membranes are shown in Figure 5.3 (a and b). The random porous network is clearly visible on the nanofibers and their surface is appeared to be rough. This porous structure can provide the large surface area to immobilize CLCH for the rapid and high quantity removal of organic dyes from the aqueous solution.

Figure 9.3 (c and d) exhibit the SEM images of PPLLA membranes after coating with 1 % CH and CLCH – 0.1. The surface of CH coated PPLLA nanofibers is relatively smooth. For CLCH – 0.1 coated membranes, the surface becomes coarser due to the addition of APTES. The tiny bright spots in PPLLA/CLCH – 0.1 membrane corresponds to the silicon elements distributed uniformly throughout the matrix, similar results were reported in the previous study **[31, 32].**

Furthermore, the morphology of CLCH – 0.1 membranes after the adsorption of dyes are shown in Figure 5.3 (e and f). The surface of the adsorbent was covered with a uniform layer due to the adsorption of MB. In contrast, the smooth molecular flakes of RB were adsorbed on the surface of adsorbent. Researchers also showed related morphologies of MB and RB on adsorbents in earlier studies **[33, 34]**.

The adsorption of MB and RB dyes on CLCH – 0.1 membrane was further confirmed by the EDS examination. The EDS spectra in Figure 5.3 (g) showed the presence of sulphur and nitrogen which are present in the MB backbone. Moreover, the presence of excessive nitrogen in Figure 9.3 (h) was an indication to the presence of RB on the adsorbent membrane. The presence of MB and RB can also be confirmed visually in Figure 5.3 (j and k). After the adsorption, the RB and MB molecules were displayed by a light pink and dark blue colour of PPLLA/CLCH – 0.1 membranes.




(c)
10 µm
(d)
10 µm
(e)
10 µm
(f)
10 µm
(g)
N
Cl
O
Si
Cl
0
2
4
6
8
Full Scale 2280 cts Cursor: -0.217 (0 cts)
(h)
N
S
Cl
S
O
Si
Cl
0
2
4
6
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Full Scale 2903 cts Cursor: -0.156 (0 cts)

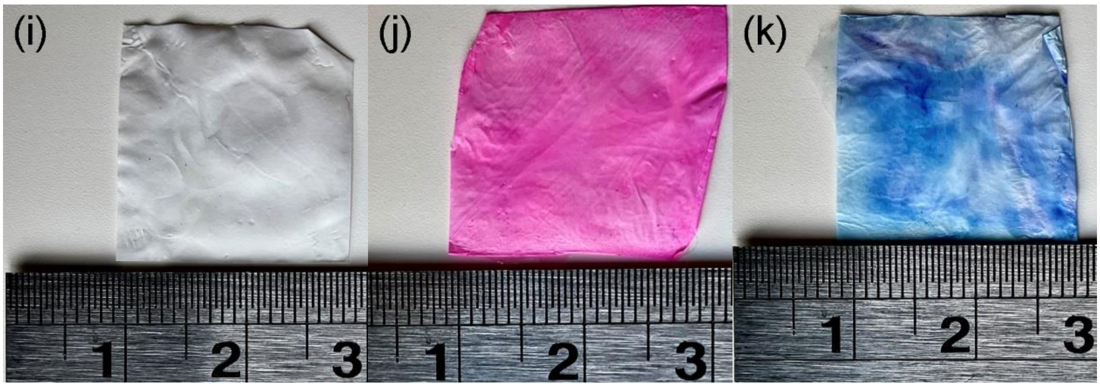


Figure 5.3 (a & b): SEM of PPLLA nanofibrous membrane, (c & d): SEM of PPLLA/CH 1% and PPLLA/CLCH – 0.1, (e and f): SEM of PPLLA/CLCH – 0.1 membrane after adsorption of RB and MB dyes, (g and h): EDS graph of RB and MB dyes after adsorption on PPLLA/CLCH – 0.1 membrane and (i, j & k): the visual contrast of PPLLA/CLCH – 0.1 before and after adsorption of RB and MB dyes.

5.10.3 Effect of varying pH

The pH of the solution has a significant effect on the adsorption process. One of the main factors that affect the adsorption efficiency of the adsorbent is the surface charge, which is dependent on the pH. In this research, the adsorption capacity of APTES/CLCH membranes for RB (pKa = 5.81) and MB (pKa = 3.80) dyes was investigated in the pH range of 3-9, initial concentration of 300 mg/L, time of 60 min, room temperature and by using APTES/CLCH – 0.1 membrane. As exhibited in Figure 5.4 (a) RB dye showed less adsorption at lower pH, while MB dye has increased adsorption at higher pH. The observed decrease in adsorption could be attributed to the presence of more hydrogen (H^+) ions in the solution which interact with the adsorbent membrane. There is steady rise in the adsorption with increase in pH, deprotonation occurs at higher pH which leads to the negative charge on the adsorbent. For MB dye, the adsorption capacity recorded highest at pH 9, a likely explanation is that OH groups on the adsorbent become completely dissociated at pH $\geq$ 8, making the adsorbent membrane more negative as compared to lower pH levels **[35]**. In contrast, it can be observed from Figure 5.4 (a) that removal of RB is less at pH > 4. Previous studies reported that **[36]**, RB exists in zwitterionic form, which promotes the interaction between carboxyl and xanthene groups in RB to form large molecules of RB and makes them difficult to be adsorbed on the adsorbent.

