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Modification of Cellulosic Fibres with Synthesized Functional Chitosan Derivatives for Ecofriendly Textile Products

ISLAM, MD. MOFAKKHARUL

University of Rajshahi

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MODIFICATION OF CELLULOSIC FIBRES WITH SYNTHESIZED FUNCTIONAL CHITOSAN DERIVATIVES FOR ECOFRIENDLY TEXTILE PRODUCTS

A Dissertation
Submitted to the Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Bangladesh for the Degree of
Doctor
of
Philosophy

By

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Bangladesh

June, 2017

Dedicated

To

Mahib, Anan, Poly

and

The Memory of late Nabuar Rahman

and

My beloved Mother Mst. Moriom Begum

DECLARATION

I hereby declare that the research work submitted as the thesis entitled **"Modification of Cellulosic Fibres with Synthesized Functional Chitosan Derivatives for Ecofriendly Textile Products"** under the supervision of Professor **Dr. Md. Ibrahim H. Mondal**, in the Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Rajshahi-6205, Bangladesh for the Degree of Doctor of Philosophy is the result of my own investigation and has not ever been submitted before in any form for any other degree at any place. I further declare that the whole work of the submitted thesis paper for the degree of Doctor of Philosophy to the University of Rajshahi is based on my original investigation except references used in the text of the thesis.

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CERTIFICATE

This is to certify that the Ph. D. thesis entitled **"Modification of Cellulosic Fibres with Synthesized Functional Chitosan Derivatives for Ecofriendly Textile Products"** submitted by **Md. Mofakkharul Islam,** Roll No. 11904, Registration No. 2555, Session: 2011-2012, Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Rajshahi, Bangladesh has been completed under my supervision. This is an authentic and bonafide record of the research carried out by the candidate.

To the best of my knowledge, this thesis has not been submitted for the award of any degree or award elsewhere.

SUPERVISOR

Professor Dr. Md. Ibrahim H. Mondal
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Md. Mofakkharul Islam
June, 2017

ABSTRACT

Cellulosic fibres, especially jute and cotton, are the most abundant agricultural renewable raw materials. They have the qualities of stiffness, low elasticity, susceptibility toward sunlight and microbial attacks etc. which are hindrances on use of those fibres. Chitinous wastes from different sources and fish processing industries always pollute the environment in different ways. A huge amount of prawn shell wastes is deposited as sea food waste in different areas of fish processing industries which have virtually no demand for its use. These indigenous, cheap and available chitinous wastes can easily be used to produce valuable chitosan (Ch) and its functional derivatives, especially N-octyl chitosan (NOCh), carboxymethyl chitosan (CMCh), carboxymethyl chitosan-grafted-acrylic acid (CMCh-g-AA), N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (NMA-HTAChC), which are commercially important and will ultimately reduce pollution problems. The purpose of this research was to develop soluble chitosan and water soluble modifiers, based on that chitosan, which have excellent textile modification properties. These new products can substitute for toxic textile chemical modifiers. In addition, cellulosic fibres like jute and cotton can enhance their effectiveness for intensified textile use through ecofriendly modification. In addition, the dyeability of unmodified and modified jute and cotton fibres, including their tensile strength, moisture absorbance, swelling capacity, chemical resistance, dye-ability and colour fastness properties were investigated.

Chitosan was prepared from chitin, which was obtained from prawn shell waste by a series of chemical processes involving demineralization, deproteinization, decolouration, and deacetylation. Chitosan (Ch) and its said derivatives were successfully prepared by deacetylation of chitin, reductive amination of chitosan, carboxymethylation of chitosan, graft copolymerization of CMCh, quarternization of chitosan and acrylamidomethylation of HTAChC, respectively, at ambient condition, which were also optimized. The optimized condition for deacetylation is 50% alkaline solution, solid to liquor ration 1:50 (w/v), at 80^0C for 4h, in presence of ethanol with

reflux system. Lower yield and substitution to higher yield and substituted products were obtained from single step to multistep reactions. Chitosan and its synthesized derivatives were characterized with their physicochemical properties, degree of deacetylation (DDA), solubility, viscosity, molecular weight, nitrogen content, degree of substitution (DS) and degree of quarternization (DQ) were investigated.

The obtained DDA of prepared chitosan was 85% and DS of prepared NOCh and CMCh in different steps of reaction ranges from 0.008 to 0.051 and 0.54 to 1.44 and DS was determined by titrimetric analysis. The moisture absorbency, ash content and molecular weight of prepared chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC were 9.79%, 8.17%, 13.76%, 6.83%, 18.43%, 17.71% and 1.34%, 0.75%, 14.87%, 8.39%, 0.84%, 0.79%, respectively and 1,39,958.73 Da for chitosan, 1,62,181 Da for NOCh, 2,06,179 Da for CMCh, 3,10,270 Da for CMCh-g-AA. The synthesized chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC are characterized by Fourier Transform Infrared Spectroscopy (FTIR) which showed prominent peaks at 1659 cm^{-1} for (-CO) at 1600 cm^{-1} for ($–NH_2$) groups of chitosan, at 1516 cm^{-1} for corresponding to C-H stretching into methyl groups of NOCh, at 1384 cm^{-1} for symmetrical $-COO^-$ group and near at 1741 cm^{-1} for −COOH group of CMCh and at 1319 cm^{-1} for poly (AA) of CMCh-g-AA, at 1480 cm^{-1} for C-H bending of trimethylammonium group of HTAChC and at 1670 cm^{-1} for C=O stretching and 1545 cm^{-1} for N–H bending of NMA-HTAChC which confirms the synthesized derivatives. The structure of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC were investigated by FTIR and ^1H NMR.

Jute and cotton fibres were modified with prepared chitosan and its functional derivatives. Optimized modification conditions for jute and cotton with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC where modifier concentration 20% on the basis of weight of fibre, 5% $K_2S_2O_8$, 5% $FeSO_4$ based on the weight of monomer, solid liquor ration of 1:50 temperature 55^0C and time for 60 min. Grafting of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC on cellulosic fibre surfaces were confirmed by graft yield percent for jute 6.79%, 6.12%,12.06%, 9.39%, 10.69% and 14.74% and for cotton 11.78%, 10.75%, 16.77%, 12.06%, 14.56% and 18.86% respectively. FTIR at 1600 cm^{-1} for the NH_2 group, at

1516 cm^{-1} for C-H stretching, at 1740 cm^{-1} for –COOH group, at 1319 cm^{-1} for poly (AA), at 1480 cm^{-1} for C=O stretching and 1545 cm^{-1} for N–H bending respectively due to incorporation of said modifier on cellulosic fibres. The surface of fibres was investigated by Scanning Electron Microscopy (SEM) and modified fibres surface was smoother than unmodified fibres. X-ray diffraction pattern showed moderate crystallinity and the order is as follows: chitosan modified > NOCh modified > CMCh modified > CMCh-g-AA modified > HTAChC modified > and NMA-HTAChC modified cellulosic jute and cotton. The thermal behavior of modified fibres was also investigated by TGA, DTA and DTG analysis. On the basis of initial decomposition temperature (T_i) thermal stability of those jute and cotton fibres follows the order, chitosan modified > CMCh modified > unmodified > NOCh modified > HTAChC modified > CMCh-g-AA modified, NMA- HTAChC modified and chitosan modified > unmodified > HTAChC modified > NOCh modified > NMA- HTAChC modified > CMCh modified > CMCh-g-AA modified respectively. It was observed that textile modifying properties of NMA-HTAChC is comperatively better than that of other functional chitosan derivatives due to higher fibre affinity of NMA-HTAChC. It was also observed that over all modification showed improved chemical resistance to acid and alkali, moisture absorbency, tensile strength, moderate thermal stability and reduced swelling resistance in different solvent, compared to unmodified jute and cotton fibres.

The modified fibres were dyed with reactive dyes (Reactive Orange 14 and Reactive Brown 10) and direct dyes (Direct Orange 31 and Direct Yellow 29). Dyeing of modified and unmodified jute and cotton fibres revealed that dye exhaustions were increased up to 10% due to modification through sorption of prepared chitosan and its functional derivatives causes the increment of reactive sites of the fibres which also enhanced the sunlight, wash, alkali and acid fastness of the dyed fibres. Chitosan and its functional derivatives are safe, biocompatible and ecofriendly substances for human use so those are valuable as textile materials for textile and garment finishing.

CONTENTS

List of Tables

List of Figures

List of Scheme

List of Abbreviations

%	=	Percentage
°C	=	Degree Celsius
cm	=	Centimetre
cm^{-1}	=	Per centimetre
gm	=	Gram
min	=	Minute
h	=	Hour
ml	=	Mililitre
ml^{-1}	=	Per mililitre
AA	=	Acrylic acid
APS	=	Ammonium persulfate
CAN	=	Ceric ammonium nitrate
Ch	=	Chitosan
CMCh	=	Carboxymethyl chitosan
CMCh-g-AA	=	Carboxymethyl chitosan grafted acrylic acid
DDA	=	Degree of deacetylation
DHSE	=	Directorate of Higher and Secondary Education
DS	=	Degree of substitution
FTIR	=	Fourier Transform Infrared
HTAChC	=	N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride
KPS	=	Potassium persulfate
MoE	=	Ministry of Education
NMA	=	N-methylolacrylamide
NMA-HTAChC	=	N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride
NMR	=	Nuclear Magnetic Resonance
NOCh	=	N-octyl chitosan
SEM	=	Scanning Electron Microscopy
UGC	=	University Grant Commission
PP	=	Poster presentation
OP	=	Oral presentation
wof	=	weight of fibres

Chapter 1
GENERAL INTRODUCTION

1.1 Cellulose

Bangladesh is an agricultural and monsoon rain country and the main sources of natural cellulose is plant kingdom specially jute, cotton etc. Cellulose is the common material of plant cell walls which was first recognized by Anselm Payen in 1838. Cellulose $(C_6H_{10}O_5)_n$ is a long chain polymer of beta-glucose. It occurs naturally almost in pure form only in cotton fibres and also in jute fibres in combination with lignin and any hemicelluloses, it is found in all plant material- wood, leaves, stalks etc. Jute and cotton are natural, biodegradable, low-cost, multicellular, cellulosic fibres, produced in large quantities every year in South and Southeast Asia, especially in Bangladesh and neighboring India. Jute plants contain three main categories of chemical compounds: cellulose (58~63%), hemicellulose (20~24%) and lignin (12~15%), and some other small quantities fats, pectin, aqueous extract, etc. [Chattopadhyay, 1998; Tanmoy et al., 2014]. Cotton fibres consist of (80-90%) cellulose, (6-8%) water, (0.5-1%) waxes and fats, (0-1.5%) proteins, (4-6%) hemicelluloses and pectins, and (1-1.8%) ash [Lewin, 1998; Hu, 1996].

Cellulose monomers (β-glucose) are linked together through β-(1→ 4) glycoside bonds. Cellulose is a straight chain polymer but no coiling occurs. In micro-fibrils, the multiple hydroxyl groups from hydrogen bond with each other, holding the chains firmly together and contributing to their high tensile strength. This strength is important in cell walls, where they are meshed in to a carbohydrate matrix, which helps to keep plants rigid.

Cellulose contains 44.4 percent of carbon, 6.2 percent of hydrogen and 49.4 percent of oxygen [Moore, 1978]. It is the principal constituent of all plant life. The empirical formula of cellulose $(C_6H_{10}O_5)_n$ corresponds to a polyanhydride of glucose. The two terminal glucose residues of a cellulose molecule contain two different end groups; one contains a reducing hemiacetal group in the position C_1 and is therefore, known as the reducing end group, whereas the other contains an extra secondary hydroxyl group in the position C_4 and is known as the non-reducing end group. The structure of cellulose

is written in **Fig. 1.1.** There are two secondary and one primary alcoholic hydroxyl group in each basic anhydro-D-glucose unit $(C_6H_{10}O_5)_n$ which are arranged in positions 2, 3 and 6 respectively, on the basic unit. The reactivity of the hydroxyl group varies in different reactions. In many reactions (mainly esterification) the primary hydroxyl groups have greater reactivity. The two secondary hydroxyls, at the second and third carbon atoms, differ somewhat in their reactivity. The primary hydroxyls of cellulose elementary units are responsible for the sorbability and dyeability of cellulose materials. Cellulose is highly stereo specific. The high hydroxyl content of cellulose might suggest the high water solubility. This is because of stiffness of the chains and hydrogen bonding between hydroxyl groups of adjacent chains [Dudley et al., 1983].

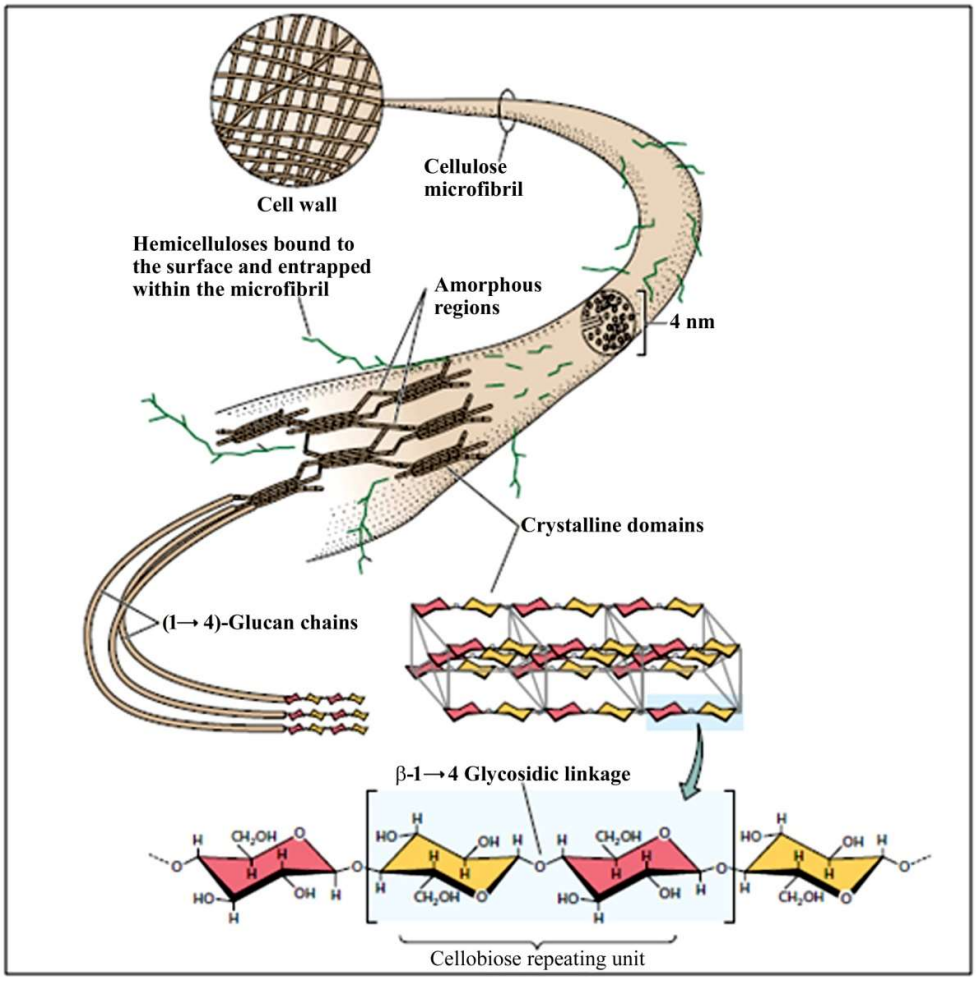


Figure 1.1: **Structural model of a cellulose microfibril as it occur in plant cell wall [Taiz and Zeiger, 2010].**

A given cellulose material, the portion that does not dissolve in a 17.5% solution of sodium hydroxide at 20°C is α-Cellulose and this is true cellulose; the portion that dissolves and then precipitates upon acidification is β-cellulose; and the proportion that dissolves but does not precipitate is called γ-cellulose. Jute and cotton are the most important sources of cellulose.

1.2 The Jute Fibre

Jute is the common name given to the fiber, which is a secondary phloem fibre obtained from the bark of the stems of plants of the two cultivated species *Corchorus capsularis* L. (White Jute) and *Corchorus olitorius* L. (Tossa Jute or Dark Jute) of the family Liliaceae [Rowell and Stout, 2007; Palit, 1999]. Jute is a long, shiny, soft and biodegradable fibre and it is second only to cotton in importance among vegetable fibres [Vaca-Garcia, 2008; Palit, 1999]. Jute is called "the golden fibre" for its silky golden colour, and high cash value [Yasmin et al., 2010]. Jute fibre is used for the manufacture of carpet backing, ropes, canvas, sackings, home textile, bags, handicrafts, blanket, nursery pots, insulation materials, soil saver, and jute based composites shown in **Fig. 1.2** [Singh, 2011]. The bulk of the world's supplies of jute is grown in Bangladesh, India, China, Thailand and Nepal [Anonymous, 1995]. Bangladesh is the largest net jute exporting country and covers 88% of total world export [IJSG, 2013].

Favorable conditions for jute cultivation are found in the deltas of the great rivers of the tropics and subtropics - the Ganges, the Irrawaddy, the Amazon, and the Yangtze, where irrigation, often by extensive flooding, and alluvial soils combine with long day lengths to provide opportunity for considerable vegetative growth before flowering [Rowell and Stout, 2007]. Generally, jute plant is grown by means of seed propagation which sown in earlier April to Mid - May. Its fibre develops in the phloem or bast, region of the stem of the plant. Usually the mature plants reach a height of 2.5-3.5 m and a basal diameter of about 25 mm and pass from vegetative to reproductive phase. The transition from the vegetative to reproductive phase is marked by forking of the apex into two or more branches. After maturation both the jute species starts flowering on late August to early September depending upon sowing period. Harvesting the plants at the correct time is most important for optimum fibre yield. The correct time is

judged when the plants are in the small-pod stage. Harvesting before flowering generally results in lower yields and weaker fibre and if the seeds are allowed to mature, the fibre becomes harsh and coarse and difficult to extract from the plant [Rowell and Stout, 2007; Palit, 1999].

Figure 1.2: **Chronological view of jute fibre processing (A) Harvesting of mature jute plant, (B) Jute plant bundle retting, (C) Collection of jute fibre after retting, (D). Drying of jute fibre in open air, (E) A bundle of dry jute fibre and (F) Jute fibre products.**

1.3 Fine Structure and Chemistry of Jute

Jute fibre is multi celled in structure **(Fig. 1.3).** The cell wall of fibre is made up of a number of layers; primary wall and the secondary wall (S), which contain three layers (the S1, S2 and S3 layer). Like other lignocellulosic fibres, these layers mainly contain cellulose, hemicellulose and lignin in varying amounts. The individual fibres are bonded together by a lignin-rich region known as the middle lamella. Cellulose attains highest concentration in the S2 layer (about 50%) and lignin is most concentrated in the middle lamella (about 90%), in principle it is free of cellulose. The S2 layer is far the thickest layer and dominates the properties of the fibres [Olesen, 1999].

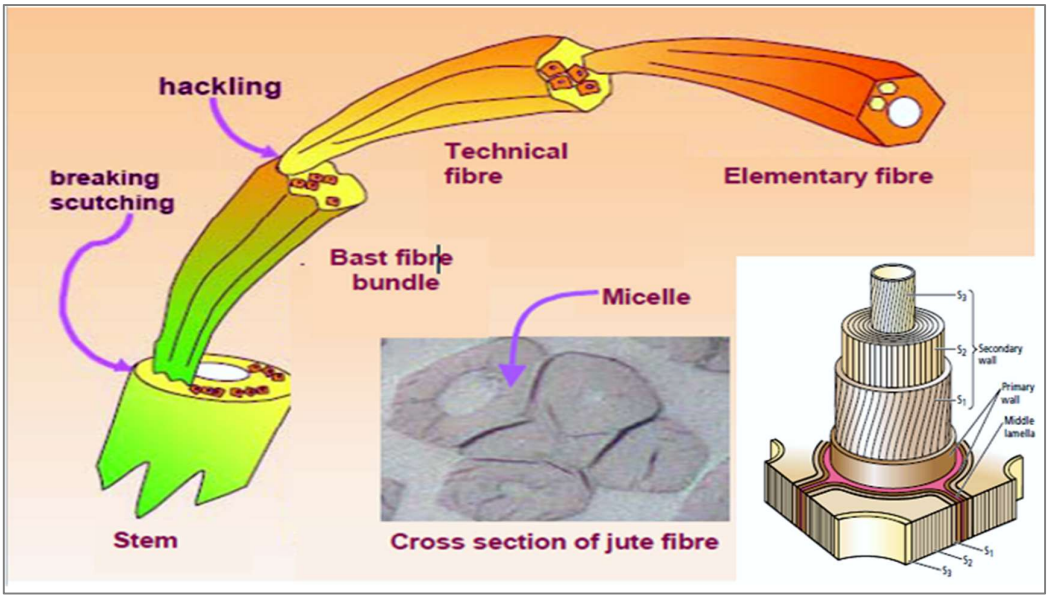


Figure 1.3: **Schematic of jute fibre structure [Snijder, 2004].**

The composition of the White and Tossa jute fibres is more or less same with minor different in constituents. The average composition of a fairly good quality of jute fibre is summarized in **Table 1.1**.

Table 1.1: Chemical composition of jute fibre [IJSG, 2015].

Constituents	Amounts (%)
α-cellulose	60.0 – 63.0
Hemicellulose	21.0 – 24.0
Lignin	12.0 – 13.0
Pectin	0.20 - 1.50
Proteins/ N_2 matter	0.20 - 1.50
Fats and Waxes	0.40 - 1.0
Total	100.00

1.4 The Cotton Plant

Cotton is a natural fibre and makes up just under half of all the fibre sold in the world. Cotton grows on a plant that is a member of the Hibiscus family and is botanically known as *Gossypium hirsutum* or *barbadense.* By nature, it is a perennial shrub which reaches a height of 3.5 m. Commercially it is grown as an annual and only reaches a height of 1.2 m. The most common type of cotton grown in Australia is *Gossypium*

hirsutum, more commonly known as American Upland. It is a leafy, green shrub that briefly has cream and pink flowers that become the 'fruit' or cotton bolls. The cotton plant has a deep taproot, which can go as deep 1.5 m. It is fairly drought-tolerant but requires a regular and adequate moisture supply to produce profitable yields [http://makinginnyc.wordpress.com/2013/01/30/4-what-is-cotton.]

Figure 1.4: The cotton plant

Figure 1.5: A ripe cotton boll

1.5 The Cotton Fibre

Cotton is grown so the fibre can be made into products we use each day, including jeans, T-shirts, sheets and towels etc. Fibre from the cotton plant is made into yarn and fabric, the seeds are crushed for oil and animal feed, and the leaves are turned into mulch. In its unprocessed form, the fibre is called lint. The lint grows inside the fruit of the cotton plant (the boll). Inside each boll are about 30 cotton seeds with many lint fibres attached to each seed. The lint is protected in the boll until it ripens and splits open.

1.6 Cultivation of the Cotton Plant

The cotton plant can be found as a perennial in treelike plants in tropical climates but is normally cultivated as a shrubby annual in temperate climates. Whereas it grows up to 6 metres (20 feet) high in the tropics, it characteristically ranges from 1 to 2 metres (3 to 6.5 feet) in height under cultivation. Within 80–100 days after planting, the plant develops white blossoms, which change to a reddish colour. The blossoms fall off after a few days and are replaced by small green triangular pods, called bolls that mature after a period of 55–80 days. During this period the seeds and their attached hairs develop within the boll, which increases considerably in size. The seed hair, or cotton fibre, reaching a maximum length of about 6 cm (2.5 inches) in long-fibre varieties, is

known as lint. Linters, fibres considerably shorter than the seed hair and more closely connected to the seed, come from a second growth beginning about 10 days after the first seed hairs begin to develop. When ripe, the boll bursts into a white, fluffy ball containing three to five cells, each having 7 to 10 seeds embedded in a mass of seed fibres. Two-thirds of the weight of the seed cotton (i.e., the seed with the adhering seed hair) consists of the seeds. Although cotton can be grown between latitudes 30° N and 30° S, yield and fibre quality are considerably influenced by climatic conditions, and best qualities are obtained with high moisture levels resulting from rainfall or irrigation during the growing season and a dry, warm season during the picking period.

To avoid damage to the cotton by wind or rain, it is picked as soon as the bolls open, but since the bolls do not all reach maturity simultaneously; an optimum time is chosen for harvesting by mechanical means. Handpicking, carried out over a period of several days, allows selection of the mature and opened bolls, so that a higher yield is possible. Handpicking also produces considerably cleaner cotton; mechanical harvesters pick the bolls by suction, accumulating loose material, dust, and dirt, and cannot distinguish between good and dicoloured cotton. A chemical defoliant is usually applied before mechanical picking to cause the plants to shed their leaves, thus encouraging more uniform ripening of the bolls.

Table 1.2: Raw cotton components [http://www.engr.utk.edu/mse/Textiles/Cotton20 fibers.htm]

Constituents	Amounts (percentage on dry basis)
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%

1.7 Processing of Cellulosic Fibres

During scouring (treatment of the fibre with caustic soda), natural waxes and fats in the fibre are saponified and pectins and other non-cellulose materials are released, so that the impurities can be removed by just rinsing away. After scouring, a bleaching solution

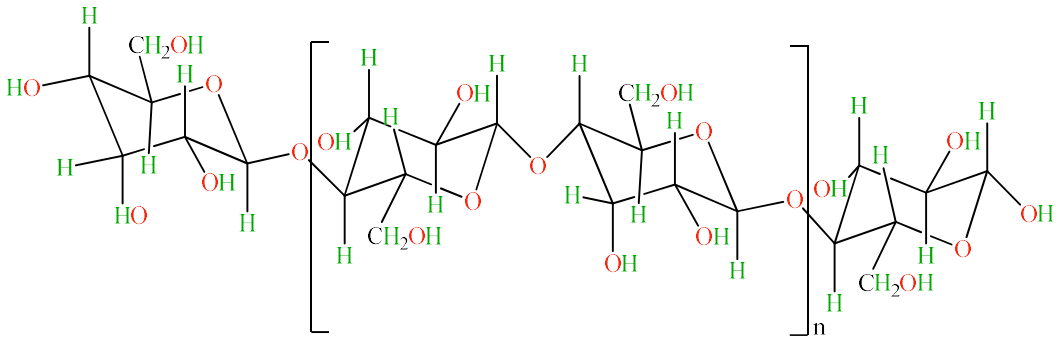
(consisting of a stabilized oxidizing agent) interacts with the fibre and the natural colour is removed. Bleaching takes place at elevated temperature for a fixed period of time [Jawaid et al., 2011]. Mercerization is another process of improving absorption properties of cotton. Cotton fibre is immersed into 18- 25% solution of sodium hydroxide often under tension [Noureddine et al., 2007]. The fibre obtains better luster and sorption during mercerization. After scouring and bleaching, the fibre is 99% cellulose.

1.8 Structural Features of Cellulose

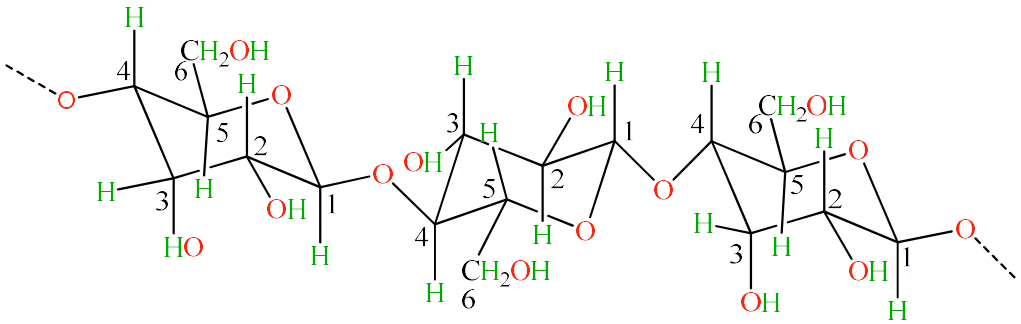
Cellulose is a natural polymer containing thousands of β-D-glucose unit by glucosidic linkages (C-O-C) at the C_1 and C_4 positions **(Sch. l.1)**. Each unit is rotated through 180° with respect to its neighbors, so that the structure repeats itself every two units.

The pair units are called cellubiose, and since cellulose is made up of repeating cellobiose units, cellulose is technically a polymer of cellobiose rather than α-D-glucose. The polymer structure stabilizes the ring configuration so that correct representation of cellulose is that in which glucose residues are rings. Cellulose contains approximately 10^4 units in the polymer chain and is about 5 μm long. The two terminal glucose residues differ from all the other glucose residues in the cellulose chain (they alone have four hydroxyl groups). The fact that the (1-4)-bond demands a rotation of 180° of each subsequent glucose unit to fit the β-configuration of the connecting hemiacetal linkage, gives the cellulose molecule a rod-link chain structure **(Sch. l.2)**. The β -glucosidic linkage in cellulose and the resulting intermolecular hydrogen bonds render the cellulose molecule straight and stiff. On the other hand, in starch the glucose units can be arranged in a helix-like chain molecule **(Sch. l.3)**.

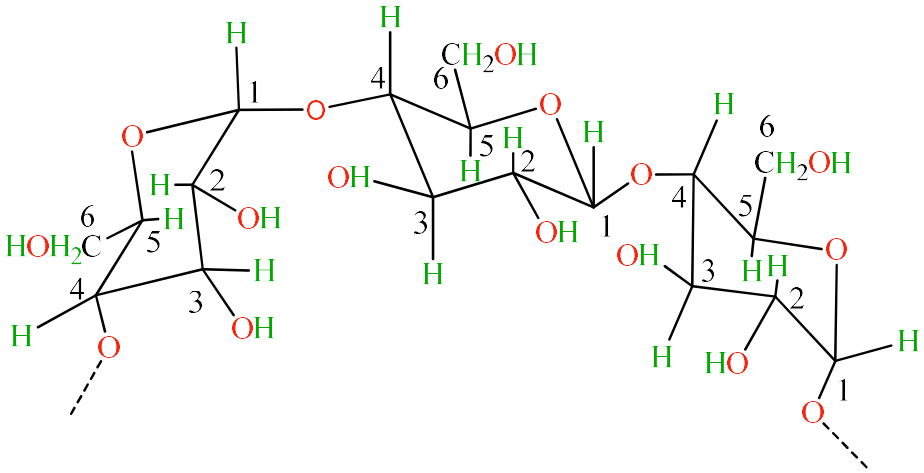
Whenever the distance between the various oxygen and hydrogen atoms in the cellulose molecule reached 0.3 nm or less, they interact with each other to form intramolecular and intermolecular hydrogen bonds. Infrared spectroscopy has verified the existence of these hydrogen bonds [George et al., 1998; Benedetto et al., 1989].



Scheme 1.1: **Cellulose molecule**



Scheme 1.2: Rod like chain structure of cellulose



Scheme 1.3: Helix like chain structure of starch

1.9 Chemistry of Cellulose

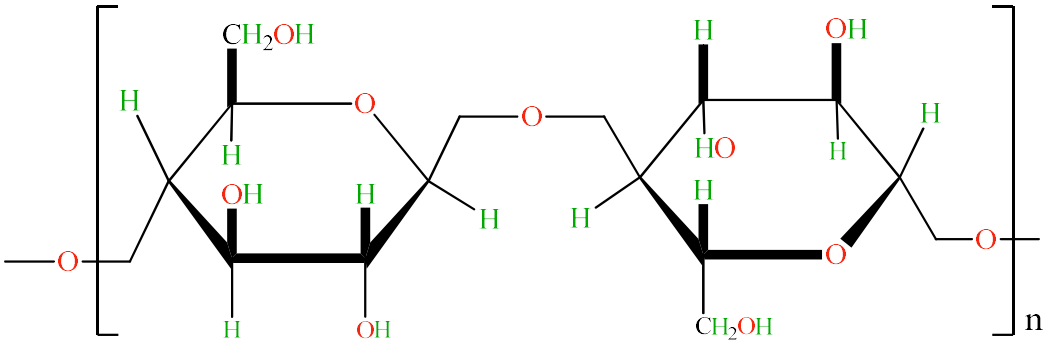
Although it took many decades after the identification of cellulose by Payen, cellulose has been shown to be a long chain polymer with repeating units of D-glucose, a simple sugar. In the cellulose chain, the glucose units are in 6-membered rings, called pyranoses. They are joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring. Since a molecule of water is lost when

an alcohol and a hemiacetal react to form an acetal, the glucose units in the cellulose polymer are referred to as anhydroglucose units.

The spatial arrangement, or stereochemistry, of these acetal linkages is very important. The pyranose rings of the cellulose molecule have all of the groups larger than hydrogen sticking out from the periphery of the rings (equitorial positions). The stereochemistry at carbons 2, 3, 4 and 5 of the glucose molecule are fixed; but when glucose forms a pyranose ring, the hydroxyl at C-4 can approach the carbonyl at C-1 from either side, resulting in two different stereo chemistries at C-1. When the hydroxyl group at C-1 is on the same side of the ring as the C-6 carbon, it is said to be in the configuration (not to be confused with cellulose, which is not related). Because of the equatorial positions of the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule. This positioning makes them readily available for hydrogen bonding. These hydrogen bonds cause the chains to group together in highly ordered (crystal-like) structures. Since the chains are usually longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between (the "fringed-micelle" model). The inter-chain hydrogen bonds in the crystalline regions are strong, giving the resultant fibres good strength and insolubility in most solvents. They also prevent cellulose from melting (*i.e.*, non-thermoplastic). In the less ordered regions, the chains are further apart and more available for hydrogen bonding to other molecules, such as water. Most cellulose structures can absorb large quantities of water (*i.e.*, it is very hygroscopic). Thus, cellulose swells, but does not dissolve, in water.

The chain is built up through oxygen links and each monomer unit, called a glucoside residue, is seal to have three OH or alcohol groups **(Sch. l.4)**. These free OH groups cause a great deal of attraction between chains through the exertion of intermolecular forces known as hydrogen bonding and polar. When hydrolysed with fuming hydrochloric acid, cellulose gives D-glucose in 95-96% yield [Irvine and Hirst, 1922] therefore the structure of cellulose is based on the D- glucose units. Methylation, acetylation, nitration of cellulose produced a trisubstituted product as a maxnum substitution product [Hers and Weltzien, 1925; Heuser and Hemer, 1925; Frendenberg and Braun, 1928; Haworth et al., 1931] and it therefore follows this fact that each

glucose unit presents three hydroxyl groups in an uncombined state when fully methylated cellulose is hydrolysed, the main product is 2, 3, 6- tri-0-methyl-D-glucose in 90%. Thus the three free hydroxyl groups in each glucose unit must be in the 2, 3 and 6 positions and 4 and 5 are therefore occupied. When subjected to acetolysis; i.e. simultaneous acetylation and hydrolysis, cellulose forms cellabiose octaacetate. Thus cellobios unit is present in cellulose.



Scheme 1.4: Repeating unit of cellulose (β-cellobiose residue)

1.10 Reactivity of Cellulose

Cellulose reacts as a trihydric alcohol with one primary and two secondary hydroxyl groups per glucose unit. The relative reactivity of the hydroxyl groups of both low molecular mass carbohydrates and cellulose has been studied [Ali et al., 1999]. In the former, the 2- and 6-hydroxyl groups are usually the most reactive. With cellulose, certain data indicate the preferential reactivity of the 2-hydroxyl and others of the 6-hydroxyl group. The manifolds reactions of cellulose may be conveniently divided into two main kinds: those involving the hydroxyl groups and those comprising a degradation of the chain molecules. The former includes the following reactions [Hebeish and Guthrie, 1981]:

(1) Esterification: nitration, acetylation and xanthation

(2) Etherification: alkylation and benzylation

(3) Replacement of –OH by $–NH_2$ and halogen

(4) Replacement of -H in –OH by Na

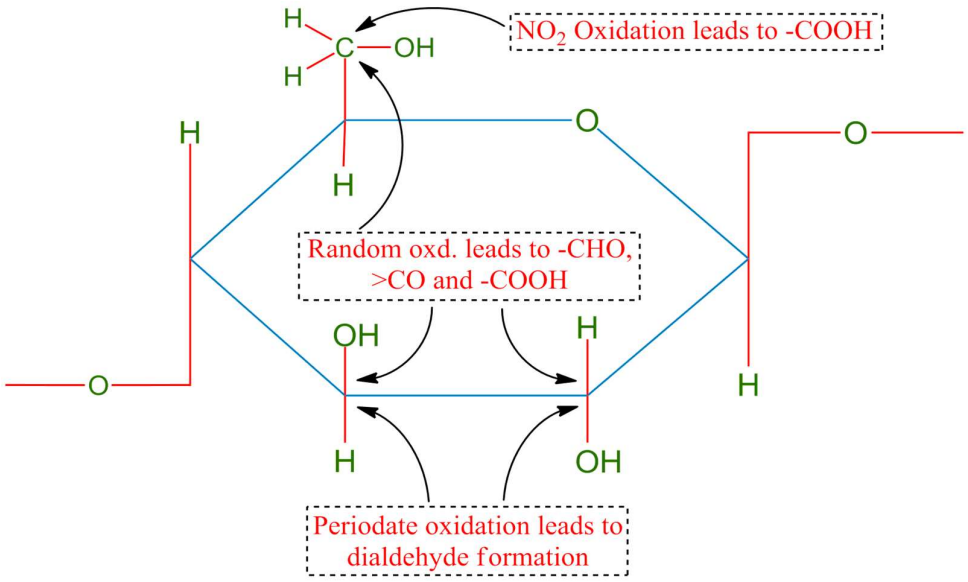
(5) Oxidation of $-CH_2OH$ to –COOH

(6) Oxidation of secondary-OH groups to aldehyde and carboxyl group

(7) Formation of addition compounds with acids, bases, and salts.

These reactions taking place without breakdown of the chain may have only a local effect, e.g., causing change in the terminal groups or in individual members of the chain, or they may affect all, or the majority of the members of the chain simultaneously. In the former case it is exceedingly difficult to detect the changes analytically in high molecular products, for which reagents of the utmost sensitivity are required. Sometimes, however, these reactions are manifested indirectly. Changes in the cellulose molecule resulting from oxidation in an acid medium affect only a few members of the chain and are scarcely to be detected by direct means; yet, later on they become clearly noticeable in that the chain splits up at the affected parts upon subsequent contact with alkaline liquids. There are many chemical reactions- the esterification and etherification of the hydroxyl groups in particular- which are liable to take place over the entire chain more or less uniformly, with often little difference in reactivity of the –OH groups in position 2, 3 and 6 though occasionally probable distinctions have been made.

When the cellulose is oxidized, the chain usually breaks down, probably as the result of opening and cleavage of the monomeric rings. Side by side with this, other reactions not interfering with chain length may occur, such as oxidation of the primary hydroxyl groups in the C-6 position to aldehyde or carboxyl groups, oxidation of the secondary hydroxyl groups at C-2 and C-3 to ketone groups, oxidative opening of rings to form two aldehyde or carboxyl groups, etc. According to the conditions of oxidation, the resulting products have either a marked acidic or equally pronounced reducing character. While the former exhibit intensified sorption towards basic dyes, the latter show an increased copper number. Mixed types also occur. The various possible types of oxidized groups formed in the cellulose molecule are shown in **Sch. l.5**.



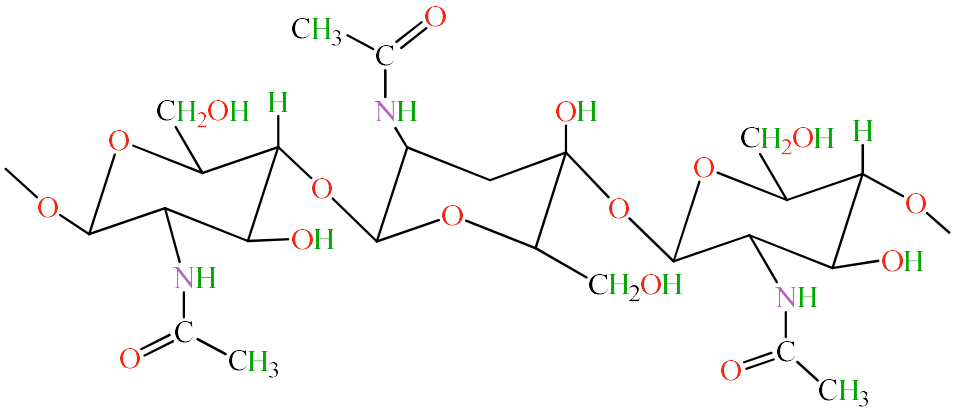
Scheme 1.5: Possible type of oxidized groups in cellulose

1.11 Chitin and Chitosan

Chitin is considered as the second most abundant polysaccharide on the planet with a production of approximately 10^{10}-10^{12} Tons [Robert, 1992]. Chitin is a homo polymer of 2-acetamido-2 deoxy-D-glucose (N-acetylglucosamine) residue linked by β-(1-4) bond [Wang et al., 2006] This structure is also known as N- acetyl glucosamine [Pradip et al., 2004] as shown in **Sch. l.6**. This structure is compact and disallows chitin to be soluble in most solvent. Therefore, it brings the demand for chitin to be transformed into chitosan [Peter, 1995].

In referred to the chemical structure, chitin is often considered as a derivative of a cellulose where both having polysaccharide as the functional group but it has acetamide groups (-$NHCOCH_3$) at the C-2 position. Physically, chitin is a white, hard, inelastic, nitrogenous polysaccharide [Pradip et al., 2004].

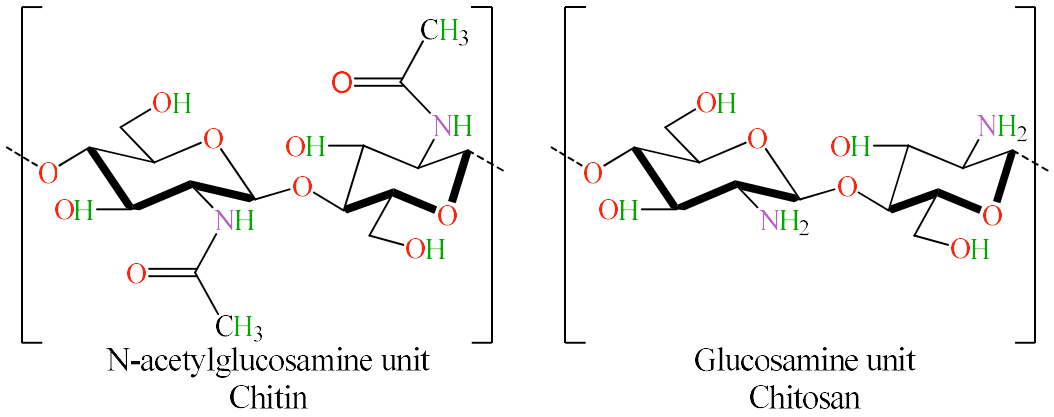
Naturally, there are three types of chitin that is different in structures, which are α-chitin, β-chitin and γ-chitin. α- chitin being the most abundant has a tightly compacted orthorhombic cell formed by alternated sheets of anti-parallel chains [Minke and Blackwell, 1978]. β- chitin having a monoclinic unit cell with polysaccharide chains attaching in a parallel manner [Gardner and Blackwell, 1975]. γ- chitin is said to be the combination of α and β structure rather than a third polymorph [Robert, 1992].



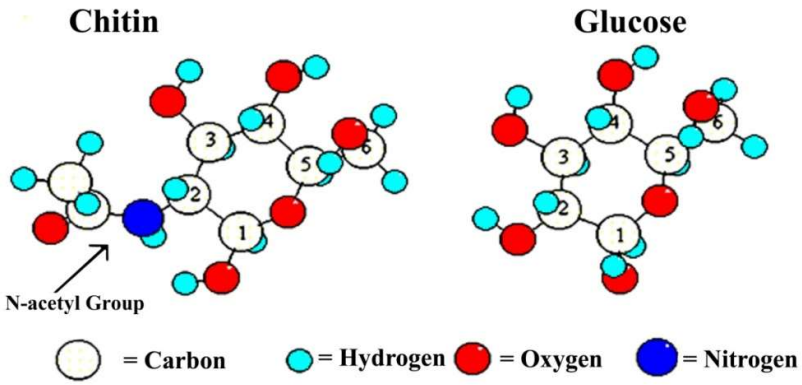
Scheme 1.6: Structure of chitin

Chitosan is one of the derivatives of chitin. Differed from chitin, chitosan are soluble in most solvent especially aqueous acidic which enable it to behave as a cationic polyelectrolyte. In recent years, chitosan has turned to be more preferable than chitin as it is more tractable in solution process. Chitosan contains properties as common biopolymers such biocompatibility, biodegradability, non-toxicity while it is unique because of some properties such as film forming ability, chelation and absorption properties, and antimicrobial activity [Kumar, 2000]. In addition, its great formability enables it to be converted into fibres, films, coating, beads, powders and solution which allow it to diverse its usefulness [Kumar, 2000; Al Sagheer et al., 2009].

Generally, chitosan is a cationic polysaccharide in a result of deacetylation of chitin with a linear chain structure consisting β-(1-4)-linked 2-acetamino-2-deoxy-β-D-glucopyranose with 2-amino-2-deoxy-β-D-glucopyranose [Marthur and Narang, 1990] consequently a homopolymer of N-acetylglucosamine and glucosamine that shown in **Sch. l.7**.



Scheme 1.7: Structure of chitin and chitosan



Scheme 1.8: The structural formula of chitin and glucose

Chitin and chitosan are valuable versatile natural materials derived from shells of prawns and crabs. The word "Chitin "comes from the Greek etymology meaning "A Coat of Mail". The product was first used by Odier in 1823.

The human use of chitosan can be traced back to 1811 when chitin, the source from which it is derived, was first discovered by Braconnot, a professor of natural history in France. According to historians, while Braconnot conducted research on mushrooms, he isolated what was later to be called chitin.

He further observed that this substance did not dissolve in aqueous acidic solutions, e.g. sulfuric acid. Later in 1823, Odier discovered that this compound is also one of the major constituent of the exoskeleton of insects and then he renamed as CHITIN (from Greek khitōn meaning tunic or envelope). Prof. C. Rouget in 1859, prepared a compound from chitin by treatment with concentrated caustic solution and observed that, unlike chitin, the resulting substance dissolved in acids. This compound was then named as CHITOSAN by Hoppe- Seiler in 1894 [Hirano, 2003]. In the mean time, in 1878, Ledderhose proposed chitin to be made of glucosamine and acetic acid. However, the existence of chitosan in nature was discovered in 1954 in the yeast Phycomyces blakesleeanus. During 1930's and 1940's, researchers in Korea, Japan, Europe and USA have tested chitin and chitosan in biomedical applications. In Japan, chitosan was first used for waste water treatment to absorb grease, oils, heavy metals and other potentially toxic substances. Researchers claim that a tooth paste made from crab's shell could cut dental infections and reduce the number of visits to dentists

[Hirano, 2003; Davis and Bartnicki-Garcia, 1984]. During 1970‘s the interest in these bio-macromolecules resulted in the first ever Chitin-Chitosan conference being held in the United States in 1977. Pioneering work of Muzzarelli during 1980‘s has greatly advanced our understanding of these materials [Hirano, 2003; Terbojevich and Muzzarelli, 2000]. Chitosan has been approved as a food additive in Korea and Japan since 1995 and 1983, respectively, and thus considerable attention has given to the use of chitosan as a natural preservative to improve the shelf-life of food [No et al., 2002]. In the United States, the food Studies on applications of chitosan and synthesized chitosan derivatives in textile processing and drug administration (FDA) has approved chitosan for fruit juice clarification, protein recovery from food process waste, edible coatings, and as an additive for animal feed [Davies et al., 1989; Hirano, 1997; Inmaculada et al., 2009].

1.12 Sources of Chitin and Chitosan

Chitin is found in a wide variety of species, from fungi to the lower animals. It is frequently present as a cell wall material in plants, and in the cuticle of animals. Arthropod shells (exoskeletons) are the most easily accessible sources of chitin. These shells contain 20-50% chitin on a dry weight basis. From practical viewpoint, shells of crustaceans such as crabs and shrimps are conveniently available as wastes from seafood processing industries and are used for the commercial production of chitin. Other potential sources for chitin production include krill, crayfish, insects, clams, oysters, jelly fish, algae and fungi. Some fungi contain chitosan; however, it is commercially produced by the deacetylation of chitin [Tsugita, 1990].

