Cellulose Isolation from Cotton Gin Waste and Synthesis of Cellulose/PVA Membrane for Heavy Metals Removal

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APPROVAL SHEET

Certified that the contents and form of this report entitled “Cellulose Isolation from Cotton Gin Waste and Synthesis of Cellulose/PVA Membrane for Heavy Metals Removal” submitted by Hamna Aamir, Iqra Javed and Wajeeha Naz have been found satisfactory for the partial requirements of the degree.

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Abstract

The scope of this project was waste minimization through resource recovery and the targeted waste was Cotton Gin Waste (CGW). The process of cellulose isolation from cotton gin waste was optimized and a fibrous membrane was fabricated using phase inversion technique. CGW was taken from industry, weighed and manually cleaned. It was then subjected to alkali treatment for 2 hours with 10% Sodium Hydroxide (NaOH) at 80^0C. The CGW was bleached with 5% Hydrogen Peroxide (H_2O_2). The CGW was then treated with 10% Sulfuric acid for 1 hour at 80^0C. After filtering, the CGW fibers were oven dried for 3 hours. As a result of which, fine cellulose powder was obtained. For the fabrication of porous membrane, 3g of Polyvinyl Alcohol (PVA) was dissolved in 30 mL of distilled water. Another solution was prepared by the dissolution of 6g of Sodium Hydroxide (NaOH) and 6g of urea in distilled water and 1g of cellulose. The two solutions were mixed in a reflux assembly for 24 hours.

This resulted in the fabrication of a cross-linked cellulose/polyvinyl alcohol (PVA) porous membrane. The fabricated membrane was used for the removal of heavy metals like copper, zinc and manganese from synthetic wastewater. The membrane was characterized by FTIR to identify the functional groups present in the membrane matrix and SEM analysis to find the pore size and morphology of the membrane. The maximum removal ofcopper was found to be 95% at 5 mg/L, 59.8% at 5 mg/L for zinc and 49.84% at 6mg/L concentration for manganese. This specified that the developed membrane could be effectively utilized for the removal of above mentioned heavy metals from wastewater.

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List of Abbreviations

RO	Reverse Osmosis
NF	Nanofiltration
UF	Ultrafiltration
MF	Microfiltration
MD	Membrane Distillation
CMC	Carboxymethyl Cellulose
PEG	Polyethylene Glycol
PVA	Polyvinyl Alcohol
SEM	Scanning Electron Microscopy
AAS	Atomic Absorption Spectroscopy
PAA	Polyacrylic Acid
FTIR	Fourier Transform Infrared Spectroscopy

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Chapter 1

Introduction

Pakistan being an agricultural country produces vast amount of cotton annually, a major portion of which is exported while some portion of cotton is used for domestic purposes. Globally, Pakistan is the fifth producer of cotton and the third biggest exporter of cotton. Cotton is used for multiple purposes in Pakistan and it has been ranked as the fourth largest consumer of cotton. The cotton crop consumes almost 15 percent of the total area available for cultivation in Pakistan. Export from cotton makes up 10 percent of the national GDP of Pakistan. Whilst cotton production provides a boost to the economy of Pakistan, it also poses a threat to the environment in the form of cotton gin waste (CGW). CGW, previously considered trash, has now opened new prospective. 227 kg of cotton can give out approximately 37 to 147 kg of cotton gin. This cotton gin waste, when disposed to certain chemical treatments, produces cellulose; a valuable product used in the manufacture of everyday items like paperboard and paper.

Cellulose is present in all plants, but its percentage varies from one species to another. Research shows that algal biomass contains 7.1% of cellulose (Ververis et al., 2007), the percentage of cellulose present in citrus peels varies from 12.7 to 13.6 (Ververis et al., 2007), wheat straw contains 35-45% of cellulose (Rio et al., 2012) and cotton gin waste contains 80-90% of cellulose component.

Evaporation-induced phase separation, interfacial polymerization, immersion precipitation, thermally induced phase separation and vapor-induced phase separation are some of the more popular techniques used for the fabrication of cellulose membranes (Lalia et al., 2013). Surface, physical and chemical properties of different types cellulose membranes vary with the techniques used for their fabrication. Membrane cross-section can be isotropic (symmetric), integrally anisotropic (asymmetric) and thin-layer or mixed matrix composite depending upon the method of their fabrication and the materials used. (Ulbritchb et al., 2006)

Cellulose membranes are used for the removal of heavy metals from wastewater. Pakistan is facing a serious environmental threat due to the high discharge of heavy metals, mainly in industrial wastewater. Tanning, electroplating, metallurgical and textile industries discharge considerable amounts of heavy metals in their wastewaters. These heavy metals are not subjected to proper treatment and go untreated into groundwater and aquatic ecosystems. (Andleeb et al., 2010). Chemical precipitation, adsorption with adsorbents, membrane filtration, electrodialysis and photocatalysis are the more popular methods for the removal of heavy metals from wastewater (Barakat et al., 2011).

Thus, in this research, optimization of cellulose isolation from cotton gin waste and fabrication of cellulose membrane was achieved. The cellulose membrane was then characterized and subjected to various tests to determine its removal efficiency of heavy metals

1.1. Project Statement

To optimize cellulose isolation from cotton gin waste and fabrication of a porous membrane on laboratory scale for heavy metals removal.

1.2. Project Objectives

Following objectives were set in the beginning of the project:

1) Optimization of cellulose isolation from cotton gin waste
2) Fabrication and characterization of cellulose/PVA membrane
3) Determination of heavy metals removal efficiency from aqueous solution

1.3. Project Background

Untreated agricultural waste poses threat to environment and puts million acres of useful land to no use. Incineration and land filling are the methods used for the disposal of agricultural waste, but they require high cost and high human resource. These practices are a burden on the economy. Instead of treating agricultural waste as 'waste', it can be put to better use by converting it into useful resources and also by using it as a renewable energy source.

Agricultural countries like Pakistan which produce large amounts of cotton annually, can take advantage of the waste product i.e. cotton gin waste by turning it into useful products like cellulose. Pakistan produces massive amount of cotton annually and the target set by the government of Pakistan for the production of cotton for 2015-2016 is 15.49 million bales, which will be cultivated over an area of 3.12 million hectare. Almost half of the cotton produced annually is converted into cotton gin waste. Cotton gin waste is the impure form of cotton and comprises of dust particles, leaves, seeds and stalks. Southern cities of Punjab and Sindh produce the highest amount of cotton.

Cotton gin waste, when subjected to different chemical process, yields cellulose, a useful component which is used in the manufacture of a large number of products. Cellulose is a useful resource for the fabrication of cross-linked porous membranes.

Surface properties of membrane like tensile strength, porosity, sorption capacity, water solubility depend upon the polymer and method used for the fabrication of the membrane.

Wastewater from tanning, metallurgic, textile and paint industries is contaminated with heavy metals like lead, copper, zinc, arsenic and cadmium. These heavy metals, if go untreated in groundwater or other aquatic bodies, can cause havoc. Heavy metals can bio accumulates and they can be passed from one organism like fish to another like the human. Also, if a living organism is exposed to this untreated water for longer times, heavy metals would accumulate in the bodies of the organisms. Bio accumulation can be very detrimental for the health of a living organism.

Porous membranes formed by the combination of cellulose and a certain polymer work by adsorption process. Heavy metals can be removed efficiently from wastewater through these porous membranes.

1.4. Project Scope

The scope of this project is waste minimization through resource recovery.For that we targeted agricultural waste; cotton gin waste to be precise. Cotton gin waste was subjected to various chemical procedures under such conditions that its isolation efficiency was optimized to 50-60%. From the isolated cellulose, porous cellulose membrane was fabricated. The methodology used for the fabrication of the membrane is discussed in detail in section 3 of this report. Characterization of membrane was achieved through different techniques and it was subjected to various tests to determine its removal efficiency of heavy metals from synthetic wastewater.

Chapter 2

Literature Review

2.1. Cellulose Isolation

Cellulose is the most abundant organic material which is found in every plant’s cell, constitutes approximately 33% of the plant’s matter. Several research works have been done on the isolation of cellulose depending upon the type of feedstock and the availability of chemical present.

Table 1: Cellulose Contents

Plant’s matter	**Cellulose Content %**	**References**
Algal Biomass	7.1	Ververis et al., 2007
Citrus Peels	12.7-13.6	Ververis et al., 2007
Rice Husk	25-35	Luduena et al., 2011
Wheat Straw	35-45	Rio et al., 2012
Cotton Gin Waste	80-90	Haleem et al., 2014

Among all these, cotton gin waste has high cellulose content. Cotton gin waste is a byproduct of the cotton ginning process and consists of the dried burr of cotton ball, stems, leaf fragments, and various dumpy or smashed cotton fibers, all of which have high content of cellulose (Wilde et al., 2010).