5.10.4 Effect of 3-aminopropyltriethoxysilane ratio

To see the effect of APTES crosslinking ratio on the removal of MB and RB dyes, PPLLA/CLCH membranes were prepared with varying ratios of APTES (0.05, 0.1, 0.2 and 3). The adsorbent membranes were evaluated at the pH of 4 and 9 for RB and MB, initial dye concentration of 300 mg/L, time 60 min and at room temperature. The results are shown in Figure 5.4 (b). The graph shows that there has been a marked increase in MB and RB adsorption as the amount of APTES is increased up to 0.1. It is anticipated that up to 0.1 ratio of APTES the OH and NH active sites on adsorbent would increase for the adsorption of dyes. The adsorption capacity of PPLLA/CLCH membrane decreased with a further increase of APTES. It could be the amine and hydroxyl groups in silanol can make hydrogen bonds with the hydroxyl or amine groups in chitosan amorphous regions which reduced the functional sites for adsorption of dyes.

5.10.5 Effect of dyes initial concentration

In this work, four different concentrations (50, 100, 200 and 300 mg/L) were prepared of RB and MB at pH 4 and 9, respectively. The effect of initial dye concentration is displayed in Figure 5.4 (c). As shown, the adsorption capacity of PPLLA/CLCH was risen for the higher quantities of MB and RB dyes. This can be attributed to the large mass transfer of dye molecules, which overcomes the resistance between the liquid and solid phase and leads to the higher probability of collision between dye molecules and adsorbent.

5.10.6 Effect of time

Figure 5.4 (d) shows the graph of MB and RB dye adsorption capacity as a function of time. This study was conducted in time range from 10 to 240 min, with PPLLA/CLCH – 0.1

membrane, pH 4 and 9, initial concentration of 300 mg/L and at room temperature. In the first 60 min of adsorption process more than 80 % removal of both dyes was achieved, which shows the rapid removal of adsorbent membrane. In the initial stages of adsorption process, there are more active sites available on the surface of adsorbent which makes easier for dye molecules to adsorb. With the increase in time, these vacant sites might be partially or completely filled up and made it difficult for dye particles to be occupied. This results in slow adsorption of dyes from the bulk solution. Equilibrium adsorption for MB dyes was reached after 150 min, whereas equilibrium value for RB was obtained after 180 min. This may indicate to the higher adsorption capacity of RB on the adsorbent membrane.

5.10.7 Effect of temperature and thermodynamic studies

The effect of temperature on the adsorption capability of PPLLA/CLCH membrane was investigated at temperatures of 25, 30, 40, 50 and 60 °C, concentration of 300 mg/L, pH of 4 and 9, and time 150 min. The results are shown in Figure 5.4 (e). As seen, the adsorption quantity of RB and MB dyes decreased with the increase in temperature. The quantity was decreased from 90.04 to 41.4 mg/g and 82.8 to 37.6 mg/g for RB and MB, respectively. It may be due to the reduction in binding force between the adsorbent and adsorbate at elevated temperatures. Table 5.1 presents the thermodynamic parameters of adsorption process calculated from the Vont Hoff’s plot Figure 5.4 (f). The negative values of enthalpy ($\Delta H°$) for RB and MB uptake shows that adsorption process exothermic. Moreover, the negative value of entropy ($\Delta S°$) indicates the decrease in randomness of the adsorption process for MB and RB dyes. Finally, as the temperature increased from 300 to 333 °K, the Gibb’s free energy ($\Delta G°$) values ranged between -1.883 to 3.459 for RB and -1.696 to 3.646 for MB. This demonstrates that the adsorption process was spontaneous and viable at room temperature, however, the process at higher temperature could not be continued.