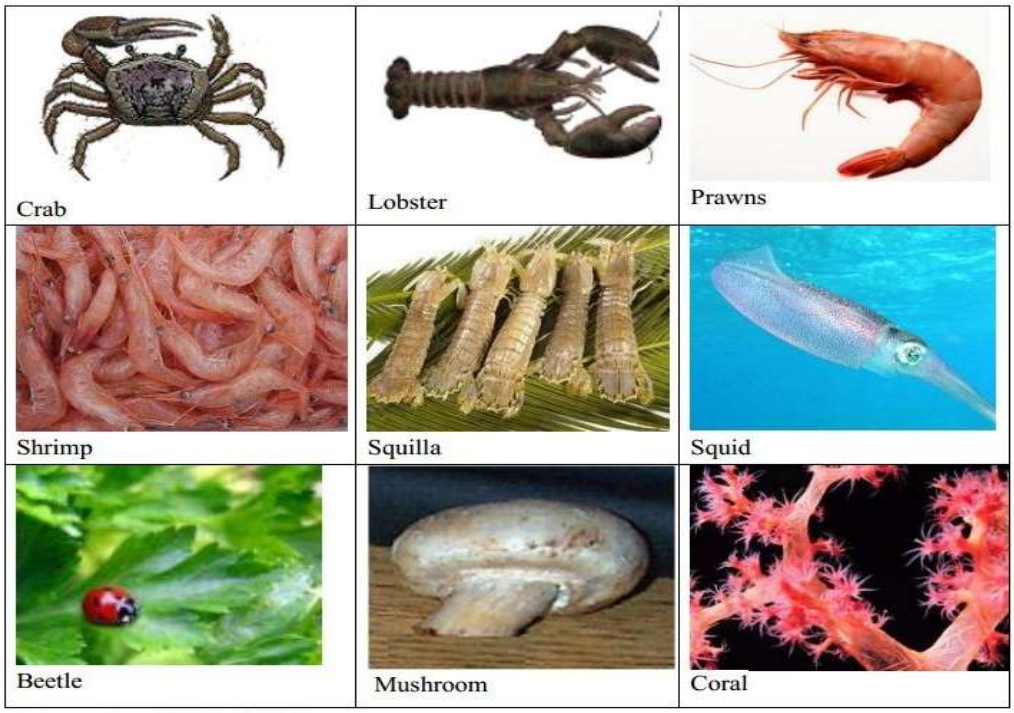


Figure 1.6: Sources of chitin

Prawn is considered as the main source of export profit of Bangladesh. Beside in expanding the national profit, industrialization, employment, opportunity and gaining foreign currency, prawn processing industry plays a vital role. In our country, white prawn (*Penaeus indicus*) is famous as "white dollar". These prawns bring away a lot of foreign currency that is dollar every year [Davis and Bartnicki-Garcia, 1984]. There is a contradiction about the nomenclature of prawn. In many countries it is known as prawn while it is known as shrimp by other countries of the world. It is known from the survey, made by fisheries department that the production of prawn was 758000 MT in Bangladesh in the year 1994 [Farkas, 1990].

1.13 Types of Prawn

There are several types of prawn grown in Bangladesh [Shahidi et al., 1999].

Table 1.3: Types of prawn

Names/Types	Scientific name	Seasons of cultivation
Fresh water giant prawn	*Macrobracium rosenbergii*	November-July
Monsoon river prawn	*Macrobracium*	May-October
Dimua river prawn	*Malcolmsonii*	April-July
Chuncho river prawn	*M. villosimanus*	May-August
Hairy river prawn	*M. lamarrei*	April-November
Short leg river prawn	*M. rude*	All seasons
Goda river prawn	*M. mirabile*	July-September
Kaira river prawn	*M. dolichoductylees*	All seasons
Roshna prawn	*M. dayanum*	April-November
Giant tiger prawn	*Paldemon styliferus*	March-November
Undian white shrimp	*P. monodon*	May-September
Kuruma prawn	*P. indicus*	November-March
Green tiger prawn	*P. japonicas*	November-March
Speckled shrimp	*P. orientalis*	May-September
White shrimp	*P. semisulculus*	July-August

1.14 Background of Study of Chitosan

Chitosan is a natural polysaccharide comprising copolymers of glucosamine and *N*-acetylglucosamine, and can be obtained by the partial deacetylation of chitin, from crustacean shells, the second most abundant natural polymer after cellulose. Chitin can be converted into chitosan by enzymatic means or alkali deacetylation, this being the most utilized method. During the course of deacetylation, part of polymer N-acetyl links is broken with the formation of D-glucosamine units, which contain a free amine group, increasing the polymer's solubility in aqueous means.

Chitosan has been widely used in vastly diverse fields, ranging from waste management to food processing, medicine and biotechnology. It becomes an interesting material in pharmaceutical applications due to its biodegradability and biocompatibility, and low toxicity. Chitosan has found wide applicability in conventional pharmaceutical devices as a potential formulation excipient. The use of chitosan in novel drug delivery is as mucoadhesive, peptide and gene delivery, as well as oral enhancer have been reported in

the literature. Chitosan exhibits myriad biological actions such as hypocholesterolemic, antimicrobial, and wound healing properties. Since chitosan is a new substance, it is important to carry out precise standardization for its pharmaceutical and biomedical applications like other auxiliary substances.

Chitosan can be characterized in terms of its quality, intrinsic properties (purity, molecular weight, viscosity, and degree of deacetylation) and physical forms. Furthermore, the quality and properties of chitosan product may vary widely because many factors in the manufacturing process can influence the characteristics of the final product. Chitosan is commercially available from a number of suppliers in various grades of purity, molecular weight, and degree of deacetylation. The variations in preparation methods of chitosan result in differences in its deacetylation degree, the distribution of acetyl groups, the viscosity and its molecular weight. These variations influence the solubility, antimicrobial activity among other properties, being that commercial chitosan usually has a deacetylation degree varying from 70% to 95%, and a molecular weight ranging from 50 to 2000 k Da.

The deacetylation degree is the proportion of glucosamine monomer residues in chitin. It has a striking effect on the solubility and solution properties of chitin. By convention, chitin and chitosan are distinguished by their solubility in dilute aqueous acids such as acetic acid. Chitin does not dissolve in dilute acetic acid. When chitin is deacetylated to a certain degree (~ 60% deactivation) where it becomes soluble in the acid, it is referred to as chitosan. A typical deacetylation process of chitin involves the reaction of chitin powder or flake in an aqueous 40-50% sodium hydroxide solution at 100-120°C for several hours to hydrolyze N-acetyl linkages. Repetition of the process can give deacetylation values up to 98% but the complete deacetylation can never be achieved by this heterogeneous deacetylation process without modification. Fully deacetylated (nearly 100%) chitosan can be prepared by the alkaline treatment of a gel form instead of the powder form of chitosan [Stephanie, 2008].

1.15 Definition and Composition of Chitin and Chitosan

Chitin, found in the shell of crustaceans, the cuticles of insects, and the cell walls of fungi, is the second abundant biopolymer in the nature [Knorr, 1984]. Structurally, chitin is a straight-chain polymer composed of β-1, 4-N-acetylglucosamine and

classified into α-, β- and γ-chitin [Cabib, 1981; Cabib et al., 1988]. Chitosan derived by partial N- deacetylation of chitin is also a straight-chain polymer of gluco-samine and N-acetylglucosamine [Muzzarelli and Rocchetti, 1985]. α- Chitin has a structure of antiparallel chains whereas β-chitin has intrasheet hydrogen-bonding by parallel chains [Minke and Blackwell, 1978; Jang et al., 2004]. However, γ-chitin has a parallel and antiparallel structure, which is a combination of α-chitin and β-chitin [Jang et al., 2004]. Because chitin possesses many beneficially biological properties such as biocompatibility, biodegradability, haemostatic activity, and wound healing property, much attention has been paid to its biomedical applications [Farkas, 1990] emulsifying, thickening and stabilizing agent in food industry [Shahidi et al., 1999]. Chitin is always made from crustaceans and therefore; crab shell is a source of chitin and chitosan. The objective of this study was to purify crab chitin from commercial crab chitin using acid and alkaline treatments followed by removal of all colour with potassium permanganate and to prepare chitosan there from by further N- deacetylation treatment with concentrated sodium hydroxide solution. The yields, degrees of N-deactivation (DD), molecular weights (Mw) and colour characteristics of various chitosan products were determined. The physicochemical properties of chitosan prepared were then studied using element analysis and X-ray diffraction patterns.

Chitosan is a heteropolymer consists of β-(1-4) 2-acetamido-2-deoxy-β-D-glucopyranose (N-acetyl glucosamine) and 2-amino-2-deoxy-β-D-glucopyranose (D-glucosamine) units, randomly or block distributed throughout the biopolymer. The chain distribution is dependent on the processing method used to derive the biopolymer. It is the N-deacetylated derivative of chitin, but the N-deacetylation is almost never complete. Chitin and chitosan are names that do not strictly refer to a fixed stoichiometry. Chemically, chitin is known as poly-*N*-acetyl glucosamine, and in accordance to this proposed name, the difference between chitin and chitosan is that the degree of deacetylation in chitin is very little, while deacetylation in chitosan occurred to an extent but still not enough to be called polyglucosamine.

The structural details of chitin and chitosan are shown in **Sch. l.9**. Chitosan has one primary amine and two free hydroxyl groups for each monomer with a unit formula of $C_6H_{11}O_4N$. This natural biopolymer is a glucosaminoglycan and is composed of two common sugars, glucosamine and N-acetylglucosamine, both of which are constituents of mammalian tissues.

Chitosan is the second abundant polysaccharide next to cellulose but it is the most abundant natural amino polysaccharide and is estimated to be produced annually almost as much as cellulose. Chitosan can be chemically considered as an analogue of cellulose, in which the hydroxyl at carbon-2 has been replaced by acetamido or amino groups. As a point of difference from other abundant polysaccharides, chitin and chitosan contain nitrogen in addition to carbon, hydrogen and oxygen. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%). As most of the present-day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives. However, these naturally abundant materials also exhibit a limitation in their reactivity and process ability. Chitosan is recommended as suitable functional material, because this natural polymer has excellent properties such as biocompatibility, biodegradability, non-toxicity and adsorption properties. Recently, much attention has been given to chitosan as a potential polysaccharide source. Chitosan can be degraded by soil microorganisms and water microorganisms. This makes chitosan environmental friendly. This was acknowledged by the US Environmental Protection Agency when it exempted chitosan from tolerance level testing [Yo, 2008]. Chitosan is a fibre-like substance derived from chitin. Chitin is the fibre in shellfish shell such as crab, lobster and prawn. It is also found in common foods we eat such as grain, yeast, bananas, and mushrooms. Chitin, a naturally abundant polymer, consists of 2-acetamido 2-deoxy-β-D-glucose through a β (1→4) linkage. In spite of the presence of nitrogen, it may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group. Like cellulose, it functions as a structural polysaccharide. Its natural production is almost inexhaustible: arthropods, by themselves, account for more than 106 species from the 1.2×10^6 of total species compiled from the animal kingdom, which produce chitin. The chitin is deproteinized, dematerialized and de-acetylated. It is a dietary fibre, meaning that it cannot be digested by the digestive enzymes of a person. Chitin is a white, hard, inelastic, nitrogenous polysaccharide and the major source of surface pollution in coastal areas.

Chitin is made up of a linear chain of acetyl glucosamine groups, while chitosan is obtained by removing enough acetyl groups (CH_3-CO) for the molecule to be soluble in most diluted acids. This process is called deactivation. The actual difference between chitin and chitosan is the acetyl content of the polymer. Chitosan having a free amino group is the most useful derivative of chitin [Stephanie, 2008].

1.16 Chemistry and Reactivity of Chitin and Chitosan

Chitin occurs naturally as one of three crystalline polymorphic forms, known as α, β and γ-chitin. The chains of α-chitin are antiparallel but the β chitin has a parallel stack structure. The γ-chitin form has not been fully classified but an arrangement of two parallel chains and one antiparallel chain has been suggested. Although both α and β-chitins possess C=O·····H−N intermolecular hydrogen bonds, the β-chitin does not have the intermolecular hydrogen bonds between $-CH_2OH$ groups, which are present in the α-chitin. This fact makes it easy for the β-chitin to swell in water to produce hydrates: unlike the α-chitin, which has a strong three-dimensional hydrogen bond network. The α-chitin is the most abundant and found in crustaceans, insects, and fungi, while the occurrence of β-chitin is less common and it is found in squid pens. Chitosan mainly occurs in two molecular conformations, namely (i) as extended two-fold helix and (ii) as extended eight-fold helix **Fig. 1.7**. The eight fold helix conformation transforms into two-fold helix under high humidity. No ordered conformation, however, is present in the aqueous acidic solution. The molecular flexibility increases with increase in deacetylation, increase in ionic strength in the solution and increase in temperature.

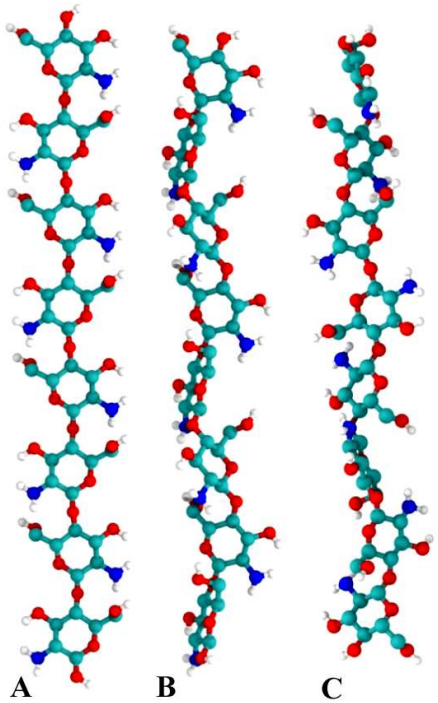
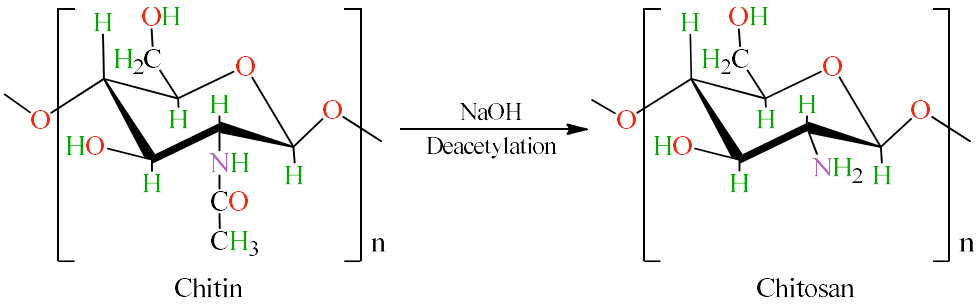


Figure 1.7: Chitosan secondary structures as determined by solid X-ray crystallography. A) two-fold, B) 5-fold and C) two-relaxed-fold (Richard et al., DOI: 10.5772/51803).

Chitosan [$(C_6H_{11}O_4N)_n$] is a polysaccharide composed of a linear (1-4) linked 2-amino-2-deoxy-β-d-glucan (i.e. β-d-glucosamine) in the chair $^4C_1$ conformation. It is derived by alkaline deacetylation of chitin i.e. (1-4) linked 2-acetaamido-2-deoxy-β-d-glucan (i.e. N-acetyl-β-d-glucosamine), **Sch. I.9**. When chitin is boiled in a highly-concentrated sodium hydroxide solution, deacetylation takes place: producing chitosan with free amino groups and sodium acetate as byproducts. The mechanism of deacetylation is similar to alkali hydrolysis acid amides [Bahl and Tuli, 1983]. In highly alkaline medium, the hydroxyl ions of sodium hydroxide (OH-) attack the electron deficient carbonyl carbon of acetamide group on chitin to form an intermediate anion. Chain scission follows and releases free amino groups on the main chain with liberation of acetic acid. The liberated acid then gets neutralized with sodium hydroxide. The overall reaction mechanism is illustrated in **Sch. I.9**.

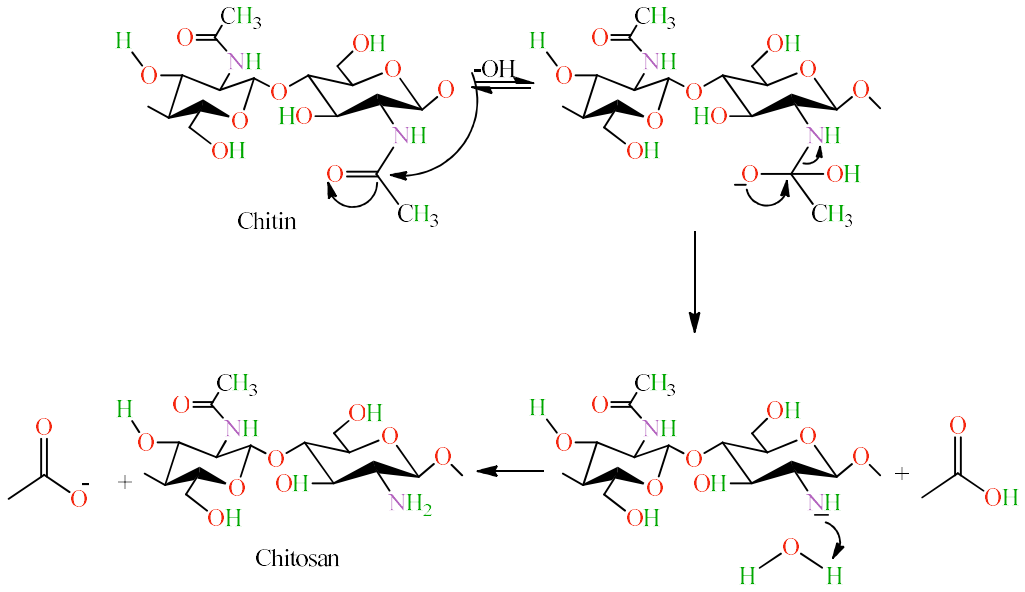


Scheme 1.9: Synthesis of chitosan by deacetylation of chitin

1.17 Chemical Reactivity

Chitosan has three reactive groups, that is, primary (C-6) and secondary (C-3) hydroxyl groups on each repeat unit, and the amino (C-2) group on each deacetylated unit. These reactive groups are readily subject to chemical modification to alter mechanical and physical properties, and solubilities of chitosan. The typical reactions involving the hydroxyl groups are etherification and esterification. Selective O-substitution can be achieved by protecting the amino group during the reaction. The presence of a nucleophilic amino group allows selective N-substitution, such as N-alkylation and N-acylation by reacting chitosan with alkyl halides and acid chlorides, respectively. The alternative method for the N-alkylation is reductive alkylation, where the amino group is converted to an imine with a variety of aldehydes or ketones, and subsequently reduced to an N-alkylated derivative. Chitosan can also be modified by either cross-linking or graft copolymerization. A number of chemically modified chitosan

derivatives are listed in the literature [Robert, 1992; Muzzarelli, 1985]. Between chitin and chitosan, a number of derivatives of partially N-acetylated chitosan exist, which is characterized by degree of deacetylation (DDA). DDA has a direct impact on the secondary structure of the polymeric chain and can also influence the solubility of the polymer in organic or aqueous solvents. As an evolved nomenclature, chitinous substances that do not dissolve in dilute organic acids, e.g. 1-2% acetic acid, are collectively called 'chitin'. On the other hand, chitinous substances that can dissolve in aqueous dilute acids are referred as chitosan: approximately 60% + deacetylated products fall in this category. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units. The structure of chitosan is very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is replaced by amino group in chitosan, **Sch. I.10** [Roberts, 1992; Ogawa, 1991; Peter et al., 2000; Mukesh, 2002; Vivek and Singh, 2005; Tahlawy, 1999].



Scheme 1.10: Reaction mechanism of deacetylation of chitin

1.18 Chitosan and Its Functional Derivatives

Chitosan displays interesting properties such as biocompatibility, biodegradability [Kumar et al., 2004; Sanford et al., 1989] and its degradation products are non-toxic, non-immunogenic and non-carcinogenic [Muzzarelli, 1997; Bersch et al., 1995]. Therefore, chitosan has prospective applications in many fields such as textiles,

biomedicine, waste water treatment, functional membranes and flocculation. However, chitosan is only soluble in few dilute acid solutions, which limits its applications.

Recently, there has been a growing interest in the chemical modification of chitosan in order to improve its solubility and widen its applications [Kurita et al., 1998; Sashiwa and Shigemasa, 1999; Heras et al., 2001]. Derivatization by introducing small functional groups to the chitosan structure, such as alkyl or carboxymethyl groups [Jayakumar et al., 2006; Lu et al., 2007] can drastically increase the solubility of chitosan at neutral and alkaline pH values without affecting its cationic character. Due to the limited solubility of chitosan, N-octyl chitosan derivative was prepared through Schiff reaction with aldehyde by reductive alkylation that was characterized by different physical and instrumental analysis. Keep in mind the solubility of chitosan in acitic acid solution at pH = 4: many researchers attempt to prepare water soluble derivatives of chitosan which are safe and friendly substances for human usage.

1.19 Chitosan Derivatives

The chitosan properties were altered by chemical modification by means of grafting onto chitosan chains to make macro molecular chains. This is done by substitution of hydrophilic group in place of amino or hydroxyl group of chitosan. The modification improves and enhances the physiochemical proprieties of chitosan. The degree of acetylating, reactivity, solubility and molecular weight were altered. The chitosan derivatives are the modified and altered form of chitosan with improved physiochemical proprieties. The hydrophilic group which took part in modification and alteration were hydroxyl propyl, hydroxyalkylamine, hydroxyethyl, and sulfate phosphate and carboxyalkyl group. The carboxyalkyl group included carboxybutyl, carboxyethyl and carboxymethyl [Mourya et al., 2010]. Among all Chitosan derivatives the carboxymethyl group placed highest in consumption and usage. It happened because of ease of synthesis, solubility, reactivity, biodegradability, biocompatibility and non-toxicity [Mourya et al., 2010].

1.19.1 N-Octyl chitosan (NOCh)

Reductive amination i.e. Bosch reduction of Schiff‘s base provides an attractive route for the synthesis of N-substituted chitosan compounds containing alkyl or aryl groups of varying chain lengths or molecular sizes. Primary amines when treated with alkyl or

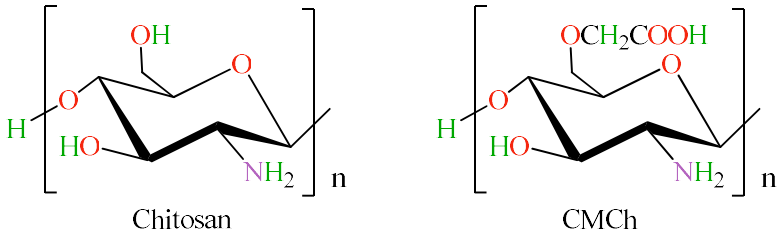
aryl aldehydes produce Schiff's base which on reduction with $NaBH_4$ or $NaBH_3CN$ results into N-alkyl or aryl substituent becoming secondary amine [Bahl and Tuli, 1983] as shown in **Sch. 2.7**. Since the reaction is carried out in acidic medium, a great degree of homogeneity is favored. These secondary amines then can further be quaternized with alkyl iodide. A series of chitosan quaternary ammonium salts containing N-alkyl and/or N-aryl substituents were prepared by different workers for various purposes are reported [Kim and Choi, 2002; Rabea et al., 2005; Rabea et al., 2006; Mobarak and Abdullah, 2010; Sajomsang et al., 2009; Bobu et al., 2011; Bayat et al., 2006; Wei et al., 2001].

1.19.2 Carboxymethyl chitosan (CMCh)

Carboxymethyl chitosan, an important water-soluble chitosan derivative, has many attractive chemical, physical and biological properties such as gel-forming capability, low toxicity, and good biocompatibility, all of which make it a promising biomaterial [Chen et al, 2006; Chen and Wang, 2001; Zhu and Fang, 2005]. Due to its unique properties, particularly its biocompatibility, carboxymethyl chitosan has been extensively used in the biomedical field as moisture-retention agent and bactericide, in wound dressings as artificial bone and skin, and in blood anticoagulants as an element in drug delivery systems [Hirano, 1996; Muzzarelli, 1988; Muzzarelli et al, 1982; Zhang et al, 2000]. Besides, carboxymethyl chitosan is an efficient metal chelater and exhibits high adsorption capacity for dyes [Gupta and Haile, 2007; Sun and Wang, 2006]. Since it has been shown to possess a variety of unique properties, the compound has attracted worldwide attention. Most of the related literatures concern their applicability in biomedical field.

The carboxymethyl chitosan was found O-Carboxymethyl chitosan, N-Carboxymethyl chitosan and N, O-Carboxymethyl chitosan. There are two methods followed up for the substitution. These are reductive alkylation method and direct alkylation method. In reductive alkylation method, by varying the conditions number of CMCh were formed differentiated by molecular weight distribution, molecular sizes and degree of deacetylation. The second method was the direct alkylation. In this method the chitosan reacted with monochloroacetic acid. The isopropanol in water were used as solvent. In this method the O-Carboxymethyl and N-O Carboxymethyl were formed by varying the

pH. At mild pH 8 to 8.5, the amino group active took part in reaction and formed N-Carboxymethyl. When sodium hydroxide concentration increase >20% and pH increases the hydroxyl group became active hence substitution of hydroxyl group done on C_6.



Scheme 1.11: Structure of chitosan and CMCh.

The degree of deacetylation puts no impact on degree of substitution however the sodium hydroxide concentration affects the chemistry of CMCh. The CMCh exists in dirty white to pure white powder form. The properties strictly influenced by experimental conditions of temperature and reactants concentrations. The presence of carboxy group in CMCh chain enables its solubility in neural, acidic and basic medium. It is highly soluble polymer. Another property of CMCh was its moisture adsorption and retention. This was very prominent characteristic which make its importance high in cosmetic industry and drug formation. The large hydrodynamic volume of CMCh is feasible in film formation and hydrogels making. The CMCh was antioxidant and antimicrobial agent specially used in wood healing drugs and cell cultures agricultural and food industry for preservation and storage of fruits and vegetables from fungus and bacterias. The carboxymethyl chitosan was most suitable organic polymer for metal adsorption and metal chelation. The flexible structural chemistry and hydrophilicity make feasible for metal complexation. The amino group and hydroxyl group were the active legends for metal chelation and dye binding [Farag and Mohamed, 2013].

1.19.3 Carboxymethyl chitosan-g-acrylic acid (CMCh-g-AA)

Carboxymethyl chitosan is a carboxymethylated polymer of chitosan which obtained after alkaline deacetylation of the chitin. It displays interesting properties such as biocompatibility and biodegradability [Ravi, 2000; Felt et al., 1998; Hirano et al., 1989] and its degradation products are non-toxic, non-immunogenic and non-carcinogenic [Muzzarelli, 1997; Bersch et al., 1995). Therefore, CMCh has prospective applications in many fields such as biomedicine, waste water treatment, functional membrane and flocculation. Recently there has been a growing interest in chemical modification of

CMCh to improve its applications [Sugimoto et al., 1998; Heras et al., 2001]. Among various methods, graft copolymerization is most attractive because it is a useful technique for modifying the chemical and physical properties of natural polymers. CMCh bears the free amino reactive groups that can be grafted. Grafting of a CMCh allows the formation of functional derivatives by covalent binding of a molecule, the graft, onto CMCh backbone. Recently researchers have also shown that after primary deviation followed by graft copolymerization; CMCh obtained much improved bioactivities such as antibacterial antioxidant properties [Xie et al., 2000; Xie et al., 2001]. Grafting of CMCh is a common way to improve its properties such as increasing chelating [Yang and Yuan, 2001] or complexation properties [Chen and Wang, 2001], the bacteriostatic effect [Jung et al., 1999] and enhancing absorption properties [Kotze et al., 1997; Thanou et al., 2001]. Although grafting of CMCh modifies its properties, it is possible to maintain some interesting characteristics such as mucoadhesevity [Hoffman et al., 1997], biocompatibility [Ono et al., 2000], and biodegradability [Singh and Ray, 1998]. Many investigations have been carried out on the graft copolymerization of CMCh in view of preparing polysaccharide-based advanced materials with unique bioactivities and thus widening their applications in biomedicine and environmental fields. The potential applications of grafted CMCh lie in various fields such as controlled drug delivery, biomedical and textile finishing.

Graft copolymerization of vinyl and acrylic monomers onto CMCh and other natural polymers can introduce desired properties and enlarge the field of potential application of them by choosing various types of side chains. In recent years, a number of initiator systems have been developed to initiate graft copolymerization. Redox systems, such as ceric ammonium nitrate (CAN), potassium persulfate (KPS) and ammonium persulfate (APS), usually produce free radical sites on polymers. The properties of grafted CMCh have been improved but only to a limited extent because of its regular structure and the strong intermolecular hydrogen bonds. Recent researchers showed that grafting onto pre-modified CMCh induced much improved bioactivities. Although, there are very limited reports about the graft copolymerization of pre-modified CMCh derivatives.

1.19.4 Water soluble fibre reactive derivative of chitosan

Chitosan, with the structural formula poly-β-(1-4)-D-glucosamine, is the deacetylated derivative of chitin, and it is the second most abundant polysaccharide found on the

earth, next to cellulose. As a natural renewable resource, it has a number of unique properties such as antimicrobial activity, nontoxicity, and biodegradability that attract scientific and industrial interest in many fields [Luca et al., 2012; Elsabee et al., 2012; Jayakumar et al., 2010]. Nowadays, chitosan has been widely used as a flocculant [Zhu et al., 2012], clarifier [Ghorbel-Bellaaj et al., 2012], thickener [Sanchez et al., 2011], fibre [Zhao et al., 2015], film [Miri et al., 2015], affinity chromatography column matrix, gasselective membrane, plant disease resistance-promotor, anti-cancer agent, wound healing promoting agent, and antimicrobial agent. However, these activities are limited to acidic conditions due to its poor solubility above pH~6.5. Because of its very stable crystalline structure with strong hydrogen bonds, researchers have focused on the preparation of chitosan derivatives soluble in water over a wide pH range; the solubility of chitosan can be improved by chemical modification.

Chitosan has reactive amino and hydroxyl groups, both of which can be used to chemically alter chitosan's properties under mild reaction conditions. Therefore, many water-soluble derivatives have been prepared by introducing hydrophilic groups such as carboxymethyl, dihydroxyethyl, sulfate, phosphate, hydroxyalkylamino, or by grafting a water soluble polymer on the macromolecular chain of chitosan [Facin, 2015, Garcia-Valdez et al., 2013, Yang et al., 2014]. Polymeric quaternary ammonium compounds have received the most attention over the years [Zhang et al., 2014].

Chitosan, which is derived from a deacetylation reaction of chitin, has attractive fibre modifying activity. However, chitosan applications as a textile modifier are only effective in acidic medium due to its low solubility in neutral and basic conditions. The positive charges carried by the protonated amine groups of chitosan (in acidic conditions) that are the driving force for its solubilization are also associated with its textile fibre modifying activity. Therefore, chemical modifications of chitosan are required to enhance its solubility and broaden the spectrum of its applications, including as textile modifier. Quarternization on the nitrogen atom of chitosan is the most used route to render water-soluble chitosan-derivatives, especially at neutral pH conditions. Recent reports in the literature demonstrate that such chitosan-derivatives present excellent fibre modification activity due to permanent positive charge on nitrogen atoms side-bonded to the polymer backbone. Recently, increasing attention has been paid to water-soluble quaternary

ammonium derivatives of chitosan and its applications. The chemical characteristics and modification properties of these derivatives can play significant role in textile areas mainly as a modifier for cellulosic and other textile fibre.

Chitosan can be dissolved under slightly acidic aqueous conditions but insoluble in neutral pH. Main features of the quaternary chitosan are the water solubility under neutral pH and cationic charge density over the whole pH range. Furthermore, the quaternary chitosan derivative presents high affinity for cellulose fibre surface and has H-bonding potential, which can improve the strength properties of treated cellulose fibre. Quaternary chitosan derivative was synthesis achieved by a process using Glycidyltrimethylammonium chloride (GTMAC), under neutral aqueous conditions. The corresponding epoxide of GTMAC, generated in the process, reacts with the primary amino groups of chitosan following a nucleophilic addition pathway. Thus the quaternary chitosan derivative obtained is.

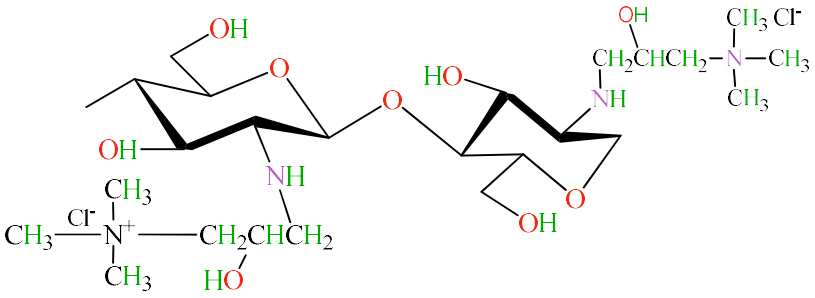
Quaternary ammonium derivatives of chitosan have received the most attention as textile finishing agent over the years. However, they have some deficiencies, such as less affinity to cellulosic as well as textile fibres. To overcome this limitation, an efficient method is the introduction of a fibre-reactive group on the HTAChC to improve laundering durability of chitosan [Yoo, 1997, Kim et al., 1998; Kim et al., 1999]. N-methylolacrylamide (NMA) was chosen as a reagent to introduce a fibre-reactive group onto the HTACC because it has often been used for crosslinking of cellulose [Gardon, 1961; Kamel et al., 1973; Hebeish and Hugazy, 1990; Hebeish and Rafai, 1991]. NMA has two reactive groups, which react under different conditions, a N-methylol group and a double bond conjugated with a carbonyl group. By reacting NMA with HTAChC under acidic conditions, N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (referred to here as NMA-HTAChC) is obtained with excellent textile finishing properties.

1.19.5 N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (HTAChC)

Chitosan, a deacetylated product of chitin, has many interesting properties, such as antimicrobial activity, biodegradability, and nontoxicity. Many attempts have been made to use chitosan in several industrial fields, such as medical, textile, food, cosmetic

industry etc. [Lee et al., 1998]. In particular, several methods were studied so as to apply this to fibre materials to improve textile properties, such as the binding of chitosan to cellulosic fibre with a crosslinker or blending chitosan with fibre-forming polymers [Hasegawa et al., 1994; Ratto et al., 1996]. But research on binding of chitosan with cellulosic fibre is limited by the difficulty of finding a common solvent for chitosan, which dissolves commonly in aqueous acid solution. On the other hand, some compounds containing quaternary ammonium groups are water soluble and impart improved textile properties of cellulosic fibre when applied to them [Seong and Ko, 1998; Washino, 1993].

Therefore, a chitosan derivative containing such a group can be water soluble and will exhibit higher textile fibre activity. HTAChC can be synthesized [Kim et al., 1998] from chitosan and GTMAC, which enhances water solubility and affinity towards cellulosic fibre of chitosan. Because many antistatic finishing reagents also contain quaternary ammonium groups [Stevens, 1983], it is expected that HTAChC can also be used as an antistatic agent for synthetic fibres. Thus, both improved textile and antistatic properties may be obtainable with HTAChC.

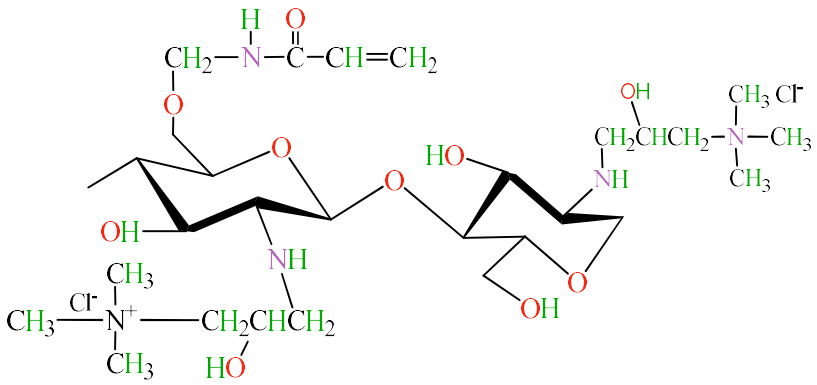


Scheme 1.12: Structure of HTAChC

HTAChC can be prepared by nucleophilic chain opening reaction between GTMAC and Chitosan. GTMAC was chosen as a quaternization reagent because of its ease of reaction with amino groups of chitosan and it is known that the reaction product HTAChC shows water-solubility as well as an excellent antimicrobial activity [Kim et al., 1998; Seong et al., 2000). The HTAChC can be prepared by reacting chitosan with GTMAC in a neutral aqueous condition, in which the hydroxyl groups of chitosan are not sufficiently nucleophilic to induce ring opening of GTMAC, whereas the amino group of chitosan is nucleophilic enough to do that.

1.19.6 N- methylolacrylamide N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (NMA- HTAChC)

The last step of synthesis is the introduction of a fibre-reactive group on the HTAChC to overcome the poor laundering durability of chitosan [Yoo, 1997; Kim et al., 1999]. NMA was chosen as a reagent to introduce a fibre-reactive group onto the HTAChC because it has often been used for crosslinking of cellulose [Gardon, 1961; Kamel et al., 1973; Hebeish and Higazy, 1990; Hebeish and Rafai, 1991].



Scheme 1.13: Structure of NMA-HTAChC

NMA has two reactive groups, which react under different conditions, a N-methylol group and a double bond conjugated with a carbonyl group. By reacting NMA with HTAChC under acidic conditions, NMA-HTAChC is obtained through acrylamidomethylation.

The proton of the acid catalyst is transferred to the hydroxyl group of NMA and H_2O is eliminated to give a carbonium ion, which is stabilized by resonance structures. This ion reacts with a nucleophilic group, i.e., the hydroxyl group (C-6) of the HTAChC, which is a primary alcohol. As an acid catalyst, ammonium chloride (NH_4Cl) [Hebeish and Rafai, 1991] was used, which is a latent acid and generates HCl at an elevated temperature.

The released acid can protonate secondary amine groups of HTAChC, which prevent the amine groups from acting as a nucleophile. Also, the amine group of the HTAChC is in a relatively bulky environment due to the quaternary ammonium salt groups. Therefore, the reaction between NMA and hydroxyl groups on C-6 position (primary alcohol) of HTAChC is predominant. The NMA-HTAChC has acrylamidomethyl groups as a fibre reactive group, which has a pendent double bond that can react with the hydroxyl groups of cellulose under alkaline condition.

1.20 Modification of Jute and Cotton Fibres

In the recent time, considering the global advancement and improvement of people's living standards with the need of environmental protection, the demand for natural, biodegradable, biocompatible and ecofriendly textile fibres, such as jute and cotton has been rising day-by-day. However, they have certain unfavorable properties such as, high stiffness, very low elasticity, susceptibility toward sunlight and microbial attacks etc, which cause hindrances on their use.

For this reason, to minimize the undesirable aspects and to enhance the effectiveness for intensified textile use, modification of jute and cotton fibres has been attempted during the recent years. This modification has been done using chemical [Mondal et al., 2007; Mondal et al., 2004; Mondal, 2003; Mondal and Haque, 2007; Mondal et al., 2006], photochemical [Ghosh and Paul, 1983] and radiation-induced [Khan et al., 2010; Zaman et al., 2012; Khan et al., 2015] methods. Many workers has been modified chemically jute and cotton fibres among them, with nitrile [Mondal et al., 2007; Mondal et al., 2004; Mondal, 2003], acrylate [Mondal and Haque, 2007; Mondal et al., 2006; Mondal, 2013], acrylic and amide monomer [Mondal et al., 2002] and the modified fibres has shown improved thermal, tensile and colour fastness properties, but there is no sincerity about ecofriendness. We are searching for health and environment friendly modification of cellulosic fibres.

1.21 Enhancement of Dye Ability of Jute and Cotton Fibres

Jute and cotton is the most widely used textile material because of its properties such as relatively low cost, fine cross section, high strength, durability, thermal stability, good mechanical properties, moisture absorbency and comfort to wear. Jute can be modified by a number of techniques to improve their performance characteristics such as dyefixation, soil repellency, crease resistance and flame retardant [Tzanko, 2006]. Chemical modification of jute and cotton will improve their dye ability and at the same time it will pollute the environment to greater level. Modification can also be possible with the help of biopolymers like chitosan is an environmentally benign route. Chitosan [(1-4)-2-amino-2-deoxy-D-glucose] is a water insoluble amino polysaccharide obtained from chitin by deacetylation process. It is a copolymer of N-acetyl glucosamine and glucosamine units and generally contains more than 90% glucosamine units and found

in the shell of crabs and shrimps [Kittinaovarut, 2003]. It is an inexpensive biodegradable, non-toxic compound and useful in many areas of applications such as waste water treatment, food and textile industry and recently in drug industry as a hydrating agent in cosmetics. However, it was reported that chitosan as an auxiliary in dyeing and printing of textile materials and leathers [Chung, 1998].

1.22 Importance of the Research Work

The purpose was to alter the petroleum based chemical modifier with biodegradable and biocompatible natural modifier for improve the resultant physical properties of cellulosic textile products. Scientists are now trying to create suitable coupling of the different chemical features on the jute and cotton reactive sites. This coupling will obtain smooth surface morphology with expected improvements in chemical, thermal and physical properties.

Many researchers have also prepared chitosan from prawns [Gopalakannan et al., 2000] crustaceans and crabs. They have synthesized N-alkyl chitosan [Aranaz et al., 2010; Bobu et al., 2011] from trade chitosan product for different types of use. No published work has yet tested the strategy used in this project. The strategy explored in this research project was the synthesis of chitosan and its water soluble functional derivative from prawn shell wastes. These were used as modifiers to develop high quality textile fibres. The modification, for the jute and cotton fibres by chitosan and its functional derivatives similarly improves the surface smoothness, chemical, thermal and physical properties. Then the potential dyeing performance of these modifiers on jute and cotton in warm exhaust dyeing was investigated. The impact of this strategy on proper waste management of crustacean shells was also considered as well as to save our environment from prawn shell waste pollution and to avoid petroleum based modifier by ecofriendly chitosan derivatives, for this waste material would be a value added products in textile sector.

1.23 Environmental Impact of the Present Research Work

Environmental pollution is a natural consequence of human activities. It is also the result of natural processes. The shell fish industry is operative among all the costal countries and contributes hugely to the food delicacies. During the processing of prawns, shrimps and lobsters mostly the meat is taken, while the shell and head

portions are generated as wastes. This results in the generation of a huge amount of waste throughout the world. It is estimated that the shell-fish industry produces about 60,000-80,000 tons of waste. The disposal of such an enormous amount of waste has become a serious environmental concern [Muzzarelli et al., 1986]. Although these wastes are biodegradable but the rate of degradation of a large amount of waste generated per processing operation is comparatively slow [Prashanth and Tharanathan, 2007]. This results in accumulation over time and the ads to environmental concerns as they not only produce obnoxious smell but also attract pathogenic insects, flies and rodents, thus creating an unhygienic atmosphere.

The immediate solution to this problem seems to be quick recycling of the crustacean shells generated and extraction of commercially viable substances to be further used in other applications [Roberts, 2008]. As we know the shell and head wastes of crustaceans contain chitin, proteins and minerals. So by demineralising and deproteinizing the wastes chitin can be obtained [Jiang et al., 2003]. Chitin can be used for various economical applications. Moreover the chitin can be further deacetylated to produce chitosan, a valuable chemical substance having a wide range of viable uses [Kumar, 2000]. Various derivatives of chitin and chitosan can also be manufactured which diversify the fields of application of these two chemicals [Thanou and Junginger, 2005].

1.24 Rationale of the Research

Synthetic polymers have all along been the major materials in our daily life. They are seen in a wide range of applications from dietary to mechanical support. However, they have also created problems in disposal as they are considered not biodegradable and take up millions years to degrade back to nature. In other words, they consume a large space and become a major issue as environmental pollution increasing the demands for biopolymers which exhibit the characteristic of biocompatibility, biodegradable and non-toxicity. Chitosan and its functional derivatives, being biopolymer extracted from chitin, as well as shrimp shells, can be developed to act in place of environmental pollution. In addition, chitosan and its water soluble functional derivatives also gain fame in waste water treatment field and medical field due to its metal absorption, antibacterial and so on respectively. These demands then create the need for mass production of chitosan and its derivatives. Therefore, understanding the effectiveness

and efficiency of chitosan extraction method will improve the quality of product and will definitely give many benefits.

1.25 Aims and Objectives of the Present Study

Jute and cotton are the most abundant renewable and biodegradable ligno-cellulosic and cellulosic biopolymers. They are called the most important cash crops of Bangladesh and play an important role in the economic development of Bangladesh. Even though jute and cotton possess great economic impact in Bangladesh, they have some inherent drawbacks viz; the coarseness and rigidity nature, photo yellowing property, poor colour fastness, poor crease resistance and drape property of jute and some inherent properties of cotton are seriously limits the general use especially for textile purposes. To overcome those inherent limitations of cellulosic fibres and trying to develop prawn shell waste as a value added product in the textile sector and to protect our environment from prawn shell waste pollution, the present research work was undertaken:

1. To prepare chitosan from prawn shell waste for key component of chitosan derivatives.
2. To prepare water soluble chitosan derivatives for cellulosic jute and cotton fibres modification.
3. To modify jute and cotton fibres with chitosan and its ecofriend functional derivatives in order to improve dyeability and colouring performances of the modified jute and cotton fibres.
4. To improve fibre tensile strength as well as elongation break and reduce susceptibility to moisture and UV by means of chitosan and its derivatives treatment of jute and cotton fibres which could be suitable for various applications.

Chapter 2
MATERIALS AND METHODS

2.1 Materials: Raw Materials, Chemicals, Modifiers and Dyestuffs

All the Raw Materials, Chemicals, Monomers and Dyestuffs employed in the present investigation are given below with their origin and purity.

2.1.1 Raw materials

In the present investigation cellulosic fibres (jute, cotton) and dry shrimp shells were used as source raw materials for fibres and chitin respectively.

2.1.1.1 Jute fibre

Corchorus olitorious (Tossa Jute) jute fibre was collected from Rajshahi Jute Mill, Bangladesh. 30 cm of the jute fibre was selected from the middle portion of the jute stream that was taken for this study.

2.1.1.2 Cotton fibre

Cotton fibres were collected from Keya spinning mills Ltd., Bangladesh.

2.1.1.3 Prawn shell

Dry prawn shell was collected from Mongla (near Sundorbon forest) and Satkhira and Khulna regions of Bangladesh that are prawn waste processing areas and used it for the production of chitin, the source material of chitosan.

2.1.2 Chemicals

All the chemicals that were used in the present investigation are listed in **Table 2.1** with sources and purity.