Randal et al., used the ground cobs for the production of white, water-swollen cellulose gel (Randal et al., 2011).

‘’Ground cobs (220 grams) was treated with NaOH (Alkali treatment) and 0.6% NaOCl at 8°C and stirred for about two hours in a resin flask, resulting in the white, water –swollen cellulose gel (11% solids) which was then frozen wet in a refrigerator’’ (Randal et al., 2011).

Guozhi et al., and their coworkers performed similar experiments in order to isolate cellulose from rice straw. From their research work, they concluded that cellulose was prepared from rice straw by pre-treatment with alkaline and acid solutions successively (Guozhi et al., 2013).

‘’Rice straws were cut into 4 to 5 cm dimensions and washed thoroughly 3 to 4 times by warm water to remove soluble aqueous substance and dirt particles, then dried at 5°C. The dried clean rice straw was crushed into powder form and was collected by passing through Tyler screens of different meshes. 10 grams powder was extracted by using 150 ml toluene-ethanol (2:1, v/v) mixture for 24 hours to remove wax, pigments and oils, followed by oven drying at 5°C. The dewaxed powder was mixed in 350 ml of 4 wt. % KOH solution with 2 wt. % H_2O_2 at 4°C for 8 hours. It was then heated at 9°C for 4 hours. The mixture was then cooled to room temperature. It was then filtered and washed thoroughly with distill water to remove any dissolved substances until the filtrate became neutral. The obtained solid was then dried overnight at 5°C. It was followed by immersing in 250 ml acetic acid solution at 7°C for 5 hours with 3 to 4 of pH value. The mixture was centrifuged and washed thoroughly with plenty amount of distill water until the filtrate became stable. It was followed by drying in ambient conditions. The content of cellulose in the mixture was calculated accordingly to the reported procedure’’ (Guozhi, Min, Chongjing, Tao, Jianfen, 2013).

Istirokhatuna et al., prepared cellulose from Tropical Water Hyacinth (Istirokhatuna et al., 2015).

“Extraction of water hyacinth fibers was done by using toluene/ethanol solvent with ratio of 2: 1 for 3 hours at 115°C. Additionally, bleaching process using 3% NaClOfor 2 hours at 80°C was performed. Then hydrolysis using NaOH 1% at 60°C for 2 hours removed the hemicellulose. Again bleaching was performed to remove the remaining lignin using 1% NaClO and stirred at 75°C for 3 hours. The end phase involves hydrolysis using 5% HCl as catalyst for 6 hours at 65°C. Then sample was filtered and the obtained solid was washed with distilled water until it is acid free” (Istirokhatuna et al., 2015).

Ibrahim et al., performed the experiments for the evaluation of cellulose from bleached rice straw pulp (Ibrahim et al., 2013).

“Alkaline pulping process was used in which the unbleached rice straw was cut into small pieces and 10 times its weight (w/w) sodium hydroxide solution was added. Bleached rice straw pulp was obtained by extracting the lignin and most of the hemicelluloses using a two stage bleaching method applying sodium hypochlorite. The liquor to fiber ratio was maintained 10:1 with pH of 9. Then pulping was allowed for 2 hours at 160°C in a rotary autoclave, after which the pulp was thoroughly washed with water till neutrality and dried in air” (Ibrahim et al., 2013).

2.2. Cellulose Membrane Fabrication

Many techniques have been performed for the fabrication of cellulose membranes depending upon the content of cellulose and molecular weight of the polymer added.

Lalia, et al. performed a review on various membrane fabrication techniques (Lalia et al., 2013).

“Depending upon the choice of a polymer, the size of the particle that can be retained and the desired structure of the membrane, they discussed the most commonly used techniques for preparation of polymeric membranes; phase inversion, interfacial polymerization, stretching, track-etching and electrospinning” (Lalia et al., 2013).

Table 2: Membrane Technologies

Technology (Membrane Processes)	**Polymers Used for Membrane Fabrication**	**Fabrication Techniques**	**Average Pore Size of the Membrane**
RO	·Cellulose acetate/triacetate ·Aromatic polyamide ·Polypiperzine ·Polybenziimidazoline	·Phase inversion ·Solution casting	3–5 Å
NF	·Polyamides ·Polysulfones ·Polyols ·Polyphenols	·Interfacial polymerization ·Layer-by-layer deposition ·Phase inversion	0.001–0.01 μm
UF	·Polyacrylonitrile (PAN)	·Phase inversion	0.001 – 0.1 μm

	·Polyethersulfone (PES) ·Polysulfone (PS) ·Polyethersulfone (PES) ·Poly(phthazine ether sulfone ketone) (PPESK) ·Poly(vinyl butyral) ·Polyvinylidene fluoride (PVDF)	·Solution wet-spinning	
MF	·PVDF ·Poly(tetrafluorethylene) (PTFE) ·Polypropylene (PP) ·Polyethylene (PE) ·PES ·Polyetheretherketone (PEEK)	·Phase inversion ·Stretching ·Track-etching	0.1–10 µm
MD	·PTFE ·PVDF	·Phase inversion ·Stretching ·Electrospinning	0.1–1 µm

Source: (Lalia et al., 2013)

Table 3: Fabrication Techniques

Technique	**Application**	**Operating Principle**
Phase Inversion		
Evaporation-induced phase separation		Demixing process
Vapor-induced phase separation		Demixing process
Immersion precipitation		Demixing process with improved efficiency
Thermally induced phase separation		Demixing process with improved efficiency
Interfacial polymerization		
	Fabrication of thin-film composite RO and NF membranes.	Cross linking of micro porous polysulfone and aqueous solution of a polymeric amine and at 110 °C.
Stretching		
	Stretching of highly	Extrusion of the heated solvent

	crystalline polymers forming porous structure.	free polymer (above melting point) into thin sheet forms and stretching to make it porous.
Track-etching		
		Linear damage tracks across the irradiated nonporous polymeric film.
Electrospinning		
	Filtration and desalination	High potential applied between the polymer solution droplet and the grounded collector.

Source: (Lalia et al., 2013)

They claimed that the immersion precipitation and thermally induced phase separation are the most commonly used method in the fabrication of polymeric membranes with several morphologies. In phase inversion process the uniformly mixed polymer solution is converted precisely from a liquid to a solid state.

They also gave reviews on the structure–property relationship of membranes and structure parameters which affect the membrane performance. The important parameters which affect the membrane performance are crystallinity of the membrane polymer, porous structure, hydrophobicity/ hydrophilicity, membrane charge and surface roughness. Crystallinity of polymers is a major property in determining the mechanical stability and permeability of the polymer, particularly for nonporous membranes" (Lalia et al.,2013).

Istirokhatuna and his work fellows again performed different experiments for membrane fabrication by phase separation methods using the cellulose acetate (Istirokhatuna et al., 2015).

"Ten gram isolated cellulose was added in 24 ml glacial acetic acid at 40°C for 1 hour. Furthermore, 1 ml sulfuric acid and 60 ml glacial acetic acid were added, and stirred again for 45 minutes at the same temperature. The mixture was cooled to 18°C and then 27 ml acetic anhydride was added. Afterwards, 1 ml sulfuric acid and 60 ml glacial acetic acid were added for 3 hours at 40°C. Furthermore 67% acetic acid was added to the mixture at 40°C for hydrolysis process as long as 15 hours at room temperature. Cellulose acetate was precipitated by adding distilled water drop by drop and stirred to obtain powder precipitate. The resulted powder precipitate was washed and dried in an oven at 50°C.

Cellulose diacetate solutions with concentration of 13-15 % were prepared using cellulose acetate and acetone as solvent. Polyethylene glycol (5%) was added drop by drop and the homogenous polymer solution was left without stirring until no bubbles were observed. The polymer solution was cast with a thickness of 200 m using a steel casting knife on a glass substrate, then left in free air contact Thereafter, the proto-membrane was solidified by inserting into a coagulation bath containing water for 1 day at room temperature. The resulting membranes were washed to remove excess solvent" (Istirokhatuna et al., 2015).

Yang et al., states that the regenerated the cellulose micro porous membranes can be made by mixing cellulose cuoxam with a water soluble polymer (polyethylene glycol and gelatin as pore former). When the PEG molecular weight was smaller than 2000, a mixture of cellulose cuoxam and PEG aqueous solution was miscible, and membranes with a micro porous structure were formed (Yang et al., 1996).