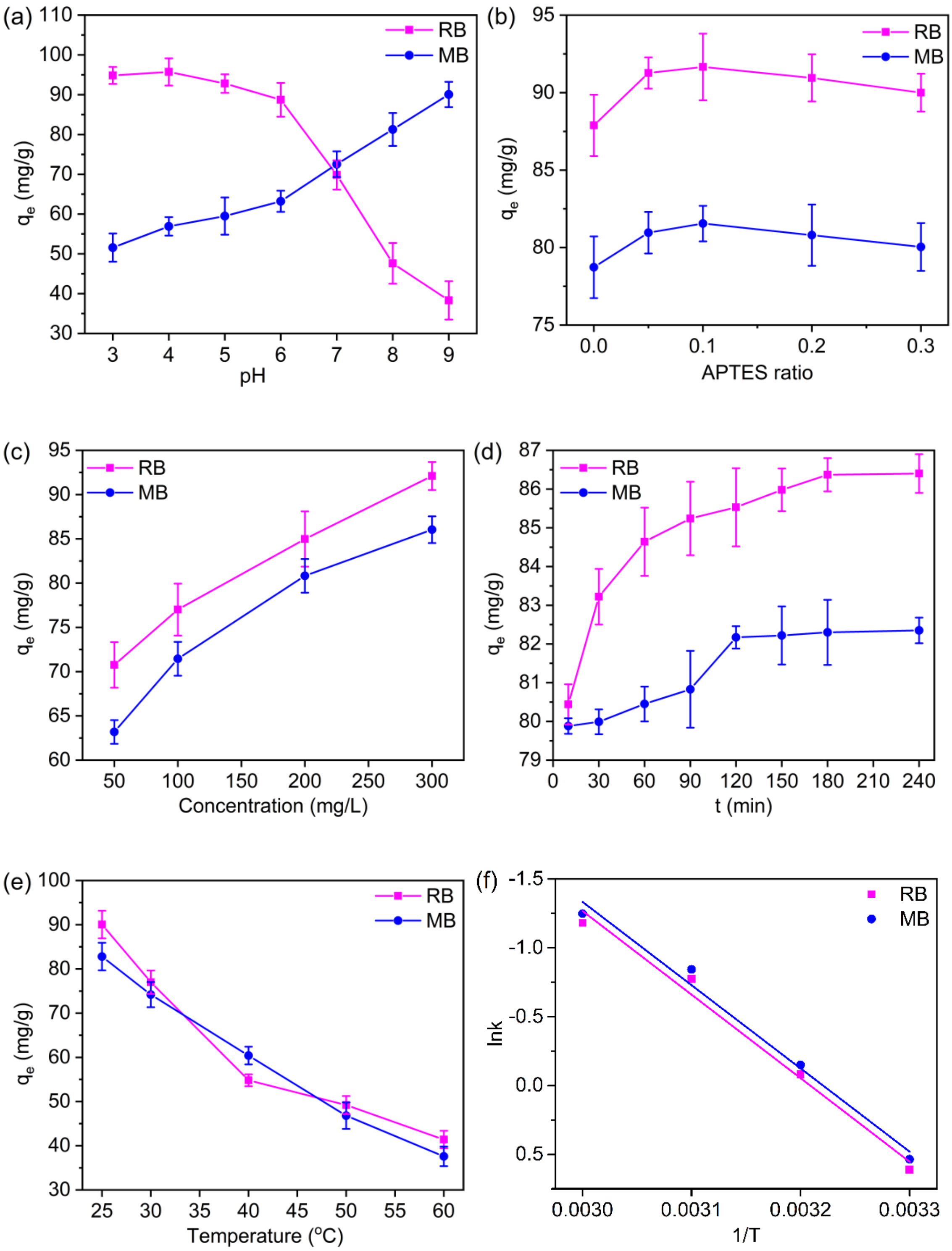


Figure 5.4 Parameters of adsorption process; (a): effect of varying pH, (b): effect of 3-aminopropyltriethoxysilane ration, (c): effect of initial concentration of dyes, (d): effect of contact time, (e): effect of temperature and (f): vont hoff's plot.

Table 5. 1 Thermodynamic parameters of RB and MB dyes.

Dyes	ΔH° (KJ/mol)	ΔS° (J/mol/K)	ΔG° (KJ/mol)			
			300	313	323	333
RB	-50.45	-161.89	-1.88	-0.22	1.84	3.45
MB	-50.26	-161.88	-1.69	0.40	2.02	3.64

5.10.8 Isotherm studies RB and MB on PPLLA/CLCH membrane

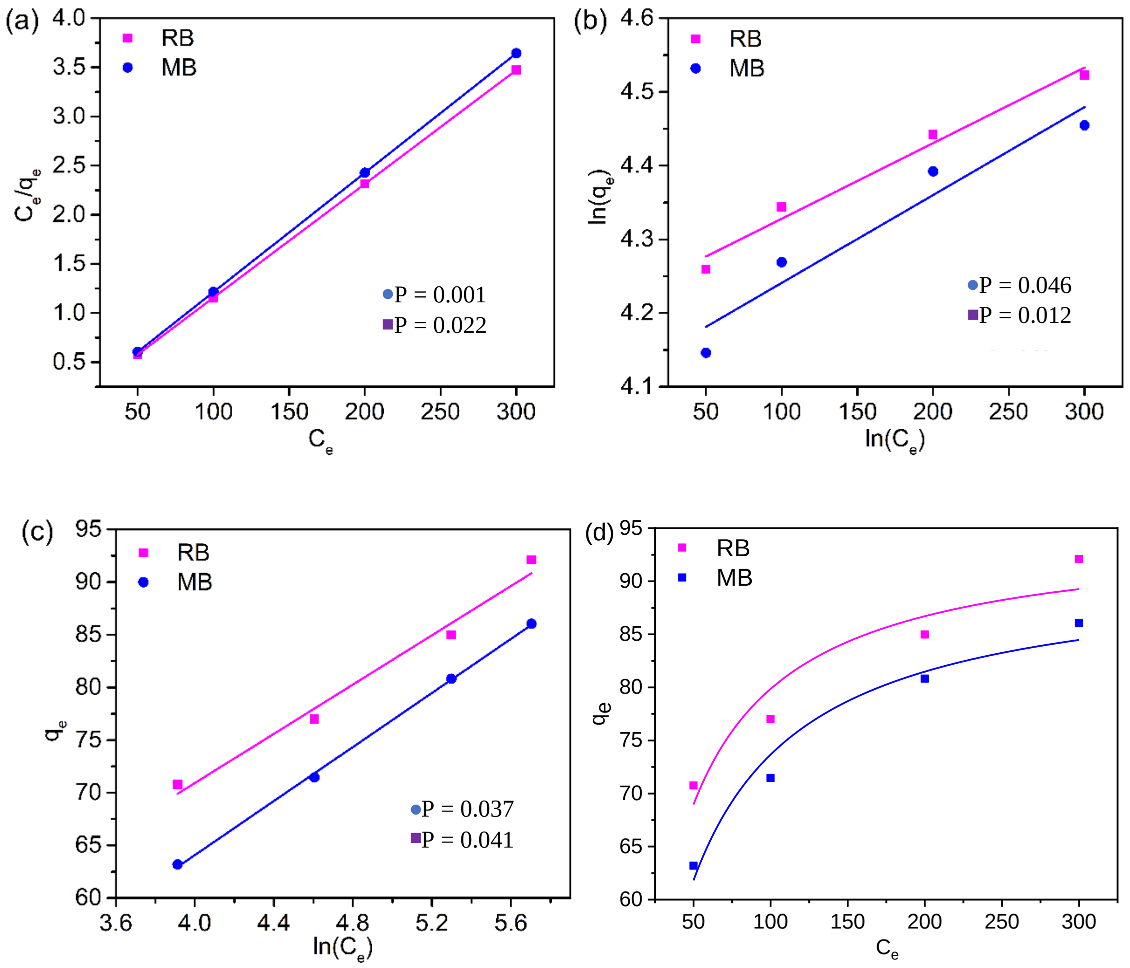
Figure 5.5 (a, b, c, d and e) show the fitted curves of linear and non-linear Langmuir, Freundlich and Temkin isotherms for RB and MB dyes. Calculated parameters of these isotherms are presented in Table 5.2. R^2 values of Langmuir isotherm for both dyes suggest that the homogenous layer of dye molecules was formed on the adsorbent surface. Also, the experimental adsorption capacities of RB and MB dyes (87.37 and 82.85 mg/g) were nearly be the same to the calculated values (86.43 and 82.37 mg/g) from Langmuir isotherm plot. In contrast, the Freundlich and Temkin isotherm data did not fit well with lower R^2.