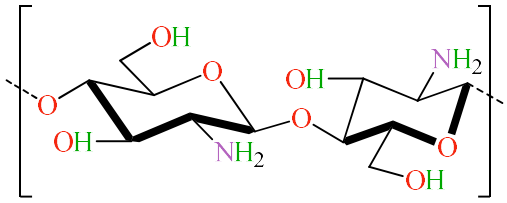
Table 2.1: List of used chemicals with source

Sl. No.	Chemicals	Producers
1	Jet (Detergent)	Kohinoor (Bangladesh)
2	Anhydrous sodium carbonate (Na_2CO_3, 99.5%)	BDH (England)
3	Sodium chlorite ($NaClO_2$, 80%)	BDH (England)

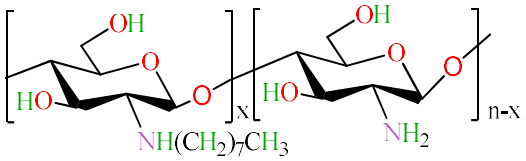
4	Sodium hypochlorite (NaOCl)	Merck (Germany)
5	Sodium acetate (CH_3COONa, 98%)	BDH (England)
6	Octanal ($C_8H_{16}O$)	Merck (Germany)
7	Sodium borohydride ($NaBH_4$)	Merck (Germany)
8	Sodium lauryl sulphate ($C_{12}H_{25}NaO_4S$)	LCP (India)
9	Magnesium chloride ($MgCl_2.6H_2O$)	LCP (India)
10	Triton X 100	LCP (India)
11	Acetic acid glacial (CH_3COOH, 100%)	BDH (England)
12	Tartaric acid ($C_4H_4O_6$, 99.5%)	BDH (England)
13	Sodium hydroxide (NaOH, 98%)	BDH (England)
14	Sodium chloride (NaCl, Extra pure)	BDH (England)
15	Hydrochloric acid (HCl, 36%)	BDH (England)
16	Absolute alcohol (C_2H_5OH, 100%)	Merck (Germany)
17	Acetone (C_3H_6O)	Merk (Germany)
18	Ammonium chloride (NH_4Cl)	LCP (India)
19	Sodium meta-bi-sulphite ($Na_2S_2O_5$, 99.9%)	Merck (Germany)
20	Potassium bromide pure (KBr)	QFC (India)
21	Methanol (CH_3OH)	Merck (Germany)
22	Carbon tetrachloride (CCl_4)	Tecno Pharm Chem (India)
23	Monochloroacetic acid ($CH_2ClCOOH$)	BDH (England)
24	Iso-propylalcohol ($CH_2CH(OH)CH_3$)	Merck (Germany)
25	Potassium persulphate ($K_2S_2O_8$)	Merck (Germany)
26	Acrylic acid ($C_3H_4O_2$)	RDH (Germany)
27	Ractified sprit	Keru (BD)
28	Silver nitrate ($AgNO_3$)	Sigma (USA)
29	Nitric acid (HNO_3)	Merck (Germany)
30	Sulphuric acid (H_2SO_4)	Merck (Germany)
31	Ether (CH_3OCH_3)	LCP (India)
32	2-mercaptoethanol ($HOCH_2CH_2SH$, pure)	Sigma (USA)
33	4-methoxyphenol (pure)	Sigma (USA)
34	Glycidyltrimethylammonium chloride (GTMAC)	Sigma (USA)
35	N-methylolacrylamide (NMA, 48 wt%)	Sigma (USA)

36	Starch	LCP (India)
37	Iodine (I_2)	Merck (Germany)
38	Potassium iodide (KI, pure)	Merck (Germany)
39	Wheel soap	Lever Brother's Bangladesh Ltd
40	Hydrogen peroxide (H_2O_2, 35%)	Merck (Germany)
41	Salicylic acid	Merck (Germany)
42	Calcium chloride ($CaCl_2$)	Merck (Germany)
43	Reactive Orange 14	Sigma (U.S.A)
44	Reactive Brown 10	Sigma (U.S.A)
45	Direct Orange 31	Sigma (U.S.A)
46	Direct Yellow 29	Sigma (U.S.A)
47	Methyl red	Merck (Germany)

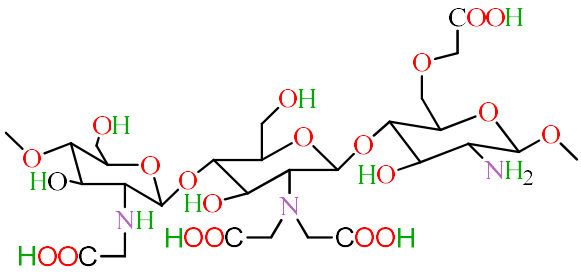
2.1.3 Modifiers



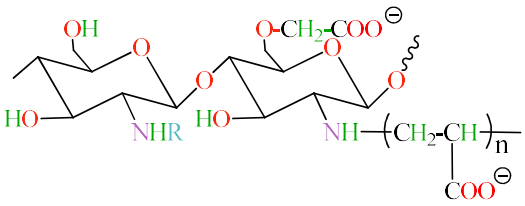
Chitosan (Ch)



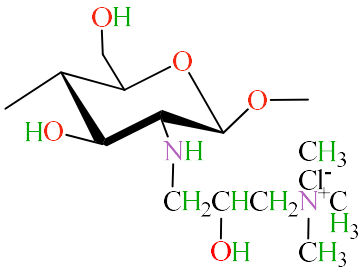
N-octyl chitosan (NOCh)



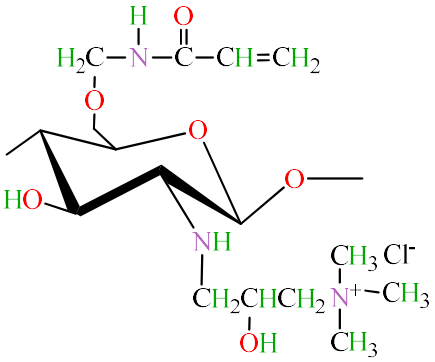
Carboxymethyl chitosan (CMCh)



Carboxymethyl chitosan grafted acrylic acid (CMCh-g-AA)



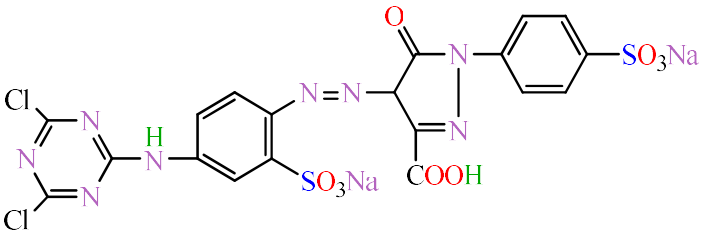
N-(2-Hydroxy) propyl-3- trimethylammonium chitosan chloride (HTAChC)



N-methylolacrylamide-N-(2-Hydroxy) propyl-3- trimethylammonium chitosan chloride (NMA-HTAChC)

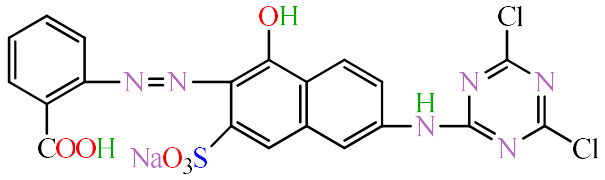
2.1.4 Dyestuffs: Structure of reactive and direct dyes

There were two reactive and two direct dyes used in the present investigation. The structures of these dyes are as follows:



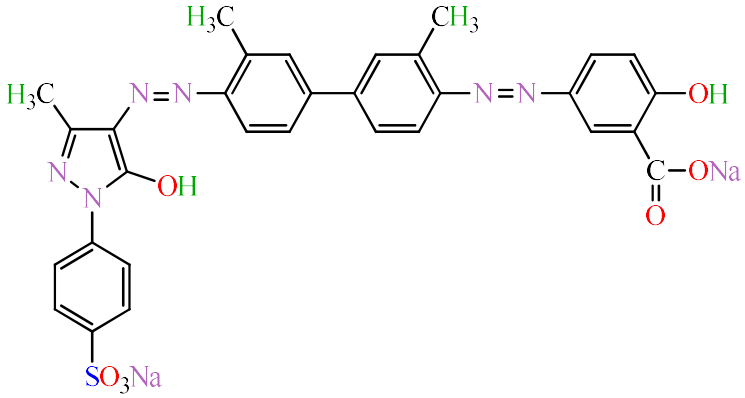
C.I. 19138, λ= 430 nm, R= 8254, 50%, Sigma, USA.

Scheme 2.1: Reactive Orange 14



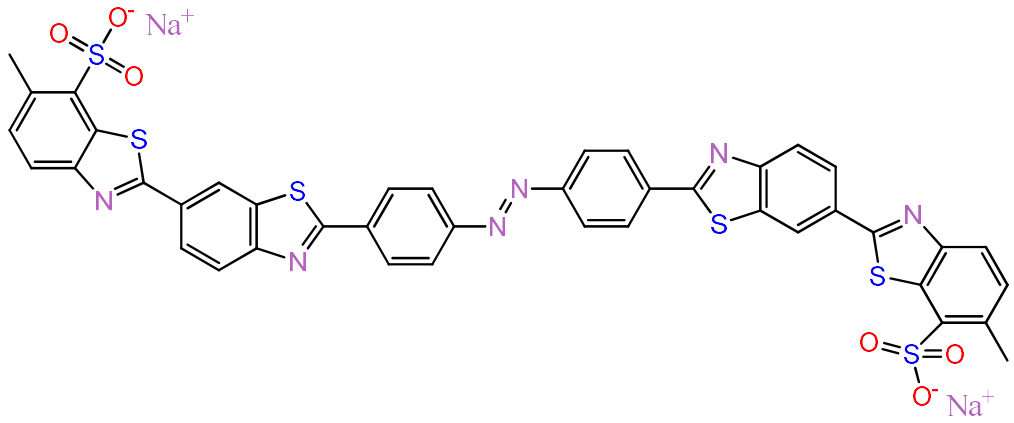
Lot 701107831, λ= 520 nm, R= 0385, 50%, Sigma, USA.

Scheme 2.2: Reactive Brown 10



C.I. 23655, λ= 430 nm, 50%, Sigma, USA.

Scheme 2.3: Direct Orange 31



C.I. 19556, λ= 618 nm, 50%, Sigma, USA.

Scheme 2.4: Direct Yellow 29

2.2 Instruments

All the apparatuses and instruments employed in the present investigation are listed in **Table 2.2**.

Table 2.2: List of main apparatuses and instruments employed in the present investigation

Sl. No.	Instruments
1.	Shaker
2.	Soxhlet Extractor
3.	Kjeldahl Machine
4.	Conductivity Metre
5.	Oven, regulated at 200°C
6.	pH Metre
7.	Humidity Chamber
8.	Moisture Analyzer
9.	Muffle Furnace
10.	Tensile Tester
11.	Infrared Spectrophotometer (FTIR)
12.	Scanning Electron Microscope (SEM)
13.	X-Ray Defractometre (XRD)
14.	Thermo Gravimetric Analyzer (TGA)
15.	NMR Spectrometre
16.	Dye bath (DYSIN partner in Bangladesh, Rapid, Taiwan)
17.	Colorimetre (Type-S104, No-221, Spectrophotometre, WPA Linton Cambridge, UK)

The instruments used for the synthesis and characterization of samples is given below:

Figure 2.1: Instruments used in the present investigation (a) Kjeldahl machine, (b) NMR spectrometer, (c) Reflux system, (d) Dye bath, (e) Centrifuge machine and (f) Shaker

Figure 2.2: Instruments used in the present investigation (a) Muffle furnace, (b) Water bath, (c) Electronic balance, (d) Magnetic stirrer, (e) Moisture analyzer and (f) Forced convection oven.

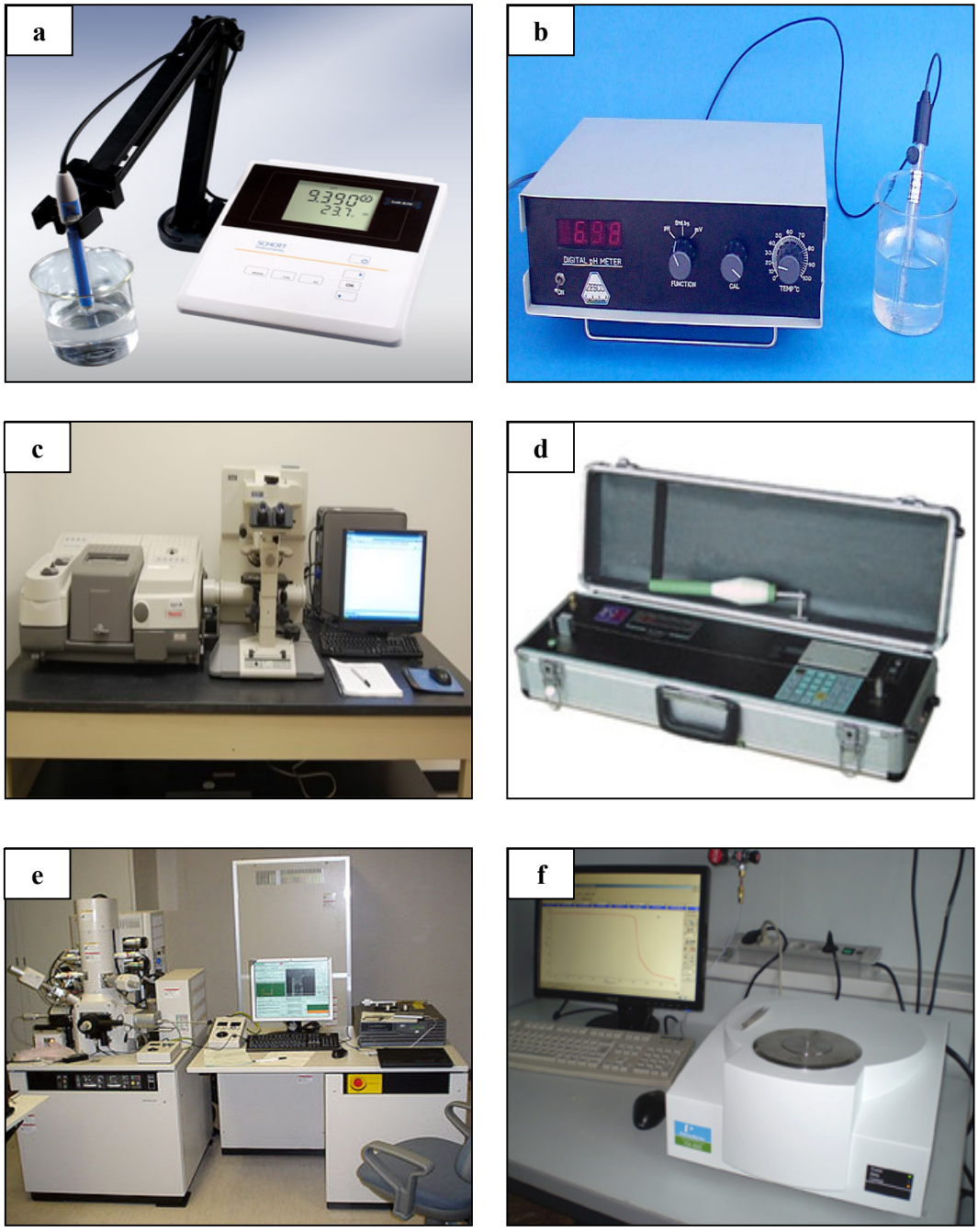


Figure 2.3: Instruments used in the present investigation (a) Conductivity meter, (b) pH meter, (c) FTIR spectroscopy analyzer, (d) Tensile tester, (e) Scanning electron microscope and (f) Thermogravimetric analyzer.

2.3 Methods

2.3.1 Preparation of jute fibre: Cleaning, bleaching and washing

2.3.1.1 Cleaning

The removal of impurities such as dirty materials, fatty, waxy and gummy substances from textile fibre materials is called scouring or cleaning. It is carried out by the use of surface active agents, such as soda and detergents. The dirty materials were removed by treating the fibre with a mixture of 6.50 gm detergent and 3.50 gm of soda in one liter at 75°C for 30 min in a beaker in the ratio 1:50 (w/w). The fibre was then washed thoroughly with distilled water and dried in sun in the open air [Farouqui and Mondal, 1989].

2.3.1.2 Bleaching

0.5% sodium chlorite ($NaClO_2$) solution or 5.0 gm per liter sodium chlorite ($NaClO_2$) solution was prepared and its pH was adjusted to 4.0 by adding 0.2M acetic acid (CH_3COOH) solution from a burette and the pH change was observed directly with a pH meter. For each gm of jute fibre 50 ml of the liquor was taken and bleaching was conducted at 85-90°C for 90 min. Prior to start of bleaching 1.0 ml of buffer solution of acetic acid and sodium acetate of pH 4.0 was added for every 10.0 ml of the liquor to maintain the constant pH throughout the process. This buffer solution was prepared by adding 0.20M acetic acid (CH_3COOH) to 0.20M sodium acetate (CH_3COONa) solution. After the completion of bleaching the fibre was washed well with distilled water and immersed in 0.20% sodium meta-bi-sulfite ($Na_2S_2O_5$) solution for 15 min. After that the fibre was washed well with distilled water and dried in open air and stored in the desiccators [Farouqui and Mondal, 1989].

2.3.1.3 Washing

The fibre samples were modified with 0.10 gm/L caustic soda solution for 20 min at 90°C and neutralized with acetic acid solution [Bhuiyan et al., 2013]. The fibres were then washed thoroughly with distilled water and dried in the open air. After that the fibres were dried in an oven at 60ºC.

2.3.2 Preparation of cotton fibre: Washing and bleaching

2.3.2.1 Washing of cotton fibre

At first, the cotton fibres were washed with 0.2% Na_2CO_3 solution at 75º C for 30 min in a beaker in the ratio of 1:50. The fibres were then washed thoroughly with distilled water and dried in the open air. After that the fibres were dried in an oven at 60ºC and then stored in desiccators [Singha and Thakur, 2009; Farouqui and Mondal, 1989].

2.3.2.2 Bleaching of cotton fibre

Scoured cotton fibre was modified with solution containing hydrogen peroxide (30%) 10 gm/L, soda ash 10 gm/L, detergent 1 gm/L at about 85ºC for 60 min. The material to liquor ratio was maintained at 1:30. After bleaching was over, the fabric was given hot wash at 80ºC for 20 min and then rinsed [Naser et al., 2015].

2.3.3 Preparation of chitin and chitosan

Chitosan was prepared from prawn shell waste by a series of chemical treatments. Collected prawn shells was washed and dried by forced air oven at 100ºC-105ºC and later the size was reduced by means of grinding (40-60 mesh) using hammer mill. The ground prawn shell was then ready for chemical treatment. The series of chemical treatments were demineralization, de-protenization and decolouration and by means of these set of chemical treatment chitin was obtained [Alam et al., 2008]. Later chitin passed through a chemical treatment named deacetylation to give chitosan. Chitin in crustacean was tightly associated with proteins, lipids, pigments, and calcium deposits. Therefore, in order to isolate chitin from crustacean shell (Shrimp is a member of Crustacean) all the steps were discussed below:

2.3.4 Prawn shell collection and processing

Collected raw prawn shell were washed with running tap water and all kinds of unwanted materials were removed by hot water spray then dried in forced air oven at 100ºC - 105ºC in the Polymer and Textile Research Laboratory of the Department of Applied Chemistry and Chemical Engineering in the University of Rajshahi. Then the dried shells were grind by a ball mill in order to get small sizes shells. After milling process, the ground prawn shells were screening to determine the particle sizes. Then powdered shell was stored in a plastic bag in desiccators.

2.3.4.1 Demineralization

The mineral content in the exoskeleton of crustacean was removed by demineralization. The demineralization of the prawn shells was carried out using 1N hydrochloric acid solution in 100 ml beakers at an extraction ratio of 1: 20 (w/v). The mixture was then heated at 104°C for 4 h with stirring with a glass rod. The demineralized prawn shells were recovered by filtration and thoroughly rinsed with distilled water through a Buchner funnel by vacuum pump. And later the resulted demineralized shells were dried at 65°C for 4 h in vacuum oven. The obtained sample kept in the desiccators to make ready for de-proteinization [Antonia, 1991; Alam et al., 2008; George, 2009].

2.3.4.2 Deproteinization

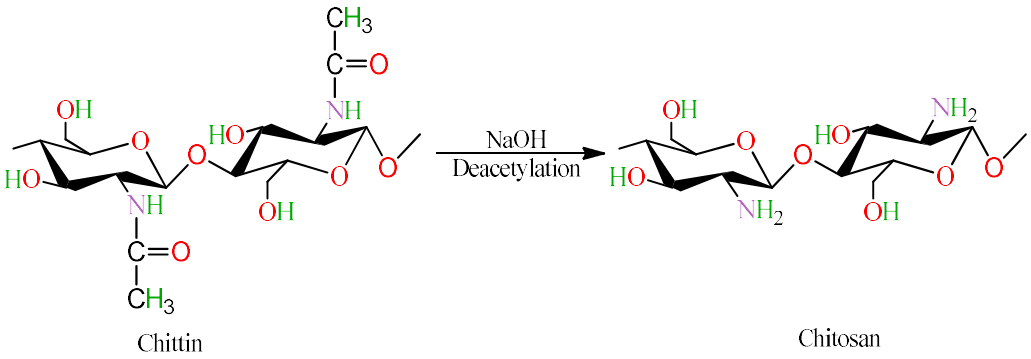
Deproteinization of chitin was carried out using 1N sodium hydroxide (NaOH) in a 100 ml beaker at shell: extractant ratio of 1: 15 (w/v). The mixture was then heated at 104°C for 4 h with stirring with a glass rod. The mixture was wished with distilled water by decantation and filtration to neutralize with vacuum pump and dried in an oven at 104°C for 24 h to produce chitin. Thus the produced chitin is an intermediate product of chitosan. The residual weight was measured to estimate the loss in weight upon de-proteinization and determined ash, mineral and total nitrogen content. The process was carried out second and third time for absolute chitin extraction [Antonia, 1991; Alam et al., 2008; George, 2009].

2.3.4.3 Decolouration

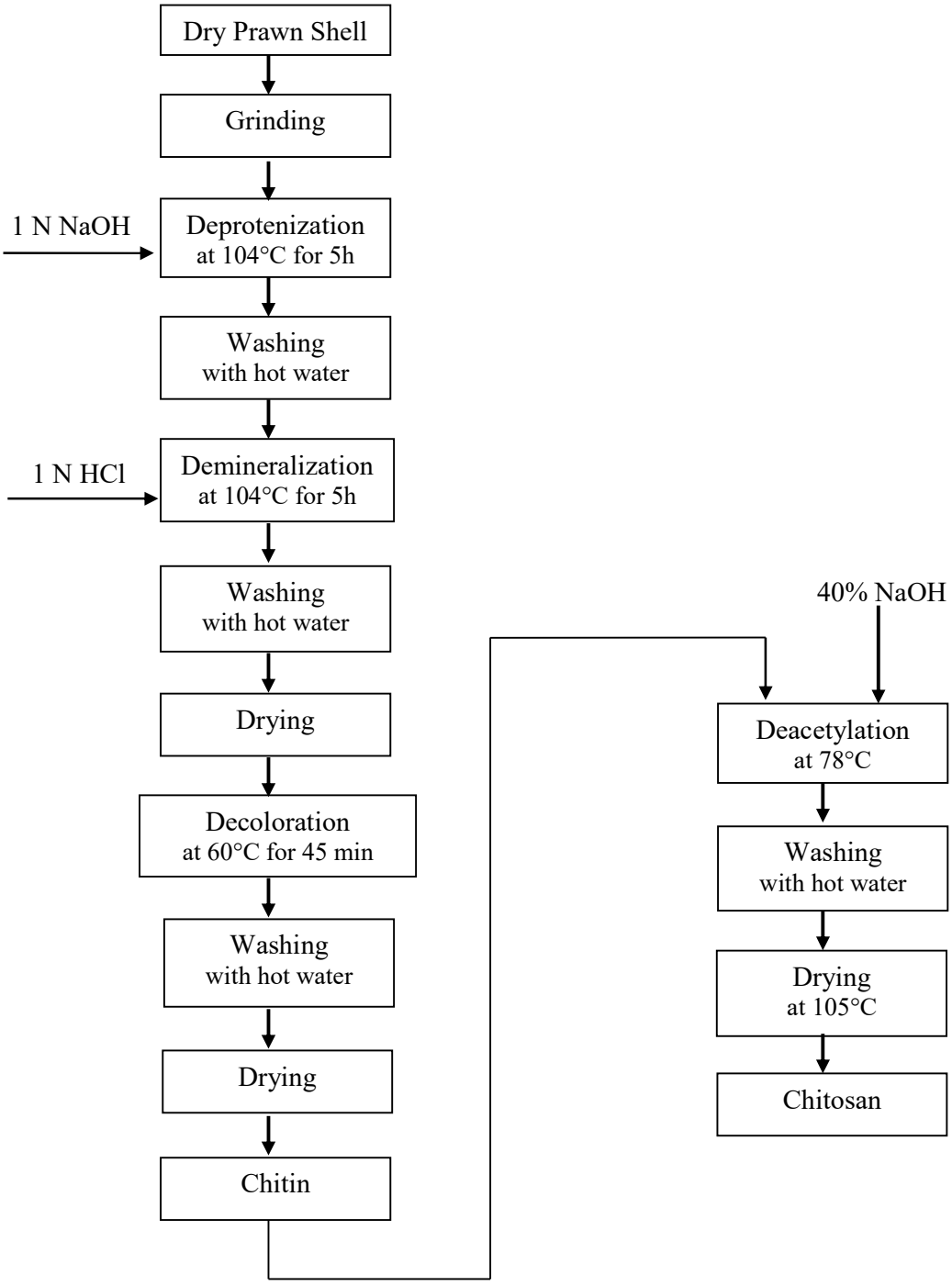
Crude chitin was discoloured using various methods (Kamasastri and Prabhu, 1961; Blumberg et al., 1951). Crude chitin sample were refluxed with absolute acetone (150 ml) for 45 min and dried at room temperature for 2 h and then modified with 70% acetone. Sample were then washed, rinsed with distilled water and then mixed with 0.315% sodium hypochlorite solution (containing 7% available chlorine) for 5 min. The residues were then removed by filtration (through a 140 μm filter paper) and then washed with distilled water and dried at 65°C for 4 h in a vacuum oven. The residual weights were measured in order to estimate the yield of crude chitin [Antonia, 1991; Alam et al., 2008; George, 2009].

2.3.5 Deacetylation of chitin into chitosan

The conversion of chitin to chitosan was achieved by the treatment of chitin with concentrated sodium hydroxide (40% w/v) at 78°C in presence of ethanol with reflux for 3 h to remove the acetyl groups from it with a solid to solvent ratio of 1: 30 (w/w). After this process solid separated from the alkali layer which were extensively washed with distilled water by vacuum pump to remove traces of alkali till neutralized. The resultant solid was dried in vacuum oven at 50°C for 24 h to produce chitosan and this way chitosan were extracted from prawn shell waste. Chitosan extraction was repeated out second and third time for absolute chitosan extraction [Antonia, 1991; George, 2009; Islam et al., 2015]. The reaction of chitin into chitosan and flow chart for chitosan preparation are given below in **schme 2.5 and 2.6** respectively.



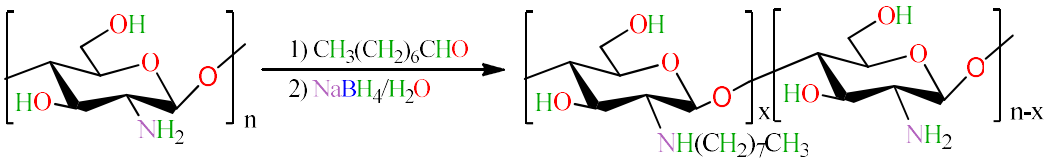
Scheme 2.5: Preparation of chitosan from chitin



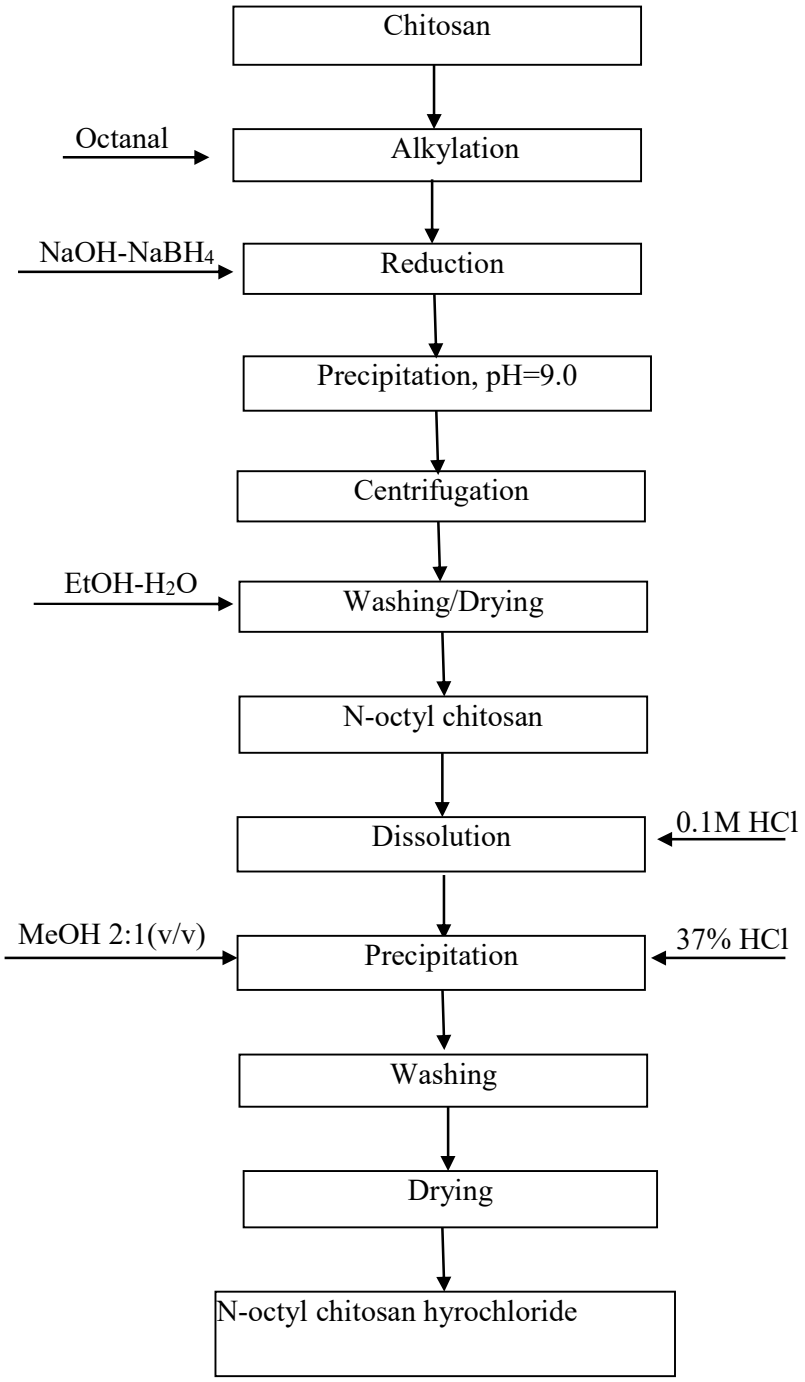
Scheme 2.6: Flow diagram of chitosan preparation

2.3.6 Preparation of N-octyl chitosan

N-octyl chitosan (NOCh) were prepared by introducing an octyl group to NH_2 on C_2 of glucosamine unit. To prepare NOCh, 1 gm of chitosan was suspended in 50 ml of methanol, and then 1 gm of octanal was added in the suspension while stirring at room temperature. After 24 h of reaction time, the pH of the reaction mixture was adjusted at 8-10 by NaOH solution and then $NaBH_4$ solution (0.5 gm in 5 ml of water) was slowly added to the reaction mixture. The reaction mixture was stirred with magnetic stirrer at ambient temperature for another 24 h, followed by neutralization using 2M HCl. The prepared NOCh was collected by precipitation using methanol into the neutralized solution and then filtered, repeatedly washed with methanol and water, and dried at 60°C overnight under a reduced pressure [Zhang et al., 2003; Vinsova and Vavrikova, 2008; Bobu et al., 2011].



Scheme 2.7: Reaction for the preparation of N-octyl chitosan

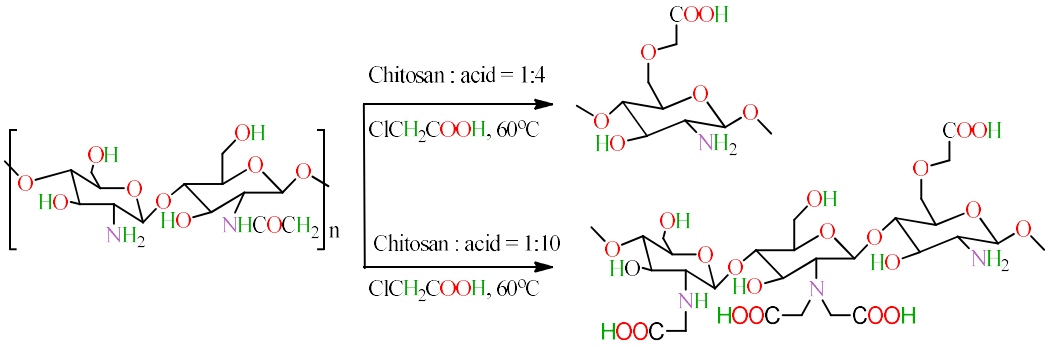


Scheme 2.8: Synthesis scheme of N-octyl chitosan

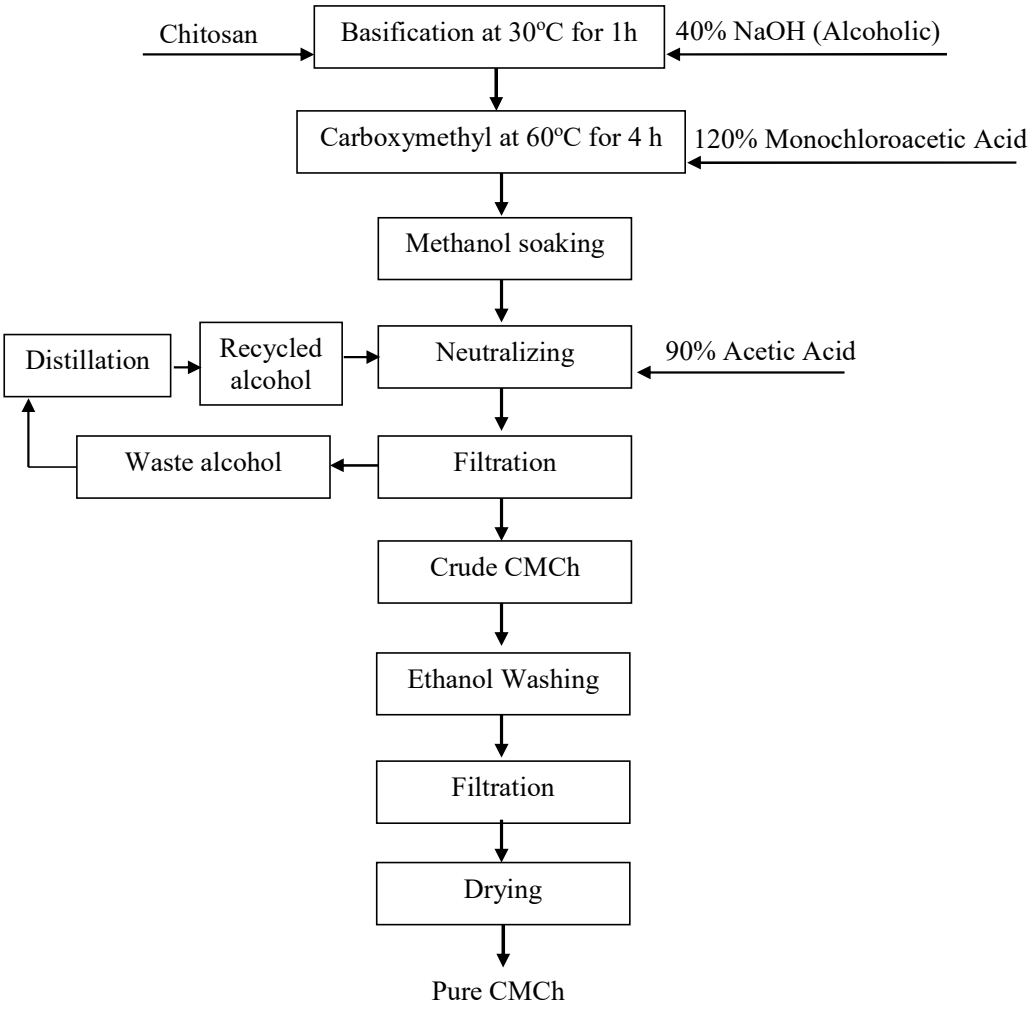
2.3.7 Carboxymethylation of chitosan

Carboxymethyl chitosan was prepared from chitosan by acid–base treatment method [Mourya et al., 2010]. Following the procedure described for the carboxymethylation of chitosan, purified chitosan (3 gm) was dispersed in 65 ml of isopropanol. After 20 min of magnetic stirring at room temperature, 20.4 gm of aqueous NaOH (40%) and 14.4 gm of monochloroacetic acid/isopropanol solution (1:1 m/m) were added to the suspension [Yeasmin and Mondal, 2015]. The reaction proceeded to the desired time at room temperature and the solid product was then filtered, suspended in 150 ml of methanol and neutralized with glacial acetic acid. The product was extensively washed with 80% ethanol and dried at room temperature.

For the purification of these derivatives, 1.5 gm of the sample was dissolved in 1.5 L of aqueous solution of 0.1M NaCl. The resulting solution was filtered and the carboxymethyl chitosan was precipitated upon addition of absolute ethanol. Then, the carboxymethyl chitosan (CMCh) was washed with ethanol/water mixtures of increasing ethanol content (75%, 80% and 90%) and finally with absolute ethanol [Yeasmin and Mondal, 2015].



Scheme 2.9: Reaction for the preparation of carboxymethyl chitosan.

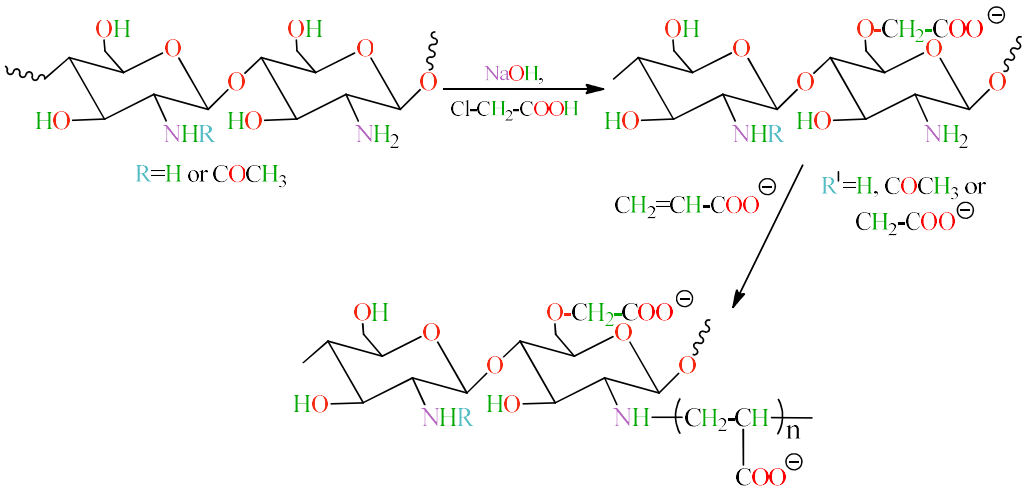


Scheme 2.10: Flow diagram of carboxymethyl chitosan (CMCh) preparation

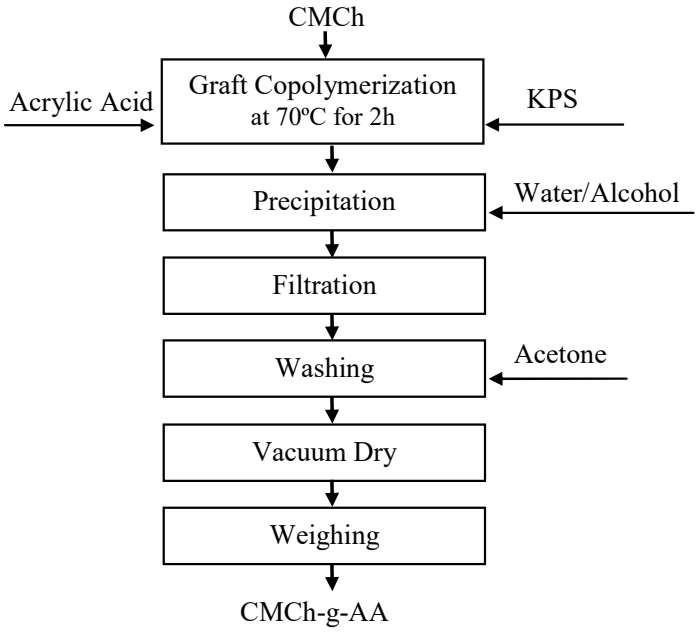
2.3.8 Graft copolymerization of CMCh

Graft copolymerization was carried out in a 250 ml two-necked glass flask using 0.1 gm CMCh. Before addition of the predetermined amount of monomer, acrylic acid (AA), the monomer was neutralized by using NaOH (4M) and then completed to the desired volume by deionized water. The used monomer concentrations were in the range of (0.25– 3M). The components were mixed through regular stirring for 30 min with bubbling of slow stream of nitrogen gas. Then the flask was placed in a thermostated bath at the desired reaction temperature (50–90ºC). Upon reaching the desired temperature, the appropriate concentration of the initiator, KPS (3–15 mmol based on the total volume of reaction mixture) dissolved in 10ml of deionized water was added drop wise with stirring. The graft copolymerization was continued for a

predetermined period (0.5–3 h). After the desired time, the reaction was stopped by letting air into the flask and rapidly cooling down the reaction. The products were precipitated by pouring the reaction mixture into acetone. The precipitate was filtered off, washed with acetone, and the crude product was dried under vacuum and weighed. The homopolymer formed was extensively extracted in a Soxhlet apparatus by refluxing with methanol for 24 h. The residual graft copolymer obtained was washed with methanol, dried, and weighed [Sherbiny and Mahdy, 2010].



Scheme 2.11: Reaction for the preparation of (CMCh-g-AA) carboxymethyl chitosan grafted acrylic acid.



Scheme 2.12: Flow diagram of CMCh-g-AA preparation

2.3.9 Preparation of HTAChC

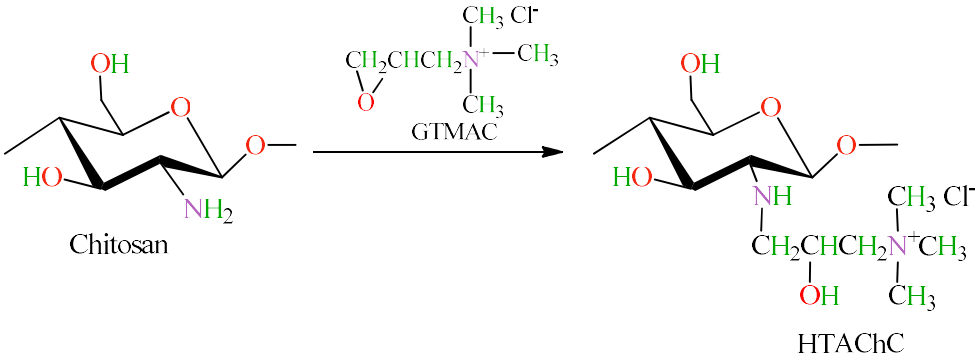
The HTAChC was synthesized by following steps [Lang et al., 1990]:

2.3.9.1 Dispersion of chitosan

The chitosan (5 gm) was dispersed in 50 ml of distilled water in a reaction vessel with constant stirring on a magnetic stirrer hot plate. After formation of a dispersion, the reaction vessel is maintained at a temperature of 85ºC by hot plate of the magnetic stirrer.

2.3.9.2 Quaternization of chitosan

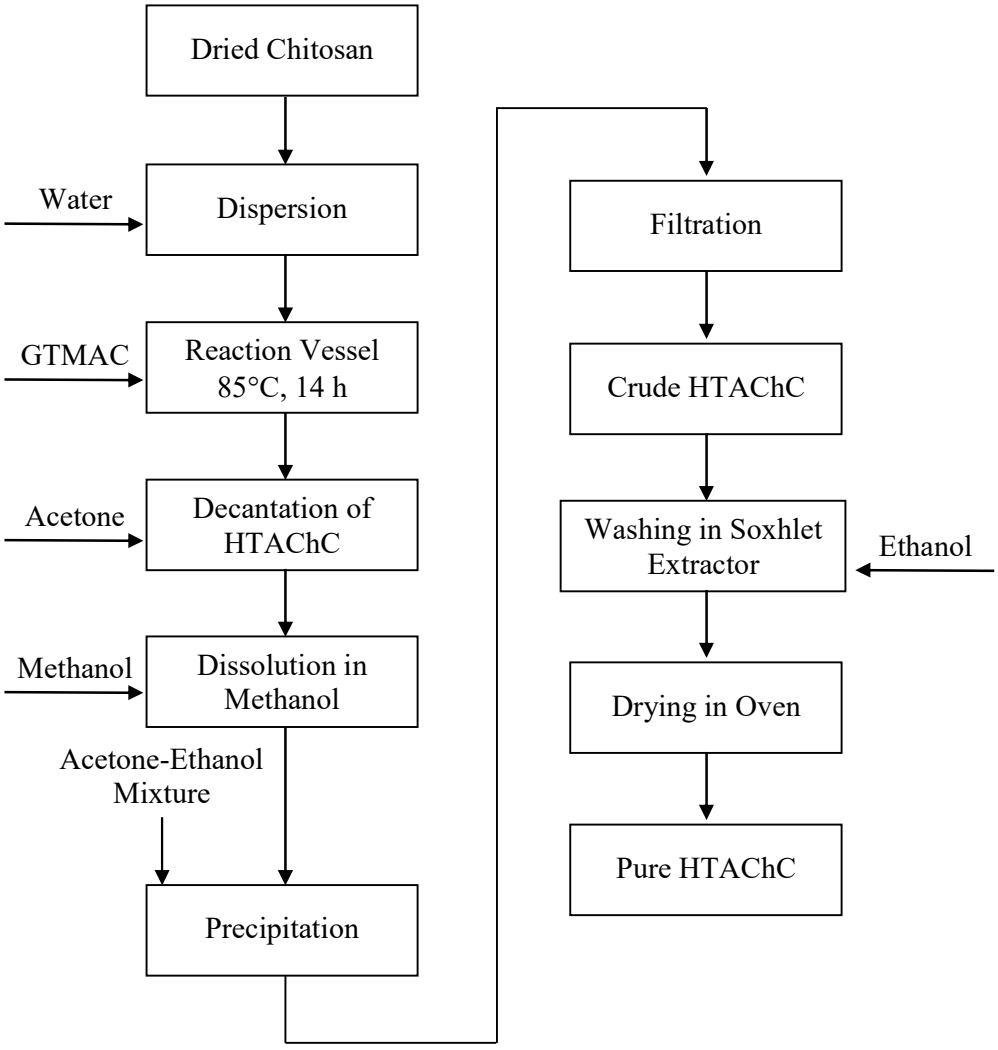
Quaternization of Chitosan was carried out by adding three mole GTMAC equivalents to one mole amino group of chitosan. As chitosan was completely dispersed into distilled water in the reaction vessel, one third of required GTMAC was added with constant stirring. Rest two third of the GTMAC was added two times at a 2 h interval. After a total 16 h reaction, the clear and yellowish reaction solution was poured in 200 ml cold acetone while stirring and kept in the refrigerator overnight. The next day, acetone was decanted and the remaining gel-like product was dissolved in 100 ml methanol. The solution was precipitated in a 250 ml acetone:ethanol (4:1) mixture. The white product was collected by filtration which was crude HTAChC and it was further needed to be purified by washing.



Scheme 2.13: Synthesis of HTAChC.

2.3.9.3 Purification of HTAChC

The crude HTAChC obtained from filtration stage need to be purified by washing with hot ethanol using a soxhlet extractor for 24 h. The final product was collected and dried at 60°C overnight. The obtained product is HTAChC.



Scheme 2.14: Flow chart for preparation of HTAChC

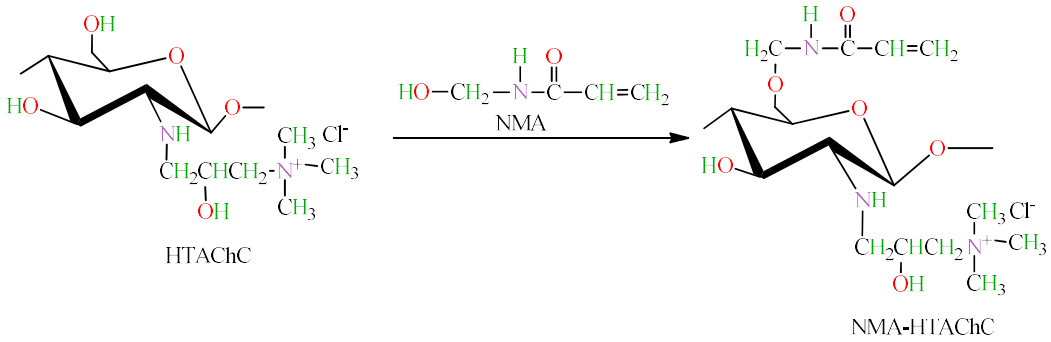
2.3.10 Preaparation of NMA-HTAChC

NMA-HTAChC was synthesized by the following steps: [Kim et al., 1998; Yoo, 1997; Park et al., 1996]

2.3.10.1 Acrylamidomethylation of HTAChC

Acrylamidomethylation of HTAChC is carried out by dissolving HTAChC to an aqueous NMA solution in presence of NH_4Cl. The HTAChC (1 g) was dissolved in 5 ml of 48 wt. % aqueous NMA solution (8 mole excess to HTAChC) with a small amount of 4-methoxyphenol (0.2% w/v) which was added as a polymerization inhibitor at room temperature. To the solution, NH_4Cl (3 - 4 mole excess to HTAChC) was

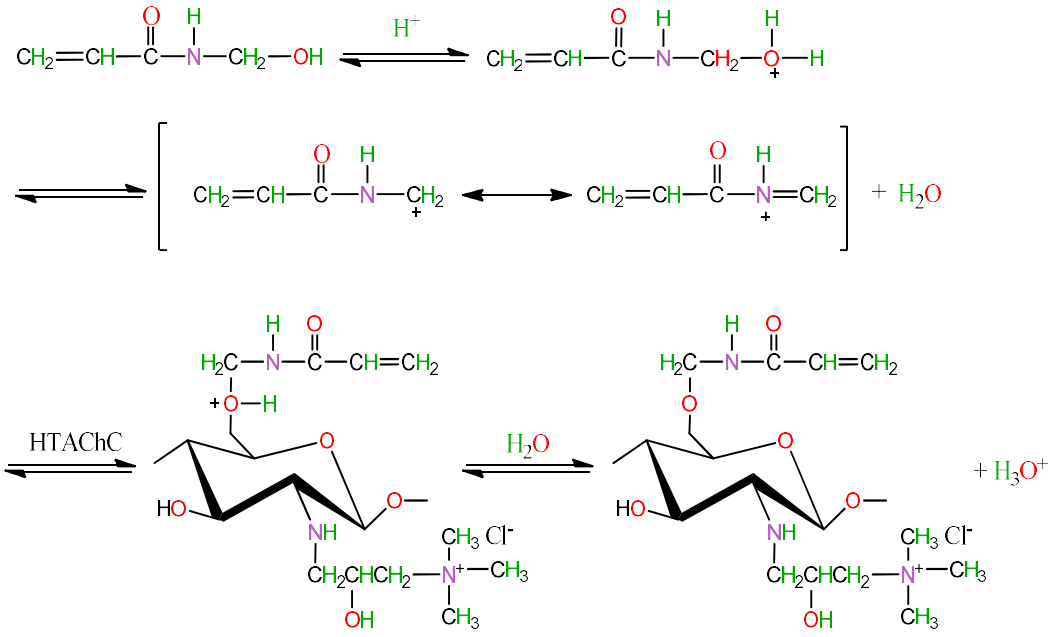
added and dissolved to maintain the acidic medium for acrylamidomethylation reaction. The reaction solution was reacted at 140°C for 8 - 20 min using an oil bath. After reaction, 15 ml of methanol was added to the reaction solution and it was stirred for 10 sec. The product was precipitated in 100 ml acetone and kept overnight for decant. The decanted product obtained is crude NMA-HTAChC which need to be purified by washing.