“A 6 wt.% cellulose cuoxam solution was prepared in which the desired amount of PEG400, aqueous solutions of 20% PEG2000, 20% PEG6000, 20% PEG20000 and 20% gelatin were respectively added. The cellulose/polymer mixture solution was filtered and then casted on a glass plate to a depth of 0.25 mm. Then immersed immediately into a coagulation bath of dilute NaOH aqueous solution and again regenerated in dilute H_2SO_4, washed in running water, then placed in iso-propanol for 10 h, and finally stored in 20% iso-propanol/2% formaldehyde aqueous solution” (Yang et al., 1996).

Ibrahim et al., further accomplished the evaluation of cellulose and carboxymethyl cellulose/polyvinyl alcohol membranes. The isolated cellulose from rice straw was converted to carboxymethyl cellulose (CMC) and both the polymers were cross-linked with polyvinyl alcohol (Ibrahim et al., 2013).

“The dried isolated cellulose from rice straw was sieved with a 0.32 mm screen, and the fine cellulose powder was weighed and dipped in a 2000 mL beaker with 20% sodium hydroxide solution. The aqueous suspension was heated and stirred at 80°C for 4.5 h, and then filtered and washed with 95% ethanol solution. The filter residue was added in a beaker with 15% sodium hydroxide solution in water bath, and then interfused by monochloroacetic acid, being stirred and heated at 70°C for 1 h. After that, the polymer was filtered off, washed with 75% aqueous ethanol solution, and dried. Then 0.5 g of extracted dried cellulose was dissolved in 20 mL dimethylacetamide at 130ºC for 2 h under stirring. After the slurry had been allowed to cool to 100ºC, 1.5 g of anhydrous LiCl were added. To this solution, 3.0 mL of 0.08% CAS, as initiator, was added and the mixture was immediately stirred at 60ºC for half hour under nitrogen. At the same time, 4 g of polyvinyl alcohol was dissolved in 30 mL of distilled water at 60ºC with a constant stirring. After cooling, the dissolved cellulose was mixed with the PVA solution by stirring and the reaction maintained for 3 h at 85ºC under N_2. The copolymerization reaction was continued up to 24 h with stirring at 25ºC. The formed gel was then poured into a petri-dish for film casting" (Ibrahim et al., 2013).

Ulbritch explains the classification of the membranes in four different categories with their respective description (Ulbritch et al., 2006).

Table 4: Classification and Description for Membranes

Classifications	Description
Membrane materials	Organic polymers, inorganic materials (oxides, ceramics, metals), mixed matrix or composite materials.
Membrane Cross-section	Isotropic (symmetric), integrally anisotropic (asymmetric), bi-or multilayer, thin-layer or mixed matrix composite.
Preparation method	Phase separation (phase inversion) of polymers, sol-gel process, interface reaction, stretching, extrusion, track-etching, and micro-fabrication.
Membrane module configuration	Flat-sheet, hollow fiber, hollow capsule

Source: (Ulbritch et al., 2006)

2.3. Removal of Heavy Metals

In wastewater, heavy metals are usually present in dilute quantities (1 - 100 mg/L) and at neutral (pH = 7.0) or acidic pH values (pH < 7.0) (Ayres et al., 1994) and are generally considered to be those whose density exceeds 5 g per cubic centimeter (Barakat et al., 2011). Their removal from the wastewater was done in many techniques depending upon the type of heavy metal and its concentration.

The discharge of heavy metals into aquatic ecosystems has become a serious matter in Pakistan over the previous decades. These pollutants are introduced into the aquatic systems as a result of different industrial operations. The chemically polluted water has seriously damaged the ecology of surface and groundwater; eventually having serious consequences on living organisms in polluted area. Tanning, electroplating, textile, mining and metallurgical waste are the most considerable sources of environmental pollution by heavy metals. In Pakistan, there are 670 textile units discharging their wastes into water bodies without waste water treatment (Andleeb et al., 2010).

Barakat et al., studied different methods used for the removal of heavy metals from industrial wastewater. A wide range of treatment technologies include chemical precipitation, adsorption, membrane filtration, electrodialysis, and photocatalysis as well as membrane filtration (Barakat et al., 2011).

Table 5: Main Advantages and Disadvantages of Various Physicochemical Methods for Treatment of Heavy Metals from Wastewater

Treatment Method	Advantages	Disadvantages
Chemical Precipitation	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal
Adsorption with new Adsorbents	Low-cost, easy operating conditions, having wide pH range, high metal binding capacities	Low selectivity, production of waste products
Membrane Filtration	Small space requirement, low pressure, high separation selectivity	High operational cost due to membrane fouling
Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumption
Photocatalysis	Removal of metals and organic pollutant simultaneously, less harmful by-products	Long duration time, limited Applications

Source: (Barakat et al., 2011)

“Among these techniques, the membrane filtration is extensively used because of its treatment performance compared to other technologies. Also methodological application and practicability are the major aspects for the selection of the most appropriate treatment system for inorganic effluent” (Barakat et al., 2011).

Ngah et al. gave reviews on the removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbent (Ngah et al., 2008).

“The extensive range of low-cost adsorbents acquired from chemically modified plant wastes were studied for the removal of heavy metal ions such as Cd, Cu, Pb, Zn, Ni and Cr (VI) ions from the wastewater. The chemically modified plant wastes vary greatly in their ability to adsorb some heavy metal ions. In general chemical modification improved the adsorption capacity of adsorbents possibly due to higher number of active binding sites after the modification, better ion-exchange properties and formation of new functional groups that favors the metal uptake. The most common chemicals used for treatment of plant wastes are acids and bases” (Ngah et al.,2008).

Table 6: Summary of Modified Plant Wastes as Adsorbents for the Removal of Heavy Metal Ions from Aqueous Solution

Adsorbent	Modifying Agent	HeavyMetals
Rice husk	Sodium hydroxide Sodium bicarbonate Epichlorohydrin	Cd(II)
Rice husk	Tartaric acid	Cu(II) Pb(II)
Sawdust (cedrus deodar wood)	Sodium hydroxide	Cd(II)
Sawdust (S. robusta)	Formaldehyde	Cr(VI)
Sawdust (Poplar tree)	Sulfuric acid	Cu(II)
Sawdust (Dalbergiasissoo)	Sodium hydroxide	Ni(II)
Banana pith	Nitric acid	Cu(II)
Banana stem	Formaldehyde	Pb(II)
Jute fibres	Hydrogen peroxide	Cu(II) Ni(II) Zn(II)
Wheat bran	Sulfuric acid	Cu(II) Cd(II)
Groundnut husk	ric acid followed by silver Impregnation	Cr(VI)
Peanut husk	Sulfuric acid	Pb(II) Cr(III) Cu(II)
Walnut sawdust	aldehyde in sulfuric acid	Cd(II)

		Ni(II) Pb(II)
Groundnut shells	Reactive Orange 13	Cu(II) Ni(II) Zn(II)
Bagasse fly ash	Hydrogen peroxide	Pb(II) Cr(III)
Carrot residues	Hydrochloric acid	Cr(III) Cu(II) Zn(II)
Cork powder	Calcium chloride Sodium chloride Sodium hydroxide Sodium hypochlorite Sodium iodate	Cu(II)

Source: (Ngah et al., 2008)

Fenglian et al. also contributed towards the different methods used to treat heavy metals from wastewater. These include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation flocculation, flotation and electrochemical methods. However the ion-exchange, adsorption and membrane filtration techniques are most commonly considered for the treatment of heavy metal from wastewater (Fenglian et al., 2011).

“Membrane filtration technologies can remove the heavy metal ions with high efficiency”.

Table 7: Heavy Metal Removal Efficiencies

Membrane	**Heavy metal**	**Initial metal Conc.**	**Removal efficiency (%)**	**Conditions**
RO	Cu $^{2+}$, Ni^{2+}	500 mg/L	99.5	Operation pressure 5 atm
RO	Cu^{2+}	20 - 100 mg/L	70 – 95	Low pressure reverse osmosis
RO	As	<500 mg/L	As(V) 91 -99, As(III) 20-55	NA
RO	Ni^{2+} , Zn^{2+}	Ni^{2+}: 44-169 Zn^{2+}: 64-170	99.3 98.9	Operational pressure 1100 kPa
NF	Cu^{2+}	10 mM	47--66	Trans membrane pressure (1-3 bar)
NF	Cr(VI)	NA	99.5	Surfactants enhanced NF
NF	Cu^{2+}	0.47 M	96-98	Flat-heet NF membranes at 20bar

RO + NF	Cu^{2+}	2 g/L	>95	Operating pressures 35 bar
RO + NF	Cu^{2+}	15 mg/L	95-99	Combination of flotation and membrane filtration, 3.8 bar

Source: (Fenglian et al., 2011)

“They claimed that the membrane filtration technology can remove heavy metal ions with high efficiency, but its complications like high cost, method complication, membrane fouling and low flux have restricted their use in heavy metal removal” (Fenglian et al., 2011).