However, when using non-linear Langmuir model the R^2 and K_l are much less as compared to the linear model. Moreover, higher values of reduced chi square (11.19 and 4.86) shows that data was not well fitted with the non-linear Langmuir isotherm. Accordingly, non-linear freundlich model showed a better relationship for RB and MB dyes adsorption with better R^2 and reduced chi square values as shown in Table 5.2.

Table 5.2 Calculated parameters of langmuir, freundlich and temkin isotherms.

Isotherms	Constants	RB	MB
Langmuir (Linear)	Q_{max} (mg/g)	86.43	82.37
	K_l (L/mg)	5.84×10^{-14}	3.92×10^{-13}
	R^2	1	1
Langmuir (Non-linear)	Q_{max} (mg/g)	94.84	91.15
	K_l (L/mg)	0.053	0.042

	R^2	0.91	0.96
	χ^2	11.19	4.86
Freundlich (Linear)	K_f	38.07	30.75
	N	6.94	5.78
	R^2	0.96	0.94
Freundlich (Non-linear)	K_f	39.43	32.21
	B_f	0.147	0.172
	R^2	0.99	0.99
	χ^2	1.25	0.10
Temkin	B	11.69	12.82
	A (L/g)	4.95	2.05
	b (J/mol)	213.36	194.55
	R^2	0.97	0.98



(e)