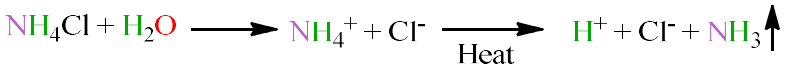
Scheme 2.15: Synthesis of NMA-HTAChC

2.3.10.2 Purification of NMA-HTAChC

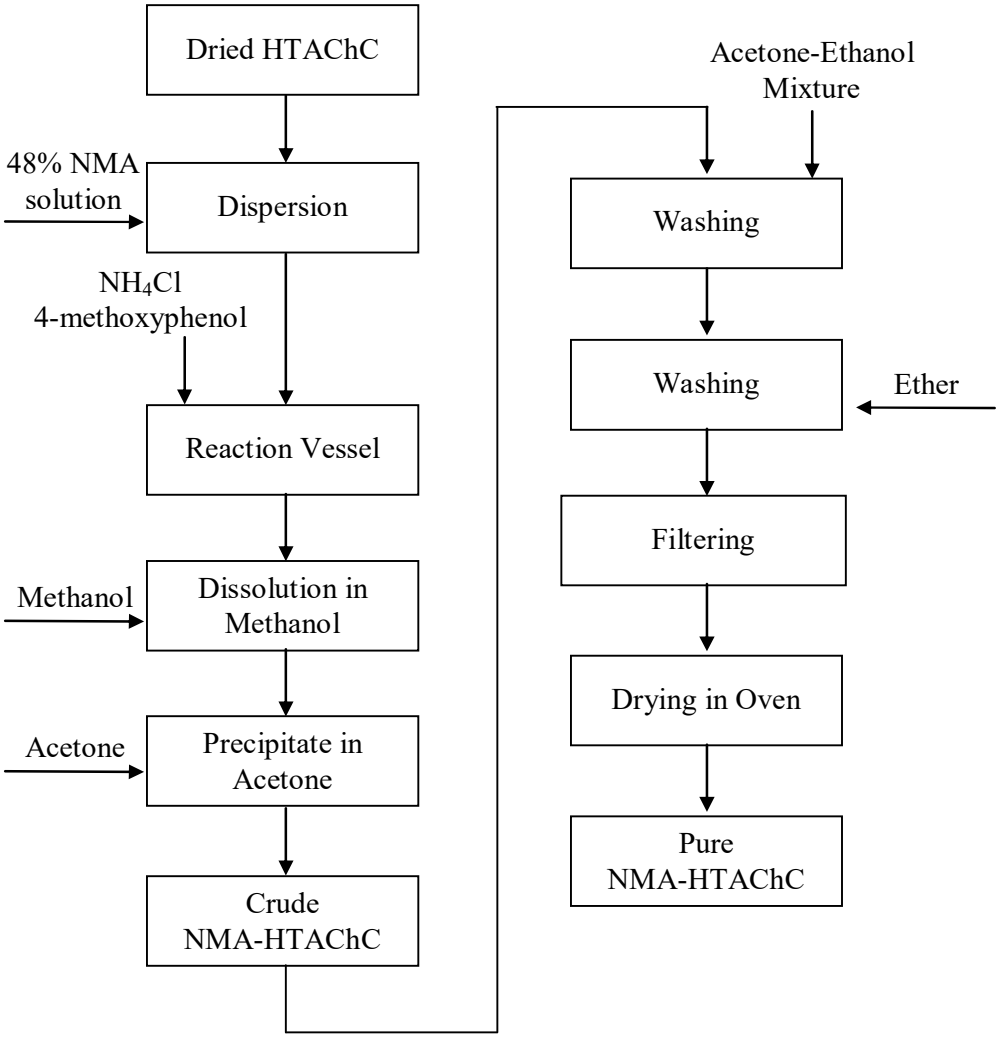
Crude NMA-HTAChC was washed thoroughly with a mixture of acetone:ethanol (1:1) for several times and finally with ether. The white reaction product was dried at 40°C under vacuum for 2 days.



Scheme 2.16: Reaction mechanism between NMA and HTAChC

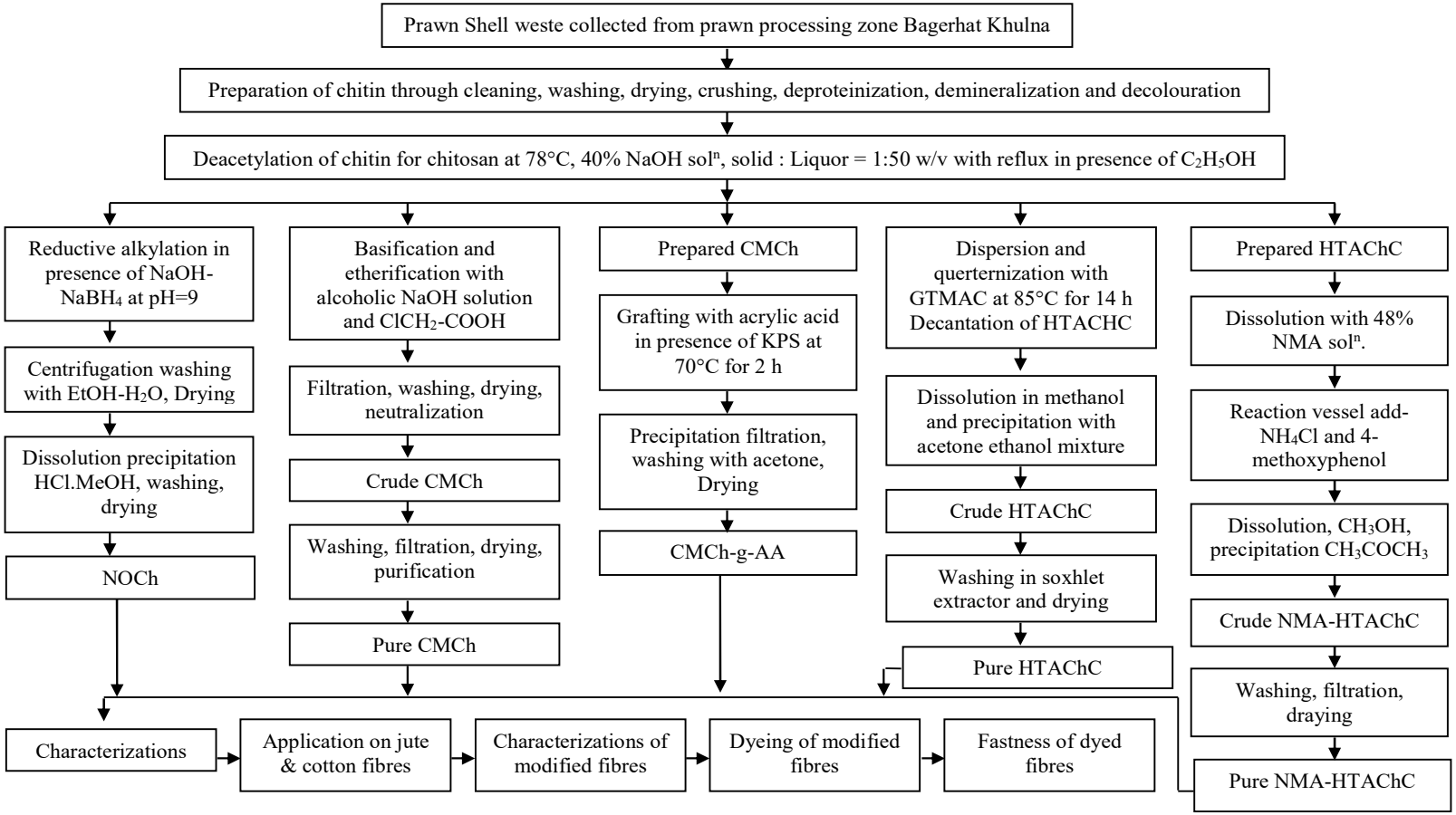


Scheme 2.17: Relase of HCl from NH_4Cl



Scheme 2.18: Flow chart for the preparation of NMA-HTAChC

Summary Flow Chart of the Present Investigation:



Scheme 2.19: Schamatic diagram of the present investigation

2.4 Characterization of Prepared Chitosan and Its Derivatives

2.4.1 Determination of yield of chitin, chitosan and its derivatives (NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC)

Yield percentage, also referred to as reaction yield percentage is the percentage of desired product obtained in a chemical reaction with respect to a key reactant. Yield percentage of chitin, chitosan, and its derivatives were determined by taking the dry weight of shrimp shells, chitin, chitosan, carboxymethyl chitosan and HTAChC before treatment and the dry weight of prepared chitin, chitosan and its derivatives respectively. Yield percentage can be determined by the following equation: [Brzeski et al., 1982, Islam et al., 2014]

$$\text{Yield percentage (\%)} = \frac{W_f}{W_i} \times 100$$

Where, W_i is the weight of dried shrimp shells, chitin, chitosan, carboxymethyl chitosan and HTAChC were taken respectively.

W_f is the weight of obtained dried chitin, chitosan and its derivatives respectively.

2.4.2 Elemental analysis

For the chemical composition of the carbonaceous materials C, N analysis is used. The carbon and nitrogen contents of the samples are determined from the quantities of CO_2 and NO_2 produced by the combustion of the dried solid in oxygen.

2.4.3 Determination of degree of deacetylation of chitosan

Various methods have been used for the determination of the degree of deacetylation (DDA) of chitosan. Among all the methods elemental analysis is simple, suitable and rapid method to determine the degree of deacetylation (DDA) value of chitin. The degree of deacetylation was calculated from the carbon/nitrogen ratio (C/N). It varies from 5.145 in completely N- deacetylated chitosan ($C_6H_{11}O_4N$ per unit) to 6.861 in chitin, the fully N-acetylated polymer ($C_8H_{13}O_5N$ repeat unit). To determine degree of deacetylation (DDA) value of chitin using the following equation [Kasaai et al., 2000].

$$DDA = \{1-(C/N-5.145)/(6.861-5.145)\}\times 100$$

Where, C is the mass of carbon in chitosan sample

N is the mass of nitrogen in chitosan sample

The above procedure was repeated at least three times for more accuracy and precision, and the average degree of deacetylation (DDA) value obtained.

2.4.4 Determination of nitrogen content

On March 7, 1883, Johan Kjeldahl presented his method of nitrogen analysis to the Danish Chemical Society. Since then, his method has been extensively studied, modified, and improved upon. Today, the Kjeldahl method for the determination of organic nitrogen is the worldwide standard for the purpose of calculating the protein content in both human food and animal food. Additionally, Kjeldahl has been adapted as a standard method of nitrogen analysis in water, wastewater, fertilizer, and fossil fuels, to name a few. The Kjeldahl method for nitrogen analysis is composed of three distinct steps. These are digestion, distillation, and titration [Kjeldahl, 2011].

Procedure

The dry sample (15-25 mg) is added to a 30 ml. Kjeldahl flask containing 2 ml of conc. sulfuric acid and 0.100 gm of reagent grade salicylic acid. The mixture is left overnight to dissolve. This length of time is necessary for sample dried from acetone solution; less time will be needed for fibrous nitrates. The accuracy of the method is dependent on complete solution of the sample.

Reagent grade sodium thiosulfate pentahydrate (0.3 gm) and 0.6 gm of reagent grade potassium sulfate are then added. The mixture is warmed gently for a few minutes and finally refluxed 6 h. The flask is cooled; the solution is dilute with 15 ml of water and the contents are transferred to an all glass distillation flask. The solution is made alkaline by addition of 20 ml of 35% (by weight) sodium hydroxide solution and then distilled into 25 ml of 0.8% boric acid solution containing the mixed indicator. This distillation will take 5-7 min. The boric acid solution is then titrated with 0.03N hydrochloric acid; 5-9 ml will be required [John, 1963].

Calculation

After all this chemistry it is now time to calculate the amount of nitrogen present in the sample. This calculation can either be performed as percent nitrogen or percent protein. For percent nitrogen:

% Nitrogen= meq. of acid × 1400/ mg. of sample

2.4.5 Determination of molecular weight of by viscometric method

In order to evaluate the molecular weight of polymeric chains, various methods can be used among them widespread are viscosity and gel permeation chromatographic techniques which ware used in this study.

Four different concentrations 0.2%, 0.4%, 0.6%, and o.8%, solution of chitosan and its derivative samples were prepared with their respective solvents. The solution was passed through a filter to remove insoluble materials. Ostwald viscometer was used to measure the passage time of the solutions flowing through the capillary in a constant temperature water bath at 25°C. Three measurements were made on each sample. The running times of the solution and solvent were recorded as seconds and used to calculate intrinsic [η].

η_{rel} (Relative viscosity)= t_2(efflux time of solution) /t_1(efflux time of solvent)

η_{sp}(Specific viscosity)= η_{rel}-1

η_{inh}(Inherent viscosity)= η_{rel}/c

η_{red}(Reduced viscosity)= η_{sp}/c

$[\eta]=\lim_{c\to 0} \eta_{sp}/c=\lim_{c\to 0} \eta_{rel}/c$

Where, c: Concentration of chitosan solution (gm/ml, %)

η_{red} was plotted on a graph. The intercept of the plots on the ordinate at c=0 gives intrinsic viscosity [η] (ml/g). The intrinsic viscosity was obtained by extrapolating reduce viscosity vs. concentration data to zero concentration. The viscosity average molecular weight of chitosan solution was calculated using the Mark Houwink equation which provides the relationship between intrinsic viscosity and molecular weight.

$[\eta]= K(Mw)^a$ (Mark Houwink equation)

Where K and a are constants for given solute-solvent system and temperature. Where values of 'K' and 'a' are 1.8×10^{-3} and 0.93, respectively [No et al., 2003; George and Julian, 1982].

From the intrinsic viscosity, the molecular weight was determined by using Ostwald viscometer at 25ºC and calculated by the following Mark-Houwink–Sakurada equation [Brandrup et al., 1998; Islam et al., 2014, Yeasmin and Mondal, 2015] as

$$[\eta] = KM^a \text{ (Mark-Houwink–Sakurada equation)}$$

Where, [η] is the intrinsic viscosity, "M" is the molecular weight, "K" is the constant and "a" is the polymer shape factor.

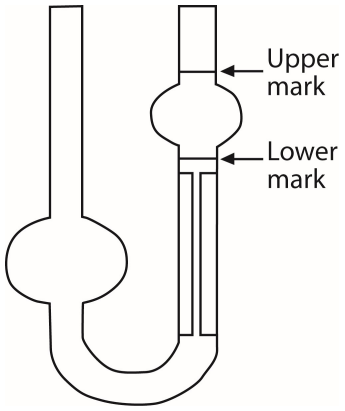


Figure 2.4: Schematic diagram of Ostwald viscometer

2.4.6 Determination of degree of substitution of CMCh

To determine the degree of substitution (DS), 0.5 gm of dried NOCh and sodium CMCh were ashed gently, between 500-600ºC, for 24 h, and then dissolved in 100 ml of distilled water. 20 ml of this solution was titrated with 0.1 N sulphuric acid using methyl red as an indicator. After the first end point, the solution was boiled and titrated to a sharp end point. The degree of substitution [Abel et al., 2011; Yeasmin and Mondal, 2015] of the carboxymethyl content was calculated as follows:

$$DS = \frac{0.162 \times B}{1 - 0.08 \times B}$$

Where, B = (0.1 × b)/a, b is the volume (in ml) of 0.1N sulphuric acid and a is the mass of pure CMCh in grams.

2.4.7 Moisture content

To study moisture content, the chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC were placed in an open air for 72 h for maintaining the saturation level at room temperature. Then the samples were analyzed by moisture analyzer as a function of weight gain [Islam et al., 2015] and was calculated using the following formula,

$$\text{Moisture content, \%} = \frac{(W_0 - W_1)}{W_0} \times 100$$

Where, W_0 is the weight of air dry sample and W_1 is the weight of dry sample.

2.4.8 Ash content

Ash content was determined using standard methods [Official Methods of Analysis, 13th ed. Association of Official Analytical Chemists. Washington D.C., 1980]. A crucible was weighed and ignited for 30 min at 600°C. It was then cooled and transferred into desiccators with the aid of tongs for 15-20 min and reweighed accurately. Approximately 0.5 gm of the vacuum dried sample was transferred into the crucible and the sample was pre-ashed in a fume hood. When the sample ceased giving off smoke, it was placed in a preheated 600°C muffle furnace for 6 h [Islam et al., 2015]. When ashing was complete the crucible was transferred directly into a desiccator, cooled and weighed.

% Ash was calculated by using the following equation:

$$\text{Ash content, \%} = \frac{\text{wt. of ash}}{\text{wt. of sample}} \times 100$$

2.4.9 Determination of degree of quarternization of HTAChC

The Degree of quarternization (DQ) of GTMAC on chitosan was measured by titration of Cl^- with aqueous silver nitrate ($AgNO_3$) solution (Lang et al., 1990). Thoroughly dried HTAChC (about 0.100 gm) was dissolved in 100 ml of deionized water and conductometrically titrated with 0.017N $AgNO_3$ aqueous solution using a burette. Solution conductivities were monitored with an Orion Benchtop Conductivity Meter (Model 162). During the titration, the temperature of the solution was kept constant (20.4 - 20.5ºC) by using a water bath because the conductivity is a function of

temperature. The titration curve for the HTAChC is constructed by plotting conductivity against the volume of Silver nitrate ($AgNO_3$). Before the inflection point, the curve has a negative slope, which corresponds to the decrease in conductivity due to the precipitation of AgCl. The positive slope after the inflection point results from the excess $AgNO_3$. The inflection point indicates the end point of the titration. Following reaction occours during the titration:

$$AgNO_3 + Cl^- \longrightarrow AgCl\ (ppt) + NO_3^-$$

Scheme 2.20: Reaction in titration of HTAChC with silver nitrate

The amount of $AgNO_3$ used at the inflection point equals to the amount of Cl^- ions present on the HTAChC. Since 1 ml of 0.017N $AgNO_3$ is equivalent to 1 mg NaCl, 0.10 gm of the HTAChC contains 3.186×10^{-4} moles of Cl^- ions.

The DQ of HTAChC can be calculated by the following equation:

$$DQ = \frac{M\times N_{Cl}}{m_{dry}}$$

Where, DQ is the Degree of quaternization of HTAChC

M is the molecular weight (gm/mol) of glucosamine repeat unit

N_{Cl} is the number of moles of Cl^- ions in the samples and

m_{dry} is the mass of dried sample in grams.

2.4.10 Determination of double bond content of NMA-HTAChC

One of the methods for determining double bonds adjacent to electron withdrawing groups is to react the compound containing double bonds with a thiol and then titrate the excess of unreacted thiol with iodine. It is known that aliphatic alcohols do not interfere with the results because the double bonds react much faster with thiols than alcohols [Gardon, 1961]. The double bond content of the NMA-HTAChC was determined by the method used by Kamel [Kamel et al., 1973]. A known amount of NMA-HTAChC (0.3 gm) was dissolved in 10 ml deionized water contained in a weighing bottle at room temperature. To the solution, 5 ml of 3% 2-mercaptoethanol ($HOCH_2CH_2SH$) aqueous solution and 1 ml 2M NaOH were added and stirred in a closed weighing bottle at room temperature for 20 min to ensure the complete

nucleophilic addition of mercaptoethanol to the double bond. The mixture was acidified with 2.5 ml 1N HCl. After the addition of several drops of starch indicator, it was titrated against a 0.1N iodine (I_2) solution until the endpoint at which the first faint blue colour that persisted for at least 30 sec. **Sch. 2.21** shows the oxidation reaction of thiol with iodine [Siggia and Hanna, 1979]. The endpoint corresponds to the complete oxidation of the remaining thiols and after that point excess iodine shows blue colour by interacting with starch indicator. A blank titration was run in an identical manner.

$$2\ R — SH + I_2 \longrightarrow R — S — S — R + 2\ HI$$

Scheme 2.21: Oxidation of thiol by iodine

$$\text{Double bond content (mmol/gm NMA-HTAChC)} = \frac{(V_B - V_S)}{W} \times 0.1$$

Where, W is the weight of sample in grams

V_B and V_S are the amount (ml) of iodine in blank and sample titration respectively

0.1 is the molarity of the iodine solution

2.4.11 Solubility

To estimate the solubility of chitosan and its derivatives were mixed with different solvent to obtain different concentrations (0.1 gm/100cc, 0.5 gm/100cc and 1 gm/100cc), stirred for 3 h at room temperature and then filtered through a 0.45 μm filter paper. Solubility was estimated from the change of filter paper weight and was calculated as percent of soluble chitosan and its derivatives related to the total mass of original sample [Chung et al., 2006, Bobu et al., 2011]. Solubility was also tested at a specific concentration in different solvents such as ethanol, acetone, dilute acetic acid, dil HCl, CCl_4, DMF, DMSO etc.

2.4.12 Modification of jute and cotton fibres

Cellulosic jute and cotton fibres were modified with different modifiers (chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA- HTAChC) by keeping it at a material liquor ratio 1:50. The optimized condition was obtained after evaluating parameters (a) concentration of modifier (2, 5, 10, 20, 50, 100, 150 and 200 %), (b) temperature (30, 40, 45, 50, 55, 60, 70 and 80°C), (c) time (30, 60, 90 and 120 min). After that the fibre was dried at room temperature [Bhuiyan et al., 2013].

Weight gain percentage for all of the above modification were calculated according to the following formula [Mohanty et al., 1986; Misra et al., 1987; Triphathy et al., 1985; Islam et al., 2015].

$$\text{Grafting percentage (\%)} = \frac{A - B}{B} \times 100$$

Where, A is the weight of the modified fibres and B is the weight of washed fibres.

2.4.12.1 Modification of jute and cotton fibres with chitosan and CMCh-g-AA

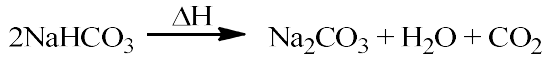
The washed jute and cotton fibres treatment was carried out with chitosan and CMCh-g-AA containing solution. First required percentage of chitosan and CMCh-g-AA solution were prepared by 2% acetic acid solution where the fibre liquor ratio was maintained at 1:50. The pH of the solution was maintained at 3.5-4 by using 0.2M acetic acid [Gerald and Witucki, 1993]. The treated fibre were washed with distilled water and subsequently dried in hot air at 60°C to be a constant weight.

2.4.12.2 Modification of jute and cotton fibres with NOCh, CMCh and HTAChC

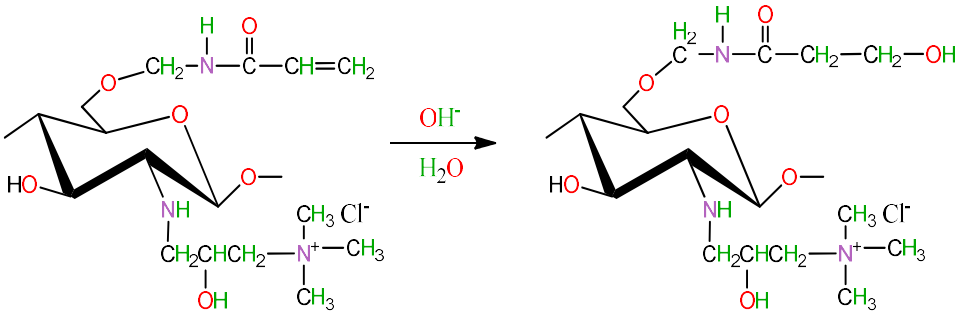
The liquor for modification of jute and cotton fibre was prepared by dissolving the modifier (NOCh, CMCh and HTAChC) and in distilled water while the liquor to fibre ratio was 1:50. The amount of modifier dissolved in the liquor was taken as a percentage on weight of fibre to be modified. $MgCl_2.6H_2O$ 0.6 mol equivalent to modifier was added to the liquor as catalyst along with Triton X-100 (0.1% of liquor) as a penetrating agent and Sodium lauyril sulfate (0.1% of liquor) as softening agent. The treated fibres were washed in distilled water to remove unfixed modifier. The fibre was dried at 60ºC to a constant weight.

2.4.12.3 Modification of jute and cotton fibres with NMA-HTAChC

The liquor for modification of jute and cotton fibre was prepared by dissolving the NMA-HTAChC and an alkaline catalyst in distilled water while the liquor to fibre ratio was 1:50. As an alkaline catalyst, sodium bicarbonate ($NaHCO_3$) was used because it is a latent alkaline catalyst [Gagliardi, 1951], which is a mild alkali at room temperature but is converted to Na_2CO_3 during the modification process as shown in **Sch. 2.22**. It is expected that the mild alkalinity of $NaHCO_3$ can minimize the hydrolysis of the NMA-HTAChC in a pad solution before application as shown in **Sch. 2.23**.



Scheme 2.22: Conversion of $NaHCO_3$ to Na_2CO_3 by heat.



Scheme 2.23: Alkaline hydrolysis of NMA-HTAChC

The amount of NMA-HTAChC dissolved in the liquor was taken as a percentage on weight of fibre to be modified. $MgCl_2.6H_2O$ 0.6 mol equivalent to NMA-HTAChC was added to the liquor as catalyst along with Triton X 100 (0.1% of liquor) as a penetrating agent and Sodium lauryl sulfate (0.1% of liquor) as softening agent. The treated fibres were washed with tap water until neutral to pH paper and further washed in distilled water to remove unfixed NMA-HTAChC. The fabric was dried at 60ºC to a constant weight.

2.5 Characterization of Modified Jute and Cotton Fibres

2.5.1 Swelling behavior study

Swelling behavior of the modified and washed fibres sample was determined by treating them with water, methanol, and carbon tetrachloride. Known initial weights W_i of the modified samples and washed sample were immersed in 100 ml of solvents at room temperature for 48 h. The samples were filtered and the excess solvent was removed with the help of filter paper and after that the final weight W_f was determined with the help of an electronic balance. The percent swelling was calculated from the increase in initial weight in the following manner [Singha and Thakur, 2009]:

$$\text{Percent swelling } (P_s) = \frac{(W_f - W_i)}{W_i} \times 100$$

2.5.2 Washing resistance

Modified cotton and jute fibres were washed with distilled water and detergent solution at different temperature. Concentration of detergent solution was 0.5% (w/v) and washing was carried out at room temperature, 40ºC and 60ºC. Amount of modified

fibre taken was about 0.2 gm and fibre to solution ratio was 1:50. Modified dried fibres of known weight were dripped into water and detergent solution at different temperature for 30 min. After that, the fibres were rinsed with distilled water and dried thoroughly at 60ºC until constant weight is obtained. Then grafting percentage after washing were calculated and loss in grafting percentage were obtained. [Mohanty et al., 1986; Misra, 1987; Triphathy et al., 1985].

$$\text{Weight gain (\%)} = \frac{A - B}{B} \times 100$$

2.5.3 Moisture absorption

The moisture absorption study of the modified fibres as well as washed fibres was performed at a constant humidity level. The modified and washed fibres were placed in a humidity chamber at room temperature for 72 h for maintaining the saturation level. The percent moisture absorption was studied by a moisture analyzer as a function of weight gain and was calculated using the following formula [Singha and Thakur, 2009].

$$\text{\% Moisture absorption } (M_{abs}) = \frac{(W_f - W_i)}{W_i} \times 100$$

Where, W_f is the final weight of the sample taken out from the humidity chamber and W_i is the weight of the dried samples.

2.5.4 Chemical resistance

Chemical resistance of modified fibres were determined by bring them in contact of acid and alkali and loss in weight of the fibres was observed. For this purpose, 1 gm of the dried modified and raw cotton fibres of known weight were immersed in 100 ml of 0.1N HCl and 0.1N NaOH solution. Similarly, 1 gm of the dried modified and raw jute fibres of known weight were immersed in 50 ml of 0.1N HCl and 0.1N NaOH solution. Fibre samples were kept in the solution for 24 h. After that, the fibres were taken out and rinsed with distilled water which later dried at 60ºC until constant weight is obtained. The losses of weight and the percent chemical resistance (P_{cr}) were calculated as follows:

$$\text{Percent chemical resistance } (P_{cr}) = \frac{(W_t - W_i)}{W_i} \times 100$$

Where, W_t is the total weight of the fibre and W_i is the weight after certain interval.

2.5.5 Tensile strength test

The experiments were performed by using a "Portable Electronic Single Yarn Strength Tester-YG021J" Fanyuan Instrument (HF) co. Ltd, China, for quick and reliable tensile strength measurement. Jute and cotton fibres were cut into equal pieces of length 25 cm and the length of each specimen between the jaws of the machine was maintained 10 cm. Each specimen was taken and the breaking strength of it was measured. The breaking load was gradually increased after starting the machine and at the point the specimen was broken down. The machine was stopped at the point of break. The breaking load was shown on the scale of the tensile tester in N.

2.5.6 Fourier transform infrared (FTIR) spectroscopy

Fourier-transform infrared spectroscopy is a technique for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". The chemical bonds can be either organic or inorganic and it can give important information about the structure of organic molecule. It can be utilized to identify compounds and investigate sample composition as well as interaction/reaction between functional groups on the different components in polymer blends and composites [Pavia et al., 1979].

Fourier Transform Infrared Spectroscopy having the acronym of FTIR is one of the commonly used methods of infrared spectroscopy. Infrared spectroscopy has been an effective technique for materials analysis in the laboratory for over few decades. In Infrared Spectroscopy, IR radiation in different wavelength is released on to the sample where certain degree of radiation will be absorbed by the sample while the remains will transmit through. An infrared spectrum represents a fingerprint of a sample with absorption peaks. This will then form a spectrum showing the absorption and transmission of the sample molecule which correspond to the frequencies of vibrations between the bonds of the atoms which compile the material. The spectrum is unique for the material as it has the unique combination of atoms and no other compound can produce the same spectrum. Therefore, infrared spectroscopy can result in a positive qualitative analysis of every different kind of material. In addition, the size of the peaks in the spectrum directly indicates the density of material present [Griffiths and Hasseth, 2007; Nishikida et al., 1995].

Study of FTIR spectroscopic measurements was carried out in Central Science Laboratory, University of Rajshahi, Bangladesh. Model: Shimadju-8900, FTIR Spectrum, Kyoto, Japan. All the samples were dried at 105°C for 10 h and then powdered in a mortar. For FTIR, test samples were prepared by mixing and grinding a small amount of material with its 100 times dry and pure KBr (Mondal, 2013). Mixing and grinding were accomplished in a mortar by a pestle. The powdered mixture was then compressed in a metal holder under a pressure to produce a pellet. The pellet was then placed in the path of the infrared beam of wave number in the range of 400-4000 cm^{-1}. Then the sample pellet were analyzed in an attenuated total reflectance (ATR) detector over a 400-4000 cm^{-1} wave number range at a resolution of 4 cm^{-1}.

2.5.7 Scanning electron microscopy (SEM) analysis

The scanning electron microscope images the sample surface by scanning it with a high energy beam of electron in a raster scan pattern. The electrons interact with the atoms that make up the sample, producing signals that contain information about the samples surface topography, composition and other properties such as electrical conductivity. In SEM the nature of the sample determines the preparation of the sample, since appropriate samples may be examined directly with little or no prior preparation. Unfortunately, most polymers present specific problems making them inappropriate. Therefore, proper sample preparation is necessary prior to characterization and these include, Plasma etching, Conductive coating through evaporation or sputtering and chemical etching method [Hunt and Jame, 1997].

Scanning electron microscopic (SEM) studies of raw and chitosan modified jute fibres were carried out on an Electron Microscopy Machine (FEI Quanta Inspect, Model: S50). Since these materials are non-conducting, they were gold plated. Scanning was synchronized with a microscopic beam in order to maintain the small size over a large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three-dimensional appearance with high resolution was obtained.

2.5.8 Thermogravimetric analysis (TGA, DTA and DTG)

The thermogravimetric analysis (TGA) is a special branch of thermal analysis, which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Not all thermal events bring

about a change in the mass of the sample (for example, melting, crystallization and glass transition) however there are some very important exceptions, which include absorption, sublimation, vaporization, oxidation, reduction and decomposition. The TGA is used to characterize the decomposition and thermo stability of materials under a variety of conditions, and to examine the kinetics of the physic-chemical process occurring in the sample. Sample weight changes are measured **[**Serkan, 2007].

Differential Thermal Analysis (DTA) is an important tool to study the structural and phase changes occurring both in solid and in liquid materials during heat treatment. The principle of DTA consists of measuring heat changes associated with the physical or chemical changes occurring when any substance is gradually heated. The thermo couple (Platinum-Platinum Rhodium 13%) for DTA is incorporated at the end of each of the balance beam ceramic tubes and the temperature difference between the holder in the sample and the holder on the references side is detected. The signal is amplified and becomes the temperature difference signal used to measure the thermal change of the sample [Serkan, 2007].

The experiments were performed using a Perkin Elmer stimulanteous thermal analyzer, STA 8000). The tests were conducted between 30-800°C under an inert atmosphere (Nitrogen). The heating rate and the air flow rate were 20°C/min and 200 ml/min respectively.

2.5.9 X-ray diffraction (XRD)

X-ray spectroscopy is unarguably the most versatile and widely used means of characterizing materials of all forms [Guo, 2009]. There are two general types of structural information that can be studied by X-ray spectroscopy: electronic structure (focused on valence and core electrons, which control the chemical and physical properties, among others) and geometric structure (which gives information about the locations of all or a set of atoms in a molecule at an atomic resolution).

2.5.10 Typical conditions of X-ray measurements

X-ray diffraction (XRD) patterns of chitin, chitosan and CMCh were recorded using Bruker D8 Advanced Germany, X-ray Diffractometer that generated Cu-Kα radiation. Powdered samples were exposed to X-ray beam at the operating voltage and current of

40 Kv and 30 mA respectively. Data were collected at a scan rate 2˚/min with the scan angle from 2 to 40˚ [Ming et al., 2009].

Clark and Smith (1937) were the first scientists to make crystal of chitin and chitosan using X-ray diffraction (XRD). They carried out those investigations using a commercial copper-target diffraction tube operated at 30 kV and 25 mA as the X-ray sources, which generated principally Cu-Kα lines. The diffraction patterns were recorded on a flat film perpendicular to the beam with the sample 5.0 cm from the film.

Apart from traditional X-ray diffraction (XRD), other X-ray techniques for determining chitin/chitosan and their derivatives have been applied: X-ray photoelectron spectroscopy (XPS), the second most popular X-ray spectroscopy technique for determining the bonding energies of C, O and N atoms on the surface of chitosan and its metal chelate, and for other chitin and chitosan investigations [Dambies et al., 2001; Gunzler and Gremlich, 2002; Minke and Blackwell, 1978]. X-ray emission spectroscopy (XES) perfect for studying the chemical bonding in chitosan and cross-linked chitosan derivatives [Smith, 1996].

2.5.11 ^{1}H NMR

Dilute solutions (5–7 mg cm^{-3}) of chitosan in a deuterated aqueous acid DCl/D_2O, at about pH 4 and, NOCh and CMCh in D_2O were prepared. 0.05 gm - 0.07 gm sample was weighted in plastic tube. Then the samples were twice freeze-dried using D_2O (99.9%) to exchange labile protons by deuterium atoms. Spectra between 0-6 ppm were recorded using a ^{1}H NMR spectrometer Bruker Avance II (700 MHz) at the temperature 300°K and at a resonance frequency of 400 MHz.

2.6 Method of Dyeing of Cellulosic Fibres

Dyestuffs were dissolved with little distilled water and after that adding cold distilled water. The dye baths were prepared by taking required amount of dye and electrolyte (NaCl). The fibre liquor ratio was maintained at 1:50. Before immersing the fibre in the dye bath it was modified well in distilled water and squeezed for even absorption of dye particles. Dyeing was started at 30°C in a thermostat control water bath, the temperature was slowly increased with occasional stirring to 60°C within about 30 min and continued for 60 min and then allowed for further 30 min as the bath cools down.

During dyeing the dye baths were slightly alkalified with 2.0% sodium carbonate solution for dye fixation and also boiled distilled water was added to the dye baths in order to maintain the fibre liquor ratio of 1:50. After dyeing the fibres were squeezed over dye baths so that not a single drop of exhausted dye liquor was lost and later rinsed with cold distilled water and dried at room temperature. The rinsed water was added to exhausted dye bath [Mathews, 1920; Hasler and Palacia, 1987, Islam et al., 2015]. To calculate the quantities of dye and assistant from stock solution the following formula was used [Charles, Hugh Giles, 1974]:

$$\text{No. of ml. of stock solution required} = \frac{W \times P}{C}$$

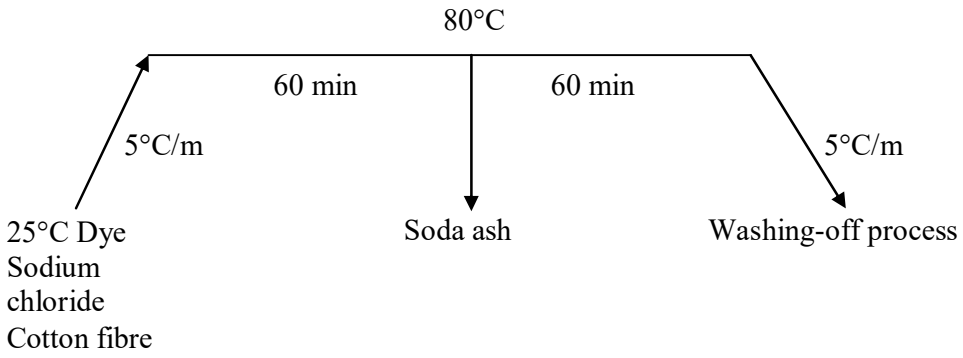
Where, W= Weight (in gm) of the fibre sample to be modified or dyed, P= Percentage of monomer, initiator, catalyst, dye or dye assistant to be used (Expressed on the basis of the weight of fibre) and C= Concentration of stock solution.

2.6.1 Method of dyeing of cellulosic fibre with reactive and direct dyes

Two reactive dyes, e.g. Reactive Orange 14 and Reactive Brown 10 and two direct dyes, e.g. Direct Orange 31 and Direct Yellow 29 were chosen for the dyeing of modified and unmodified cellulosic fibres. Dyestuffs were dissolved by first pasting with little distilled water and then, by adding cold distilled water. The dye baths were prepared by taking (50 gm/L) NaCl as an electrolyte solution on the basis of the weight of fibre. The fibre liquor ration was maintained at 1:50. All dyeing were carried out using 0.5% prepared dye (on the weight of fibre) in a dyeing machine (DYSIN partner in Bangladesh, Rapid, Taiwan, China). During dyeing 0.5 gm of bleached cellulosic fibre were immersed in the dye pot. Before immersing the fibre in the dye bath it was treated well in distilled water and squeezed for even absorption of dye particles. Exhaustion was done at 80^{o}C for 120 min.

Dyeing was started at 30°C in a thermostat control water bath, the temperature was slowly increased with occasional stirring to 80°C within about 30 min. After 1 h, the pot was taken out and then Na_2CO_3 solution (20 gm/L) was added on the basis of the weight of fibre to attain the fast reaction. The fixation of dye was continued for further 60 min, then allowed for further 30 min as the bath cools down to normal temperature. After dyeing, the fibres were squeezed over dye baths so that not a single drop of

exhausted dye liquor was lost, rinsed with cold distilled water and dried at room temperature. The rinsed water was added to exhausted dye bath [Mathews, 1947; Hasler and Palacin, 1987].



Scheme 2.24: Dyeing sequence of cellulosic fibres with different dyes

2.6.2 Preparation of calibration curves

Several standard solutions (0.0001, 0.0003, 0.0005, 0.0007, 0.0009 gm per 50 ml) of a dye were prepared and optical densities were measured with the aid of Spectrophotometer (Type-S104, No-221, Spectrophotometer, and WPA Linton Cambridge, UK) at the selected wavelength. The calibration curves were constructed by plotting the optical densities against dye content gm per 50 ml of the liquor for basic. From these calibration curves unknown concentrations were determined by taking the optical densities of diluted exhausted baths left after dyeing cotton fibre.

2.6.3 Determination of the amount of residual dye in the exhausted baths

The exhausted liquor in the reserved dye bath was adjusted to 30.0 ml or multiples to 30.0 ml to have the optical density in the exhausted liquors within the range of spectrophotometer. The amount of dye corresponding to these optical densities was read off from the calibration curve of the respective dye content of the exhausted liquor [Hasler and Palacin, 1987]. The difference between the dye content in the bath before and after dyeing gave the amount of dye absorbed by each gm of jute fibre, and hence exhaustion of baths in course of dyeing was determined.

$$\text{Exhaustion of dye, \%} = \frac{(D_0 - D_e)}{D_0} \times 100$$

Where, D_0 is the original dye bath concentration

D_e is the exhausted dye bath concentration

2.7 Fastness Test of Dyed Cellulosic Fibres

2.7.1 Colour fastness to washing

Colour fastness to washing means ability of a specimen of the dyed textile fibre to withhold its colour when subjected to washing that means mechanically agitated under specified conditions of time and temperature in a soap solution following rinsing and drying. The change in colour of the specimen and the dyed fibre are assessed with the grey scales. A bath was prepared with 5.0 gm of Jet (Detergent) in one liter of distilled water. The fibre liquor ratio was 1:50. One gram of dyed jute fibre which was 10 cm of length was entered in the bath and the bath temperature was maintained at 40 ± 2°C for 30 min. The bath solution was kept under agitation. After treatment the fibre was washed thoroughly with distilled water and dried in air at room temperature. The changing colour and the staining of the fibre were assessed with the Grey scale [ISO, 1978]. Similarly wash fastness was assessed at 40, 60, 80, and 100°C.

2.7.2 Colour fastness to spotting: Water

Dyed washed and modified fibres were combed and compressed enough to form a sheet 10 cm × 4 cm. The specimens were spotted with two drops of distilled water. Then the specimens were dried by hanging them in air at room temperature. The changes in colour of the specimens were assessed after drying with Grey scale [Shore, 1995].

2.7.3 Colour fastness to spotting: Acid

Dyed washed and modified fibres were combed and compressed enough to form a sheet 10 cm × 4 cm. The specimens were spotted with two drops of sulfuric acid solution containing 50 gm of sulfuric acid (relative density 1.84) per litre at room temperature. The specimens were dried by hanging them in air at room temperature.

The changes in colour of the specimens were assessed after drying with Grey scale [Shore 1995]. In the same way the change in colour was assessed by the solution given bellow.

I. Acetic acid solution containing 300 gm of glacial acetic acid per litre.
II. Tartaric acid solution containing 100 gm of crystalline tartaric acid per litre.
III. Hydrochloric acid solution containing 50 gm of hydrochloric acid per litre.
IV. Sulfuric acid solution containing 50 gm of sulfuric acid per litre.

2.7.4 Colour fastness to spotting: Alkali

Dyed unmodified and modified fibres were combed and compressed enough to form a sheet 10 cm × 4 cm. The specimens were spotted with two drops of sodium hydroxide solution containing 50 gm of anhydrous sodium hydroxide per litre at room temperature. The surface of the specimen was gently rubbed with the glass rod to ensure penetration. The specimens were dried by hanging them in air at room temperature and were brushed to remove sodium hydroxide residues. The change in colour was assessed after drying with Gray scale [Shore, 1995].

In the same way the change in colour of the specimens was assessed by the solutions given below:

I. Sodium Hydroxide containing 40 gm Sodium Hydroxide per litre.

II. Ammonia solution containing 10% of ammonia.

III. Sodium carbonate solution containing 100 gm anhydrous sodium carbonate per liter.

IV. Ammonium carbonate solution containing100 gm ammonium carbonate per liter.

2.7.5 Colour fastness on exposure to sunlight

Light fastness test was carried out on both the dyed and undyed bleached and modified jute and cotton fibres. The sample was exposed directly on a flat board under sunlight without any protection from weathering, but was protected from rain. At the same time and in the same place bleached and grafted fibres were exposed under the sun for 7 h in each day and continued for 250.0 h. After every 50.0 h the changes in colour of the specimens were assessed by the Grey scale with respect to control [Sayeed et al., 1987].

Chapter 3
RESULTS AND DISCUSSION

3.1 Potentiality of the Processes

The synthesis of chitosan and its functional derivatives such as, N-octyl chitosan (NOCh), Carboxymethyl chitosan (CMCh), Carboxymethyl chitosan grafted acrylic acid (CMCh-g-AA), N-(2-Hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (NMA-HTAChC) from prawn shell wastes was carried out according to the flow diagram as given in the previous chapter. The potentiality of the processes is the re-use of methanol and ethanol after washing of crude NOCh and Na-CMCh. The effect of solvent system, concentration of monomer, alkali concentration for basification, concentration of monochloroacetic acid for etherification, concentration of modifier, pH, time and temperature of the reactions for the synthesis of chitosan and its derivatives, degree of substitution (DS) and degree of querternization were studied. Some of the reactions were optimized with respect to the DS, grafting percentage etc. by varying each of the parameters.

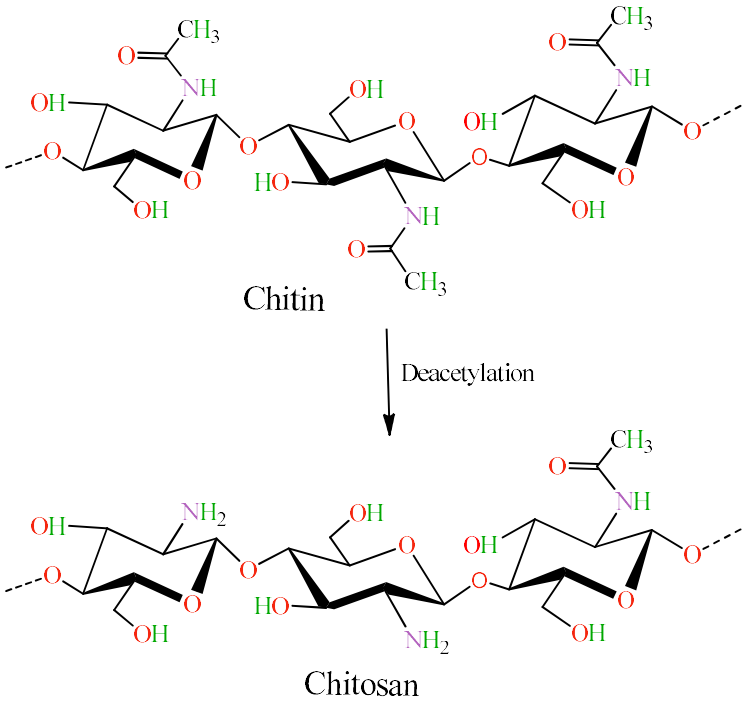
3.2 Preparation of Chitosan

Chitin is widely available from a variety of sources among which prawn shell is an important source. Generally, the prawn shell consists of protein, calcium carbonate and calcium phosphate and chitin [Knorr, 1984]. Prawn shell waste is closely associated with chitin, protein, lipid, pigment and different calcium deposits. In processing of prawn waste to chitin and conversion of chitin to chitosan involved three main steps, such as deproteinization to remove proteins, demineralization to remove calcium carbonate and calcium phosphate and deacetylation to convert acetyl groups to amino groups for chitosan. During the demineralization period, excessive undesirable foams were produced due to break down of calcium salts and generation of CO_2 gas, and, in deproteinization colour of the filtrate were brick red due to formation of sodamide. The

following reactions were took place during the preparation of chitosan from prawn shell waste.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 (\uparrow) + H_2O$$

$$Ca(PO_4)_2 + 6HCl = 3CaCl_2 + 2\ H_3PO_4$$



Scheme 3.1: Deacetylation of chitin

3.3 Solubility

Solubility of the prepared chitosan and its functional derivatives were tested in different solvents such as water, dilute acetic acid and hydrochloric acid, acetone, ethanol, DMF (Dimethylformamide), DMSO (Dimethyl Sulphoxide), THF (Tetrahydrofuran) etc. The results were shown in the **Table 3.1**. It is commonly thought that the main physical differences between chitin, chitosan and its functional derivatives is the ability to be soluble in distilled water, organic or inorganic acid such as acetic acid and hydrochloric acid and some organic solvents. Chitosan with a higher content of protonated amino groups are able to form a well-ordered arrangement in Vander Waals force and hydrogen bond which exceed its tendency for intramolecular chemical bonds [Zhang et al., 2012]. This explains its solubility in acidic chemical and partial solubility in

hydrogen containing solvent. CMCh with DS less than 0.40 was insoluble. Above this value of DS, CMCh was increasingly soluble, as its hydro-affinity increased with the increase of DS [Varshney et al., 2006]. Among them CMCh-g-AA was only soluble in some organic or non-aqueous solvents such as acetone, DMF (Dimethylformamide), DMSO (Dimethyl Sulphoxide), THF (Tetrahydrofuran) etc. but insoluble in aqueous solvents such as water, ethanol etc. The prepared functional derivatives of chitosan are almost soluble in water due to having consequent Zwitter ionic or cationic tendency of the molecular parts.