“All above techniques could be used for the treatment of heavy metal, it’s vital to state that the selection of the suitable handling techniques depends on the initial metal concentration, component of the wastewater, capital investment and operational cost, and environmental impact etc” (Kurniawan et al., 2006).

Qdais et al. presented a comparative study on the removal of heavy metals from wastewater by membrane processes (Qdais et al., 2004).

“They presented the reverse osmosis (RO) and nanofiltration (NF) membrane technologies for the treatment of wastewater containing copper and cadmium ions. It was observed that high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). However, NF was capable of removing more than 90% of the copper ions existing in the feed water. They also examined the performance of RO and NF membranes in treating wastewater containing more than one heavy metal and observed that the average removal efficiency of RO is 99.4% while that of NF was 97%" (Qdais et al., 2004).

Swaminathan et al. performed similar experiments for the separation of Ni $^{2+}$, Cu^{2+} and Cr^{2+} ions from water by complexation micro filtration technique using the synthetic polymer membranes. These ions were removed from water sample by metal ion and metal-complex separation method using the commercially accessible nylon and cellulose nitrate membrane filters. PAA and PEG were used as metal complexing agents (Swaminathan et al., 2013).

"Initially well-known concentrations of metal complexes; nickel sulphate, copper sulphate and potassium-di-chromate solutions were prepared separately from corresponding solutions using water soluble PAA and PEG polymers. These metal ions (using Nylon and CN membrane) and metal complexes (using Nylon membrane filter) were separated by using lab made membrane filtration unit with 47 mm membrane diameter and 30 mm Hg pressure (applied using vacuum pump) to suck the solution from input feed. The filtrate was tested and p% rejection was determined using UV – Visible spectrophotometer. Both the membranes showed good percentage rejection (80-90%) for all the metal complexes with PAA and PEG" (Swaminathan et al., 2013).

Copper is one of the substantial toxic heavy metal found in wastes and not decomposable, travels through the food chain. However too much intake results in buildup in the liver causing haemolysis, liver and kidney damage, irritation to upper respiratory tract, chronic asthma, gastrointestinal disturbance, anemia and diarrhea etc. (Cheriti et al, 2009, Kurniawan et al., 2006).

Heavy metals are hazardous since they tend to bioaccumulate. Bioaccumulation results in concentration rise of a chemical in a biological organism with time. The compounds accumulate in living things any time they are taken up and stored faster than they are digested or excreted. Heavy metals can enter a water supply system by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

As copper does essential work in animal metabolism but its unnecessary consumption generate severe toxicological distresses, as vomiting, convulsions, cramps, or even death (Paulino et al., 2006).Cheriti et al. claims that the biosorption process results in copper ions removal from aqueous solution, governed by the function of some parameters such as contact time, concentrations of Cu^{2+} ions, solution pH and temperature(Cheriti et al., 2009).

“Biosorption was done by shaking 100 mg of biosorbent mixed with 100 ml of copper sulfate solution of known concentration in 200 ml Erlenmeyer flasks stirred at constant speed in a magnetic shaker in a thermostatic bath. After, the solid was removed by filtration through a filter paper. Blank runs, with only the sorbent in 100mL of double distilled water, were conducted at similar conditions. The equilibrium metal concentration in the filtrates as well as in the initial solution was analyzed using AAS. The process has nearly reached equilibrium in four hours and is metals pH and temperature dependent, respectively optimal pH was 5 and temperature was 25-30^{o}C” (Cheriti et al., 2009).

Chapter 3

Research Methodology

This chapter comprises of various techniques used to produce the cellulose powder from cotton gin waste and cellulose membrane later on, which was further used for the removal of heavy metals. These techniques were analyzed to formulate a method of our own which involves:

- Isolation of Cellulose from Cotton Gin Waste
- Fabrication of Cellulose/PVA Membrane
- Characterization of Membrane
- Physicochemical Testing of Membrane
- Removal of Heavy Metals using Fabricated Membrane

3.1. Raw Material

3.1.1. Source of sample

Pakistan is the fifth largest manufacturer of cotton in the world, third largest exporter of raw cotton and the fourth largest consumer of cotton. Punjab has defeated all the former records and produced 32.35 percent more cotton than past years. Raw cotton and its by-products contribute about 69 percent of our total foreign exchange earnings. There are numerous by-products produced from the processing of cotton. These include entire cottonseed, cottonseed meal, cottonseed hulls, cotton mote, textile mill waste and cotton gin waste. Out of these, cotton gin waste is a key by-product of cotton ginning industry. Essentially, cotton ginning is the process of splitting the raw fibers into the seed bolls and dust particles and cotton gin waste. Our sample of cotton gin waste was brought from Rahim Yar Khan, Punjab, Pakistan.

Figure 1: Cotton Gin Waste

3.1.2. Composition of Cotton Gin Waste

Physically, the cotton gin waste consists of sticks, leaves, burs, soil particles, other plant materials, and mote and cotton lint. We had chosen cotton gin waste because it comprise of the product of our interest in large proportion chemically. This product is cellulose $[(C_6H_{10}O_5)_n]$. Cellulose fibers are highly stable homopolymer chains of up to 12,000 β 1-4 linked glucose units.

Table 8: Chemical Composition of CGW

Composition	Percentage
Cellulose	80 - 90%
Water	6 - 8%
Waxes and fats	0.5 - 1%
Proteins	0 - 1.5%
Hemicelluloses and pectins	4 - 6%
Ash	1 - 1.8%

Source: (Haleem et al., 2014)

3.2. Isolation of Cellulose

3.2.1. Dust Particles Removal

The cotton gin waste is washed a number of times with tap water, then with distilled water at 80°C for 15-20 minutes. Now, in order to take out the sample from beaker, first fill the beaker with tap water. Allow sample to settle down and then remove water from beaker. Repeat this process three times. After that take out sample from beaker by squeezing it and then place it in petri plate. Also use filter paper in order to avoid the removal of small size CGW sample and then place it in petri plate. At last, place sample in oven for 1 hour at 95°C. This results in decrease in weight of sample which indicates removal of dust particles from sample.

3.2.2. Carbonates and Sulphates Removal

Since, the sample was free of carbonates and sulphates, so treatment of sample with 1.5% HCl was not required in our case.

3.2.3. Alkali Treatment (Mercerization)

Take 25 grams of NaOH (99% pure) in 400 mL distilled water in a beaker and mix it. Place sample in a beaker and heat and stir at 150°C for 1 hour. Now, in order to take out sample from beaker, first allow the sample to settle down. Then remove the alkali in a conical flask and put aside for further usage. After that, fill the beaker with tap water. Allow sample to settle down and then remove water from beaker. Repeat this process three times. After that take out sample from beaker by squeezing it and then place it in petri plate. Also, use filter paper in order to avoid removal of small size CGW sample and then place it in petri plate. Dry the sample for 1 hour at 95°C. A decrease in weight of sample is observed which is due to the wax, fats etc.

3.2.4. Bleaching

Add distilled water in beaker and heat till its temperature reaches 70°C. Once it reaches 70°C then, allow heating at this particular temperature. Then add almost 6% NaOH, 5% Hydrogen peroxide solution (35% by volume) and place sample in a beaker. Heat the sample at 70°C with continuous stirring for 1 hour. In order to take out sample from beaker, first fill the beaker with tap water. Allow sample to settle down and then remove water from beaker. Repeat this process three times. After that take out sample from beaker by squeezing it and then place it in petri plate. Also, use filter paper in order to avoid removal of small size CGW sample and then place it in petri plate. Then allow sample to dry in oven at 105^{o}C for 45 minutes. This will result in decrease in weight of sample which shows the removal of lignin from sample.

3.2.5. Acid Treatment

Add distilled water, 10% H_2SO_4 (98.7% pure) and sample in beaker. Heat and stir at 80^{o}C by using hot plate for 1 hour. After heating, in order to take out sample from beaker, first allow the sample to settle down. Then remove the acid in a conical flask and put aside for further usage. After that, fill the beaker with tap water. Allow sample to settle down and then remove water from beaker. Repeat the process three times. After that take out sample from beaker by squeezing it and then place it in petri plate. Also, use filter paper in order to avoid removal of small size CGW sample and then place it in petri plate.