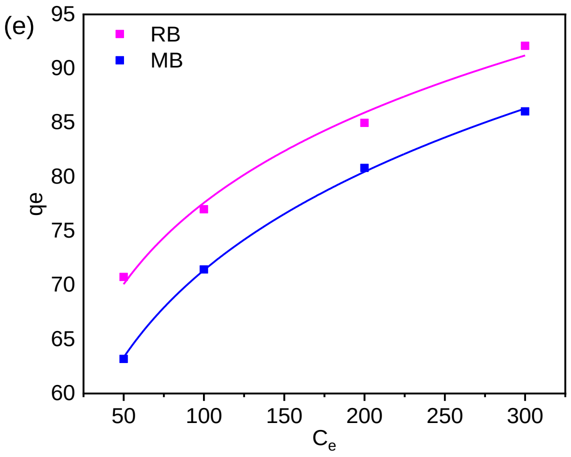
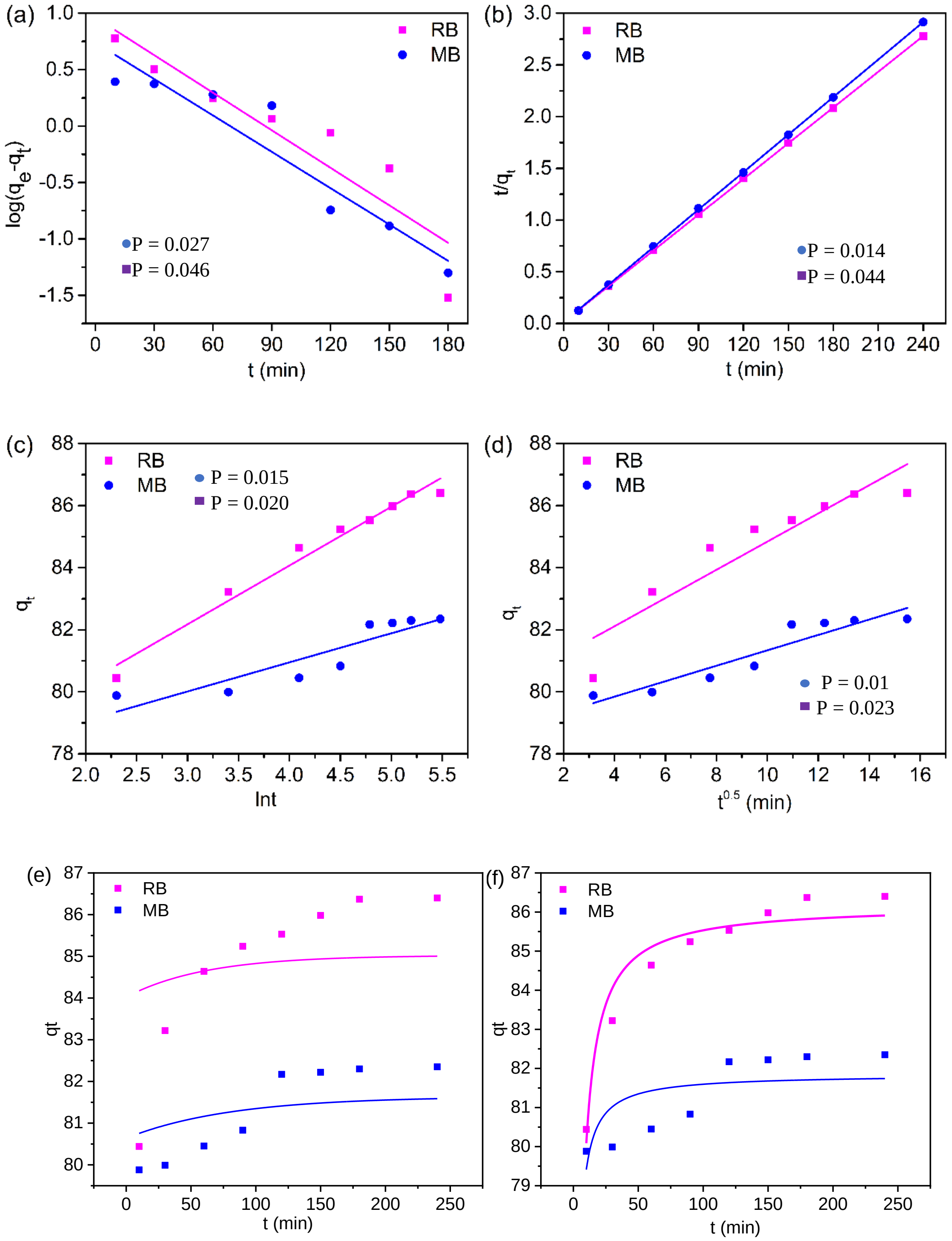


Figure 5.5 (a) Linear Langmuir isotherm, (b) Linear Freundlich isotherm (c) Temkin isotherm, (d), Non-linear Langmuir isotherm and (e) Non-linear Freundlich isotherm.

5.10.9 Kinetic studies of RB and MB on PPLLA/CLCH membrane

The fitted curves and calculated parameters of linear and non-linear pseudo first order, pseudo second order, Elovich and interparticle diffusion models are presented in Figure 5.6 (a, b, c, d, e, f and g) and Table 5.3. Large R^2 values of linear pseudo second order kinetics can be seen for RB and MB and Elovich model showed greater R^2 value for RB only. This proposes that, pseudo second order and Elovich models are suitable for describing the kinetics of adsorption system. Moreover, lower values of R^2 for pseudo first order and interparticle diffusion model confirmed that adsorption of MB and RB dyes cannot be described by these kinetic models.

Moreover, in the current study, non-linear adsorption kinetics of RB and MB dyes on PPLLA/CLCH membrane were fitted well by elovich model followed by the pseudo second and pseudo first order isotherms. The elovich model was better fitted with higher R^2 and reduced chi square values for both RB and MB dyes adsorption.


(a)
log(q$_e$-q$_t$)
t (min)
1.0
0.5
0.0
-0.5
-1.0
-1.5
0
30
60
90
120
150
180
RB
MB
P = 0.027
P = 0.046
(b)
t/q$_t$
t (min)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
30
60
90
120
150
180
210
240
RB
MB
P = 0.014
P = 0.044
(c)
q$_t$
lnt
88
86
84
82
80
78
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
RB
MB
P = 0.015
P = 0.020
(d)
q$_t$
t$^{0.5}$ (min)
88
86
84
82
80
78
2
4
6
8
10
12
14
16
RB
MB
P = 0.01
P = 0.023
(e)
qt
t (min)
87
86
85
84
83
82
81
80
0
50
100
150
200
250
RB
MB
(f)
qt
t (min)
87
86
85
84
83
82
81
80
79
0
50
100
150
200
250
RB
MB

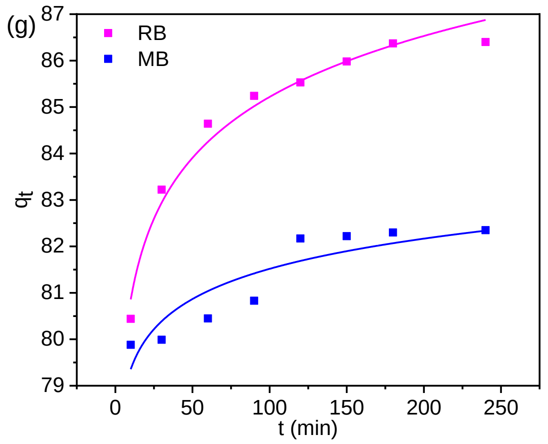


Figure 5.6 (a) Linear pseudo first order kinetics, (b) Linear pseudo second order kinetics, (c) Linear elovich kinetic model, (d) Interparticle diffusion kinetic model, (e) Non-linear pseudo first order kinetics, (f) Non-linear pseudo second order kinetics and (g) Non-linear elovich model.