Table 3.1: Solubility at different solvents

Name of compound	Water	Dil. CH_3COOH	Dil. HCl	Ethanol	Acetone	DMF	DMSO
Chitin	–	–	–	–	–	+	+
Chitosan	–	+	+	–	–	–	+
NOCh	+	+	+	+	–	+	+
CMCh	+	+	+	+	–	+	+
CMCh-g-AA	–	–	–	–	partial	+	+
HTAChC	+	+	+	+	–	+	+
NMA-HTAChC	+	+	+	+	–	+	+

To estimate the percent of solubility of chitosan and other functional derivatives were individually mixed with corresponding solvents such as chitosan in acetic acid, CMCh-g-AA in acetone and DMSO and other chitosan derivatives to obtain different concentrations (0.5 gm/L, 1 gm/L and 2 gm/L), left at room temperature for 2 h and then filtered through a filter paper. Solubility was estimated from the change in filter paper weight and was calculated as percent of soluble chitosan related to the total mass of chitosan [Chung et al., 2006]. The water solubility values of the chitin, chitosan and its functional derivatives are listed in **Table 3.2**.

Table 3.2: Solubility at different concentrations

Name of compound	Concentration, gm/100ml	Solubility, %
Chitin	0.1	98.90
	0.5	93.90
	1.0	92.10
Chitosan	0.1	99.45
	0.5	98.90
	1.0	97.10
NOCh	0.1	100
	0.5	98.90
	1.0	98.10
CMCh	0.1	100
	0.5	100
	1.0	100
CMCh-g-AA	0.1	89.90
	0.5	88.50
	1.0	87.10
HTAChC	0.1	99.99
	0.5	98.60
	1.0	97.10
NMA-HTAChC	0.1	99.90
	0.5	99.10
	1.0	97.30

3.4 Yield

The yield percent of chitin from dry prawn shell wastes treated with 1M NaOH and 1M HCl was 29.69% 25.62% and 24.12% on the first, second and third reaction steps, respectively, and obtained yields of chitosan from chitin were 15.29%, 11.26% and 9.80% on the first, second and third successive reaction steps. In general, the results were similar to those found by [Alimuniar et al., 1992]. It has been repeatedly reported that the yield was dependent on the source and size of shell powder and reaction condition and on the reaction steps. Percent yield decreases with respect to reaction step due to the removal of protein, pigment, lipids, inorganic salts and acetyl groups (-$COCH_3$)

present in chitin. Some carotenoid pigment remaining in the chitin powder caused a brown colour in the first step product and light brown in both the second and third step products, with little or no odor. For the first step, about 50% of the acetyl groups, with pigments and lipids, were removed by alkali treatment. On the second and third steps a trace amount of acetyl group was removed with no remaining pigments. The final product obtained is white and odorless [Brzeski et al., 1982]. The obtained yield percent of N-octyl chitosan synthesis from chitosan in three duplicate steps were 92.10%, 93.25% and 95.60% respectively by reductive amination with octanal [Bobu et al., 2011]. The percent yield of CMCh and CMCh-g-AA were calculated on the basis of weight of chitosan to get 275%, 281%, 285% and 300%, 289%, 296.11%, respectively, for carboxymethylation of chitosan [Rachtanapun and Suriyatem, 2009] and grafting on CMCh with acrylic acid due to successive attachment of sodium (Na^+) and carboxymethyl group (-CH_2-COOH) with chitosan and acrylic acid with CMCh. The percent yield of HTAChC and NMA- HTAChC were also determined three times: and obtained 113%, 109%, 101% and 101%, 103%, 97%, respectively, due to substitution of a H from the amino group of chitosan by GTMAC, which increases the weight of produced HTAChC, and substitution of a H from hydroxyl group of chitosan backbone of HTAChC by NMA, which increases the weight of produced NMA-HTAChC.

Table 3.3: Yield percentage (average) of chitosan and its derivatives

Name of compound	Yield percentage	Basis
Chitin	26.47%	On the weight of dried prawn shell
Chitosan	12.11%	On the weight of chitin
NOCh	93.65%	On the weight of chitosan
CMCh	280.33%	On the weight of chitosan
CMCh-g-AA	295.03%	On the weight of CMCh
HTAChC	107.66%	On the weight of chitosan
NMA-HTAChC	100.33%	On the weight of HTAChC

3.5 Degree of Deacetylation of Chitosan and Effect of Time

Degree of deacetylation is one of the important chemical characteristics which could influence the performance of chitosan and many of its applications [Li et al., 1992]. Moreover the degree of deacetylation which determines the content of free amino groups

in the polysaccharide can be employed to differentiate between chitin and chitosan. For instance, the degree of deacetylation of chitosan ranges from 56% to 99% with an average of 80%, depending on the crustacean species and the methods of preparation [No and Meyers, 1995]. The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin, leaving behind a complete amino group ($-NH_2$), and chitosan versatility depends mainly on these highly chemically-reactive amino groups. This makes the degree of deacetylation an important property in chitosan production, as it affects the physicochemical properties, hence determines its appropriate applications [Rout, 2001]. Deacetylation also affects the biodegradability and immunological activity [Tolaimate et al., 2000]. The degree of deacetylation depends mainly on source, reaction conditions such as temperature, alkaline concentration and reaction time and method of purification [Li et al., 1997]: it is therefore essential to characterize chitosan by determining its degree of deacetylation prior to its utilization. From **Fig. 3.1**, it is seen that the degree of deacetylation, maximized at 85%, at optimized conditions, is: temperature 80°C, 50% alkaline solution, solid to liquor ratio of 1:50 (w/v) for 4 h refluxing in presence of ethanol.

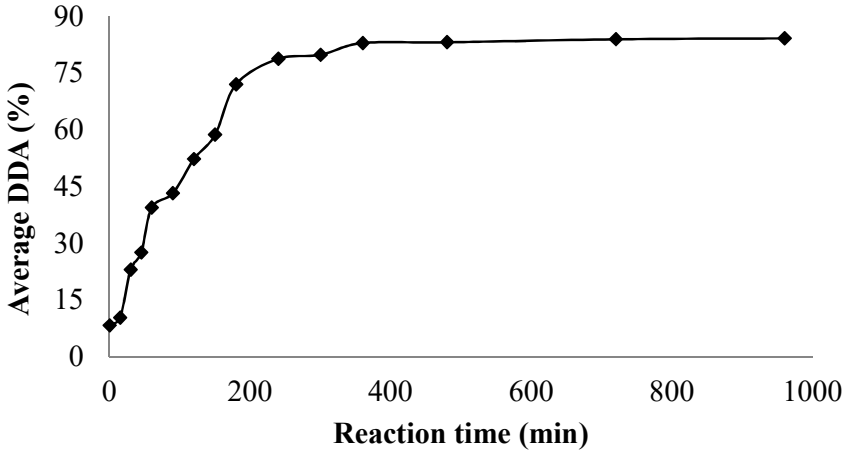


Figure 3.1: Effect of time on deacetylation percent

3.5.1 Moisture content of chitin, chitosan and its derivatives

The moisture content of prepared chitin, chitosan, N-octyl chitosan (NOCh), Carboxymethyl chitosan (CMCh), Carboxymethyl chitosan grafted acrylic acid

(CMCh-g-AA), N-(2-Hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (NMA-HTAChC) samples were observed by a moisture analyzer and the results presented in **Table 3.4**. The lowering of moisture content in the present study is due to the lack of homogeneity of the sample. The moisture content of chitin is 7.95% which is lower than the value (12.90% for mussel shell) reported by [Karim et al., 2013]. This may be due to the source of chitin and drying conditions. According to [Li et al., 1992] commercial chitosan products contain less than 5% moisture. The prepared chitosan samples had 9.79% moisture. Chitosan is hygroscopic in nature and its amine groups form hydrogen bond with water molecules [Khan et al., 2002], hence it can be affected by moisture absorption during storage. Moisture content of NOCh is 8.17% which is lower than chitosan and some other chitosan derivatives due to attachment of octyl group reductive amination, which is comparatively more hydrophobic in nature.

Moisture content of the high-solubility carboxymethyl chitosan is up to 13.76%. This value is higher than that of chitosan, which is 9.79%. The high moisture content suggests that carboxymethyl chitosan is hygroscopic and has stronger ability to bind with water. The high ability of moisture content is due to the formation of hydrogen bonds between carboxylic groups of CMCh with water molecules. Water content of the acrylic acid grafted carboxymethyl chitosan (CMCh-g-AA) is up to 6.83%. This value is less than the moisture content of the carboxymethyl chitosan (CMCh). The lower water content suggests that CMCh-g-AA is not as hygroscopic as CMCh. In addition, the water content also depends on the humidity level around the storage area of samples.

Moisture content of HTAChC and NMA-HTAChC were 18.43% and 17.71% respectively. Moisture absorption capacity of HTAChC is much higher than chitosan because of its high affinity to moisture (due to the presence of quaternary amino group and secondary alcoholic group). Moisture absorption capacity of NMA-HTAChC is

also higher than chitosan but slightly less than HTAChC because hydroxyl group of chitosan backbone of HTAChC is occupied by NMA in NMA-HTAChC.

Table 3.4: Moisture absorbance and ash content of chitosan and its derivatives

Name of compound	Moisture absorbance , %	Ash content, %	Molecular weight, Da
Chitin	7.95	5.23	--
Chitosan	9.79	1.34	1,39,958
NOCh	8.17	0.75	1,62,181
CMCh	13.76	14.87	2,06,179
CMCh-g-AA	6.83	8.39	3,10,270
HTAChC	18.43	0.84	2,13,205
NMA-HTAChC	17.71	0.79	2,17,113

3.5.2 Ash content of chitin, chitosan and its derivatives

Ash of the prawn shell waste chitin, chitosan, N-octyl chitosan (NOCh), Carboxymethyl chitosan (CMCh), Carboxymethyl chitosan grafted acrylic acid (CMCh-g-AA), N-(2-Hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (NMA-HTAChC) samples were calculated by according to the standard methods [AOAC, 1980] and also represented in the **Table 3.4**. Water and other volatile materials are vaporized and organic substances are burned in the presence of the oxygen in air to CO_2, H_2O and N_2. Most minerals are converted to oxides, sulfates, phosphates, chlorides or silicates. Although most minerals have low volatility at these high temperatures, some are volatile and may be partially lost, e.g., iron, lead and mercury. The average ash content of chitin and chitosan were 5.23% and 1.34% respectively. Chitosan has a low ash content as it is a polymeric compound having trace metal content. Ash measurement is an indicator of the effectiveness of the demineralization step for removal of calcium carbonate. The ash content in chitosan is an important parameter. Some residual ash of chitosans may affect their solubility, consequently contributing to low viscosity, or can affect other more important characteristics of the final product.

The results on high solubility carboxymethyl chitosan show the ash content of 14.87% which is greater than that of chitosan and is 0.84%. This values show that the mineral content of the synthetic carboxymethyl chitosan is higher than chitosan. The increased value of ash content in carboxymethyl chitosan may be due to the sodium salt formation of CMCh [Kurniasih et al., 2014]. Again, the acrylic acid grafted carboxymethyl chitosan (CMCh-g-AA) shows the ash content of 8.39% which is less than that of CMCh. This is due to the grafting of acrylic acid onto the CMCh which increases the overall mass of the polymer without increasing the mineral content. The average ash content of HTAChC and NMA-HTAChC were 0.84% and 0.79% respectively. HTAChC and NMA-HTAChC have lower ash content compared to chitosan because of addition of extra functional groups to chitosan backbone. HTAChC and NMA-HTAChC may affect their solubility, consequently contributing to low viscosity, or can affect some other important characteristics of the final product.

3.6 Molecular Weight

Molecular weight of polymer compound is one of the characteristic that indicate the magnitude of the degree of polymerization of that polymer. Viscosity of a polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. The intrinsic viscosity of a polymer solution is related to the polymer molecular weight according to the Mark–Houwink–Sakurada (MHS) equation [Flory, 1953]. Molecular weight of chitosan can be determined by different techniques. GPC is the most powerful technique for characterizing the molecular weight of polymers. However, it is a relative method and needs molecular weight standards for calibration to obtain the relation between elution volume and molecular weight. Viscosity techniques are very popular because they are experimentally simple. They are, however less accurate and the determined molecular weight, the viscosity average molecular weight, is less precise. Therefore, the measured molecular weight depends on the solvent used. Despite these drawbacks, viscosity techniques are very valuable [Zhang and Yang, 1986].

The physicochemical, biological and rheological properties of chitosan and its derivatives vary significantly as a function of its molecular weight and molecular weight distribution [Rodriguez et al., 2004]. More over molecular weight of polymer depends largely on the

raw materials and reaction variables. It is therefore important, and in some cases critical, to know precise and accurate values of the molecular weight. It is well known that the determination of the molecular weight of polyelectrolyte is complex. In the case of chitosan, this situation is exacerbated due to the marked tendency of this polymer to form resilient aggregates in solution. For the determination of viscosity average molecular weight (Dalton), chitosan was dissolved in a mixture of 0.1M acetic acid with 0.2M NaCl. Different concentrations of chitosan were prepared and then the Ostwald viscometer was used to measure the relative viscosity (η_{rel}) [Antonia, 1991] at room temperature. Then the specific viscosity (η_{sp}) and reduced were calculated. The flow time data was used to calculate the intrinsic viscosity by extrapolating the reduced viscosity to zero concentration. Intrinsic viscosity (η) was obtained from graph plotted reduced viscosity against concentration of the solution in gm/ml. The value of intrinsic viscosity was then recalculated into the viscosity-average molecular weight using Mark-Houwink equation. $[\eta] = (KM)^a$, Values for "K" and "a" where 1.8×10^{-3} and 0.93 respectively [No et al., 2003, Geprge and Julian, 1982]. So the obtained molecular weight of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC were 1,39,958.73 Da, 1,62,181 Da, 2,06,179 Da, 3,10,270 Da, 2,13,205 Da and 2,17,113 Da respectively.

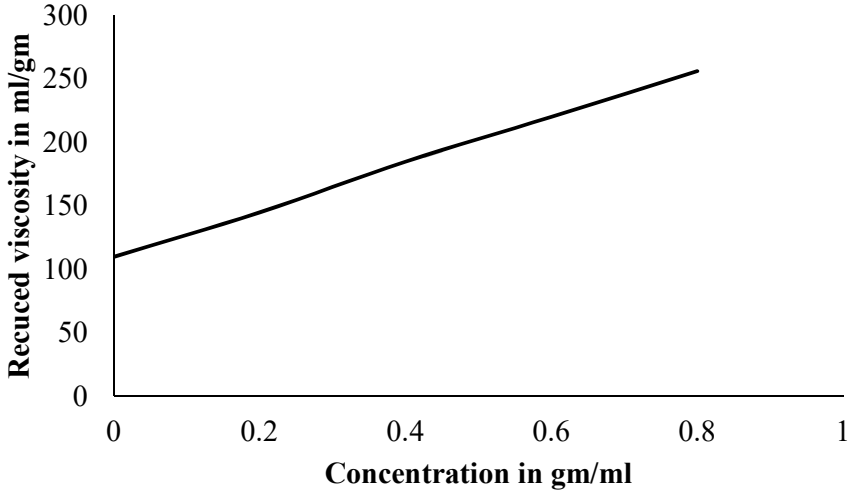


Figure 3.2: Reduced viscosity vs concentration graph of chitosan solution

The analysis shows that the molecular weight of high solubility carboxymethyl chitosan (206,179 Da) is higher than the molecular weight of chitosan (1,39,958 Da). This is due

to the addition of carboxymethyl group in Na salt form on chitosan backbone [Kurniasih et al., 2014].

Also, it was investigated that the molecular weight of acrylic acid grafted carboxymethyl chitosan (CMCh-g-AA) was around two times of CMCh. This high molecular weight is due to the high graft copolymerization reaction. The molecular weight of CMCh-g-AA is varied depending on the graft copolymerization reaction conditions.

3.7 Effect of NaOH Concentration on Yield of NOCh and CMCh

The chitosan powder from prawn shell was modified by reductive amination and carboxymethylation reaction using octanal and sodium cyanoborohydride and, monochloroacetic acid as an etherifying agent and activation with several amount of NaOH for NOCh and CMCh respectively. The percent yield of NOCh and CMCh synthesized with various NaOH concentrations (10, 20, 30, 40, 50 and 60%) were calculated and shown in **Fig. 3.3**. The result provided that increasing of NaOH concentrations affected to increase the percent yield of NOCh and CMCh. However, the percent yield of NOCh and CMCh slowly declined more than 30% and 40% NaOH concentration respectively. This observation could corroborate substitution of carboxymethyl group from carboxymethylation because of the higher molecular weight than hydroxyl group of carboxymethyl group [Rachtanapun and Suriyatem, 2009].

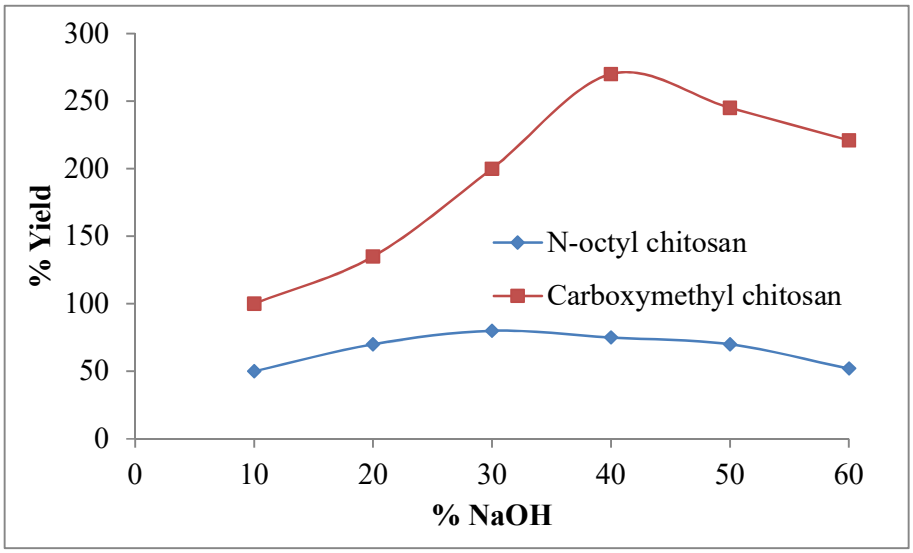


Figure 3.3: Percent yield of CMCh synthesized with various NaOH concentrations

3.8 Degree of Substitution (DS) of NOCh and CMCh

The DS of the prepared NOCh and CMCh were determined [Bobu et al., 2011, Barai et al., 1997; ASTM, 1961) and the DS data of each step are listed in **Table 3.5**

Table 3.5: Determination of DS in NOCh and CMCh prepared from chitosan at different steps

No. of reaction steps	N-octyl chitosan		Carboxymethyl chitosan	
	Degree of substitution	Yield percent	Degree of substitution	Yield percent
01	0.008	65.90	0.54	167.75
02	0.020	79.93	0.78	245.78
03	0.037	87.29	1.17	263.56
04	0.048	90.91	1.39	280.23
05	0.049	92.87	1.43	296.31
06	0.051	93.74	1.44	298.31

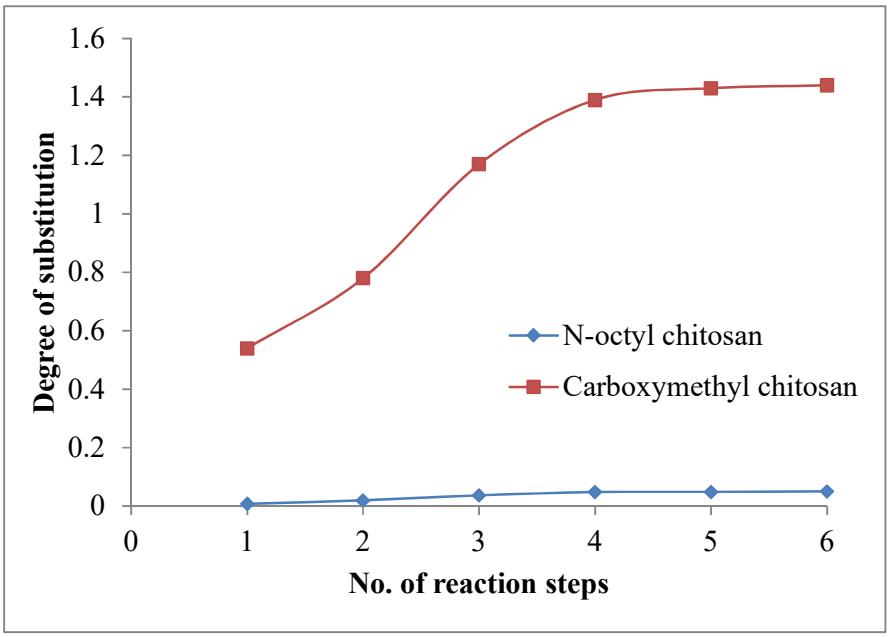


Figure 3.4: Effect of reaction steps on degree of substitution.

It can be seen from **Table 3.5** and **Fig. 3.4** that DS increased very fast at the initial step but after the 4th step, the increasing rate of DS is slow. The reason of this phenomenon was due to the fast substitution reaction for initial steps under alkaline conditions. The hydroxyl group of chitosan was very active and could be replaced by carboxymethyl group, which decreased the number of OH groups very fast up to saturation.

3.9 Effect of DS on Yield of NOCh and CMCh

The yield of NOCh and CMCh were increased gradually from initial step with the increase of DS. Complete reductive amination and carboxymethylation of chitosan i.e, theoretically possible highest degree of substitution of NOCh and CMCh are below 0.07 and 3, but practically that we were obtained maximum 0.051 and 1.44 respectively and which depends on reaction conditions (glucose-amine unit/aldehyde ratio, temperature, alkyl chain) and also supported by [Bobu et al., 2011, Yeasmin and Mondal, 2015]. That is why near the end of reaction steps; DS change was shown slowly down as well as yields of NOCh and CMCh. This might be occurred due to successive treatment with aldehyde and sodium cyanoborohydride formed chitosan imminium ion and, NaOH generated activated hydroxyl groups for substitutions. The carboxymethylation depends upon the accessibility of reagent and the availability of the activated groups. Increased substitution by successive treatment clearly showed activation of the secondary hydroxyl groups.

3.10 Degree of Quaternization of HTAChC

Degree of quaternization (DQ) is one of the important chemical characteristics which could influence the performance of HTAChC of its many applications. Moreover, the degree of quaternization which determines the substitution of GTMAC in amino groups in the polysaccharide of chitosan which is estimated by measuring the amount of Cl^- in HTAChC. The DQ of HTAChC was measured by conductometric titration of Cl^- with aqueous silver nitrate ($AgNO_3$) solution. Solution conductivities were monitored with a Benchtop Conductivity Meter (Model BC 3020). During the titration, the temperature of the solution was kept constant (25.4°C - 24.5ºC) by using a water bath because the conductivity is a function of temperature. The titration curve for the HTAChC is provided in **Fig. 3.5**. Before the inflection point, the curve has a negative slope, which corresponds to the decrease in conductivity due to the precipitation of AgCl.

The positive slope after the inflection point results from the excess $AgNO_3$. The amount of $AgNO_3$ used (6.5 ml) at the inflection point equals to the amount of Cl^- ions present on the HTAChC.

The DS of the derivatives can be calculated by the following equation:

$$\text{DQ of HTAChC} = \frac{M \times N_{Cl^-}}{m_{dry}}$$

Where, DQ is the degree of quaternization of HTAChC

M is the molecular weight (g/mol) of glucosamine repeat unit,

N_{Cl^-} is the number of moles of Cl^- ions in the samples, and

m_{dry} is the mass of dried sample in grams.

The value of DQ obtained was 0.94.

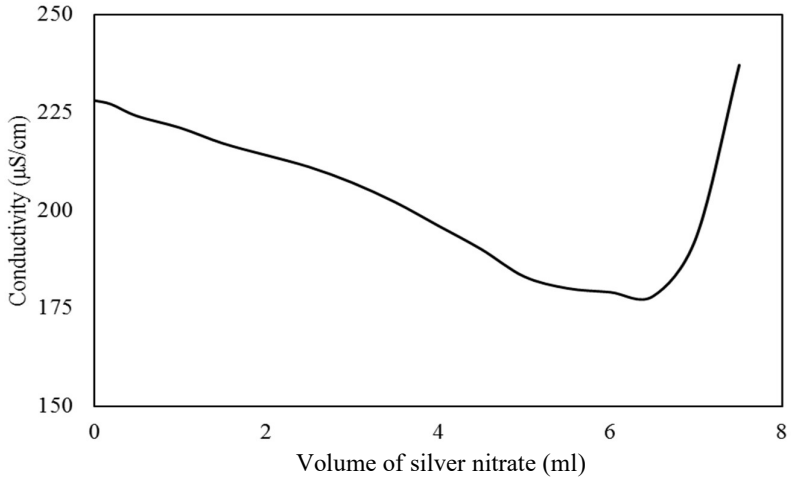


Figure 3.5: Conductometric titration curve for determination of DQ of HTAChC

3.11 Double Bond Content of NMA-HTAChC

One of the methods for determining double bonds adjacent to electron withdrawing groups is to react the compound containing double bonds with a thiol and then titrate the excess of unreacted thiol with iodine. It is known that aliphatic alcohols do not interfere with the results because the double bonds react much faster with thiols than alcohols. A known amount of NMA-HTAChC (0.3 gm) was dissolved in 10 ml deionized water contained in a reagent bottle at room temperature. To the solution, 5 ml of 3% previously prepared 2- mercaptoethanol aqueous solution and 1 ml of 2N NaOH were added and stirred in a closed reagent bottle at room temperature for 20 min to ensure the complete nucleophilic addition of mercaptoethanol to the double bond of NMA-HTAChC. The mixture was acidified with 2.5 ml 1N HCl solution to ensure acidic medium which favours the titration. After the addition of several drops of starch

indicator, it was titrated against a 0.1N iodine (I_2) solution until the endpoint at which the first faint blue colour that persisted for at least 30 sec. The endpoint corresponds to the complete oxidation of the remaining thiols and after that point excess iodine shows blue colour by interacting with starch indicator. A blank was run in an identical manner.

The double bond content was calculated using the following equation,

Double bond content (mmol/g NMA-HTAChC) = $\frac{(V_B - V_S) \times 0.1}{W}$

Where, *W* is the weight of sample in grams

V_B and V_S are the amount (ml) of iodine in blank and sample titration respectively

0.1 is the molarity of the iodine solution.

Here, *W*= 0.054 gm

V_B = 5.8 ml

V_S = 5.3 ml

Double bond content of NMA-HTAChC was calculated and that was 0.926 (mmol/gm NMA-HTAChC)

3.12 FTIR Spectroscopic Analysis of Chitin, Chitosan and Its Derivatives

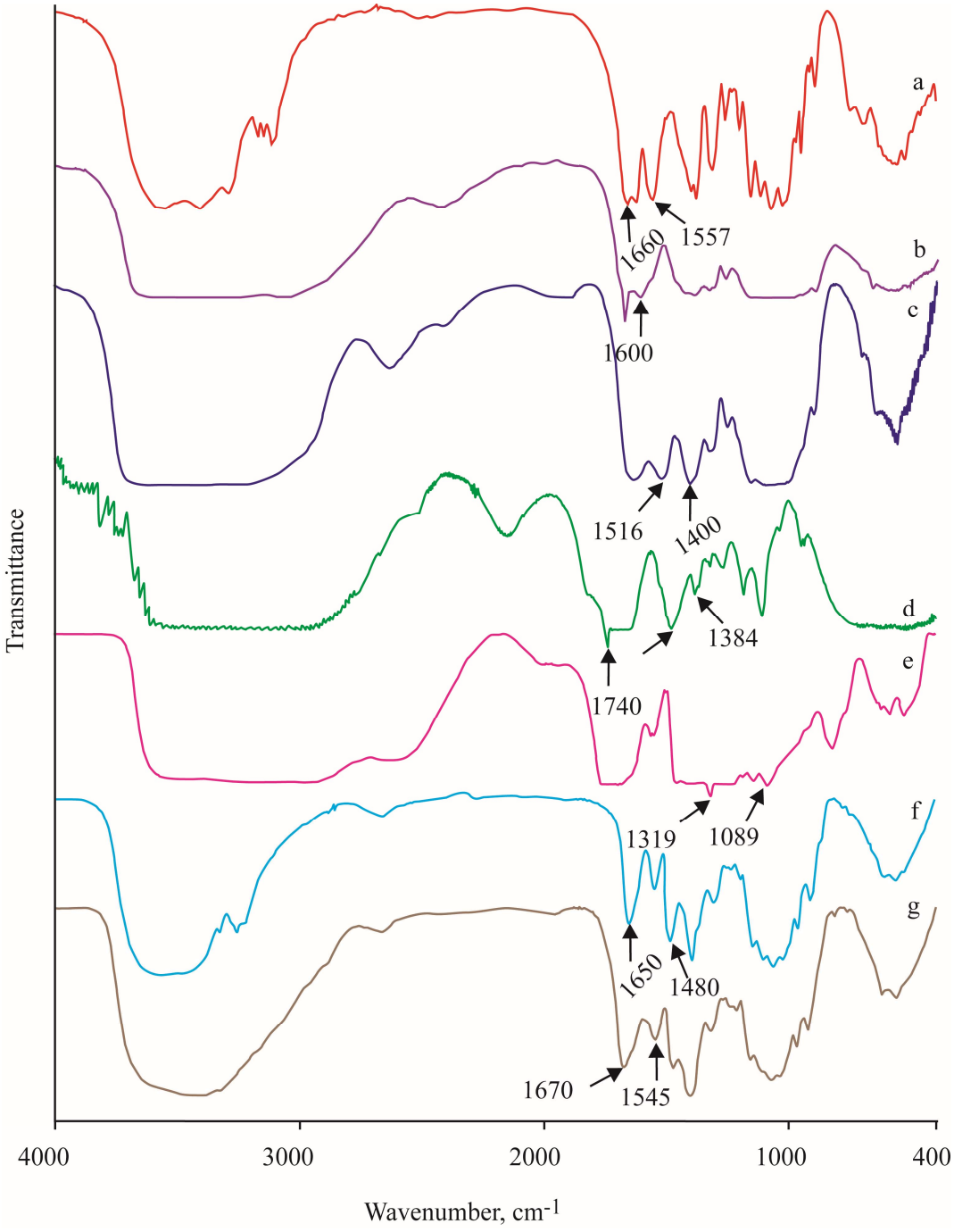


Figure 3.6: FTIR Spectra of prepared (a) Chitin, (b) Chitosan, (c) NOCh, (d) CMCh, (e) CMCh-g-AA, (f) HTAChC and (g) NMA-HTAChC

Infrared spectroscopy is one of the most important and widely used analytical techniques available to scientists working on chitosan and its derivatives. The growing interest in synthesis of various derivative of chitosan to improve its solubility and applications established that the most important application of infrared spectroscopy in this respect is the structural analysis of the chemically modified forms of chitosan. The structural changes of chitosan, N-octyl chitosan (NOCh), Carboxymethyl chitosan (CMCh), Carboxymethyl chitosan grafted acrylic acid (CMCh-g-AA), N-(2-Hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (NMA-HTAChC) samples were confirmed by FTIR. The IR spectra of chitin, chitosan and its functional derivatives are given in the **Fig. 3.6** which were obtained from prawn shell and shows the following functional groups:

Table 3.6: Assignment of major absorption bands of raw chitin, chitosan and chitosan derivatives

Name of compound	Wave numbers (cm^{-1})	Assignment
Chitin	3443.90	OH hydroxyl group
	3261.34	NH group-stretching vibration.
	2961.81,2933.51, 2891.39, 1380.09	Symmetric or asymmetric CH_2 stretching vibration
	1659.87	C=O in amide group (amide I band)
	1556.82	Vibration of N-H of amide I band
	1314.46	Vibrations of OH, CH in the ring
	1205.22,1261.71	C–O group.
	1157.02,1116.21, 1074.66	–C–O–C– in glycosidic linkage
	952.86, 896.28, 702.03	CH_3COH group
	561.80	OH out of plane bending
	3251.87	Vibration of N-H of amide II band
Chitosan	1651.04	NH-bending vibration in amide group.
	1600	N−H bending of the primary amine [Sundrarajan, et al., 2012].
	1382.97	-CH_2 bonding
	1068.02	–C–O–C– in glycosidic linkage

	587.28	OH out of plane bending
NOCh	1650	Amide-I
	1516	Asymmetric stretching of C-H in -CH_3 groups [Bobu, et al., 2011]
	1320	Amide-III
CMCh	3400-3200	O-H and N-H stretching vibration
	1741	–COOH (carboxyl) group (Mourya, et al., 2010)
	1384	carboxylate C=O
CMCh-g-AA	1319	poly (Acrylic Acid) [El-Sherbiny and Elmahdy, 2010]
	1089	polysaccharide
	1640	Vinyl group
HTAChC	3400	Increased number -OH hydroxyl group
	1660	C=O group [Lim and Hudson, 2004]
	1595	N−H bending
	1480	C-H bending of trimethylammonium group [Lim and Hudson, 2004]
NMA-HTAChC	1670	C=O stretch [Lim and Hudson, 2004]
	1590	N−H bending
	1545	N–H bending of the secondary amide in the acrylamidomethyl group [Lim and Hudson, 2004]

Chitin and chitosan can be differentiated by IR peak analysis. Chitin shows two strong absorption peaks in the range of 1659.87 cm^{-1} and 1556.82 cm^{-1} for C=O stretching and the N-H bending of the secondary amide respectively. Whereas, for chitosan shows a medium to strong peak in the range of 1650 cm^{-1} - 1580 cm^{-1} for the N−H bending of the primary amine [Stuart, 2004, Sabnis and Block, 1997]. **Fig. 3.6(b)** the spectra of the deacetylated chitosan showed a reduction of the peak at 1600 cm^{-1}, indicating that most of the secondary amide has been further changed to primary amine by the alkaline deacetylation.

The IR spectrum of CMCh [**Fig. 3.6(d)**] shows a strong new peak at 1384 cm^{-1} could be assigned to the symmetric stretching vibration of carboxylate C=O. The C-O absorption

peak of the secondary hydroxyl group becomes stronger and moves to 1089 cm^{-1}. This tends to indicate that the substitution occurs mainly at the C_6 position. The spectrum of CMCh shows also a peak at 1480 cm^{-1} which refers to the $–CH_2–COOH$ group. The broad peak in CMCh at 3400–3200 cm^{-1} is caused by both O-H and N–H stretching vibrations.

In case of IR spectrum of CMCh-g-AA [**Fig. 3.6(e)**] the peak appeared at 1319 cm^{-1} is characteristic of poly (AA). Also, in the IR spectra of the copolymer, the characteristic absorption peaks of polysaccharide at around 1089 cm^{-1}became weaker and that may be due to the high grafting percentage. The IR spectrum of CMCh-g-AA shows also the absence of clear absorption due to vinyl unsaturation around 1640 cm^{-1}. This tends to indicate the disappearance of the vinylic double bond of AA monomer due to grafting. Various studies in literature have reported that the initiation site in this type of free radical-induced graft copolymerization onto CMCh backbone is the primary amino group on C_2 position [Sherbiny, 2009; Sabaa et al., 2010].

The profiles of FTIR spectroscopy of HTAChC and NMA-HTAChC synthesized from chitosan were almost similar but have different characteristic peak which shows evidence of the conversion of chitosan to HTAChC and NMA-HTAChC. There were two absorption peaks at 1660 cm^{-1} and 1595 cm^{-1}, which correspond to the C=O stretch of the secondary amide and the N−H bending of the primary amine, respectively. Obvious changes of the FTIR spectra are observed after quaternization of chitosan with GTMAC.

In the IR spectrum of HTAChC, a characteristic peak at 1480 cm^{-1} indicates the C-H bending of trimethylammonium group which shows evidence of the quaternary ammonium salt group. It should be also noted that the N−H bending (1595 cm^{-1}) of the primary amine disappeared due to the change of the primary amine to the secondary aliphatic amine. [Pavia et al., 1996]. A new peak at 1650 cm^{-1} was assigned for the C=O stretch of the secondary amide, which was a shoulder of the N−H bending peak at 1590 cm^{-1} as shown in **Fig. 3.6(f)** In addition, the spectrum shows a broad band at around 3400 cm^{-1}, probably due to the increased number of hydroxyl groups.

The IR spectrum of the NMA-HTAChC, as shown in **Fig. 3.6(g)**, indicates the acrylamidomethylation occurred as the result of the peaks at 1670 and 1545 cm^{-1}. These peaks are most likely due to the C=O stretch and N–H bending of the secondary amide in the acrylamidomethyl group, respectively.

3.13 Thermogravimetric Analysis of Chitin, Chitosan and Its Derivatives

Table 3.7: Data obtained from TGA, DTG and DTA thermograms of chitin, chitosan and its derivatives

Samples	T_i (°C)	Char yield at 600°C (%)	DTG peak maxima temp. (°C)	DTA maxima (°C)	Nature of DTA peak	DTA peak range (°C)
Chitin	300	28	300	690	Exo.	660-700
Chitosan	280	21	310	675	Exo.	650-690
NOCh	100	14	210	600	Exo.	575-630
CMCh	90	63	330	575	Exo.	575-600
CMCh-g-AA	85	42	308	578	Exo.	570-615
HTAChC	110	16	250	650	Exo.	650-675
NMA-HTAChC	102	9	295	652	Exo.	650-680

Thermal behavior of chitin and chitosan were examined by the study of TGA, DTA and DTG thermogram. Thermogram of chitin and chitosan are represented in **Fig. 3.7** to **3.9**. Each of the figures represents three thermogram curves namely TGA, DTA and DTG.

TGA thermogram shows that decomposition paths for chitosan and its derivatives have three stages of thermal degradation. There was a weight loss in first stage between 100 - 120°C, due to dehydration of samples. In second stage between 80 - 300°C, rapid weight losses were observed for thermal degradation of the polymer backbone. In third stage, residual char is formed through weight loss which reaches to be a fixed weight. On the basis of initial decomposition temperature (T_i), the thermal stability of chitosan and its derivatives shows the following order: chitin > chitosan > HTAChC > NMA-HTAChC > NOCh > CMCh > CMCh-g-AA.

From DTA curve, a large exotherm peak was observed, due to oxidative decomposition of products, which involves formation of carboxyl and carbonyl groups as well as evolution of N_2, CO_x and NO_x and formation of carbonaceous residue [Muralidhara and Sreenivasan, 2010].

The DTG curve represents the decomposition rate at different temperature ranges. So, this clearly indicates that the amino polymer is less thermally stable than the N-acetyl one [Dahiya et al., 2008].

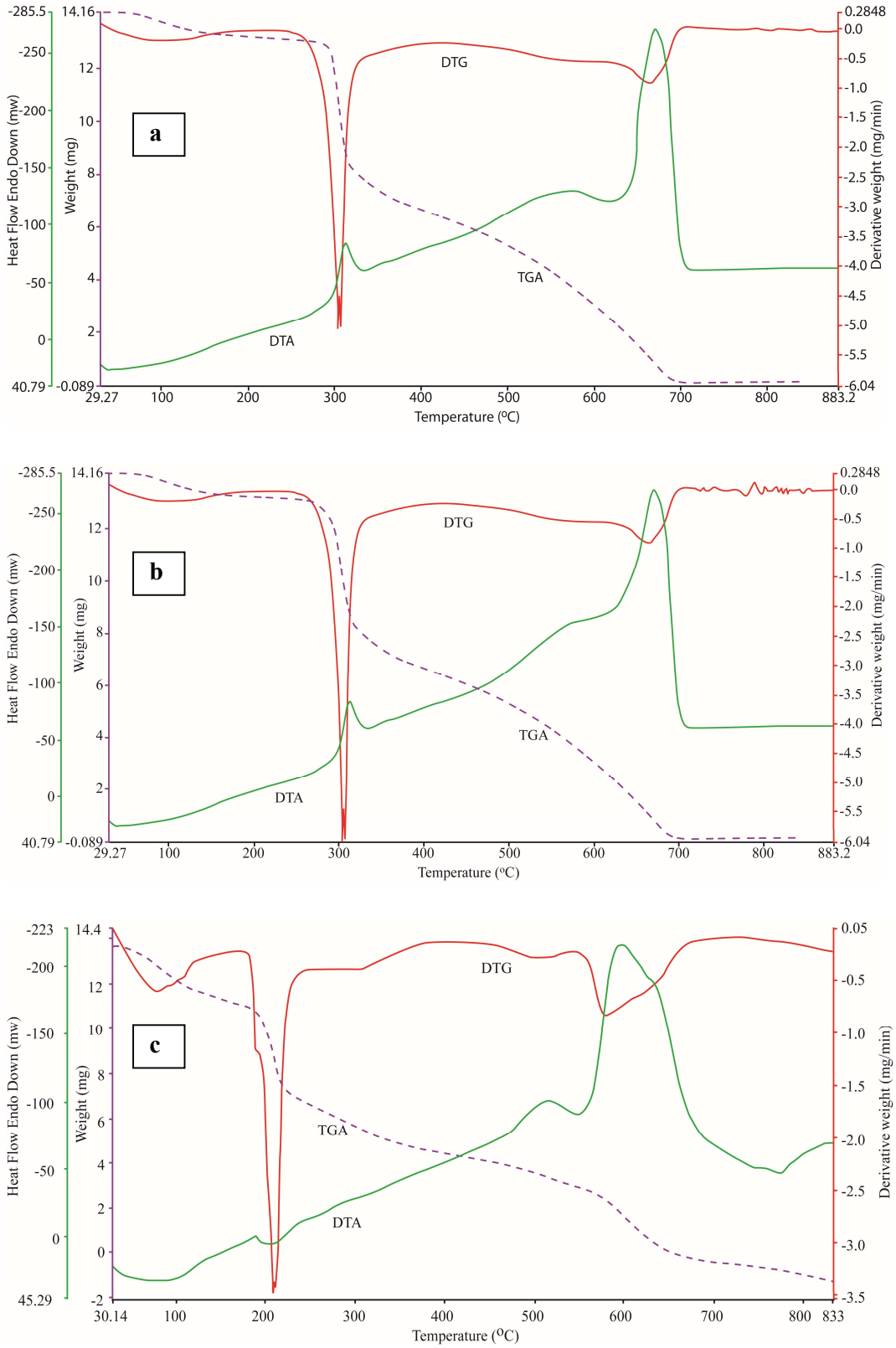


Figure 3.7: TGA, DTA and DTG curve of (a) Chitin, (b) Chitosan and (c) NOCh

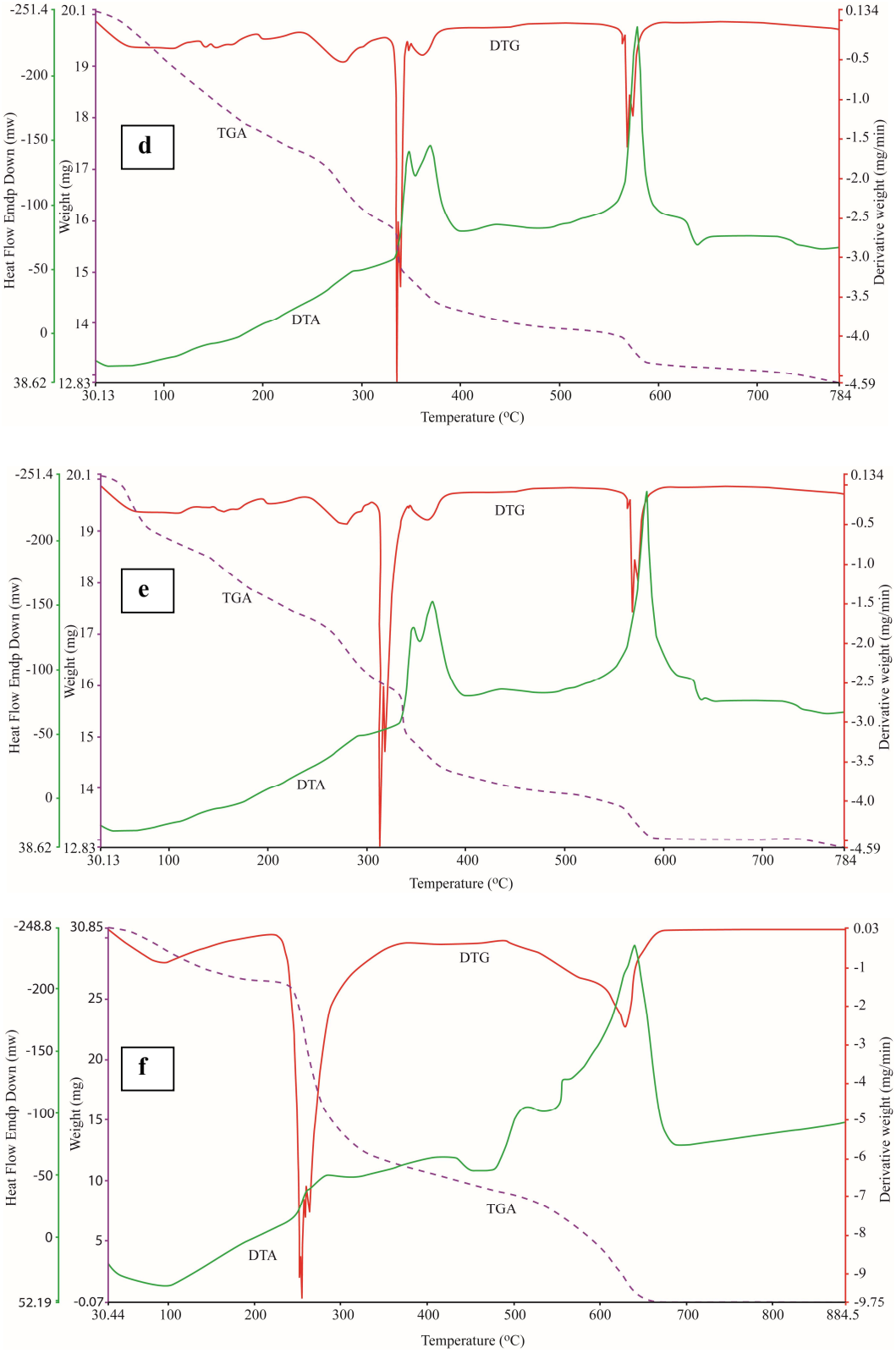


Figure 3.8: TGA, DTA and DTG curve of (d) CMCh, (e) CMCh-g-AA and (f) HTAChC

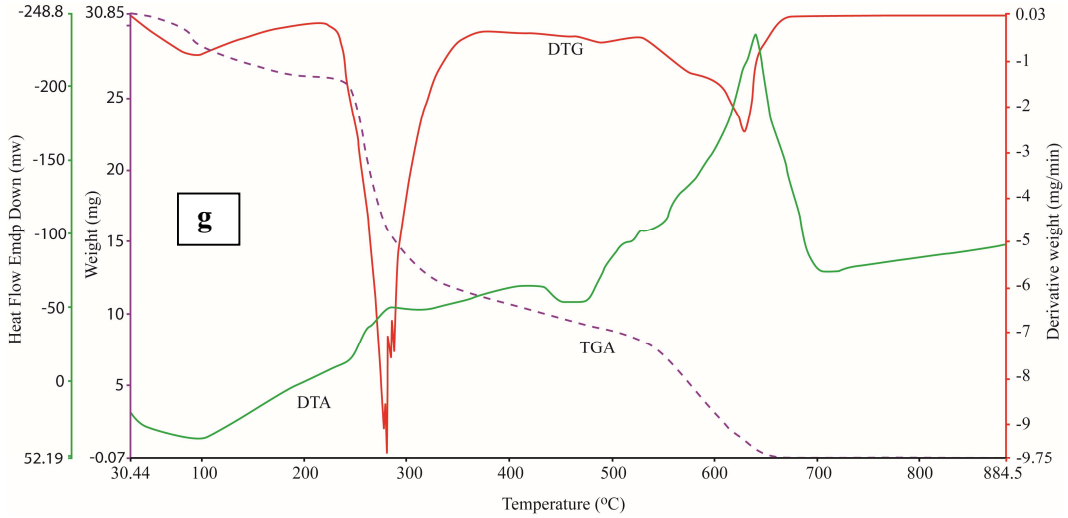


Figure 3.9: TGA, DTA and DTG curve of (g) NMA-HTAChC

3.14 X-ray Diffraction Analysis of Chitin, Chitosan and Its Derivatives

The degree of crystallinity for chitin, chitosan and its biopolymer derivatives was investigated through X-ray diffractometry. In an X-ray diffraction measurement, a crystal is mounted on a goniometre and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections [Dahiya et al., 2008]. The two-dimensional images taken at different rotations are converted into a three dimensional model of the density of electrons within the crystal.

XRD analysis was applied to detect the crystallinity of the extracted chitin, chitosan and its derivatives such as NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC. **Fig. 3.10 (a-g)** represents XRD pattern of chitin, chitosan and its prepared derivatives from prawn shell waste. The most intense peak height for the chitin sample was recorded at $2\theta = 20^{o}$ with a spacing of 4.25946 Å as shown in **Fig. 3.10(a)**. A gradually decrease in peak and increase in broadness is observed from chitosan to its prepared different derivatives in **Fig. 3.10(b-g)**. The broad peaks indicate lower crystallinity; this is to say that chitin is more crystalline than chitosan and its derivatives, which is similar to the observation reported in literature [Al Sagheer et al., 2009]. The crystallinity of chitin, chitosan and its derivatives follows the following order chitin > chitosan > NOCh > CMCh > CMCh-g-AA > HTAChC > NMA-HTAChC.