3.2.6. Stabilizing pH and Oven Drying

Maintain the pH of the sample close to 7 - 8 at the final stage. Then allow the sample to dry in oven at 100^{o}C for 3 hours. Grind the dried sample with piston and mortar, then poured through sieve to get the fine powdered cellulose.

3.3.Fabrication of Cellulose/PVA Membrane

The cross-linked cellulose/PVA composite membrane was produced by the process of phase inversion. Steps involved for the preparation of membrane are as follows:

Initially a solution of 6g of NaOH and 6g of Urea was prepared in a beaker. Solution was allowed to cool, either by putting it in a refrigerator or by the help of liquid nitrogen, till the temperature reaches to -10^{o}C. Then 1 g of cellulose was added into solution with constant stirring. Solution was put in the centrifuge at 4000 rpm for 10 minutes. After centrifuge, pH of the solution was adjusted to 7 by the addition of dilute HCl.

Another solution of 3 g Polyvinyl Alcohol (PVA), dissolved in 30 ml water, was prepared at a temperature of 50°C using hot plate with constant stirring. 2.5 ml of Polyethylene glycol (PEG) was added into the solution with constant stirring.

The two solutions prepared above were allowed to mix in a reflux assembly using hot plate magnetic stirrer bar, initially heated at 100°C for 3 hours and then kept at room temperature for next 24 hours. After the completion of reaction time, the sample mixture was carefully poured on the petri plate. Petri plate was allowed to dry. It was then heat dried in an oven at 60°C for 5 hours. Cellulose/PVA membrane can be extracted on butter paper by immersing the heated dry petri plate in the water bath.

3.4. Removal of Heavy Metals from Aqueous Solution

The prepared cellulose/PVA composite membrane was tested for the removal of Copper (Cu) metal. Initially, the stock solutions of concentration (2, 4, and 6 ppm) of copper metal were prepared separately from the standard solutions using deionized water to prepare synthetic wastewater. These solutions were passed through the fabricated membrane by using the filtration assembly. The filtrate and infiltrate was collected and analyzed using Atomic Absorption Spectroscopy (AAS) to determine percentage removal of copper metal from the membrane.

3.4.1. Analysis of Metal Permeate

Atomic absorption spectroscopy (AAS) is a spectro-analytical instrument which is mostly used to determine the concentration of the elements. In the present study, Atomic absorption spectroscopy (AAS Biotech Phoenix 986-UK) was used to analyze the percentage removal of copper metal. The known concentration solutions of 0, 2, 4, and 6 ppm were run on the instrument to obtain a standard curve.

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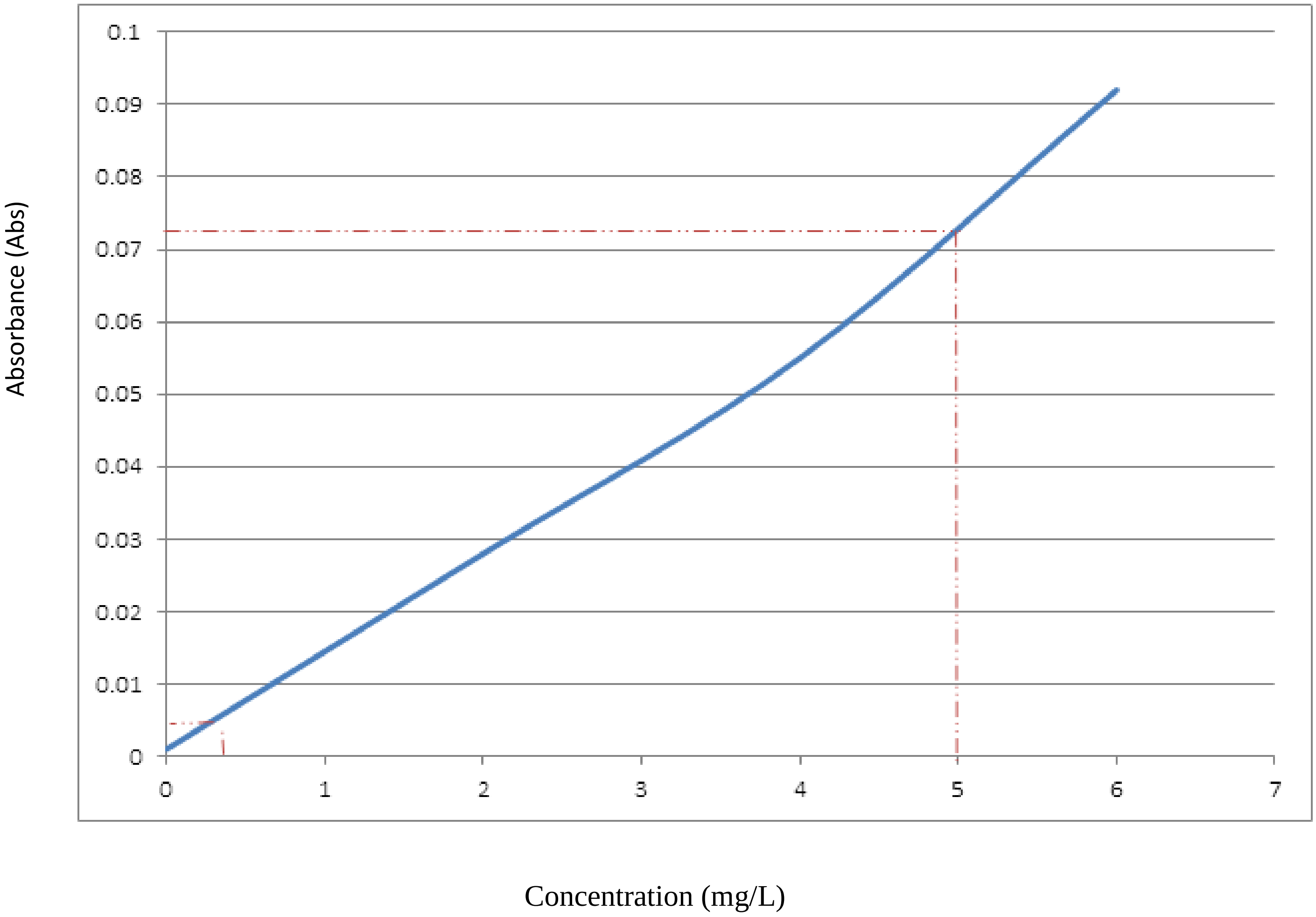


Fig 2: Infiltrate Solution Absorbance Graph

Then absorbance of both the infiltrate and filtrate solutions were observed by AAS and compared with standard curve to get the concentrations.

Table 9: Concentration Vs Absorbance

Concentration (mg/L)	**Absorbance (Abs)**
5	0.072
0.25	0.005

This gives the residual metal ion content in the filtrate. The percentage removal was expressed as

$$\textbf{Removal (\%)} = (C_i - C_f) / C_i \times 100$$ [11]

Where C_i and C_f are the initial and final concentrations of metal ion respectively.

Removal (%) = (5 - 0.25) / 5 x 100

= 95.00%

The membrane showed percentage removal of 95% at 5 mg/L concentration for the copper metal.

3.5. Morphological Analysis by Scanning Electron Microscopy (SEM)

In the present study, scanning electron microscopy (SEM) (Model-JEOL JSM-6490-A) was used to comprehend the surface morphology; pore size distribution, surface porosity, pore geometry and inspection of defects and asymmetry in the sample. A portion of membrane was installed in quick auto coater (Model JFC-1600 Ion sputtering device) who coated the membrane with Au. Scanning electron microscope uses focused and high energy narrow electron beam (in vacuum), which was normally in raster scan pattern, to produce multi signals at the surface of the membrane. As a result of the detection of signals using electron collectors, scanned images of the membrane at various magnifications were produced. Improved resolutions better than 1 nm can be visualized using SEM analysis.

3.6. Spectroscopic Characterization by Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is generally used for the identification of functional groups in a sample. In this study, Fourier Transform Infrared spectrometer (Model -Model-Perkin Elmer spectrum 100)was used to identify the functional group peaks in the spectrum. The test was carried on a small piece of the membrane and the spectrum produced was analyzed for the functional groups present in cellulose/PVA membrane. FTIR works on the basic principle that IR radiation passes through the sample, some of the radiation is absorbed by the sample and other get transmitted and the resultant spectrum is obtained by plotting absorption or transmission against frequency of the sample which ranges from 4000 to 450 cm^{-1} and a maximum resolution of 0.1 cm^{-1}.