Table 5. 3 Calculated parameters of pseudo first order, pseudo second order, Elovich model and interparticle diffusion model.

Kinetic models	Constants	RB	MB
Pseudo first order (Linear)	K_1 (min^{-1})	0.0255	0.0247
	R^2	0.83	0.87
Pseudo first order (Non-linear)	K_1 (min^{-1})	0.016	0.012
	R^2	0.26	0.43
	χ^2	3.49	0.78
Pesudo second order (Linear)	$Q_{e\ calculated}$ (mg/g)	86.80	82.71
	K_2 (g/mg/min)	0.0086	0.011
	R^2	0.99	0.99
Pesudo second order (Non-linear)	$Q_{e\ calculated}$ (mg/g)	86.18	81.84
	K_2 (g/mg/min)	0.015	0.039
	R^2	0.94	0.51
	χ^2	0.28	0.67
Elovich (Linear)	α (mg/g.min)	5.2×10^{15}	1.02×10^{36}
	β (g/mg)	0.5281	1.065
	R^2	0.97	0.78

Elovich (Non-linear)	α (mg/g.min)	6.67×10^{17}	5.07×10^{35}
	β (g/mg)	0.52	1.066
	R^2	0.97	0.81
	χ^2	0.11	0.25
Interparticle diffusion	C (mg/g)	80.29	78.84
	K_{diff} (mg/g.min$^{-1/2}$)	0.4543	0.2488
	R^2	0.84	0.86

Table 5.4 Comparison of adsorption capacity of MB and RB dyes with other reported adsorbents.

Adsorbent	RB	MB	Reference
Humic acid based membrane	18.81 mg/g	20.83 mg/g	[35]
Red mud	5.5 mg/g	19.55 mg/g	[37]
Bagasse fly ash	69 %	70 %	[38]
Graphene 3D hydrogels	50.1 mg/g	227 mg/g	[39]
Chitosan IPN hydrogels	21.90 mg/g		[40]
PPLLA/CLCH – 0.1 membrane	86.43 mg/g	82.37 mg/g	This work

5.10.10Chitosan crosslinking and adsorption mechanisms

The crosslinking reactions between APTES and chitosan are shown schematically in Figure 5.7 (a). To begin the crosslinking process, HCL was added as an acid catalyst in the solution to hydrolyse the APTES and make silanol groups. After hydrolyses, the hydroxyl groups in one silanol group made siloxane bonds with other silanol groups or with the amine groups present in CH backbone via dehydration reaction. Moreover, amino and hydroxyl groups in silanol may form hydrogen bonds with the dissociative hydroxyl or amino groups present in CH amorphous regions. These siloxane and hydrogen bonds work as crosslinking points between APTES and CH.

Adsorption mechanism of MB and RB dyes can be explained by electrostatic attraction and hydrogen bonding between dye and CH molecules. Figure 5.7 (b and c) schematically show the removal mechanism of RB and MB. For MB, at pH > 7, the hydroxyl groups of CH are completely deprotonated and have negative charge on them. These hydroxyl groups can form hydrogen bonds with positively charged amino groups present in MB or amino groups in chitosan can form a bond with amine groups in MB via electron sharing. However, for RB, at pH > 4 it exists in zwitterionic form. This increases the interaction between carboxyl and xanthene groups of RB monomers and results in the formation of dimers hence adsorption of RB becomes difficult. At pH < 4, the carboxylic groups of RB do not dissociate and can make hydrogen bond with the amine groups of CH.