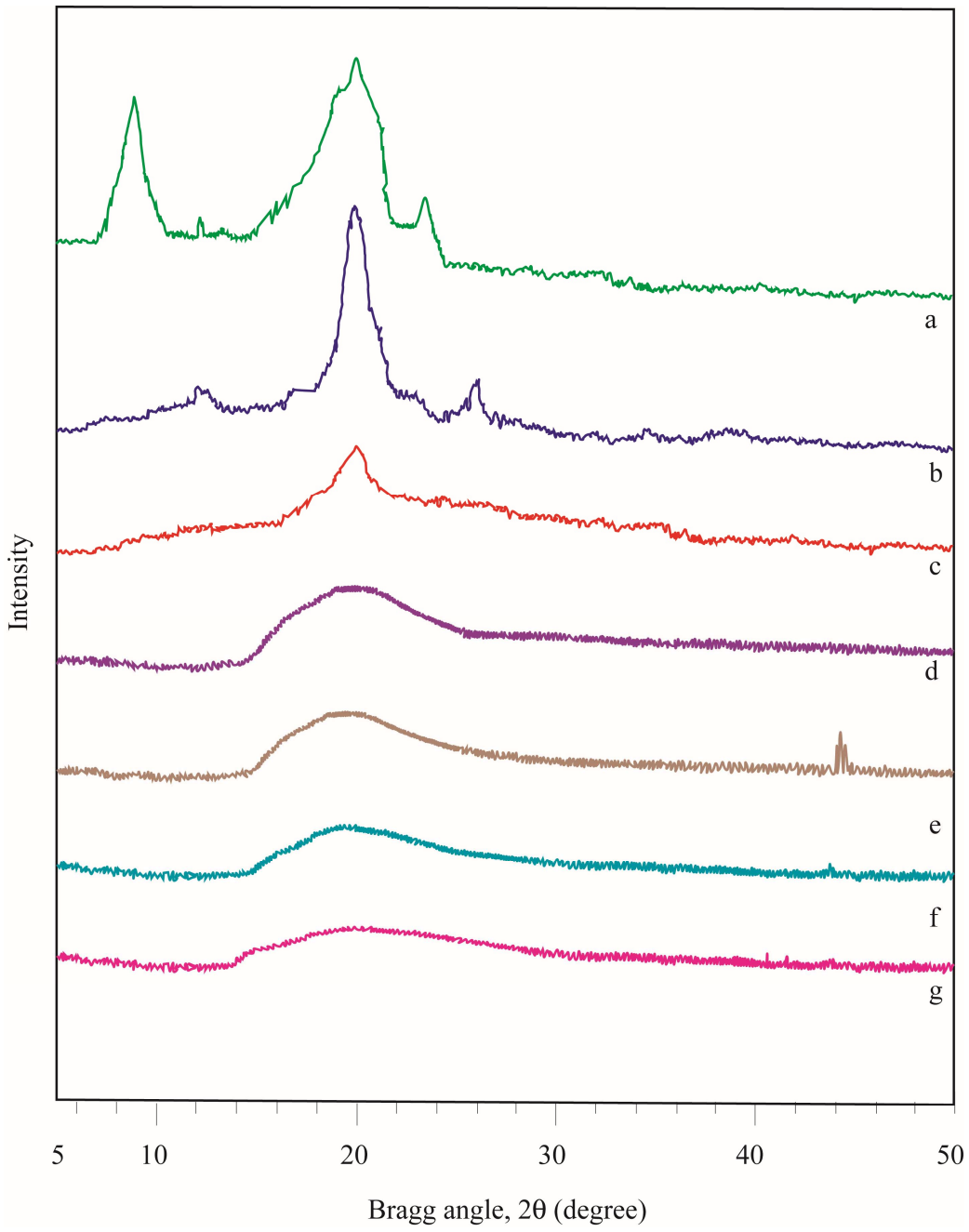


Figure 3.10: X-ray diffraction patterns of (a) Chitin, (b) Chitosan, (c) NOCh, (d) CMCh, (e) CMCh-g-AA, (f) HTAChC and (g) NMA-HTAChC

3.15 ^{1}H NMR Analysis of Chitin, Chitosan and Its Derivatives

The ^{1}H NMR spectra of chitosan and its derivatives NOCh, CMCh in D_2O, obtained by a Bruker Avance DRX 400 spectrometer, at a resonance frequency of 400 MHz, are shown in **Fig. 3.11** to **3.13**. The ^{1}H NMR spectra were performed at a temperature of 300°K. The ^{1}H NMR spectrum of chitosan presents a signal between 3.40 and 3.60 ppm, corresponding to the hydrogen bonded to the carbon atom C_2 of the glucosamine ring, while the signals between 4.10 and 4.40 ppm correspond to the hydrogen atoms bonded to carbons C_3, C_4, C_5 and C_6 of the glucopyranose units. The ^{1}H NMR spectrum of N- octyl chitosan displays broadening of the characteristic peaks and signals in the 1.7-2.0 ppm region, attributed to the protons of the methyl (-CH_3) and methylene (-CH_2-) groups grafted onto the chitosan chain, which evidences the chemical modifications resulting from the alkylation reaction. The broad multiple peaks from 1.1 to 1.3 ppm are attributed to the methylene hydrogens of the -CH_2- groups, while a typical peak at 0.7 ppm corresponds to the methyl protons at the terminal groups -CH_3, both belonging to the -C_8H_{17} aliphatic chain. [Bobu et al., 2011]

The ^{1}H NMR chemical shifts of signals of carboxymethyl chitosan is shown in **Fig. 3.13**. The resonance signal of the protons from NCH_2COOD groups can be found at 3.65 ppm which can be found at the ^{1}H NMR spectrum of carboxymethyl chitosan described by Muzzarelli et al., 1994.

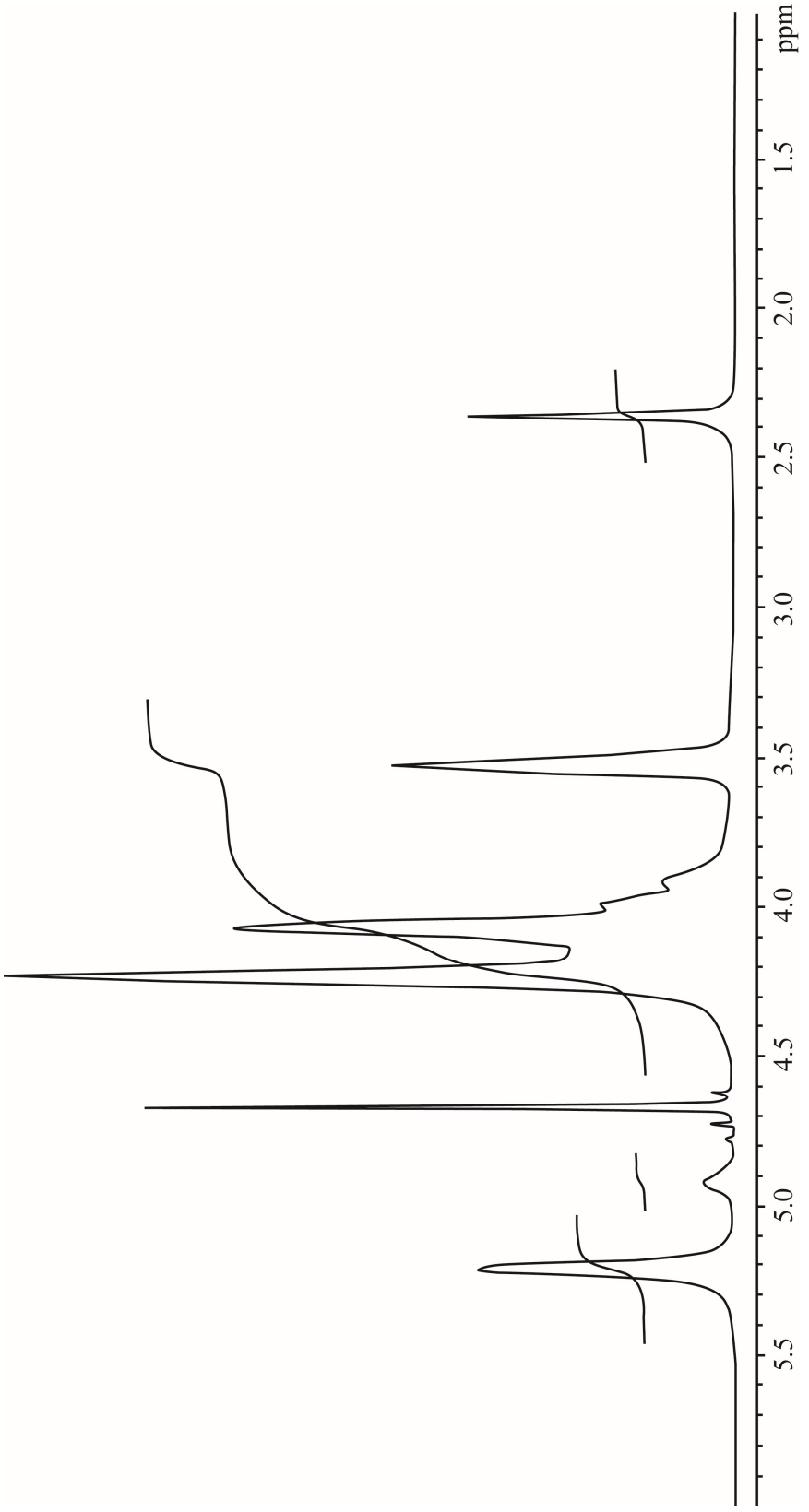


Figure 3.11: ^{1}H-NMR Spectra of Chitosan [Lavertu et al., 2003]

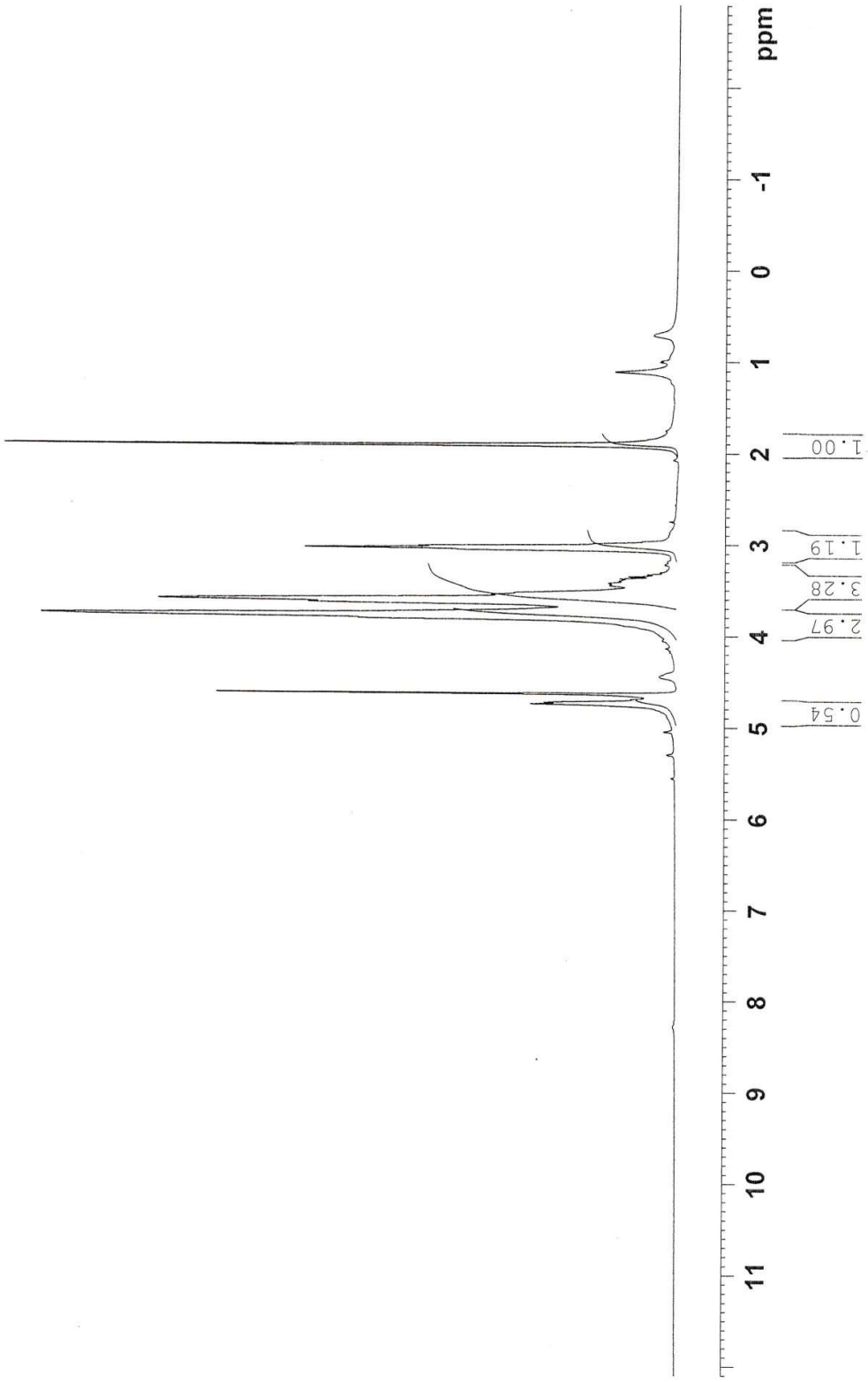


Figure 3.12: ^{1}H-NMR Spectra of NOCh

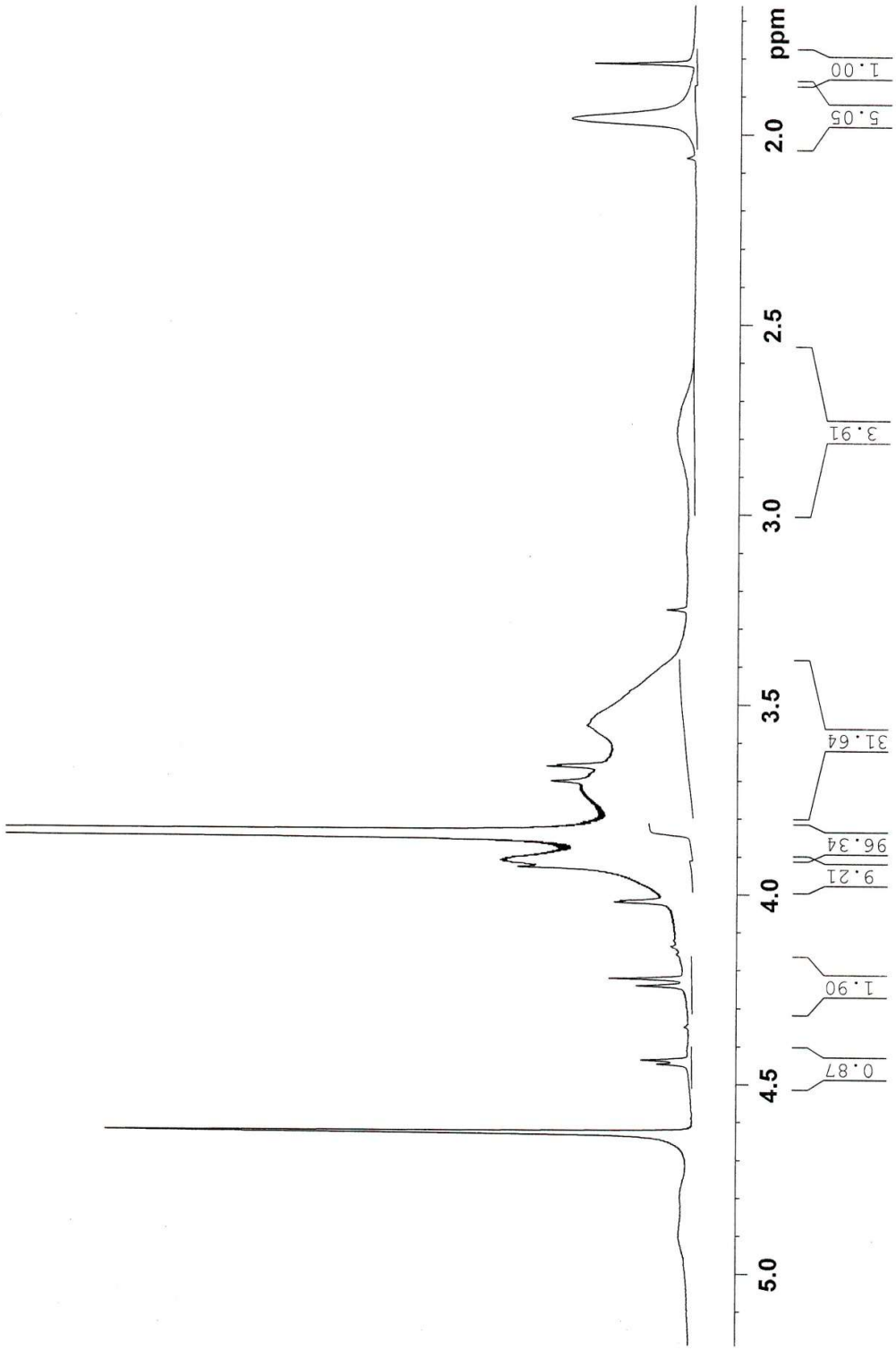


Figure 3.13: ^{1}H-NMR Spectra of CMCh

3.16 Modification of Jute and Cotton Fibres with Chitosan and Its Functional Derivatives

Fibre modification is a pioneer step for the development of textile sectors and which depends on processes and some parameters. Modification parameters such as modifier concentration, temperature and time play the significant effect on modification of jute and cotton fibres. In this study jute and cotton fibres were modified with prepared chitosan and its functional derivatives, especially NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC and were obtained optimum conditions.

3.16.1 Effect of modifier concentration

The weight gain percent that were obtained from the present investigation were represented as graft yield (%) from the **Fig. 3.14- 3.15** it can be seen that the weight gain percentage increases considerably with the increase of modifier (chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC) concentrations. This gradually increasing weight gain percentage was due to the absorption, adsorption and excess deposition of modifier on jute and cotton fibres at higher concentration. After a certain level of modifier concentration the grafting percentage was slightly varied with increase the modifier concentrations. It was found that 20% modifier concentration on the weight of fibres is sufficient to produce effective and efficient modification of jute and cotton fibres, but when the fibre was modified with more than 20% of modifiers solution caused flexibility reduction due to excess deposition of modifier and the fibres became crispy in nature. In case of highest modifiers concentrations grafting yield is highest but the increment of concentrations is not sequential with increment of grafting yield.

Grafting yield ranged from 6.12 to 14.74% and 10.75 to 18.86% for jute and cotton fibres respectively, that indicates the absorption capacity of cotton is higher than that of jute due to presence some noncellulosic matters in jute fibres. Again the modifier NOCh showed lowest and NMA-HTAChC showed highest grafting yield, due to lower affinity of NOCh to cellulosic backbone and presence of double bond on NMA-HTAChC side chain caused higher affinity to cellulosic fibres backbone. In case of CMCh grafting percent is comparatively higher due to presence of the –OH and –COONa groups that helps to create reacting side to react with fibres. The sequence of grafting is same for all the modifiers in case jute and cotton fibres.

Modification condition: Temperature: 55ºC, Time: 1 h, Fibre: Liquor = 1:50

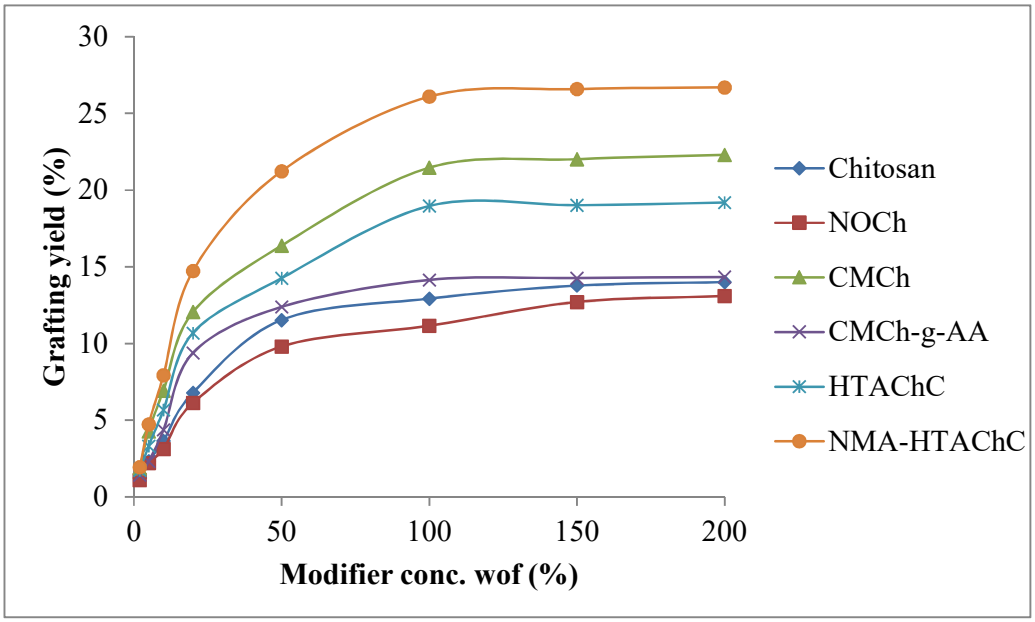


Figure 3.14: Effect of modifier concentration on grafting of jute fibres

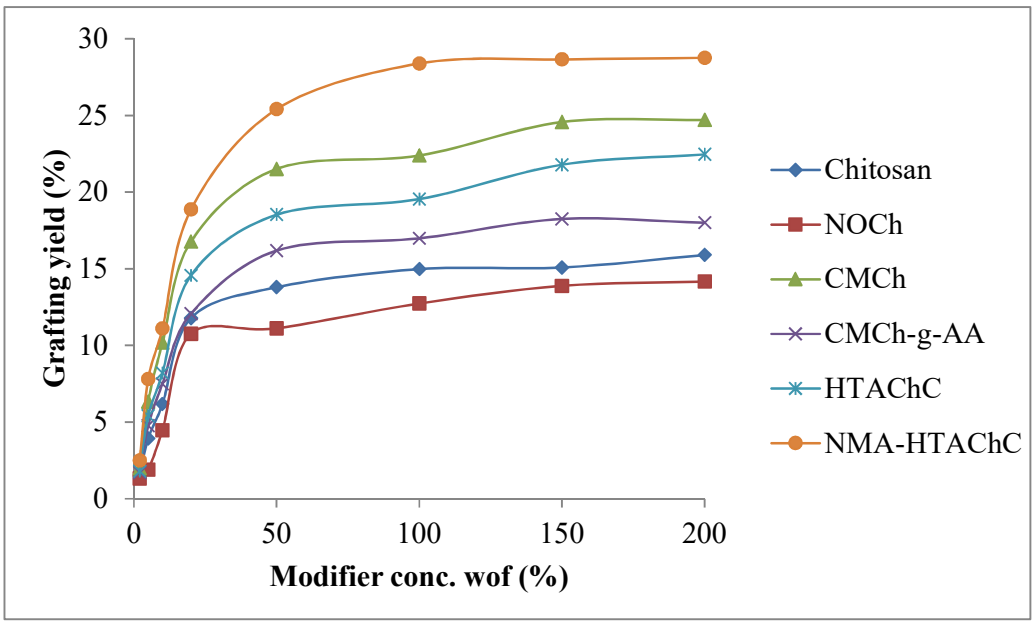


Figure 3.15: Effect of modifier concentration on grafting of cotton fibres

3.16.2 Effect of concentration on grafting efficiency of jute and cotton fibres

Grafting efficiency (%) of modified jute and cotton fibres with chitosan and its derivatives i. e NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC were obtained in this study depicted in the **Fig. 3.16-3.17** which indicates the effectiveness and economical aspect of the modification process for textile sectors. Grafting efficiency of chitosan and its functional derivatives on jute and cotton fibres is considerably affected by the modifier concentration.

From the figures, it is clear that the grafting efficiency is maximum when concentration of modifier is minimum as shown here 2% (on weight of fibre) that means almost all the dissolved modifier was exhausted from the solution by jute and cotton fibres. As concentration of modifier increased, grafting efficiency decrease considerably that means a certain amount of modifier remained in the solution after modification. Modification should be carried out in such a concentration in which grafting is sufficient and grafting efficiency is satisfactory. In this study optimum concentrations were found here is 20% of fibre weight.

The overall grafting efficiency among all the modifiers CMCh showed 67.69% and 70.01% and, NMA-HTAChC showed 68.70% and 72.00% for jute and cotton fibres respectively which are comperatively higher values than that of others may due to the higher affinity of CMCh and NMA-HTAChC to jute and cotton fibres backbone. In case of NOCh grafting efficiency showed 48.29% and 49.30% for jute and cotton fibres respectively and it is lowest due to presence of octyl side.

Experimental condition: Temperature: 55ºC, Time: 1 h, Fibre-Liquor ratio: 1:50

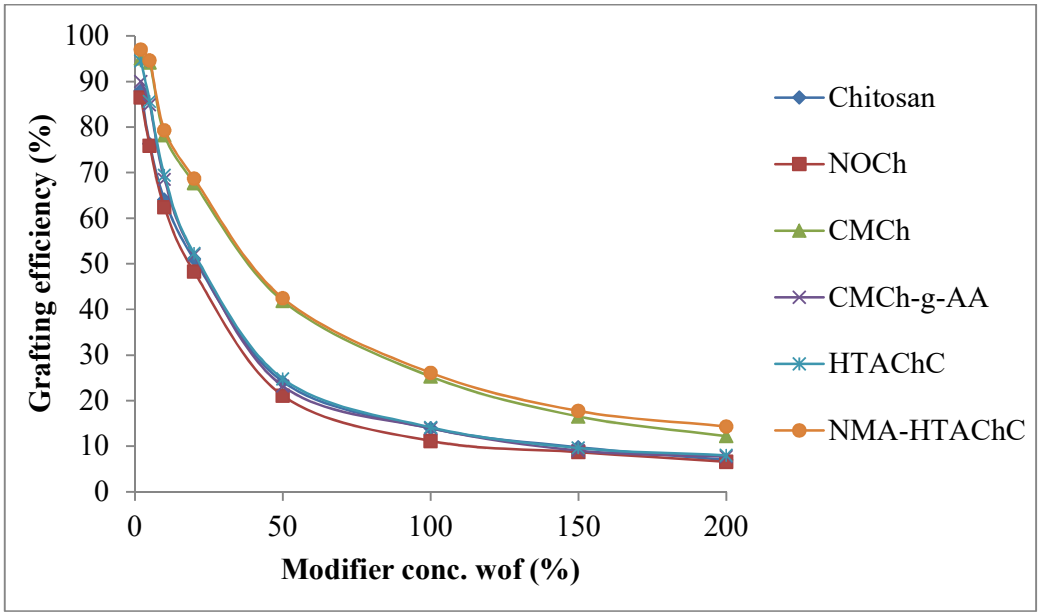


Figure 3.16: Effect of modifier concentration on grafting efficiency of jute fibres

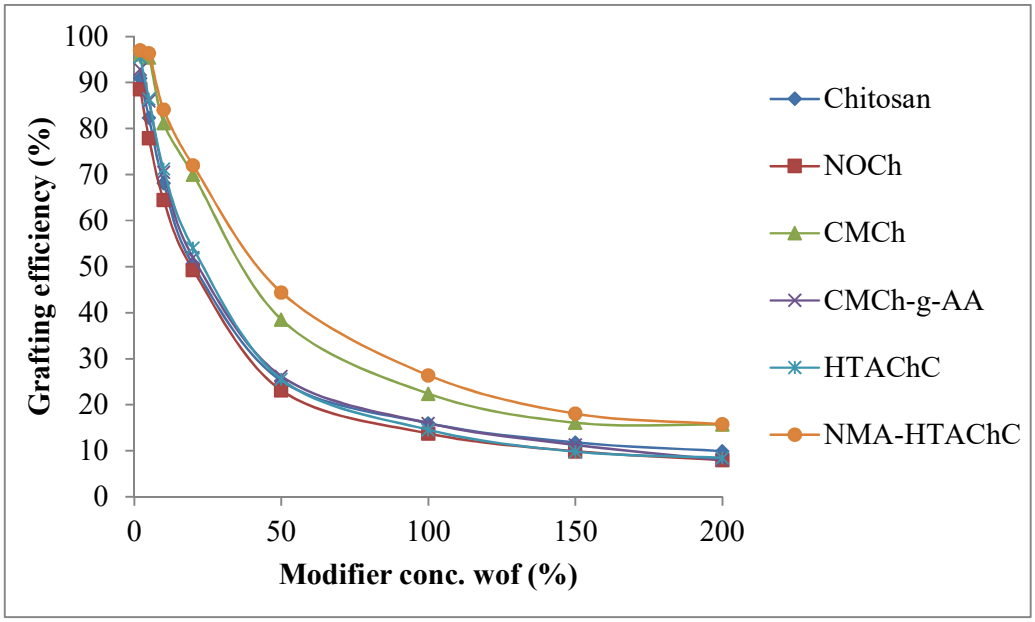


Figure 3.17: Effect of modifier concentration on grafting efficiency of cotton fibres

3.16.3 Effect of temperature on grafting of jute and cotton fibres

Grafting of jute and cotton fibres considerably depends on temperature at which the modification process was carried out. Grafting percentage obtained at different modification temperature and at a certain modifier concentration for jute and cotton fibres with chitosan and its derivatives i,e NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC has shown in **Fig. 3.18-3.19**. At a certain temperature, the grafting yield was maximum for a certain concentration of modifiers in the solution.

From the figures, it can be said that the modification of jute and cotton fibre with chitosan and its fibre reactive functional derivatives, at first the grafting percentage increases considerably with the increase of temperature. After a certain temperature, there is no increase of observable grafting yield, with the increase of temperature. The first issue is due to the increase of fibre pores diameter at higher temperature which allows more penetration of modifiers from solution to the cellulosic fibres and the second issue is due to the increase of solubility of modifiers with the increase of temperature in water which favors dissolution of modifiers rather than grafting with cellulosic fibres. The optimum temperature for chitosan and its derivatives was 55ºC. At higher temperature, cross linking occurs in between modifier and fibres, both of these are resulting to higher crispy in nature. If temperature was further increased then grafting percentages decrease because strength loss occurs due to rupture of normal fibres [Sundrarajan et al., 2012]. Among the prepared chitosan and its derivatives NMA-HTAChC showed highest grafting yield that was 14.74% and 18.86% and NOCh showed lowest that was 6.12% and 10.75% for jute and cotton fibres respectively at 55ºC due to maximum cellulose surface contact with NMA-HTAChC modifier and less contact of NOCh with fibre reactive sites.

Modification condition: Modifier concentration: 20% on the basis of weight of fibre, Time: 1 h, Fibre-Liquor ratio: 1:50

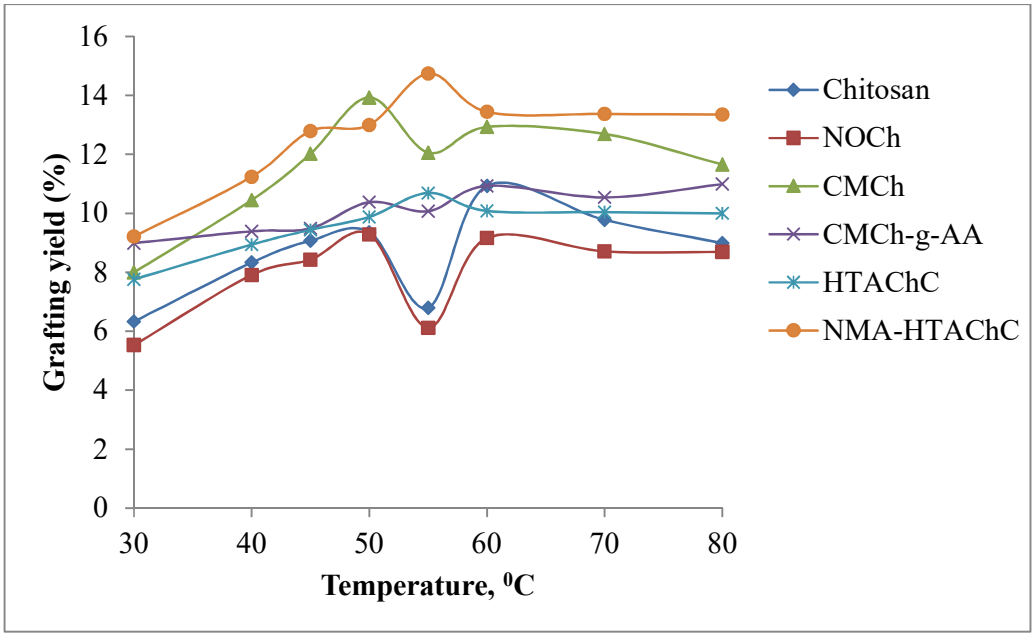


Figure 3.18: Effect of temperature on grafting yield of jute fibres

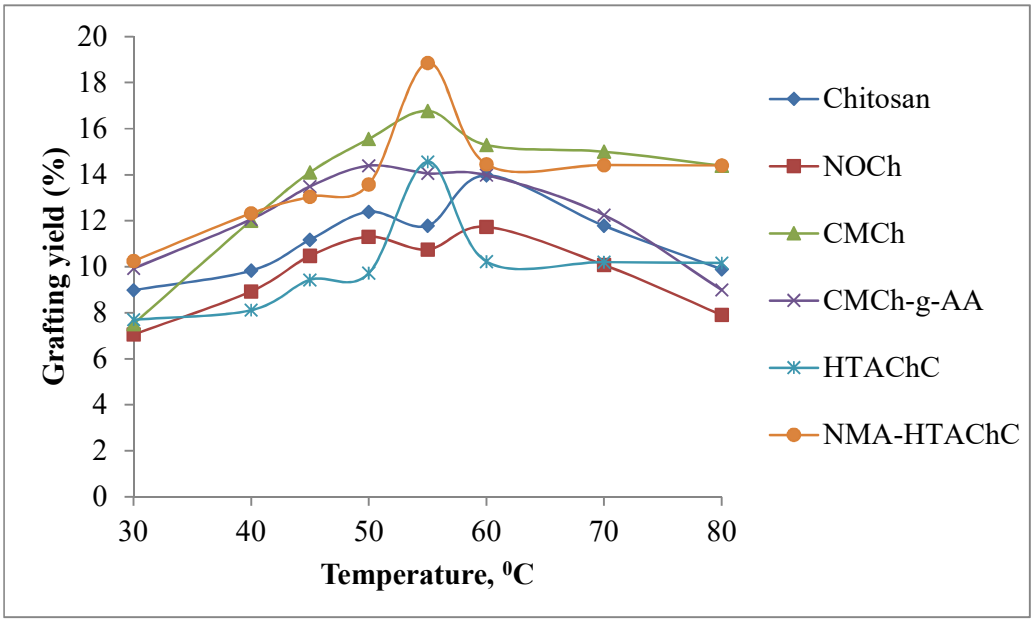


Figure 3.19: Effect of temperature on grafting yield of cotton fibres

3.16.4 Effect of temperature on grafting efficiency of cotton and jute fibres

Grafting efficiency of prepared chitosan and its derivatives i, e NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC at different temperature with a certain condition were measured through the modification of jute and cotton fibres and shown in **Fig. 3.20-3.21**. It's also a measure of effectiveness and economical aspect of the modification process. Modification temperature affects grafting efficiency considerably. From the figures it was observed that grafting efficiency increase as the temperature increases up to 55°C as microscopic pores of the fibre surface enlarge which allow the penetration of chitosan and its derivatives to the cellulosic fibres. After that, grafting efficiency tends to decrease because of increase in solubility of modifiers at higher temperature. Among the modifiers NMA-HTACC showed highest grafting efficiency, 66.96% and 72.68% for jute and cotton respectively, due to higher affinity towards cellulosic fibres compared to others at 55°C.

Modification condition: Modifier concentration: 20% on the basis of weight of fibre, Time: 1 h, Fibre-Liquor ratio: 1:50

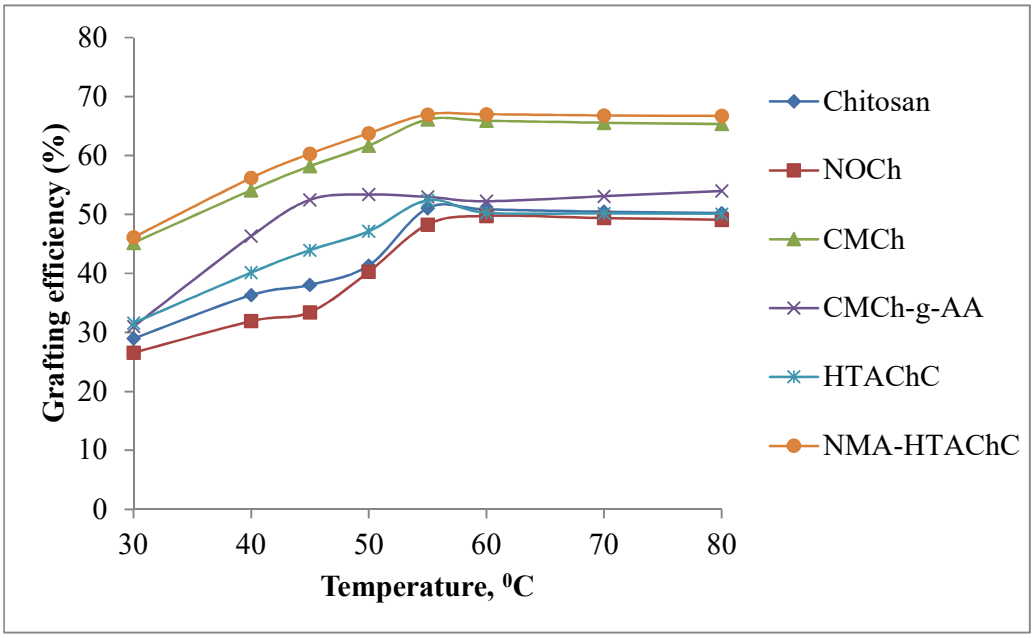


Figure 3.20: Effect of temperature on grafting efficiency of jute fibres

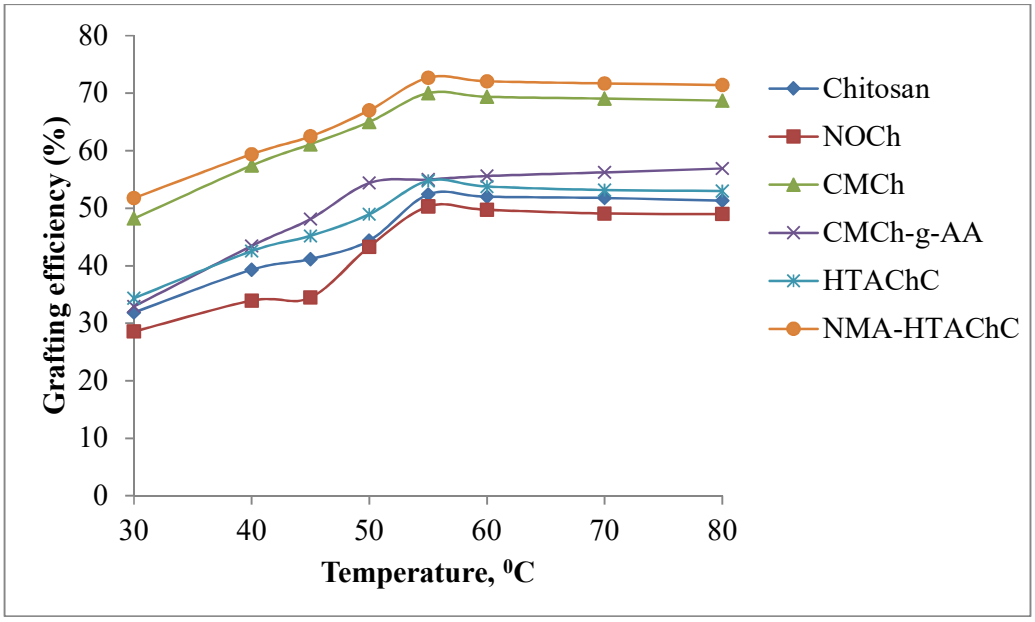


Figure 3.21: Effect of temperature on grafting efficiency of cotton fibres

3.16.5 Effect of time on grafting yield of cotton and jute fibres

Jute and cotton fibres were modified with synthesized chitosan and its functional derivatives i, e NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC at a certain concentration, temperature, and fibre-liquor rationon and obtained in this study depicted in the **Fig. 3.22-3.23**. It can be observed that graft yield increases with increasing the reaction time and leveled off after 1 h, reaching near about saturation value of grafting. The optimum modification time is 1 h and maximum graft yield for 1 h was 14.35% for jute and 18.90% for cotton fibres. If temperature and time were further increased then grafting percentages decrease because strength loss occurs due to rupture of normal fibres [Sundrarajan et al., 2012]

Modification Condition: Concentration: 20% on fibre weight, Temperature: 55ºC, Fibre: Liquor = 1:50

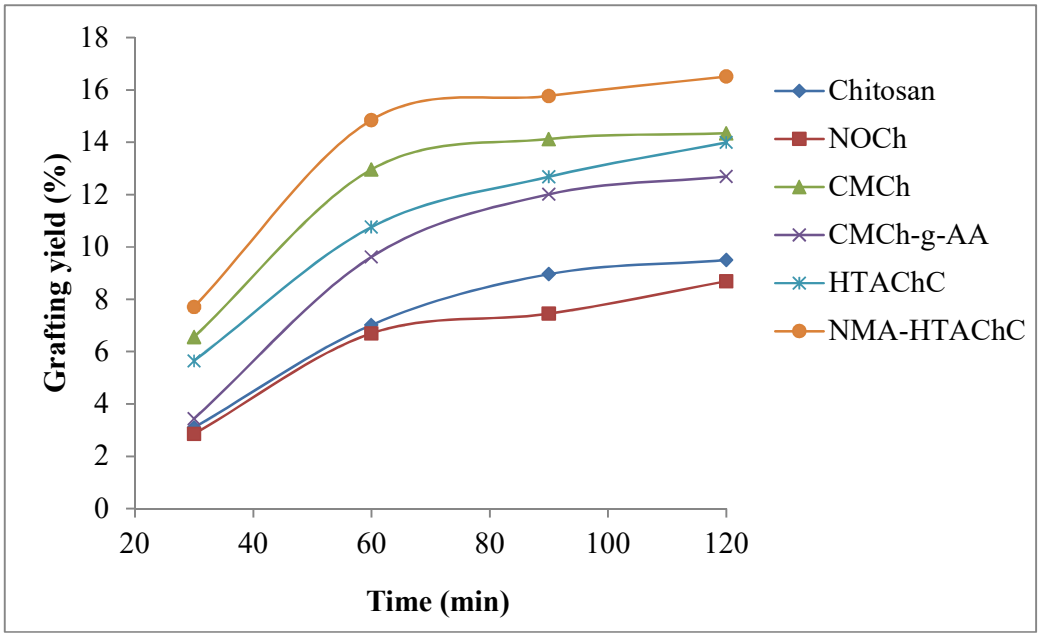


Figure 3.22: Effect of time on grafting of jute fibres

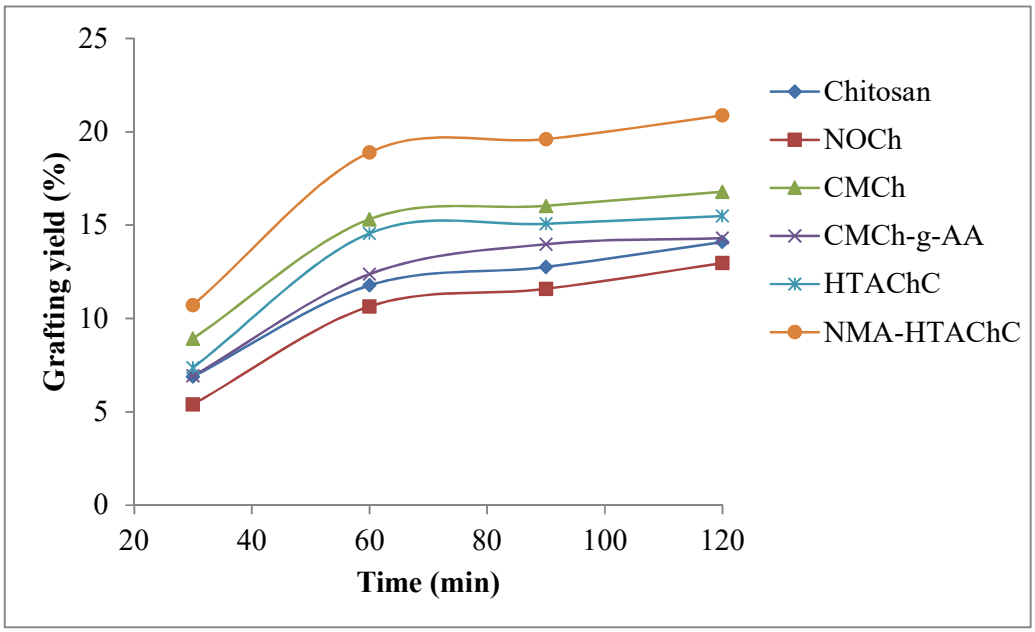


Figure 3.23: Effect of time on grafting of cotton fibres

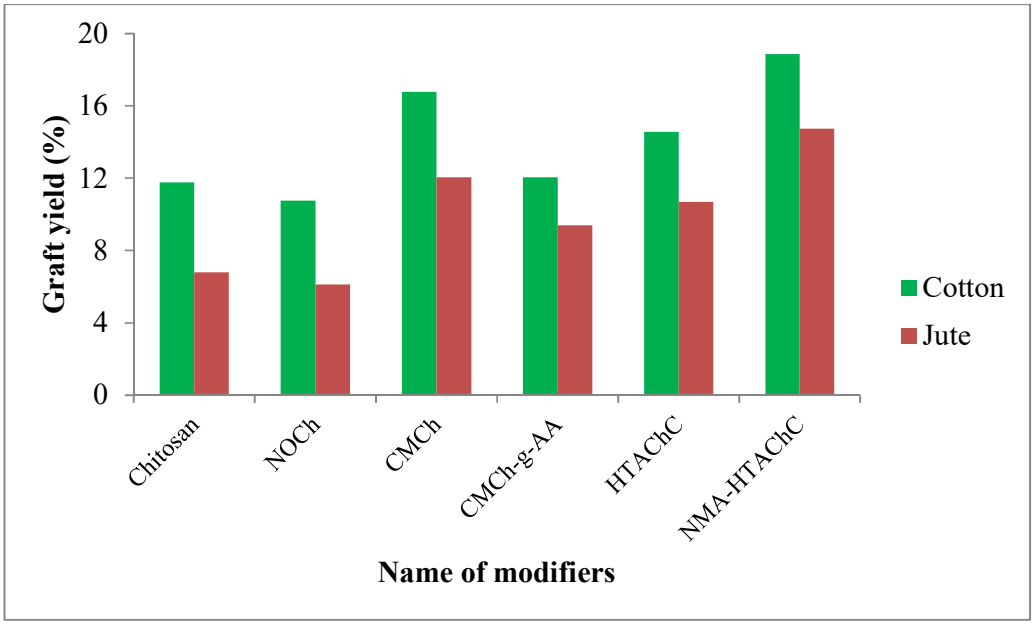


Figure 3.24: Effect of modifiers on jute and cotton fibres

3.16.6 Selected modification conditions and graft yield

Table 3.8: Graft Yield of cotton and jute fibres at selected modification conditions

Name of modifier	Modifier conc. (%) wof	Tempe-rature (°C)	Time (min)	Material liquor ration (w/v)	Graft yield (%)	
					Cotton	Jute
Chitosan	20	55	60	1:50	11.78	6.79
NOCh	20	55	60	1:50	10.75	6.12
CMCh	20	55	60	1:50	16.77	12.06
CMCh-g-AA	20	55	60	1:50	12.06	9.39
HTAChC	20	55	60	1:50	14.56	10.69
NMA-HTAChC	20	55	60	1:50	18.86	14.74

3.17 Characterization of Modified Cellulosic Fibres

3.17.1 Washing resistance of modified jute and cotton fibres

Washing resistance of modified jute and cotton fibres were determined by washing the fibres with distilled water and 0.5% (w/v) detergent solution at different temperature. The chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC modified jute and cotton fibres were washed with distilled water and detergent solution at room temperature, 40ºC and 60ºC temperature respectively while the fibre: liquor ratio was 1:50 and the experimental result is shown in **Table 3.9-3.10**.

Table 3.9: Resistance of modified jute fibres to washing with water at different temperatures

Expt. No.	Types of modified fibres	Washing temp. (º C)	Grafting before wash (%)	Grafting after wash (%)	Grafting loss in (%)
1	Chitosan	Room	6.79	5.71	1.08
2		40	6.79	5.63	1.16
3		60	6.79	4.56	2.23
4	NOCh	Room	6.12	6.01	2.11
5		40	6.12	2.95	3.00
6		60	6.12	3.02	3.10
7	CMCh	Room	12.06	10.93	1.13
8		40	12.06	10.10	1.96
9		60	12.06	10.01	2.05
10	CMCh-g-AA	Room	9.39	8.35	1.04
11		40	9.39	7.94	1.45
12		60	9.39	6.88	2.51
13	HTAChC	Room	10.69	9.14	1.55
14		40	10.69	8.54	2.15
15		60	10.69	6.67	4.02
16	NMA-HTAChC	Room	14.74	13.62	1.12
17		40	14.74	13.04	1.70
18		60	14.74	11.53	3.21

Washing condition: Fibre: Liquor = 1:50, Time: 30 min.