In this study, FTIR analysis was performed for cellulose, PVA and cellulose/PVA membrane separately to identify the functional groups present in the fabricated membrane and to determine the degree of substitution of functional groups in the cellulose/PVA membrane.

3.7. Physicochemical Testing of Membrane

3.7.1. Water Sorption Test

Water sorption test was carried out to determine the water absorbing capacity of the membrane. A piece of the membrane having dimensions of 1x1 inch^2 was cut on which the tests were carried out. The dry weight (W_1) of the membrane was obtained by placing the membrane on a weight balance. The membrane was then immersed in a water bath for two hours. The wet membrane was weighed on a weight balance and the weight (W_2) of the wet membrane was noted. The membrane was then subjected to oven drying for 12 hours at a constant temperature of 60◦ C. After 12 hours of oven drying, the membrane was taken out and weighed on a weight balance. The weight of oven dried membrane was denoted as W_3.

The respective weights of the cellulose membrane came out to be:

$W_{1} = 0.0841$ g , $W_{2} = 0.1172$ g , $W_{3} = 0.069$ g

Water sorption for membrane was calculated using:

% water sorption = $(W_2 - W_3) / W_3 \times 100$[3]

= (0.1172 - 0.063) / 0.063 x 100

= 86.03 %

3.7.2. Water Solubility Test

Water solubility test was carried out to determine the % water dissolution of cellulose in water. The solubility test determines the life of membrane and for how long it can be used for the removal of heavy metals from wastewater. The water solubility test was carried out by using the following formula:

% water solubility = (W_1 - W_3 /) W_1 x 100[3]

= (0.0841 - 0.069) / 0.0841 x 100

= 17.95 %

Chapter 4

Results and Discussions

4.1. Isolation of Cellulose and Fabrication of Cellulose/PVA Membrane

Isolation of cellulose from CGW was performed by extraction, alkali treatment, bleaching and acid treatment. During these processes the mass of cotton gin waste was reduced due to removal of dust particles, lignin, wax and fats etc. and as a final product, 25 g fine cellulose powder was isolated which was further used for the fabrication of cellulose/PVA composite membrane. The fabricated membrane was then used for the removal of copper metal from wastewater and the percentage removal was determined. 95% removal of copper was obtained using cellulose/PVA membrane at 5 mg/L concentration. Similar tests were carried out to determine the removal efficiencies for zinc and manganese metals. The membrane showed 59.8% removal efficiency for zinc at 5 mg/L and 49.84% removal efficiency for manganese at 6mg/L.

4.1.1. Optimization of Cellulose Isolation

Optimization of cellulose was performed at different concentrations of H_2SO_4 keeping the NaOH and H_2O_2 concentration constant. And at different concentrations of NaOH keeping the H_2SO_4 and H_2O_2 concentrations constant. The maximum cellulose was obtained at 10% H_2SO_4, 10% NaOH and 5% H_2O_2 concentration.