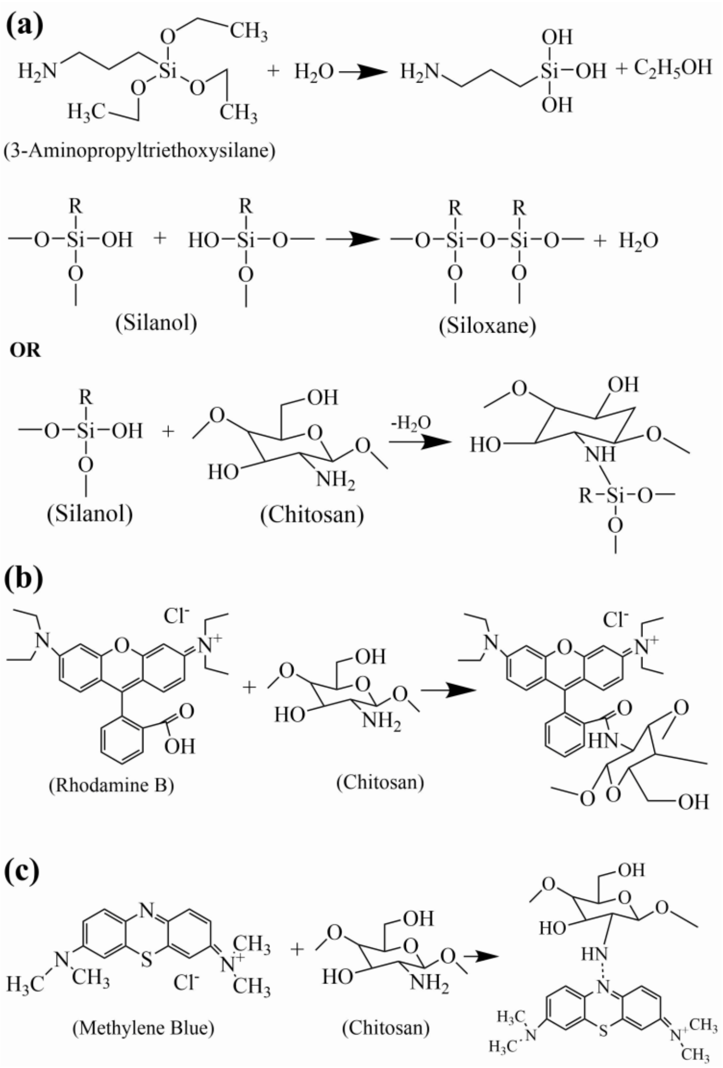


Figure 5.7 (a) mechanism of crosslinking of CH with APTES, (b & c) removal mechanism of RB and MB dyes.

5.10.11Reusability of PPLLA/CLCH membrane

The adsorbents which can be reused multiple times for the adsorption process are considered to be environment friendly and economical. Figure 5.8 shows the reusability of PPLLA/CLCH membrane for the removal of MB and RB dyes. As seen, there was no significant difference in the adsorption capacity for the first three cycles of adsorption. However, after fourth and fifth cycle sorption capability was decreased by approximately 40 % of the original value. This might be due to the degradation of crosslinked chitosan coating from surface of the membrane.

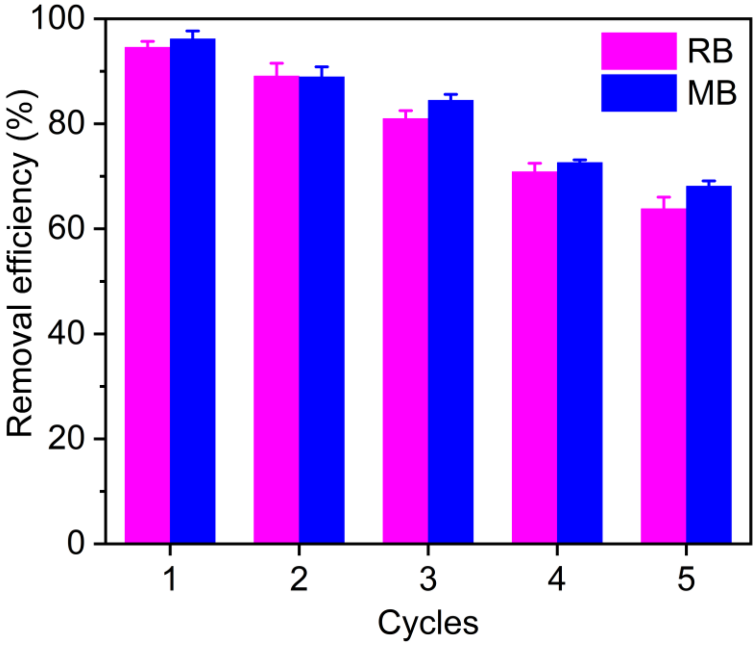


Figure 5.8 Reusability of adsorbent membranes for MB and RB dyes.

5.11 Conclusion

APTES crosslinked CH immobilized PPLLA adsorbent membrane was fabricated to adsorb synthetic dyes from the aqueous solution. FTIR study confirmed that number of active sites on the membrane were increased up to crosslinking ratio of 0.1 and there was a little or no change in amine and hydroxyl groups with the increase in APTES ratio. The adsorption capacity for RB and MB dyes was improved with the increase in initial dye concentration because of the increased mass transfer of dye molecules on the adsorbent surface. However, the adsorption capability was reduced at elevated temperatures because of the increased mobility of dye molecules and decreased binding force with the adsorbent. The pH study showed maximum capacity at pH 4 and 9 for RB and MB dyes, respectively. Moreover, adsorbent membrane had the capability to remove more than 80 % of both dyes in first 60 min and the equilibrium adsorption was reached after 150 min. Thermodynamic studies of adsorbent revealed that the adsorption process was exothermic and spontaneous. The Langmuir isotherm and pseudo second order model best interpreted the equilibrium and kinetics of dye adsorbent system. The prepared adsorbent membrane was successfully reused after five cycles. Hence, a versatile biodegrade adsorbent membrane was applied to get the clean water from the synthetic dye contaminated water.

5.12 Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

5.13 Acknowledgements

The authors acknowledge the support of the Electron Microscopy Center in The University of Manchester.

5.14 Novelty statement

According to author's knowledge, little work has been carried out to crosslink the chitosan with APTES then coated this on the hydrophobic nanofibrous membranes. Moreover, previous studies have not comprehensively considered these membranes for the adsorption of textile waste dyes from the aqueous solution. In this research, we have developed porous PLLA membranes with very high specific surface to support the adsorbents and assist them to adsorb rhodamine B and methylene blue dyes in very high quantities as compared to previous studies.