It was found that, when the different modified fibres were washed with distilled water and detergent solution at room temperature there was minor change in grafting percentage

whereas when it was washed with distilled water and detergent solution at 40ºC and 60ºC temperature there were occurred a considerable decreases in grafting percentage.

This was due to the fact that when fibres were washed with water and detergent solution at room temperature, only some extra deposition of compounds on fibre surfaces were removed. In case of high temperature washing, loosely bonded substances and impurities which were deposited on the fibre surface were removed finally resulting some weight loss and decreased the grafting percentage. Loss in grafting percentage in case of NOCh, CMCh, HTAChC, NMA-HTACC modified jute and cotton fibres were comperatively greater than that of chitosan and CMCh-g-AA modified jute and cotton fibres. This is due to the higher solubility of NOCh, CMCh, HTAChC, NMA-HTACC modifiers in water and detergent solution. Also, loss in grafting is slightly higher in case of detergent washing compare to distilled water washing due to the more surface activity of detergent solution.

Table 3.10: Resistance of modified cotton fibres to washing with water at different temperatures

Expt. No.	Types of modified fibres	Washing temp. (ºC)	Grafting before wash (%)	Grafting after wash (%)	Grafting loss in (%)
1	Chitosan	Room	11.78	10.73	1.05
2		40	11.78	10.48	1.30
3		60	11.78	9.02	2.76
4	NOCh	Room	10.75	8.41	2.34
5		40	10.75	7.20	3.55
6		60	10.75	6.52	4.23
7	CMCh	Room	16.77	15.51	1.26
8		40	16.77	14.67	2.10
9		60	16.77	13.57	3.20
10	CMCh-g-AA	Room	12.06	11.06	1.00
11		40	12.06	10.46	1.60
12		60	12.06	9.51	2.55
13	HTAChC	Room	14.56	12.6	1.96
14		40	14.56	12.04	2.52
15		60	14.56	10.13	4.43
16	NMA-HTAChC	Room	18.90	17.69	1.21
17		40	18.90	17.03	1.87
18		60	18.90	15.05	3.85

Washing condition: Fibre: Liquor = 1:50, Time: 30 min.

3.17.2 Washing resistance of modified jute fibres

Table 3.11: Resistance of modified jute fibres to washing with detergent at different temperature

Expt. No.	Types of modified fibres	Washing temp. (ºC)	Grafting before wash (%)	Grafting after wash (%)	Grafting loss in (%)
1	Chitosan	Room	6.79	5.64	1.15
2		40	6.79	5.11	1.68
3		60	6.79	4.29	2.50
4	NOCh	Room	6.12	3.81	2.31
5		40	6.12	3.00	3.12
6		60	6.12	2.89	3.23
7	CMCh	Room	12.06	10.83	1.23
8		40	12.06	10.01	2.05
9		60	12.06	9.96	2.10
10	CMCh-g-AA	Room	9.39	8.10	1.29
11		40	9.39	7.85	1.54
12		60	9.39	6.83	2.56
13	HTAChC	Room	10.69	9.05	1.65
14		40	10.69	8.45	2.24
15		60	10.69	6.57	4.12
16	NMA-HTAChC	Room	14.74	13.42	1.32
17		40	14.74	12.79	1.95
18		60	14.74	11.41	3.33

Washing condition: Fibre: Liquor = 1:50, Time: 30 min., Detergent conc.: 0.5% (w/v)

3.17.3 Washing resistance of modified cotton fibres

Table 3.12: Resistance of modified cotton fibres to washing with detergent at different temperature

Expt. No.	Types of modified fibres	Washing temp. (ºC)	Grafting before wash (%)	Grafting after wash (%)	Grafting loss in (%)
1	Chitosan	Room	11.78	10.67	1.11
2		40	11.78	10.06	1.72
3		60	11.78	9.03	2.75
4	NOCh	Room	10.75	8.21	2.54
5		40	10.75	7.03	3.72
6		60	10.75	6.20	4.55
7	CMCh	Room	16.77	15.03	1.74
8		40	16.77	14.37	2.40
9		60	16.77	13.32	3.45
10	CMCh-g-AA	Room	12.06	10.75	1.31
11		40	12.06	10.18	1.88
12		60	12.06	9.44	2.62
13	HTAChC	Room	14.56	12.24	2.32
14		40	14.56	11.59	2.97
15		60	14.56	9.69	4.87
16	NMA-HTAChC	Room	18.86	17.19	1.65
17		40	18.86	16.63	2.23
18		60	18.86	14.75	4.11

Washing condition: Fibre: Liquor = 1:50, Time: 30 min., Detergent conc.: 0.5% (w/v)

3.17.4 Swelling behavior of jute and cotton fibres

Swelling behavior of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC modified and unmodified cellulosic jute and cotton fibres were studied by immersing them in different polar and non-polar solvents namely water, methanol and carbon tetrachloride as shown in the **Table 3.13**. Swelling ability reflects the relationship between void structure in backbone polymer and size of solvent molecules both for polar and non polar solvents [Singha and Thakur, 2008; Singha et al., 2008, Singha and Thakur, 2009].

The bleached raw jute and cotton fibres show maximum swelling with polar solvents like water and methanol and least swelling with the non polar solvents like CCl_4. In case of different modified jute and cotton fibres, water and alcohols do not interact to the same extent as with bleached raw fibres due to blockade of active sites on the fibres backbone by chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC treatment, which causes change in the sorption behavior. The higher cellulosic hydroxyl group content makes it higher swelling in polar solvent. On the other hand, cotton contains large amounts of fibre hair than jute fibre. So, the swelling of cotton fibre is more than jute fibre.

From the **Table 3.13** it is clear to us the swelling behavior of chitosan and CMCh-g-AA modified fibres were decreased at lower value for the polar solvent but slightly increased for non-polar solvents. In the case of chitosan and CMCh-g-AA modified fibres, water and alcohols do not interact to the same extent as with raw fibres due to blockade of active sites on natural fibre backbone by chitosan and CMCh-g-AA, which causes change in the sorption behavior.

Therefore, the unmodified cellulosic fibre shows maximum swelling, this due to the presence of hydrophilic functional groups on cellulosic fibre surface. But swelling behavior of modified cellulosic fibre in case of non-polar solvent is opposite to that of polar solvent and swelling increase slightly in case of modified cellulosic fibre due to an increase in number of hydrophobic functional groups on cellulosic fibres surface. Swelling in polar solvents for NOCh, CMCh, HTAChC and NMA-HTAChC modified

cellulosic fibre is greater than that of chitosan and CMCh-g-AA modified fibres which is due to more hydrophilic nature of those modifier compare to chitosan and CMCh-g-AA. Swelling percentage in polar solvents is comparatively higher due to most probably the formation of more hydrogen bond.

Table 3.13: Effect of modification on swelling behavior of jute and cotton fibres in different polar and non polar solvents.

Expt. No.	Fibre status	Name of solvents	Swelling of cotton (%)	Swelling of jute (%)
1	Bleached	Water	95.86	87.00
2		Methanol	80.15	65.67
3		CCl_4	11.28	9.02
4	Chitosan modified	Water	56.45	45.76
5		Methanol	48.54	42.44
6		CCl_4	45.33	36.78
7	NOCh modified	Water	65.45	42.76
8		Methanol	54.11	43.32
9		CCl_4	21.76	17.98
10	CMCh modified	Water	86.22	77.49
11		Methanol	62.31	53.18
12		CCl_4	3.46	3.20
13	CMCh-g-AA modified	Water	56.57	41.98
14		Methanol	38.30	31.59
15		CCl_4	32.85	24.61
16	HTAChC modified	Water	73.22	70.22
17		Methanol	45.93	25.76
18		CCl_4	36.34	22.64
19	NMA-HTAChC modified	Water	81.75	77.65
20		Methanol	51.89	32.98
21		CCl_4	39.76	32.77

Experimental conditions: Immersion Time: 48 h and Temperature: 30ºC

3.17.5 Moisture absorption study

The moisture absorption of washed unmodified and modified cellulosic jute and cotton fibres were studied in the present investigation and the obtained results were shown in **Table 3.14**. Mainly cellulosic fibres contain multiple hydroxyl groups which is hydrophilic (attracts water). This is due to the electronegativity of the oxygen atom in OH which makes the functional group polar. This polarity attracts the polar H_2O molecule creating a hydrophilic effect.

From the **Table 3.14**, it was observed that treatment of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC onto bleached raw jute and cotton fibres has a great impact on the moisture absorption behavior. There was a decrease in percent moisture absorption when raw cellulosic fibres modified with chitosan, NOCh, CMCh or CMCh-g-AA, which is due to the fact that the sites for maximum moisture absorption are blocked after incorporation of chitosan, NOCh, CMCh or CMCh-g-AA through surface modification by showing less affinity for moisture than the original fibres.

In the present investigation it was found that HTAChC and NMA-HTAChC modified cellulosic fibres, jute showed 11.81% and 13.22% and cotton showed 13.70% and 15.43% moisture absorption when kept in open air for a week as shown in **Table 3.14**. However, HTAChC and NMA-HTAChC modified fibre showed greater moisture absorption compared to unmodified fibres due to hydrophilicity of cellulosic fibre backbone and water soluble chitosan derivatives or due to hygroscopic in nature due to presence of quaternary ammonium group and secondary amino group in their structure.

Table 3.14: Effect of modification on moisture absorption behavior of jute and cotton fibres

Expt. No.	Fibre status	Moisture absorption of cotton (%)	Average moisture absorption of cotton (%)	Moisture absorption of jute (%)	Average moisture absorption of jute (%)
1	Bleached	13.86	13.10	10.13	9.77
2		12.37		9.25	
3		13.08		9.93	
4	Chitosan modified	11.87	10.77	8.44	8.56
5		10.12		8.12	
6		10.32		9.10	
7	NOCh	8.65	8.73	8.10	7.70

8	modified	8.23		7.90	
9		9.32		7.12	
10	CMCh modified	11.09	11.14	8.26	8.28
11		10.64		9.00	
12		11.70		7.59	
13	CMCh-g-AA modified	10.09	9.85	6.36	6.10
14		8.95		6.05	
15		10.50		5.90	
16	HTAChC modified	14.33	13.70	11.36	11.81
17		13.56		12.43	
18		13.21		11.65	
19	NMA-HTAChC modified	15.60	15.43	11.54	13.22
20		14.72		12.76	
21		15.98		15.38	

3.17.6 Tensile strength testing

Tensile strength of washed unmodified and modified with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC cellulosic jute and cotton fibres were measured in this research work were shown in **Table 3.15**.

It was observed from the **Table 3.15** the tensile strength of cellulosic fibres was increased after treatment. These are due to the modification of cellulosic fibre with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC and reduction of crystallinity of fibre due to the incorporation of amorphous copolymers. This may also happen, during modification the fibres were swelled and decrystallization of cellulose takes placed. During the decrystallization, it is generally accompanied by the increase of randomness of cellulose macromolecule, so some physical changes in the cellulosic chain accompanied during modification by the decrease of randomness which may reinforce the fibre and consequently the strength of modified cellulosic fibres.

From the results, it has also seen the CMCh-g-AA modified fibre shows highest tensile strength which is 208 N/yarn for jute and 298 N/yarn for cotton fibres and lowest for unmodified fibres. The improvement in fibre strength of CMCh-g-AA modified cellulosic fibre may be attributed to greater penetration of CMCh-g-AA particles and crosslink the adjacent fibre molecules. Similarly, improved strength of

NMA-HTAChC modified cellulosic fibre is due to the penetration of the modifier in fibre pores resulting crosslink adjacent cellulosic fibre molecules assisted by double bond on NMA-HTAChC. It is also clear that NMA-HTAChC has higher fibre strength improving properties compare to HTAChC which is due to more deposition of NMA-HTAChC on cellulosic fibre and also for better cross linking activity than HTAChC.

Table 3.15: Tensile strength of bleached raw and modified jute and cotton fibres.

Expt. No.	Fibre status	Tensile strength of cotton (N)	Average tensile strength of cotton (N)	Tensile strength of jute (N)	Average tensile strength of jute (N)
1	Bleached	210	214	144	147
2		218		136	
3		214		161	
4	Chitosan modified	274	264	191	172
5		265		170	
6		253		154	
7	NOCh modified	244	250	185	165
8		255		160	
9		249		166	
10	CMCh modified	284	270	177	192
11		266		190	
12		260		209	
13	CMCh-g-AA modified	295	298	208	208
14		318		227	
15		281		189	
16	HTAChC modified	273	263	180	174
17		253		178	
18		264		164	
19	NMA-HTAChC modified	280	284	182	193
20		292		201	
21		282		197	

3.17.7 Chemical resistance study

Chemical resistance of unmodified and, chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC modified cellulosic jute and cotton fibres were studied by immersing the fibre samples in 0.1N HCl and 0.1N NaOH solution for a time period

of 48 h and the results were putted in **Table 3. 16**. From the experimental data, it has seen that the unmodified cellulosic fibres showed lower resistance in alkali solution but moderate resistance to acid solution. In case of modified fibres, fibre surface is protected by a film of modifier which protects the cellulosic fibre from contact of alkali solution causing reduction in weight loss.

The removal of hemicellulose and lignin from the unmodified jute fibre surface at strong alkaline media also increases the weight loss. At the same time the removal of fibre hairs also increase the weight loss. The washed jute and cotton showed 2.54% , 2.14% and 6.65%, 5.33% weight loss in 0.1N HCl and 0.1N NaOH solution respectively. The lower weight loss of the cotton fibre is due to the absence of hemicellulose and lignin in its backbone structure. Among chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC modified jute and cotton fibres, chitosan modified fibres shows better chemical resistance whereas NMA-HTAChC modified fibres shows lower chemical resistance.

Table 3.16: Effect of treatment on chemical resistance behavior of jute and cotton fibres.

Expt. No.	Loading media	Fibre status	Weight loss of cotton (%)	Weight loss of jute (%)
1	0.1N HCl	Bleached	2.14	2.54
2		Chitosan modified	1.65	3.47
3		NOCh modified	3.44	4.21
4		CMCh modified	4.75	6.80
5		CMCh-g-AA modified	3.21	3.76
6		HTAChC modified	4.28	4.30
7		NMA-HTAChC modified	4.95	5.88
8	0.1N NaOH	Bleached	5.33	6.65
9		Chitosan modified	1.42	2.31
10		NOCh modified	2.43	3.78
11		CMCh modified	1.35	2.35
12		CMCh-g-AA modified	0.99	1.40
13		HTAChC modified	4.85	4.80
14		NMA-HTAChC modified	4.78	4.61

Experimental conditions: Fibre weight: 1 gm, Temperature: 30°C, Time: 48 h,
Volume of acid or alkali solution: 50 ml.

3.17.8 FTIR spectroscopy analysis of washed and modified jute and cotton fibres

The FTIR spectra of bleached and modified (with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA- HTAChC) cellulosic jute and cotton fibres were recorded by a spectrophotometer and were shown in **Fig. 3.25-3.26**.

Fig. 3.25(a) and **Fig. 3.26(a)** shows the spectra of unmodified jute and cotton respectively. The FTIR spectra of raw and modified jute and cotton fibres were mostly similar as the adsorption peaks were obtained in the spectra for entire sample except the new additional peak in the modified fibre. All of the spectra had same absorption peaks at around 1033-1060 cm^{-1} (C-O stretching), 1400 cm^{-1} (-CH_2 bending) and 1637-1637cm^{-1} (C=C stretching) (Singha and Thakur, 2009).

The **Fig. 3.25(b-g)** and **Fig. 3.26(b-g)** shows the evidence of incorporation of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC on jute and cotton fibres respectively. Because modified jute and cotton fibres show an additional peak at 1600 cm^{-1} for the N–H bending of the primary amine for chitosan, 1516 cm^{-1} corresponding to the asymmetric stretching of C-H in -CH_3 group for NOCh, 1480 cm^{-1} refers to the –CH_2–COOH group for CMCh, 1319 cm^{-1} for the –CH_2–CH(COOH)– group for CMCh-g-AA, 1480 cm^{-1} refers to the C-H bending of trimethylammonium group for HTAChC and 1545 cm^{-1} for the N–H bending of the secondary amide in the acrylamidomethyl group for NMA-HTAChC.

These analytical data were indicated the functionalization of jute and cotton fibres surfaces with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC.

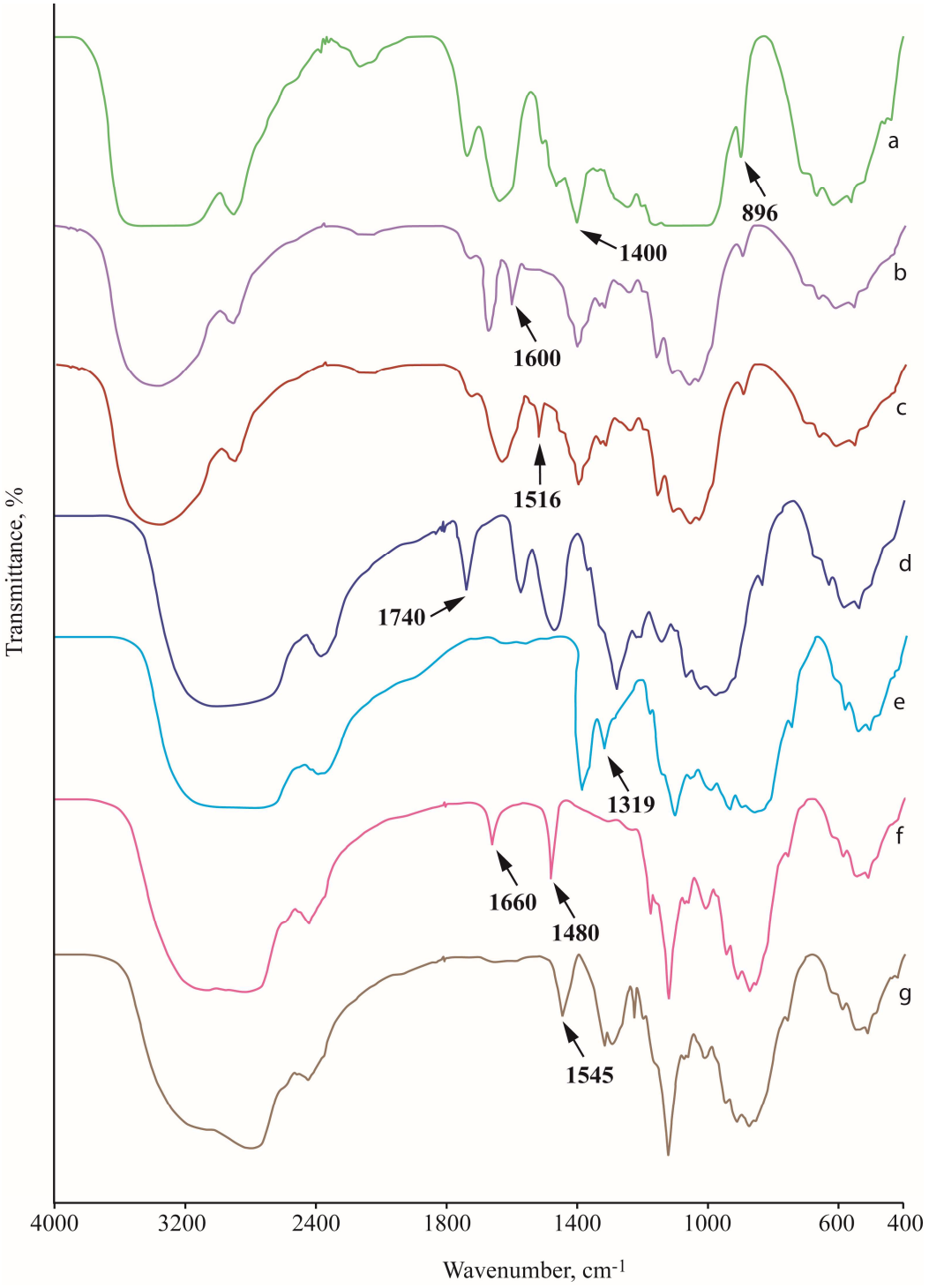


Figure 3.25: FTIR Spectra of (a) Bleached jute, (b) Chitosan, (c) NOCh, (d) CMCh, (e) CMCh-g-AA, (f) HTAChC and (g) NMA-HTAChC modified jute fibres.

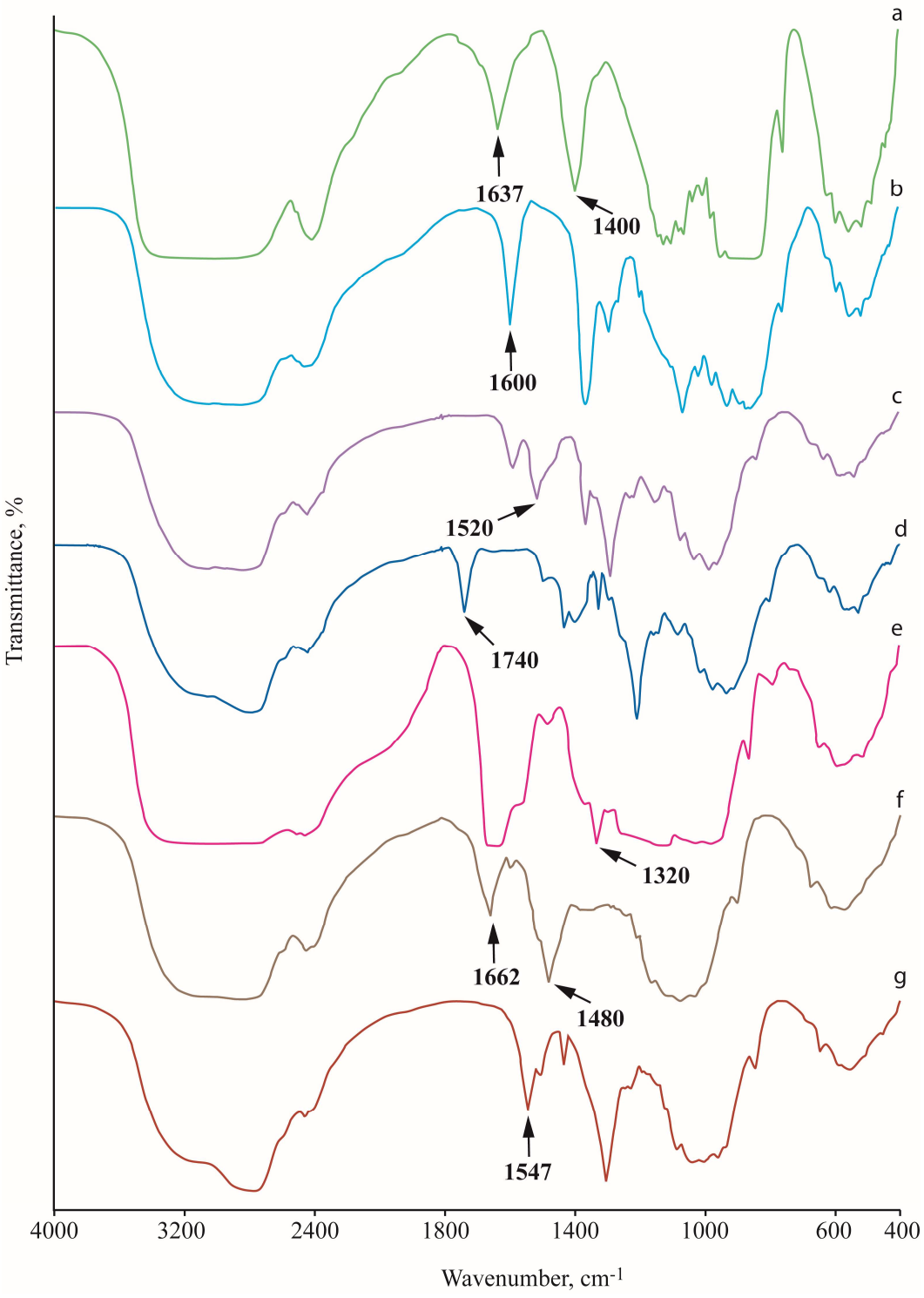


Figure 3.26: FTIR Spectra of (a) Bleached cotton, (b) Chitosan, (c) NOCh, (d) CMCh, (e) CMCh-g-AA, (f) HTAChC and (g) NMA-HTAChC modified cotton fibres.

3.17.9 Surface morphology of unmodified and modified jute and cotton fibres

Scanning Electron Micrograph (SEM) has several potential advantages in morphological investigation and has been extensively applied in the field of metallurgy, natural and modified fibres, polymers, biomaterials, composites [Sikdar et al., 1995] and so forth. The surface morphology of the modified fibre was studied which showed a characteristics structure on cellulosic fibres after treating with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC which were supported by FTIR analysis.

Fig. 3.27(a-g) and **3.28(a-g)** shows the SEM micrograph of unmodified and modified cellulosic jute and cotton fibres respectively. The SEM micrograph represents the microporous surface of the washed jute and cotton fibres. Whereas, in **Fig. 3.27 (b-g)** and **3.28 (b-g)** marked position shows the deposition of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC on to the jure and cotton fibres respectively. The micrograph of the modified fibre indicates that it is smoother than that of the washed fibre. This is because chitosan and its derivatives exhibit inherent property of film formation, which is clearly seen as a gloss on the fibre surface. According to the micrograph, modifiers were spread on the fibre in a homogeneous way, without agglomerated deposition on the fibre surface.

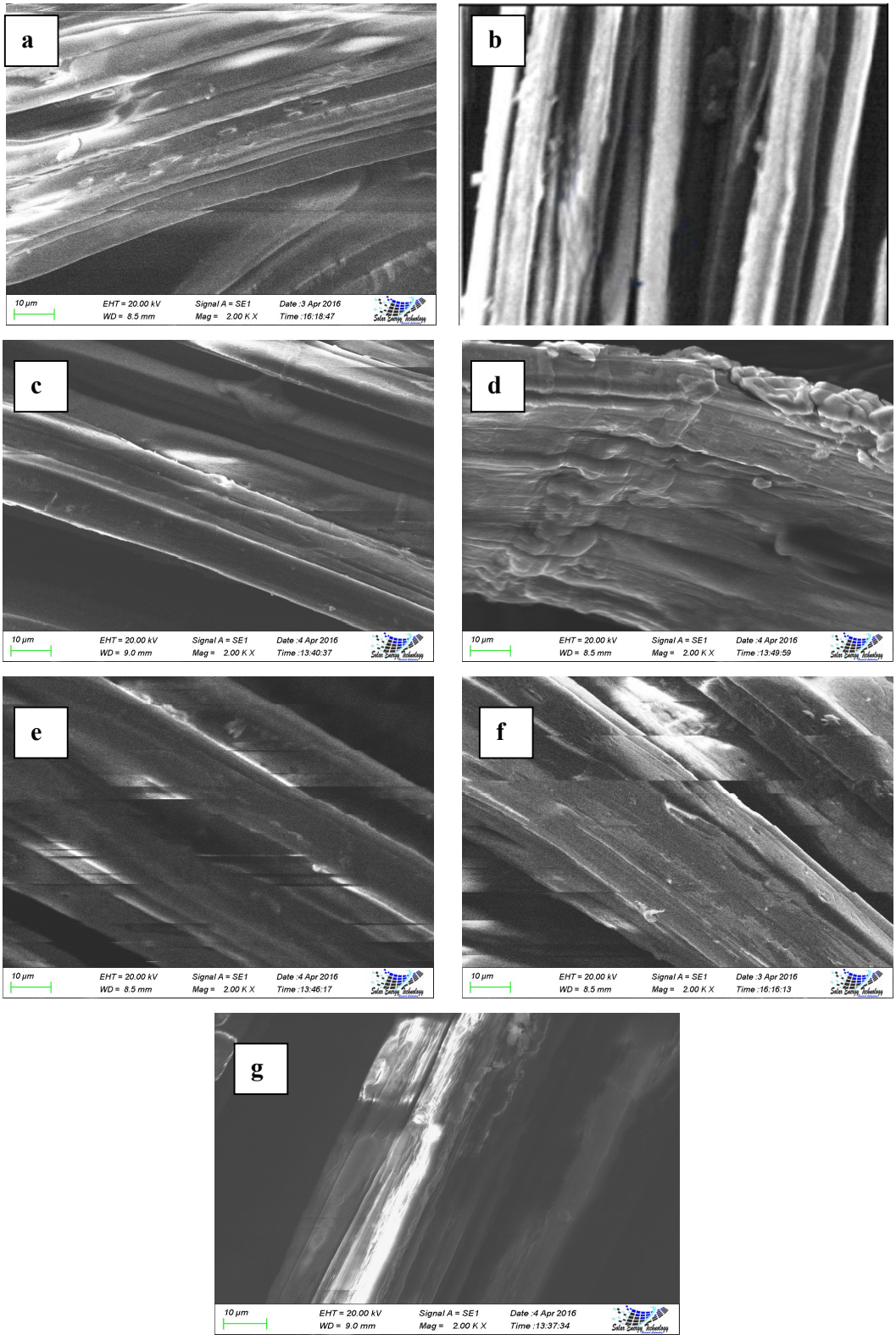


Figure 3.27: SEM of (a) Unmodified jute, (b) Chitosan modified, (c) NOCh modified, (d) CMCh modified, (e) CMCh-g-AA modified (f) HTAChC modified and (g) NMA-HTAChC modified jute fibres.

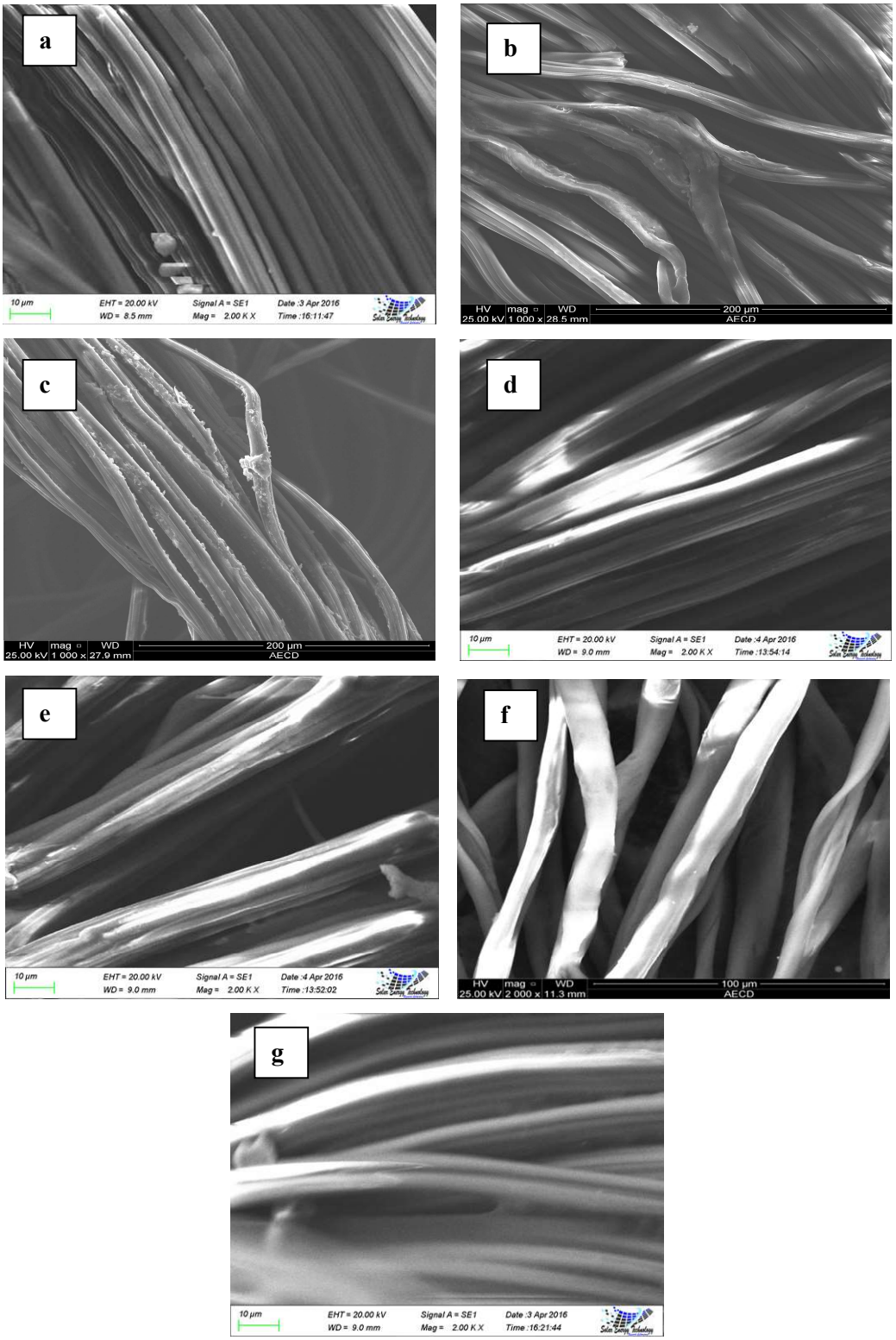


Figure 3.28: SEM of (a) Unmodified cotton, (b) Chitosan modified, (c) NOCh modified, (d) CMCh modified, (e) CMCh-g-AA modified, (f) HTAChC modified and (g) NMA-HTAChC modified cotton fibres.

3.17.10 Thermal analysis

The Thermo Gravimetric Analysis describes the thermal degradation of samples. **Fig. 3.29** to **3.34** shows the thermal behavior of raw and chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC modified jute and cotton fibres. From the thermograms, necessary thermal informations of jute and cotton fibres are enlisted in **Table 3.17** and **3.18**. TGA thermogram shows that decomposition paths for unmodified and modified cellulosic fibres have three stages of thermal degradation. There was a weight loss in first stage between 100 - 120°C, due to dehydration of cellulose. In second stage between 200 - 270°C, rapid weight losses were observed for thermal degradation of the cellulosic fibres. In third stage, residual char is formed through weight loss which reaches to be a fixed weight. On the basis of initial decomposition temperature (T_i), the thermal stability of unmodified and modified jute fibres shows the following order: chitosan modified > CMCh modified > unmodified > NOCh modified > HTAChC modified > CMCh-g-AA modified, NMA- HTAChC modified jute whereas cotton fibre shows: chitosan modified > unmodified > HTAChC modified > NOCh modified > NMA- HTAChC modified > CMCh modified > CMCh-g-AA modified.

From DTA curve, a large exotherm peak was observed, due to oxidative decomposition of products, which involves formation of carboxyl and carbonyl groups as well as evolution of CO and CO_2, and formation of carbonaceous residue [Muralidhara and Sreenivasan, 2010].

Table 3.17: Data calculated from TGA, DTG and DTA thermograms of unmodified and modified jute fibres.

Samples	T_i (°C)	Char yield at 600°C (%)	DTG peak maxima temperature (°C)	DTA maxima (°C)	Nature of DTA peak	DTA peak range (°C)
Unmodified jute	250	5	415	430	Exo.	420-440
Chitosan modified	270	16	435	458	Exo.	435-475
NOCh modified	240	12	390	415	Exo.	405-440
CMCh modified	260	16	437	450	Exo.	430-450
CMCh-g-AA modified	200	10	335	455	Exo.	430-470
HTAChC modified	230	12	340	452	Exo.	425-465
NMA-HTAChC modified	200	6	445	470	Exo.	445-475

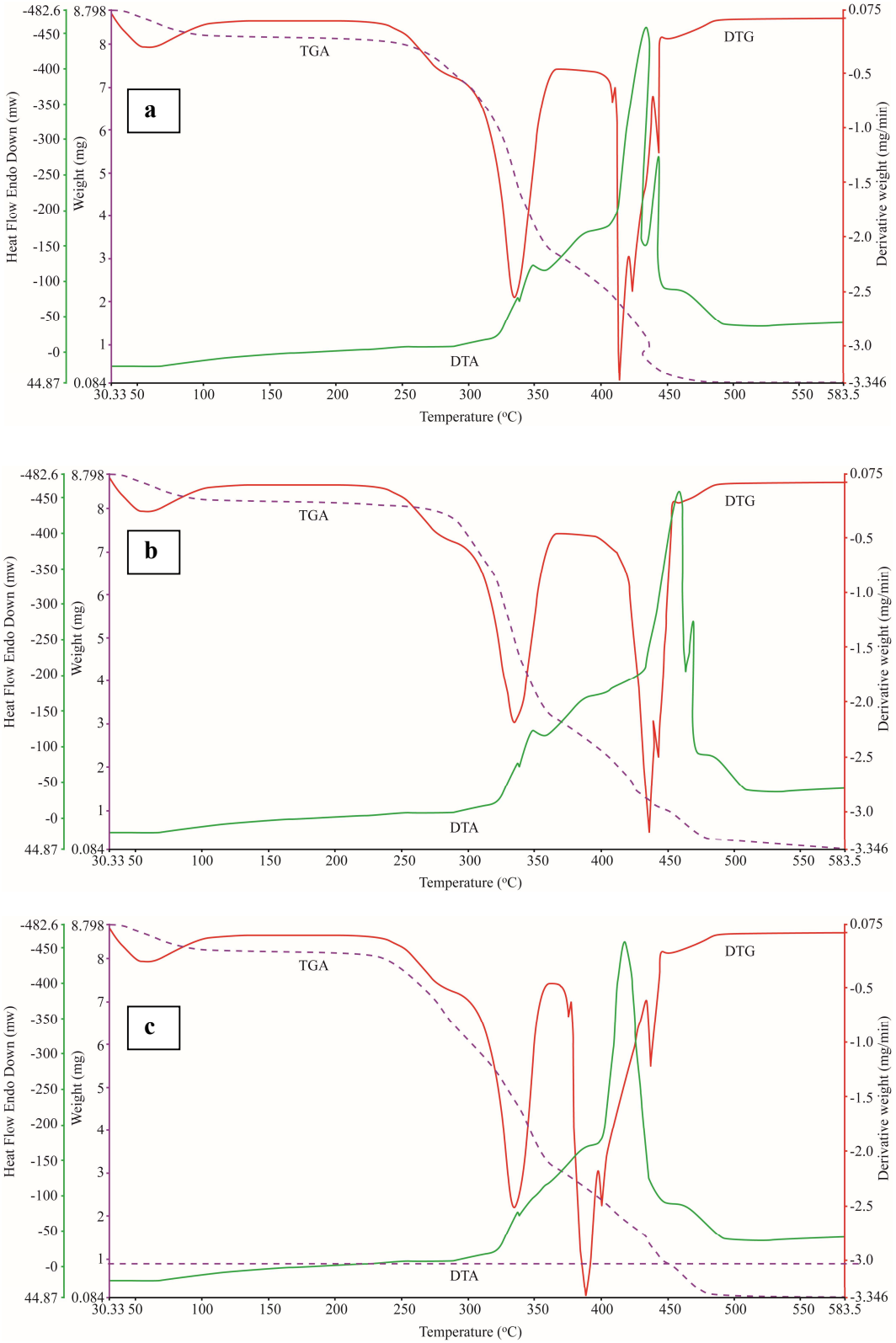


Figure 3.29: TGA, DTA and DTG curves of (a) Raw jute, (b) Chitosan modified and (c) NOCh modified jute fibres.

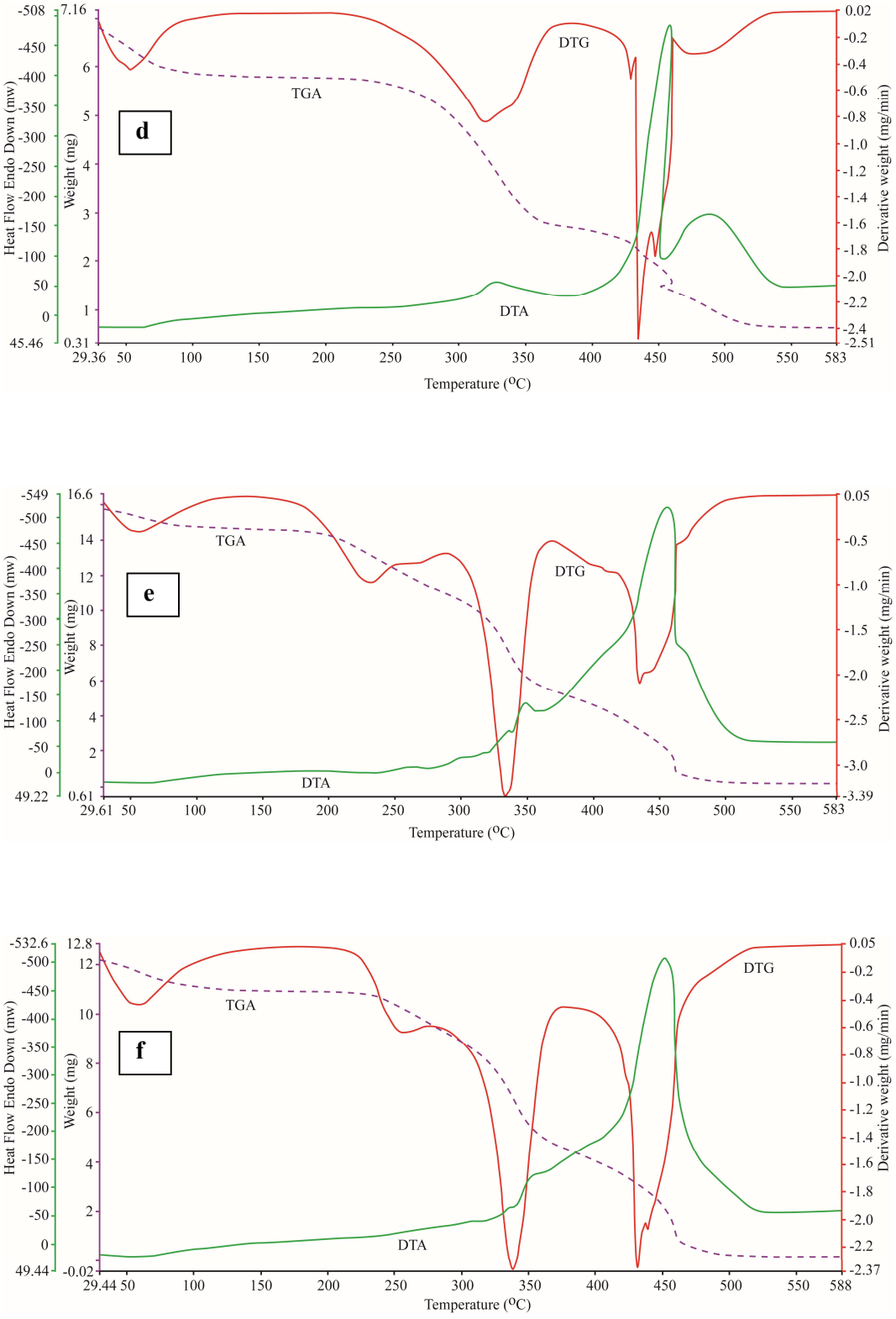


Figure 3.30: TGA, DTA and DTG curves of (d) CMCh modified, (e) CMCh-g-AA modified and (f) HTAChC modified jute fibres.

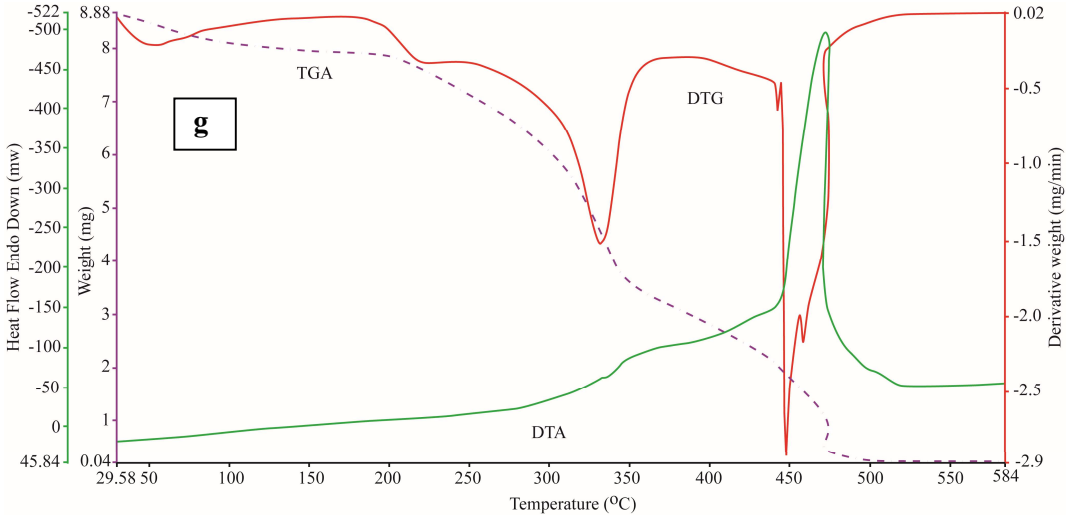


Figure 3.31: TGA, DTA and DTG curve of (g) NMA-HTAChC modified jute fibres.

Table 3.18: Data calculated from TGA, DTG and DTA thermograms of unmodified and modified cotton fibres.

Samples	Initial decomposition temp. (T_i °C)	Char yield at 460 °C (%)	DTG peak maxima temperature (°C)	DTA maxima (°C)	Nature of DTA peak	DTA peak range (°C)
Unmodified cotton	260	9.2	460	480	Exo.	450-470
Chitosan modified	275	17	450	458	Exo.	445-475
NOCh modified	230	14	400	415	Exo.	395-430
CMCh modified	220	25	450	480	Exo.	440-480
CMCh-g-AA modified	210	17	345	530	Exo.	450-550
HTAChC modified	245	19	460	470	Exo.	420-520
NMA-HTAChC modified	225	16	450	475	Exo.	450-470

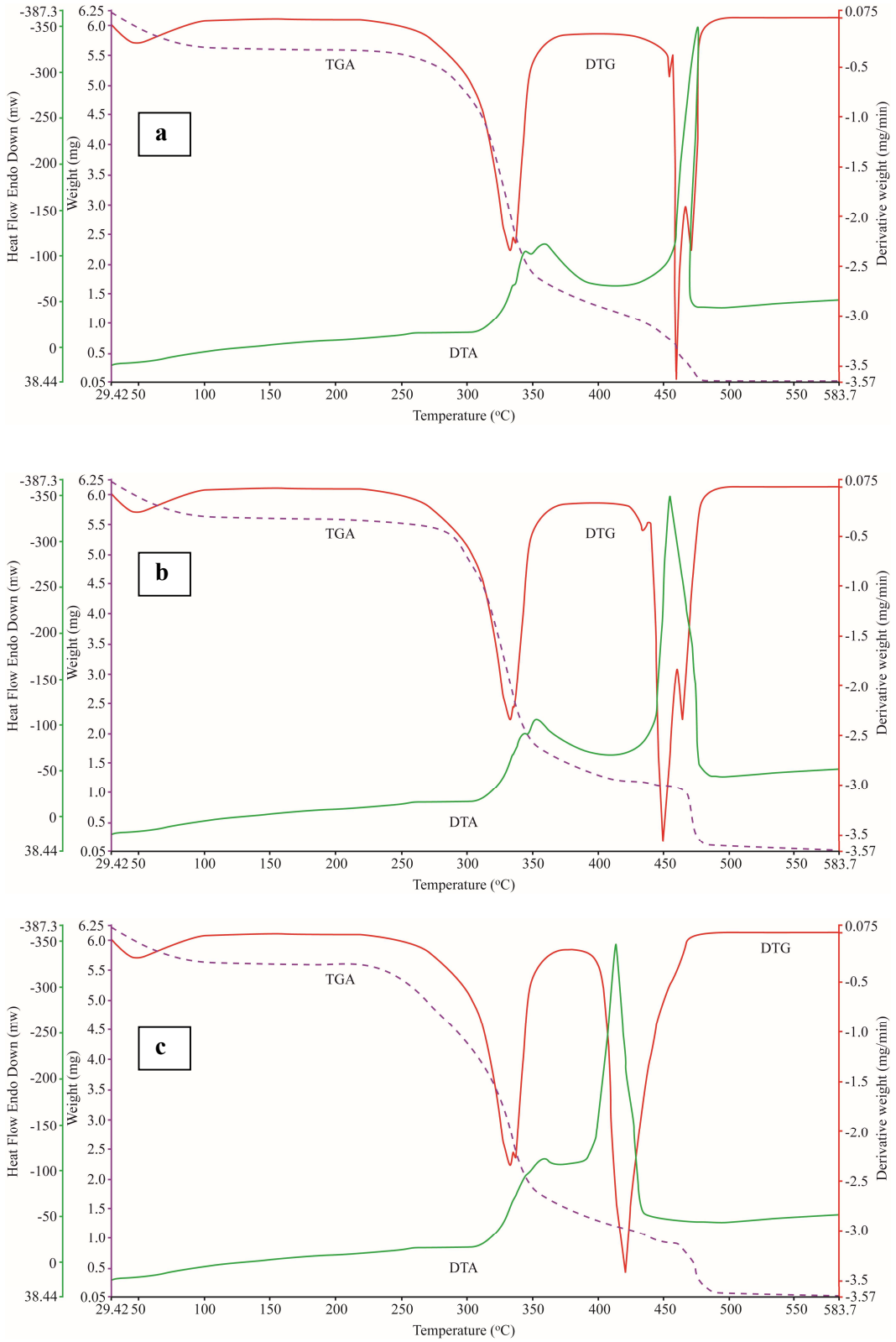


Figure 3.32: TGA, DTA and DTG curve of (a) Raw cotton, (b) Chitosan modified and (c) NOCh modified cotton fibres.