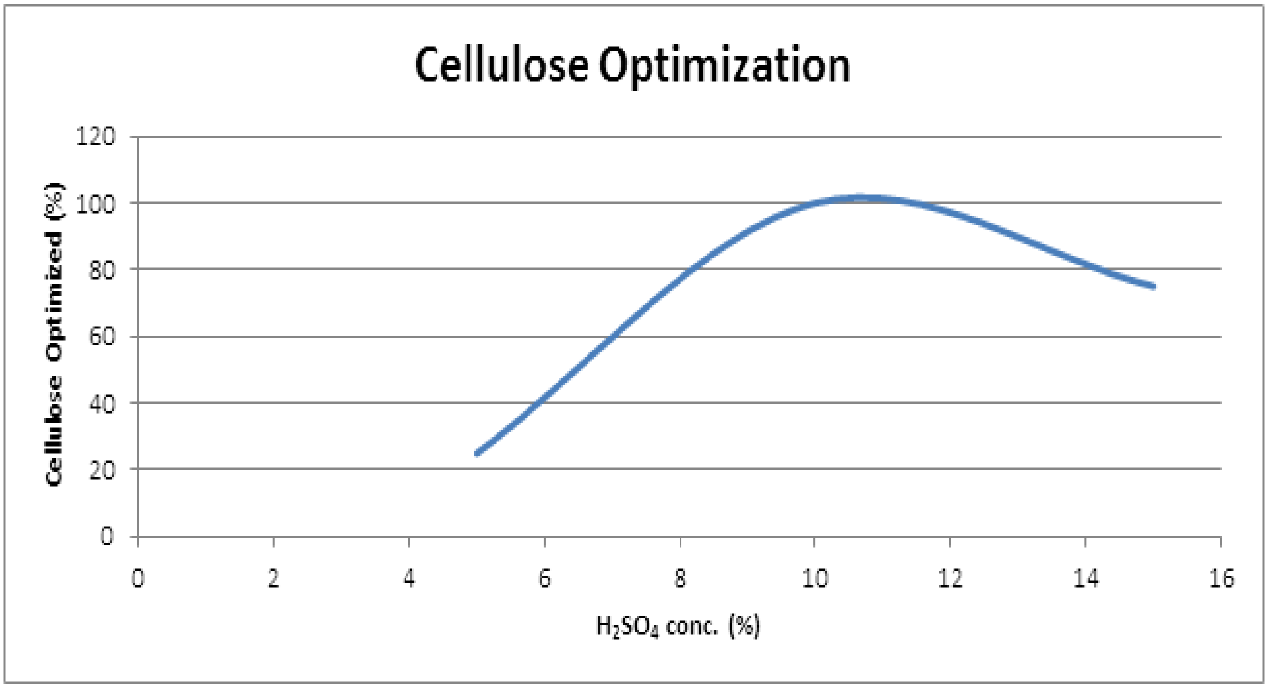


Fig 3: cellulose optimization with respect to H_2SO_4 Conc

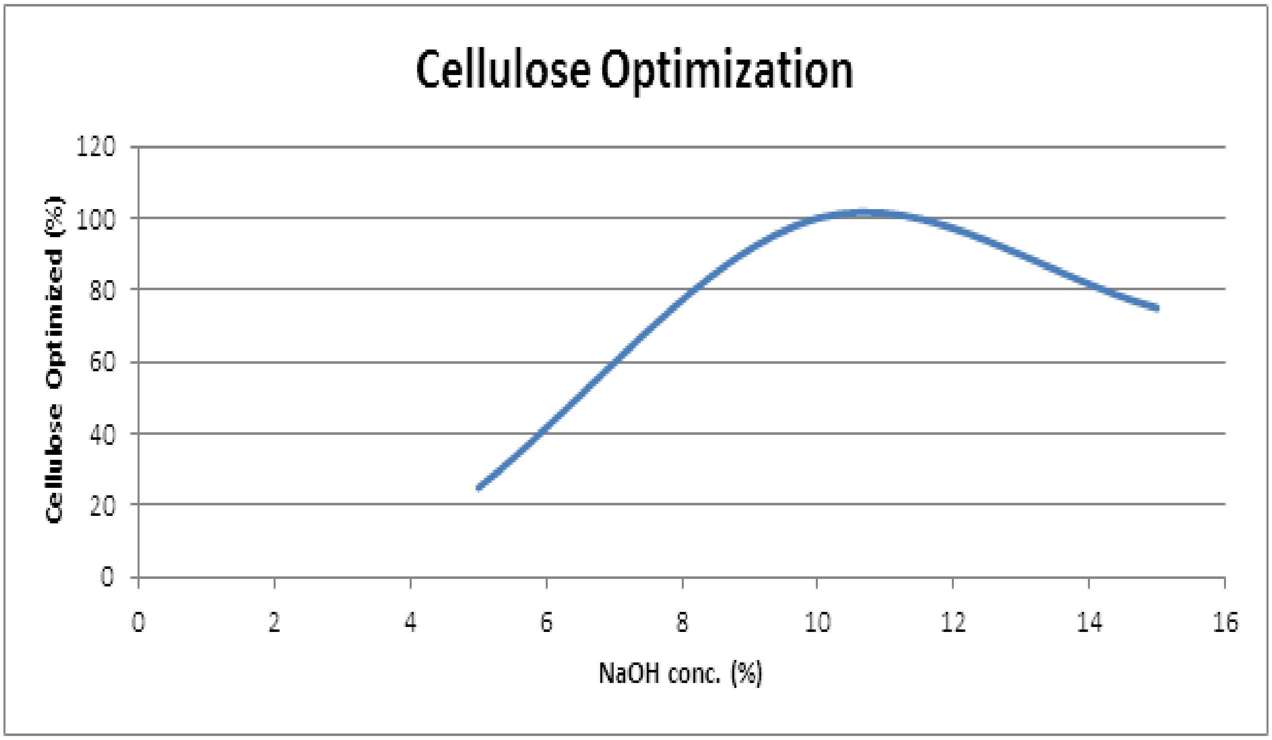
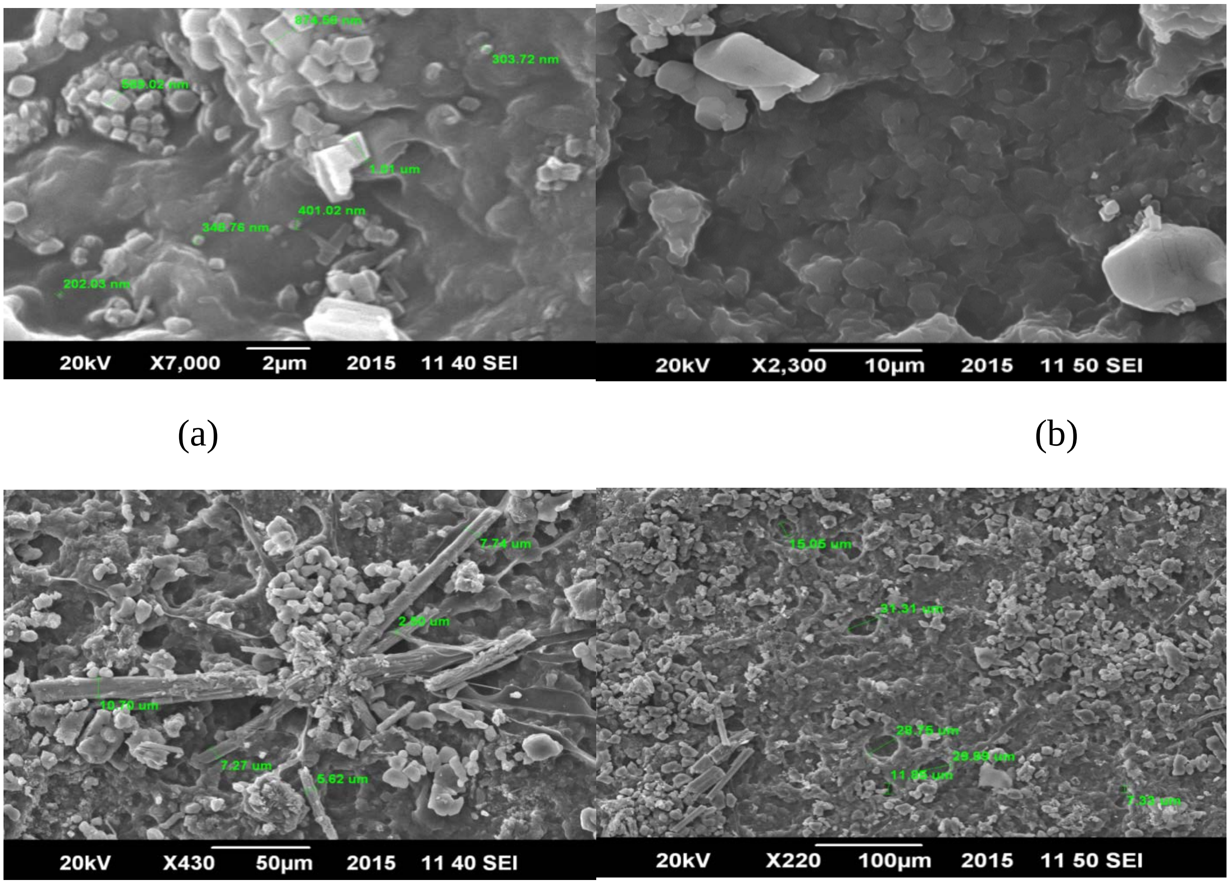


Fig 4: cellulose optimization with respect to NaOH Conc

4.2. SEM Analysis

4.2.1. SEM ofCellulose/PVA Membrane

Scanning Electron Microscopy images of the cellulose/PVA membrane at various magnifications i-e. 7000X, 2300X, 430X, 220X were established. From the SEM images as seen from **Fig.** 3 (a-d), micro porous nature of the membrane can be clearly established.



(a) (b)

(c) (d)

Fig. 3 SEM images of cellulose/PVA membrane (surface view a-d)

4.3. FT-IR Analysis

Three different spectra were obtained from FTIR analysis which was performed on cellulose; which was isolated from CGW, PVA; an important component of the membrane, and the fabricated cellulose/PVA membrane itself. The results from FTIR analysis have been discussed below:

4.3.1. FT-IR Analysis of Cellulose

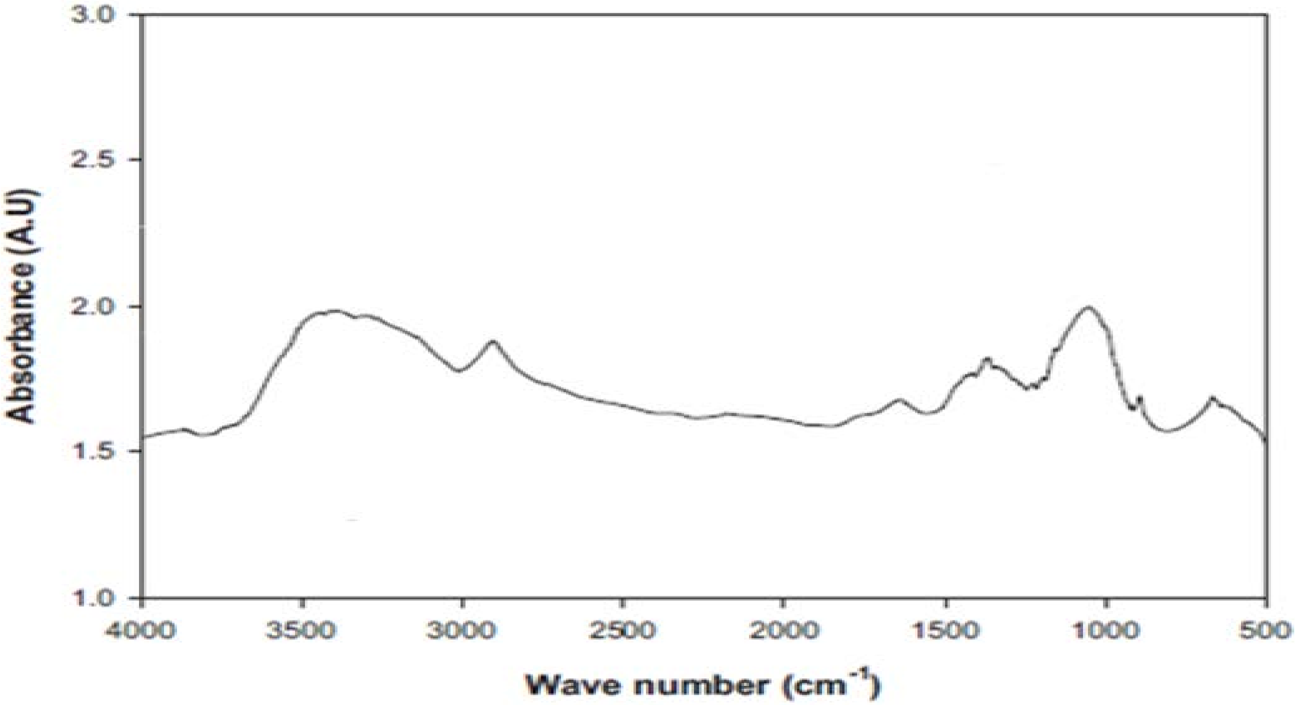


Fig 6: FT-IR Analysis of Cellulose

This spectrum was obtained by the FTIR analysis of cellulose. It is analogous to cellulose spectra which have been obtained through several studies conducted before. It spotlighted the extent of pure cellulose. The absence of non-cellulosic materials i.e. lignin and hemicellulose at peaks 1600 cm^{-1} and 1510 cm^{-1} indicated the extent of purity of isolated cellulose.