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6.Chapter 6

Conclusion & Future Work

6.1 Conclusions

This research has demonstrated the development of porous PLLA nanofibers coated chitosan based adsorbents with the aim to improve the adsorptive capacity for toxic pollutants in the water. Three routes for the development of new adsorbents were developed and evaluated.

The first route considers the immobilization of chitosan on porous PLLA nanofibrous membrane fabricated via electrospinning and use it as an adsorbent for the removal of copper ions from aqueous solution. The scanning electron microscopy, fouier transform infrared spectroscopy and x-ray diffraction analysis of adsorbents proved that chitosan was successfully immobilized on the porous PLLA nanofibrous support. Moreover, energy dispersive x-ray spectroscopy and visual observation confirmed the presence of copper ions after the adsorption on chitosan coated adsorbents. The efficacy of adsorbent was examined in varying adsorption parameters such as: pH, initial copper ion concentration, time, and temperature and chitosan concentration. This study has shown that, maximum adsorption (111.66 mg/g) for copper ions can be achieved in 10 min in optimum adsorption conditions. This adsorption ability is five times greater as well as six times faster than the previously reported study on the chitosan coated polyethylene terephthalate. Moreover, the adsorption kinetics related closely with the pseudo second order model, and adsorption experiments fitted well with the Langmuir isotherm. Finally, the thermodynamic studies revealed that the adsorption process is spontaneous and exothermic. Taken together, these findings suggest the role for surface area in promoting the adsorption capacity of toxic pollutants.

Following the understanding of chitosan coating on porous substrates, chitosan was grafted on the porous PLLA nanofibrous membrane to increase the adsorption sites and possible increase in the removal of copper ions.

Dopamine can adhere to potentially any surface type and form a uniform and layered structure on the substrate and therefore could be used as an interlayer between porous PLLA support and chitosan. This study shows that, chitosan was successfully grafted on polydopamine modified porous PLLA surface without significantly compromising the surface area of the porous substrate. The chemical grafting of chitosan was proved by x-ray photoelectron spectroscopy and fourier transform infrared spectroscopy analysis and its mechanism was discussed in detail. Furthermore, this study has identified that the adsorption capacity for copper ions was increased by two and a half times after chitosan grafting as compared to our previous study. However, the equilibrium adsorption time was increased to 40 min which is 4 times higher than our previous research. This may be due to the fact that more time is needed to adsorb higher number of copper ions. Finally, the developed adsorbent retained its capability by 80 % after three regeneration cycles.

Another viable approach towards the increasing of adsorption capacity is to cross-link the chitosan with the material that has amine groups on its backbone. These amine groups act as the adsorption sites. In the manuscript three, 3-aminopropyltriethoxysilane was used to cross-link the chitosan and coat this on porous PLLA surface. The ratio of chitosan to 3-aminopropyltriethoxysilane was optimized to utilize maximum number of adsorption sites. Fourier transform infrared spectroscopy was used to study optimization of crosslinking ratio. In this research, toxic dyes such as methylene blue and rhodamine B that are released from various clothing sectors were tested for adsorption. Moreover, in this work, linear and non-linear kinetic and isotherm models were studied. Non-linear elovich kinetic model and freundlich isotherm was fitted well for both the dyes. Also, the adsorption was higher as compared to previously reported adsorbents. Furthermore, the mechanism of chitosan crosslinking and adsorption of dyes was discussed in detail. Finally, the adsorbent was tested against five adsorption cycles and it was found that the prepared adsorbent can reuse for three cycles successfully.

6.2 Limitations of current study

The limitations of this study are:

- The current batch adsorption method is affected by the surrounding environment of aqueous solution such as pH, concentration and temperature. To control the environment in large setups can be expensive due to the higher cost of chemicals associated with it.
- There is no suitable method to dispose the chemical waste coming after the adsorption and regeneration processes.
- Moreover, degradation of chitosan coating during the regeneration process is reducing the capability of prepared adsorbents to be reused after three cycles.

6.3 Future Work

The proposed development route for the adsorption of toxic pollutants from aqueous solution in this thesis can be further expanded with the aim of removal of hazardous materials from the industrial and municipal wastewater. New directions leading towards the adsorption by using chitosan coated porous substrates are described below;

A natural progression of this work is to analyse the removal performance of prepared adsorbents in the industrial or municipal wastewater. Considerably more work will need to be done to determine the effect on adsorption capability of porous adsorbents in the presence of different ions in the wastewater such as, sodium, calcium, nitrogen, phosphorus and sulphur. Also, an investigation about the ability to adsorb other pollutants like chromium, uranium, ammonia and pesticides, would be advisable. The main recommendation in the form of methodology is, further research using the column adsorption experiments is required.

The chitosan coating on porous PLLA nanofibrous membrane showed to be the most effective adsorbent but chitosan can sometime reduce the surface area of porous nanofibers. Thus, the coating of chitosan nanoparticles or incorporation of chitosan particles during the electrospinning can help to overcome this restriction. It would be advisable to investigate the other materials different to chitosan in order to modify the surface of porous PLLA substrates.

Copper is widely used in the electronic products, building industry, transportation and industrial machinery. Further research might explore the recovery of copper from the adsorbents and reuse it various applications. This will offer a solution which ensures both a high effluent quality and a circular economy approach.

Finally, in this work porous PLLA nanofibers was evaluated, but the fabrication of different types of hydrophobic porous nanofibrous membrane can be good alternative in order to investigate and compare adsorption capacity and selectivity.