4.3.2 FTIR Analysis of PVA

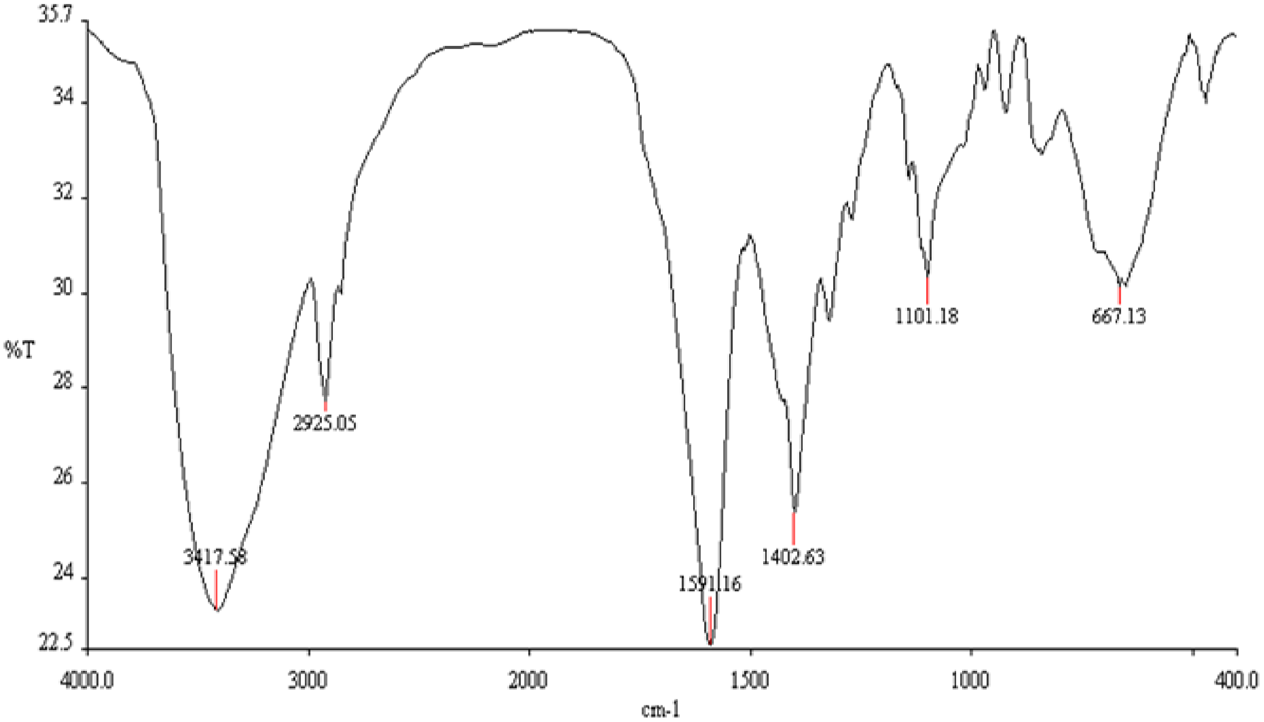


Fig 7: FT-IR Spectrum of PVA

This is the FTIR spectrum of Polyvinyl Alcohol. It shows various peaks at different wavelengths, indicating the presence of different functional groups.

4.3.3. FTIR Analysis of Cellulose/PVA Membrane

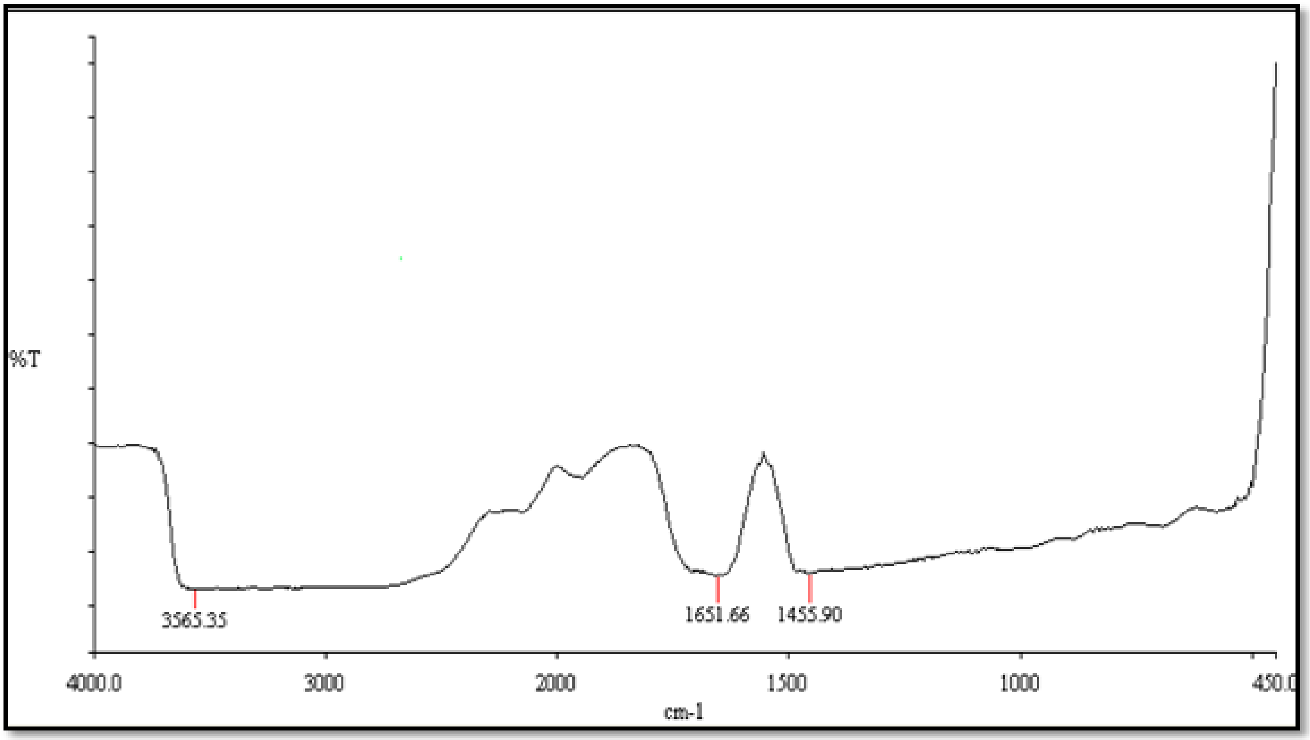


Fig 8: FT-IR Spectrum of Cellulose/PVA Membrane

This is the spectrum obtained from the FTIR analysis of fabricated cellulose/PVA membrane. FTIR analysis of the sample shows the presence of basic components which were used for the fabrication of the membrane. O-H stretching at peak 3655 is analogous with O-H stretching observed in the spectrum of cellulose and C-H bending at 1455 is analogous with C-H bending observed in the spectrum of PVA. Thus the fabricated membrane shows properties of both cellulose and PVA.

4.4. Sorption Test

Pure PVA membranes show a higher tendency for water sorption. The water sorption capacity is reduced in case of PVA/cellulose membranes. This varying trend is attributed to the conclusion that the presence of cellulose decreased the mobility of hydroxyl groups.

4.5. Solubility Test

Cellulose prevents the leaching out of PVA molecules when exposed to water. For longer life time of membrane, equal proportions of PVA and cellulose should be used during its fabrication process. Pure PVA membranes show a higher percentage of water solubility.

4.6. Percentage Removal Efficiency

The membrane showed percentage removal of

- 95% at 5 mg/L concentration for copper metal
- 59.8% at 5 mg/L concentration for zinc metal
- 49.84% at 6 mg/L concentration for manganese metal

Chapter 5

Conclusion

Cellulose was productively isolated from cotton gin waste by a multi-step process and further processed into porous cellulose membrane. Resulted cellulose had similar chemical structure with commercial cellulose. The polymer was crosslinked with poly (vinyl alcohol) (PVA) by phase inversion kinetics which was mainly responsible for formation and growth of macro voids in the membrane. PVA was used as a surface modifying agent. The physical properties of cellulose membrane were characterized by FT-IR, SEM, water sorption, solubility and salinity test. SEM study confirmed that the fabricated membrane is a microporous cellulose membrane. The present study reveals the usage of this fabricated cellulose membrane for the removal of copper ions from wastewater, which was found to be 95% at 5 mg/L concentration. The membrane showed 59.8% removal efficiency for zinc at 5 mg/L and 49.84% removal efficiency for manganese at 6mg/L. Further work is required in order to determine the removal of other heavy metals.

Recommendations

- Further work is required to improve the removal efficiencies of copper, zinc and manganese metals
- Further work is required to test the membrane for the removal of other harmful heavy metals like lead, mercury etc.

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