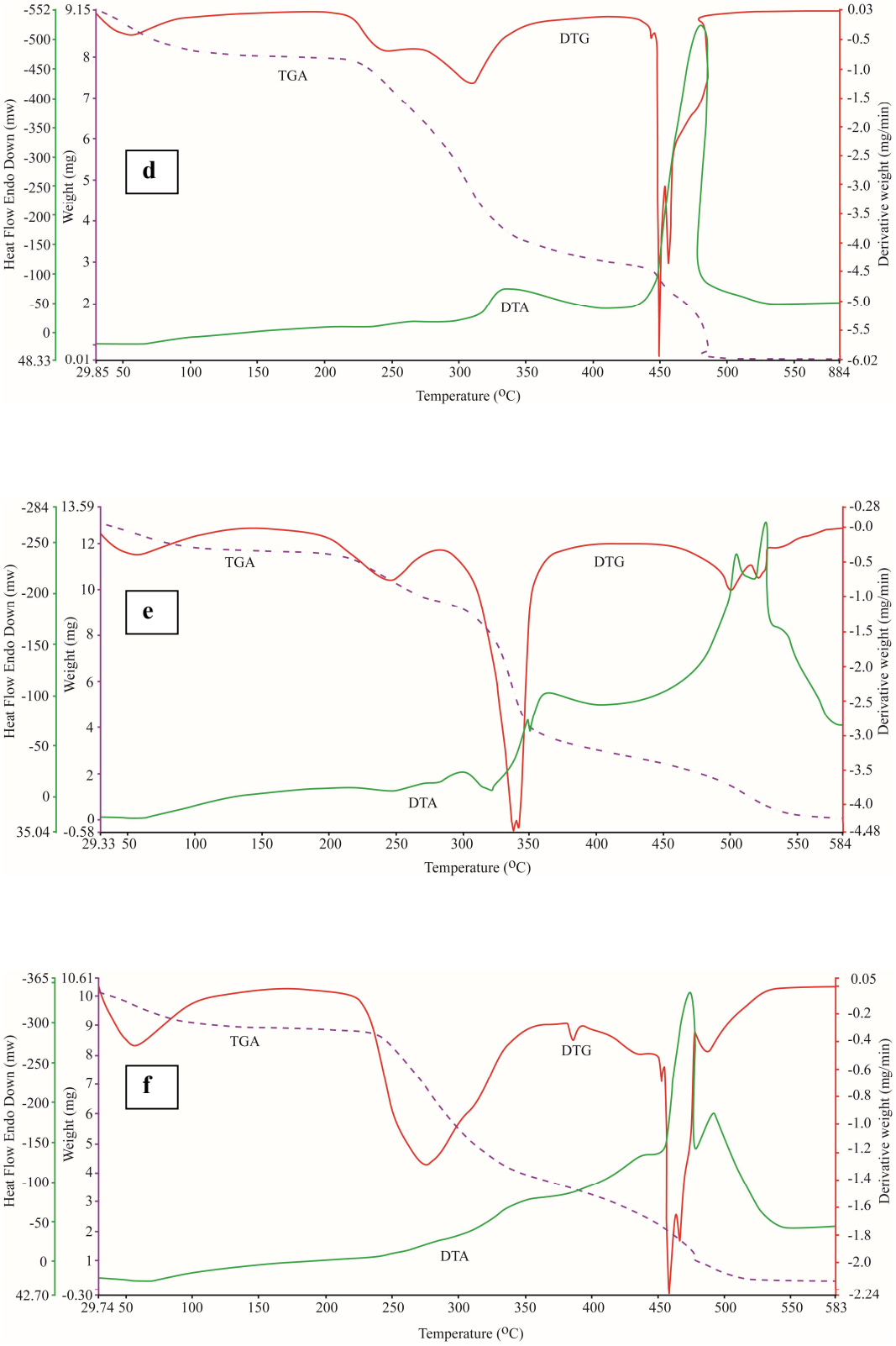


Figure 3.33: TGA, DTA and DTG curve of (d) CMCh modified, (e) CMCh-g-AA modified and (f) HTAChC modified cotton fibres.

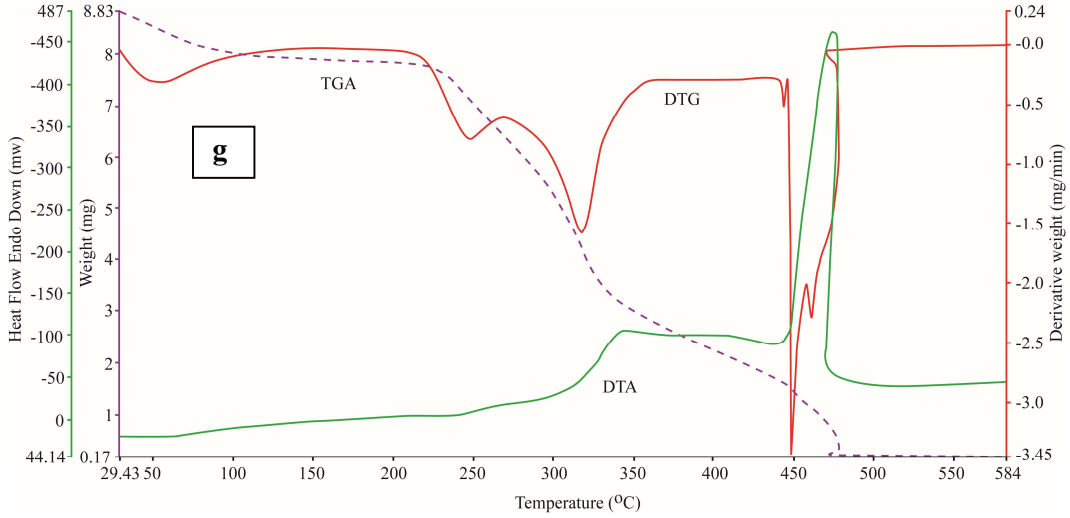


Figure 3.34: TGA, DTA and DTG curve of (g) NMA-HTAChC modified cotton fibres.

3.17.11 XRD Analysis of unmodified and modified jute and cotton fibres

The degree of crystallinity of unmodified and modified (with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA- HTAChC) jute and cotton fibres were investigated through X-ray diffractometry and the X-ray defractograms were shown in **Fig. 3.35** and **Fig. 3.36** respectively. From the figures we can conclude that the order of crystallinity of the modified and unmodified jute and cotton fibres is as follows: chitosan modified jute or cotton > NOCh modified jute or cotton > CMCh modified jute or cotton > CMCh-g-AA modified jute or cotton > HTAChC modified jute or cotton > and NMA-HTAChC modified jute or cotton.

The XRD profile of unmodified jute and cotton fibres exhibits comperetively well resolved and intense peaks, while broad diffuse scattering and less intense peaks are found for modified jute and cotton fibres. This indicates that modifier affects on crystallinity of cellulosic fibres.

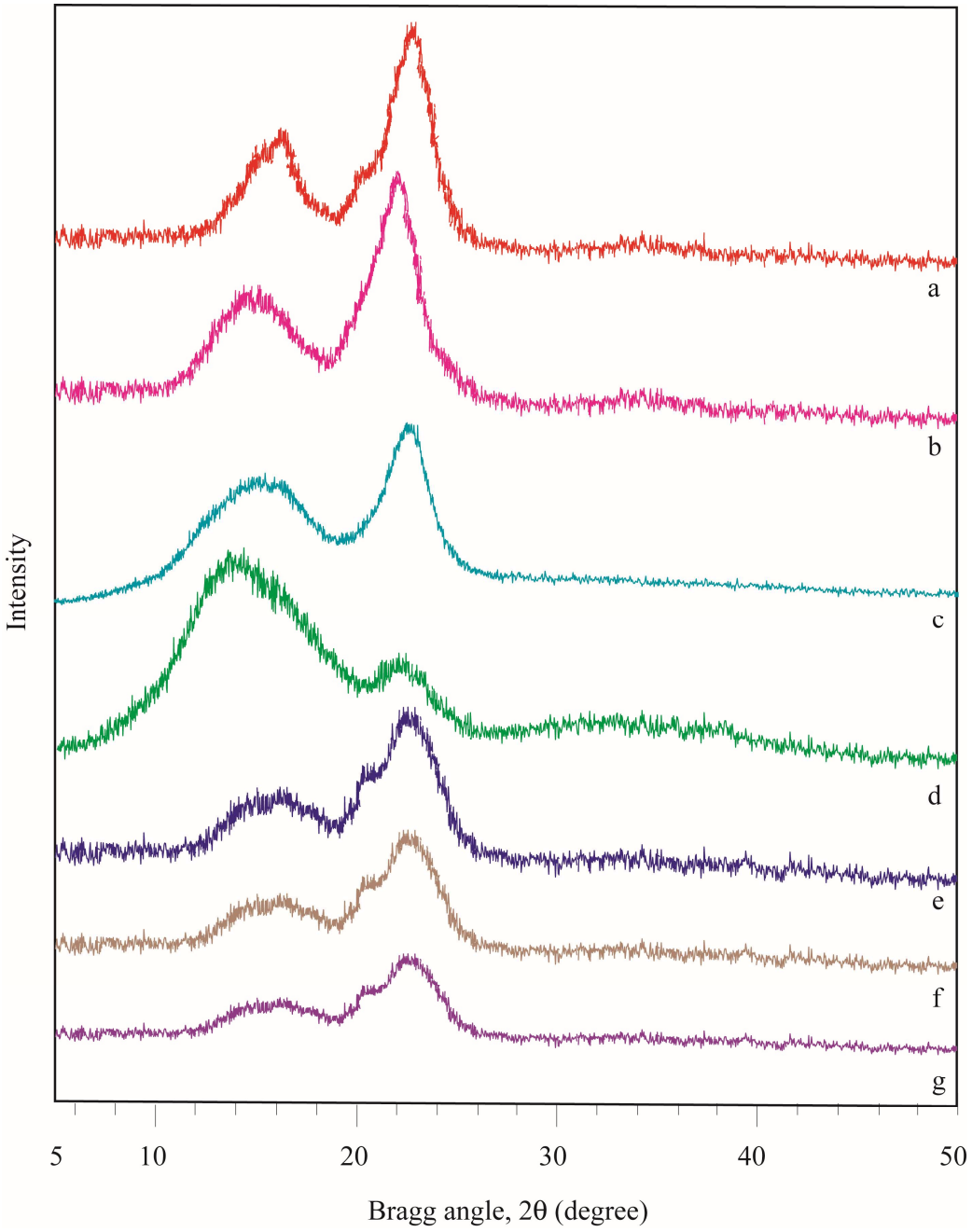


Figure 3.35: X-ray diffraction patterns of (a) Raw jute, (b) Chitosan modified, (c) NOCh modified, (d) CMCh modified, (e) CMCh-g-AA modified, (f) HTAChC modified and (g) NMA-HTAChC modified jute fibres

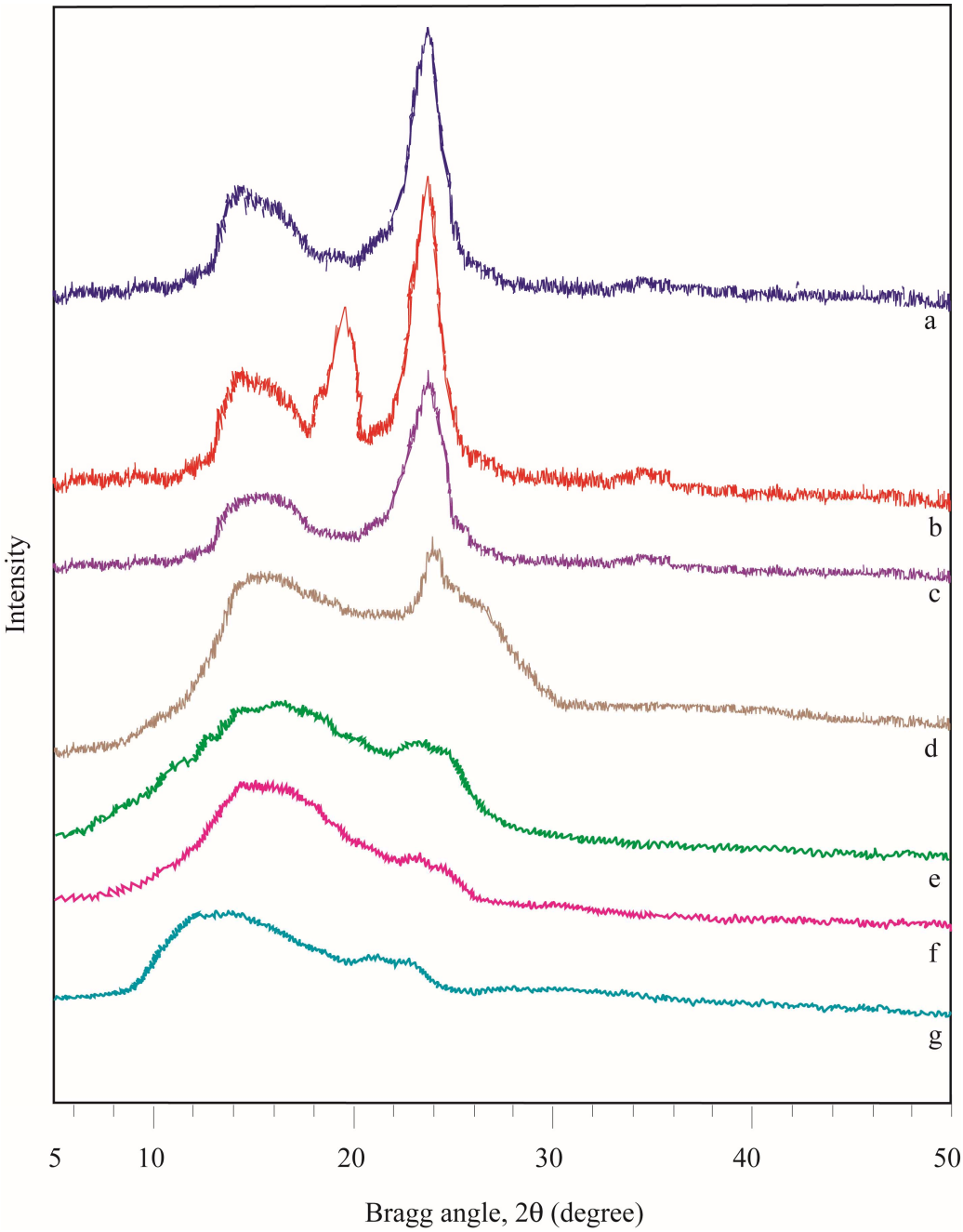


Figure 3.36: X-ray diffraction patterns of (a) Raw cotton, (b) Chitosan modified, (c) NOCh modified, (d) CMCh modified, (e) CMCh-g-AA modified, (f) HTAChC modified and (g) NMA-HTAChC modified cotton fibres.

3.18 Dyeing of Jute and Cotton Fibres

3.18.1 Calibration curves analysis

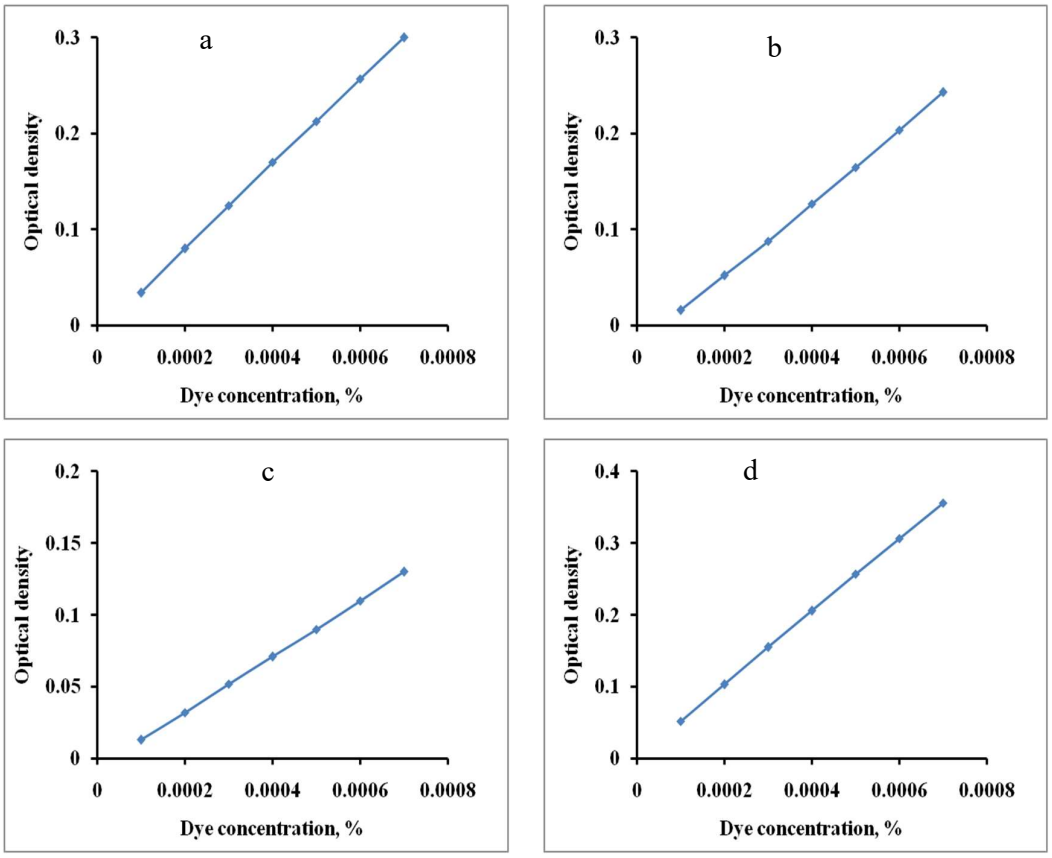


Figure 3.37: Calibration curve analysis (a) Reactive Orange 14, (b) Reactive Brown 10, (c) Direct Orange 31and (d) Direct Yellow 29.

3.18.2 Effect of modification on dye exhaustion in dyeing with various dyes

The dying was conducted following the reference with minor modification of the dye bath [Bhuiyan et al., 2013]. The dye exhaustion behavior of unmodified (bleached) and chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC modified cellulosic jute and cotton fibres are shown in **Table 3.19** and **3.20.** From the tables**,** it is observed that the dye exhaustion percent of modified fibres is higher than that of unmodified fibres. The modifier chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC make the fibres hydrophilic. Due to their hydrophilic properties the dyeability of the fibres increased. Again, from the above mentioned two tables it is also observed that, among the modified fibres, the exhaustion of dye by the NMA-HTAChC modified fibres is maximum, it also may due to the more water solubility of NMA-HTAChC and to presence of secondary amino group and vinyl group in NMA-

HTAChC. Generally reactive and direct dyes formed covalent bond with fibre polymer. The reactive system of those dyes enables it to react with the hydroxyl groups in cellulose by nucleophilic addition reaction. As the reactive dyes are anionic and cellulosic fibres gain anionic surface charge in water, the charge repulsion adversely affects the dye bath exhaustion. For this reason, unmodified fibre shows low exhaustion of dye. Their exhaustion behavior is also shown in **Fig. 3.38** and **3.39**. Fifty percent exhaustion would mean that 50% of the total amount of dye has been attached to the fibre and 50% is still in solution.

The treatment of the fibre with modifier has enhanced the dye sites in the cellulose macromolecules of cellulosic fibres. This could be due to attachment of modifier to the cellulosic fibres backbone, which helps to increase the functionality and the measure of reactivity. As a result, the modified fibre absorbed more dye than the unmodified fibres. This absorption increased the exhaustion percentage of dye in the modified fibre [Bhuiyan et al., 2013]. All the modified cellulosic jute and cotton fibres exhibit considerably better colour absorption.

Experimental condition

Jute or cotton fibre: 1 gm, Dye: 0.5% (on wt. of fibre),

Electrolyte (NaCl): 20% (on wt. of fibre),

Catalyst (Na_2CO_3): 20% (on wt. of fibre)

Table 3.19: Determination of dye absorption by washed and modified jute fibres dyed with Reactive Orange 14, Reactive Brown 10, Direct Orange 31 and Direct Yellow 29.

Name of dyes	Exhaustion (%)						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Reactive Orange 14	45.23	55.45	53.76	67.02	68.78	66.31	70.78
Reactive Brown 10	49.22	58.12	55.11	67.04	69.61	69.11	72.87
Direct Orange 31	55.56	64.34	62.03	69.34	73.40	71.09	77.67
Direct Yellow 29	52.41	61.54	58.03	70.52	73.52	69.19	75.99

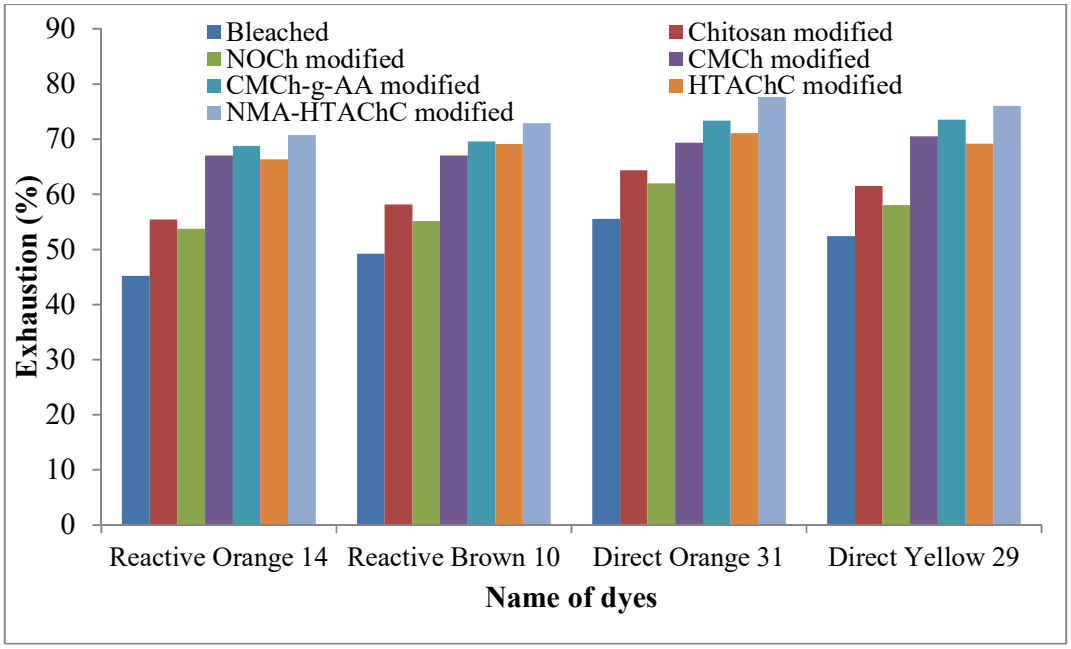


Figure 3.38: Effect of dye absorption on dyeing of washed and modified jute fibres

Table 3.20: Determination of dye absorption by washed and modified cotton fibres dyed with Reactive Orange 14, Reactive Brown 10, Direct Orange 31 and Direct Yellow 29.

Name of dyes	Exhaustion (%)						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Reactive Orange 14	57.02	66.77	64.23	78.73	79.41	76.54	81.90
Reactive Brown 10	59.23	68.02	66.31	80.65	81.31	79.05	83.78
Direct Orange 31	66.33	75.60	72.02	84.45	86.09	84.06	88.01
Direct Yellow 29	62.04	71.43	69.03	82.08	83.33	81.43	85.65

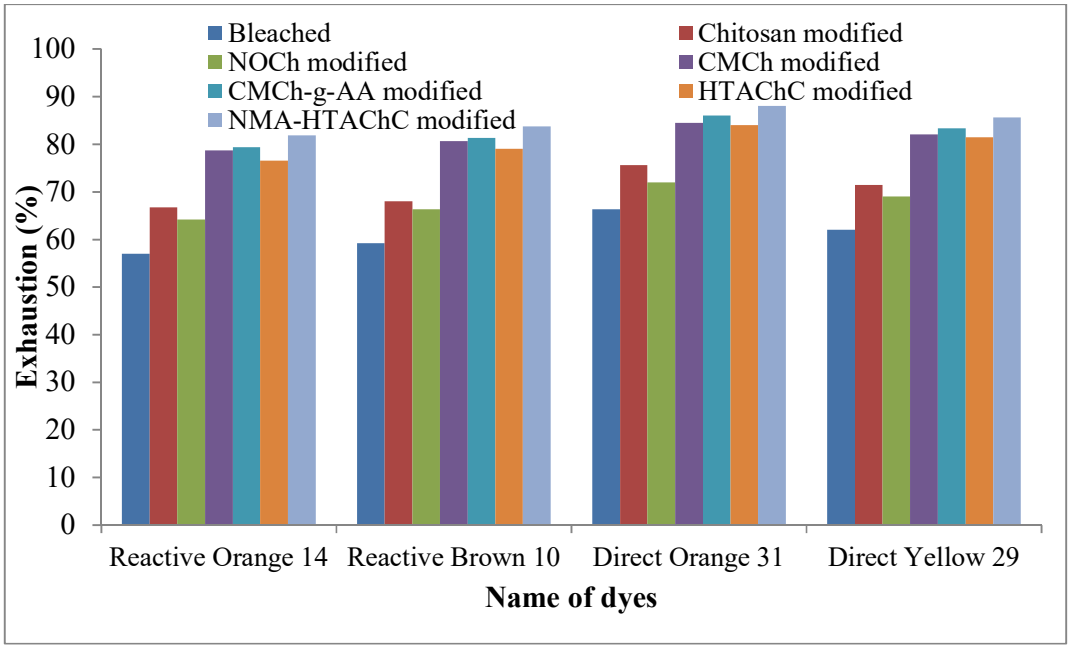


Figure 3.39: Effect of dye absorption on dyeing of washed and modified cotton fibres

3.19 Test of Colour Fastness

3.19.1 Colour fastness to sunlight in air

Colour fastness of washed and modified jute and cotton fibres on exposure to sunlight in air.

Table 3.21: Colour fastness and change in colour of washed and modified jute fibres on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 cream white	5 cream white	5 cream white	5 cream white	5 off white	5 cream white	5 cream white
50	4 cream white	5 cream white	5 cream white	4-5 whiteness decrease	4-5 cream white	5 cream white	5 cream white
100	4 slightly yellowish	4 whiteness decrease	4 whiteness decrease	4 whiteness decrease	4-5 whiteness decrease	4 whiteness decrease	4 whiteness decrease

150	3-4 slightly yellowish	4 whiteness decrease	4 whiteness decrease	4 whiteness decrease	4 whiteness decrease	4 whiteness decrease	4 whiteness decrease
200	3-4 yellowish	3 slightly yellowish	3 slightly yellowish	3 slightly yellowish	3-4 slightly yellowish	3-4 slightly yellowish	3-4 slightly yellowish
250	3-2 dull yellowish	3-2 dull yellowish	3-2 dull yellowish	3-2 dull yellowish	3 slightly yellowish	3-2 dull yellowish	3-2 dull yellowish

Table 3.22: Colour fastness and change in colour of washed and modified cotton fibres on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 white	5 slightly yellowish	5 cream white	5 cream white	5 white	5 cream white	5 cream white
50	4-5 whiteness decrease	4-5 slightly yellowish	5 cream white	5 cream white	5 white	5 cream white	5 cream white
100	4 whiteness decrease	4-5 yellowish decrease	4-5 whiteness decrease	4-5 whiteness decrease	4-5 whiteness decrease	4-5 whiteness decrease	4-5 whiteness decrease
150	3-4 slightly yellowish	4-5 yellowish decrease	4-5 whiteness decrease	4-5 whiteness decrease	4-5 whiteness decrease	4-5 whiteness decrease	4-5 whiteness decrease
200	3 slightly yellowish	4 slightly yellowish	4 slightly yellowish	4 slightly yellowish	4 slightly yellowish	4 slightly yellowish	4 slightly yellowish
250	3 slightly yellowish	3 slightly yellowish	3 slightly yellowish	3 slightly yellowish	3 slightly yellowish	3 slightly yellowish	3 slightly yellowish

It is seen from the **Table 3.21** and **3.22,** that with the progress of exposure time to sunlight in open air, colour change appears to be very slight from white to slightly yellowish for washed jute and cotton and colour change appears from cream white to dull yellowish for washed jute fibre. Yellowing is one of the main features of the photochemical changes in cellulosic fibre. Yellowing of washed jute fibre may be caused by lignin which by the action of light undergoes degradation with some loss of

methoxyl groups lead to the formation of orthodiphenols and ultimately to orthoquinones which is the main cause of yellowing of jute fibre [Callow and Speakman, 1949]. Due to the presence of negligible amount of lignin in washed cotton fibre, a slight change in colour is occurred.

From the T**able 3.21** and **3.22**, It is also observed that the light fastness rating of washed and modified fibres after 250 h exposure to sunlight in open air nearly same. The colour fastness of modified jute and cotton fibres are better than that of washed jute and cotton fibres because all the modifiers (chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA- HTAChC) form a protective layer on the jute and cotton fibres surface which itself partial protective uv– radiation and decrease the rate of uv- light penetration into the fibre backbone. This effect decreases the action of the uv – light on the change of the colour fastness. The protective layer of all the modified fibres which reduce the rate of moisture diffusion to the site of fibres. So modification lowers the access of both moisture and oxygen of which are known to participate in fading or yellowing.

Table 3.23: Colour fastness and change in colour of washed and modified jute fibres dyed with Reactive Orange 14 on exposure to sunlight in air

Exposure period, hours	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
50	4-5 yellow	4-5 orange	4-5 orange	4-5 orange	5 deep orange	4-5 orange	4 medium orange
100	4-5 yellow	4 light orange	4 light orange	4-5 orange	4-5 orange	4-5 orange	4 orange
150	4 light yellow	3-4 orange	3-4 orange	4 light orange	4-5 orange	4-5 orange	3-4 orange
200	3-4 fade orange	3 light orange	3 light orange	4 light orange	4 light orange	4 light orange	4 light orange
250	3 fade yellow	3 light orange	3 light orange	3 fade orange	3 light orange	3 light orange	3 light orange

Table 3.24: Colour fastness and change in colour of washed and modified cotton fibres dyed with Reactive Orange 14 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
50	4-5 orange	5 orange	4-5 orange	5 deep orange	5 deep orange	4-5 orange	4 medium orange
100	4 orange	4-5 orange	4-5 light orange	4-5 orange	4-5 orange	4-5 orange	3-4 orange
150	3-4 light orange	4 orange	4 light orange	4-5 orange	4-5 orange	4 orange	4-5 orange
200	3 light orange	3-4 light orange	3 light orange	4-5 light orange	4-5 light orange	4 light orange	3 light orange
250	2-3 dull orange	2-3 dull orange	2 dull orange	4 light orange	4 light orange	4 light orange	4 light orange

Table 3.25: Colour fastness and change in colour of washed and modified jute fibres dyed with Reactive Brown 10 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
50	4-5 brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown	5 deep brown
100	4 light brown	4 light brown	4 light brown	4-5 brown	4-5 brown	4-5 brown	4 medium brown
150	3-4 light orange	4 Light brown	4-5 brown	4 light brown	4-5 brown	4 light brown	4 light brown
200	2-3 dull brown	4-5 brown	4-5 brown	4 light brown	4 light brown	4 light brown	4 light brown
250	2-3 dull brown	3 Light brown	2-3 Light brown	3-4 light brown	4 Light brown	4 light brown	4 light brown

Table 3.26: Colour fastness and change in colour of washed and modified cotton fibres dyed with Reactive Brown 10 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 bright brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
50	4-5 brown	4-5 brown	4-5 brown	5 deep brown	5 deep brown	4-5 brown	4-5 brown
100	4 brown	4-5 brown	4-5 brown	4-5 brown	4-5 orange	4 brown	4 medium brown
150	3-4 light brown	3-4 light brown	3-4 light brown	4-5 brown	4-5 brown	3-4 light brown	3-4 light brown
200	3 light brown	4 light brown	4 light brown	4 light brown	4 light brown	4 light brown	4 light brown
250	2-3 dull brown	3 light brown	3 light brown	4 light brown	4 light brown	4 light brown	4 light brown

Table 3.27: Colour fastness and change in colour of washed and modified jute fibres dyed with Direct Orange 31 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
50	4-5 orange	5 orange	5 orange	4-5 orange	5 bright orange	5 orange	5 bright orange
100	3-4 light orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange	4 medium orange
150	3-4 light orange	4-5 orange	4 orange	5 orange	4-5 orange	4-5 orange	4 orange
200	3 light orange	4 light orange	3 light orange	4 light brown	4 orange	4 orange	4 light orange
250	2-3 dull orange	4 light orange	2 dull orange	3 light brown	3 light orange	3 light orange	3 light orange

Table 3.28: Colour fastness and change in colour of washed and modified cotton fibres dyed with Direct Orange 31 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
50	4-5 orange	4-5 orange	4-5 orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
100	4 orange	4 orange	4 orange	5 bright orange	4-5 bright orange	4-5 bright orange	4-5 bright orange
150	3-4 light orange	4 orange	4 orange	4-5 orange	4-5 orange	4-5 bright orange	4-5 bright orange
200	3 light orange	4 light orange	4-5 orange	4 orange	4 orange	4 orange	4 orange
250	2-3 dull orange	3 light orange	2-3 dull orange	4 light orange	4 light orange	4 light orange	4 light orange

Table 3.29: Colour fastness and change in colour of washed and modified jute fibres dyed with Direct Yellow 29 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
50	4-5 yellow	4-5 yellow	4 yellow	4-5 yellow	5 deep yellow	4-5 yellow	5 deep yellow
100	3-4 light yellow	4 yellow	3-4 light yellow	4-5 yellow	4-5 yellow	4-5 medium yellow	4-5 medium yellow
150	3-4 light yellow	4 yellow	4 yellow	4-5 yellow	4-5 yellow	4-5 yellow	4-5 yellow
200	3 dull yellow	4 light yellow	3 light yellow	4 light yellow	4 light yellow	4 light yellow	4 light yellow
250	2-3 dull yellow	3 light yellow	2-3 dull yellow	3-4 light yellow	4 light yellow	4 light yellow	4 light yellow

Table 3.30: Colour fastness and change in colour of washed and modified cotton fibres dyed with Direct Yellow 29 on exposure to sunlight in air.

Exposure period, hours	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
0	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
50	5 yellow	5 yellow	4-5 yellow	5 deep yellow	5 deep yellow	4-5 yellow	5 deep yellow
100	4 yellow	4-5 yellow	4-5 yellow	4-5 yellow	5 deep yellow	4-5 yellow	4-5 medium yellow
150	3-4 light yellow	4-5 yellow	4 yellow	4-5 yellow	4-5 yellow	4-5 medium yellow	4 yellow
200	3 light yellow	4 yellow	3 light yellow	4 light yellow	4-5 yellow	4 yellow	4 light yellow
250	2-3 dull yellow	3 light yellow	2-3 dull yellow	3-4 light yellow	4 light yellow	3-4 light yellow	4 light yellow

The light fastness of the different types of washed and modified with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC jute and cotton fibres dyed with two reactive and two direct dyes have been studied according to grey scale and the rating are shown in the **Table 3.23** to **Table 3.30**.

From the **Table 3.23** to **Table 3.30** it is observed that jute and cotton fibres dyed with Reactive Orange 14 exhibit considerably better colour fastness on exposure to sunlight in air than other reactive dye. It is also evident that the Reactive Brown 10 exhibits somewhat better colour fastness. This may be explained from the structural features of the dyes. From the structure of dyes it is observed that Reactive Orange 14 and Reactive Brown 10 contain one dichlorotriazinyl and one dihalidetriazinyl group

respectively. Thus the number of covalent bonds between the dyes and the fibres cellulose will be more and stronger in order of Reactive Orange 14 > Reactive Brown 10. So Reactive Orange 14 exhibit better colour fastness on exposure to sunlight. Dichlorotriazinyl group of reactive dyes has two electron deficient carbon groups and is therefore, susceptible to nucleophilic substitution reaction with partially ionized hydroxyl ions of the cellulose can be formed by either nucleophillic substitution or addition and the presence of more in number of these bonds will give better colour fastness properties [Farouqui et al., 1997; Trotman, 1984]. The oxidation reaction varies from dye to dye and due to the variation of covalent bonds between the dye and the fibre molecules [Farouqui and Hossain et al., 1997].

From these tables it is also observed that the change in colour of dyed fibres occurs within 50-250 h exposure and then no or slight change occurs on further increase of exposure time. This is probably, due to the mechanism of the light action produced by dye on the fibres and it is also observed that modified dyed fibres give better colour fastness properties than washed dyed fibres when they are exposed to sunlight in air. An intensive oxidation of the fibre is due to the capacity of the dye molecule, excited by the absorption of the short wave of uv-light, to be reduced because of the hydrogen contained in cellulose. As a result, further oxidation of the reduced dye by the oxygen of the air, intermediate form dye-hydrogen peroxide may be formed which is also capable of oxidizing the fibre [Sadov et al., 1973]. This oxidation reaction rapidly occurs at the earlier time of light exposure. The oxidation reaction varies from dye to dye due to the variation of covalent bonds between the dye and the fibre molecules [Farouqui et al., 1986]. It also may be explained that after modification, the –OH groups on fibre backbone are blocked by graft co-polymerization reaction. As a result the atmospheric oxygen cannot react with the fibre to form peroxy radicals. So, the change in colour or fading does not occur or slightly occurs.

3.19.2 Colour fastness on washing with soap solution

Table 3.31: Colour fastness and change in colour of Reactive Orange 14 dyed unwashed and washed modified jute fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 deep yellow	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
40	4 light yellow	4-5 orange	4-5 orange	4 orange	4-5 orange	4 medium orange	4-5 orange
60	4 yellow	4-5 orange	3-4 orange	4 orange	4-5 orange	3-4 orange	4 orange
80	3 yellow	3-4 light orange	3 light orange	3-4 orange	4-5 orange	3 light orange	3-4 light orange
100	2 poor orange	3 light orange	2 fade orange	3 light orange	4 light orange	3 light orange	3 light orange

Table 3.32: Colour fastness and change in colour of Reactive Orange 14 dyed unwashed and washed modified cotton fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
40	3 light orange	3-4 medium orange	4 bright orange	4-5 medium orange	4-5 orange	4 medium orange	4-5 orange
60	3 light orange	4 bright orange	4 bright orange	4 bright orange	3-4 medium orange	4-5 orange	4 orange
80	3 light orange	4 medium orange	3 light orange	4 bright orange	3-4 medium orange	3-4 light orange	3-4 light orange
100	3 poor orange	3 light orange	3 fade orange	3 light orange	3 light orange	3 light orange	3 light orange

Table 3.33: Colour fastness and change in colour of Reactive Brown 10 dyed unwashed and washed modified jute fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
40	4 medium brown	5 brown	4 medium brown	5 brown	5 deep brown	4-5 bright brown	4-5 bright brown
60	3-4 light brown	4-5 brown	4 brown	4 medium brown	5 brown	4-5 brown	4-5 brown
80	3-4 light brown	4 brown	3 light brown	4 light brown	4-5 brown	4 medium brown	4-5 brown
100	2 dull brown	3 light brown	2 dull brown	4 light brown	4 light brown	3 light brown	4 light brown

Table 3.34: Colour fastness and change in colour of Reactive Brown 10 dyed unwashed and washed modified cotton fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
40	4-5 brown	4-5 brown	4-5 brown	5 deep brown	5 deep brown	4-5 brown	4-5 brown
60	4 brown	4-5 brown	3-4 light brown	4-5 brown	4-5 brown	4-5 bright brown	4 bright brown
80	3-4 light brown	4 light brown	3 fade brown	4-5 brown	4-5 brown	3 fade brown	4 bright brown
100	2 dull brown	3 fade brown	2 dull brown	3 fade brown	4 light brown	2-3 fade brown	3 fade brown

Table 3.35: Colour fastness and change in colour of Direct Orange 31 dyed unwashed and washed modified jute fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
40	4-5 orange	4-5 medium orange	5 orange	5 orange	5 orange	4-5 medium orange	5 orange
60	3-4 light orange	4-5 medium orange	5 orange	4-5 medium orange	4-5 medium orange	4-5 orange	4-5 medium orange
80	3-4 light orange	4 light orange	3-4 light orange	3-4 light orange	4-5 medium orange	3-4 light orange	4-5 medium orange
100	2 light orange	3 light orange	3 light orange	3 light orange	4 light orange	3 light orange	4 light orange

Table 3.36: Colour fastness and change in colour of Direct Orange 31 dyed unwashed and washed modified cotton fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
40	4-5 orange	5 orange	5 orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
60	4 orange	4-5 orange	4-5 orange	4-5 orange	4-5 bright orange	4-5 orange	4-5 bright orange
80	3-4 light orange	4 orange	3 light orange	4 orange	4 orange	4 orange	4-5 orange
100	2 fade orange	3 light orange	2 fade orange	3 light orange	3 light orange	3 light orange	3 light orange

Table 3.37: Colour fastness and change in colour of Direct Yellow 29 dyed unwashed and washed modified jute fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
40	4 yellow	4-5 medium yellow	4-5 medium yellow	5 yellow	5 bright yellow	5 yellow	5 deep yellow
60	4 yellow	4 yellow	4 yellow	4-5 medium yellow	4-5 yellow	4 yellow	5 yellow
80	3-4 light yellow	3 light yellow	3 light yellow	4-5 medium yellow	4-5 medium yellow	4 yellow	4-5 yellow
100	2 fade yellow	3 light yellow	2 fade yellow	3 light yellow	4 light yellow	3 light yellow	4 light yellow

Table 3.38: Colour fastness and change in colour of Direct Yellow 29 dyed unwashed and washed modified cotton fibres on washing at different temperatures.

Washing temp. (°C)	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unwashed	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
40	4-5 yellow	5 yellow	4-5 yellow	5 deep yellow	5 deep yellow	5 yellow	5 deep yellow
60	4 yellow	4-5 yellow	4 yellow	4-5 yellow	4-5 yellow	5 yellow	5 yellow
80	3 light yellow	4 yellow	3-4 light yellow	4-5 yellow	4-5 yellow	4-5 yellow	4-5 yellow
100	2 fade yellow	3 light yellow	3 light yellow	3 light yellow	4 light yellow	3 light yellow	4 light yellow

The colour fastness on washing and change in colour of unmodified with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC jute and cotton fibres dyed with two reactive and two direct dyes have been studied according to grey scale and the rating are shown in the **Table 3.31** to **Table 3.38** cellulosic fibres dyed with Reactive Orange 14, Reactive Brown 10, Direct Orange 31 and Direct Yellow 29 have been studied at 40, 60, 80, and 100 °C temperature and the results are tabulated in the **Table 3.31** to **Table 3.38**.

It is observed that the **Table 3.31** to **Table 3.38** colour fastness of modified dyed fibres on washing with soap solution is slightly better than washed dyed fibres. This may be related to the symmetry of substitution of dyes in the fibres. The physical and chemical structure alterations of the modified fibres might affect the wash fastness properties. Another way, it may be explained that the compact or rigid structure of the modified fibres which require high activation energy for migration, made it difficult to remove dye molecules from the fibres fibre surface.

It is evident that the wash fastness decreases with the increase of temperature. It seems that at higher temperature, dissolution of the dye particles from the fibre surface takes place and hence more dye is easily washed off the fibre. Noted that, the solubility of dye increases with the increase of washing temperature

In conclusion, Reactive Orange 14 and Direct Orange 31 dyes have comparatively good wash fastness except Reactive Brown 10 and Direct Yellow 29. This is attributed to the very stable covalent bond that exists between the dye molecules and the fibre polymers.

3.19.3 Colour fastness to acid spotting

Table 3.39: Colour fastness and change in colour to acid spotting of Reactive Orange 14 dyed unspotted and spotted modified jute fibres with different acids.

Acid used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 deep yellow	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
Acetic acid	4 yellow	4-5 orange	4-5 orange	3 bright orange	4-5 orange	4-5 bright orange	4-5 medium orange
Tartaric acid	4 yellow	4-5 orange	4-5 orange	4-5 orange	4-5 orange	4-5 bright orange	4-5 bright orange
Hydroch-loric acid	4 yellow	3 light yellow	3 dull yellow	4-5 orange	4-5 orange	4 medium orange	3-4 orange
Sulfuric acid	3 dull yellow	3 light yellow	3 dull yellow	3 light orange	4-5 orange	4 medium orange	3-4 orange

Table 3.40: Colour fastness and change in colour to acid spotting of Reactive Orange 14 dyed unspotted and spotted modified cotton fibres with different acids.

Acid used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
Acetic acid	3 light orange	5 bright orange	4 bright orange	4 bright orange	3-4 medium orange	4-5 bright orange	4 medium orange
Tartaric acid	3 light orange	4-5 bright orange	3-4 bright orange	4 bright orange	3-4 medium orange	4-5 bright orange	4-5 bright orange
Hydroch-loric acid	3 dull orange	4 light orange	3 light orange	4 bright orange	3-4 medium orange	4 medium orange	4 medium orange
Sulfuric acid	3 dull orange	4 light orange	3 light orange	3-4 medium orange	4-5 orange	4 medium orange	3-4 orange

Table 3.41: Colour fastness and change in colour to acid spotting of Reactive Brown 10 dyed unspotted and spotted modified jute fibres with different acids.

Acid used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
Acetic acid	3 light brown	3-4 brown	3-4 brown	4-5 medium brown	4-5 brown	3-4 brown	4 brown
Tartaric acid	3 light brown	3-4 brown	3-4 brown	4-5 medium brown	4-5 brown	4-5 bright brown	3-4 light brown
Hydroch-loric acid	3-4 light brown	3 light brown	3 light brown	4 light brown	4 medium brown	4-5 brown	3-4 brown
Sulfuric acid	2 black	3 light brown	3 light brown	2 black	2-3 black	3 light brown	3 light brown

Table 3.42: Colour fastness and change in colour to acid spotting of Reactive Brown 10 dyed unspotted and spotted modified cotton fibres with different acids.

Acid used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 bright brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
Acetic acid	4 light brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown	3-4 light brown
Tartaric acid	4 light brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown	4 brown
Hydroch-loric acid	3-4 light brown	3 light brown	3 light brown	4-5 brown	4-5 brown	3-4 brown	3-4 light brown
Sulfuric acid	2 black	2 light brown	2 light brown	2-3 black	2-3 black	3 light brown	3 light brown

Table 3.43: Colour fastness and change in colour to acid spotting of Direct Orange 31 dyed unspotted and spotted modified jute fibres with different acids.

Acid used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
Acetic acid	3 light orange	4-5 orange	4-5 orange	3-4 medium orange	4-5 orange	4-5 bright orange	4 medium orange
Tartaric acid	3 light orange	4-5 orange	4-5 orange	3-4 medium orange	4-5 orange	4-5 orange	4-5 orange
Hydroch-loric acid	3-4 light orange	3-4 light orange	3-4 light orange	3-4 light orange	4-5 medium orange	3-4 medium orange	4 light orange
Sulfuric acid	2 fade orange	3-4 light orange	3-4 light orange	3 light yellow	3 light yellow	3-4 medium orange	3-4 light orange

Table 3.44: Colour fastness and change in colour to acid spotting of Direct Orange 31 dyed unspotted and spotted modified cotton fibres with different acids.

Acid used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
Acetic acid	4 light orange	4-5 bright orange	4-5 bright orange	4-5 orange	4-5 orange	4-5 bright orange	4 medium orange
Tartaric acid	4 light orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange
Hydroch-loric acid	3-4 light orange	4 medium orange	4 medium orange	4-5 orange	4-5 orange	4 medium orange	4 light orange
Sulfuric acid	2 fade orange	3-4 light orange	3-4 light orange	3 light yellow	4 yellow	3-4 medium orange	3-4 light orange

Table 3.45: Colour fastness and change in colour to acid spotting of Direct Yellow 29 dyed unspotted and spotted modified jute fibres with different acids.

Acid used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
Acetic acid	4 light yellow	4-5 yellow	4-5 yellow	4 medium yellow	4-5 yellow	4-5 yellow	4-5 deep yellow
Tartaric acid	4 light yellow	4-5 yellow	4-5 yellow	4 medium yellow	4-5 yellow	4-5 yellow	4-5 deep yellow
Hydroch-loric acid	3-4 light yellow	3-4 light yellow	3-4 light yellow	4-5 medium yellow	4-5 medium yellow	3-4 light yellow	4 yellow
Sulfuric acid	2 fade orange	3-4 light yellow	3-4 light yellow	3 light yellow	3 light yellow	3 light yellow	3-4 light yellow

Table 3.46: Colour fastness and change in colour to acid spotting of Direct Yellow 29 dyed unspotted and spotted modified cotton fibres with different acids.

Acid used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
Acetic acid	4 medium yellow	4-5 yellow	4-5 yellow	4-5 yellow	5 bright yellow	4-5 yellow	4-5 yellow
Tartaric acid	4 medium yellow	4 yellow	4 yellow	4-5 yellow	5 bright yellow	4 yellow	4 yellow
Hydroch-loric acid	3-4 light yellow	3 light yellow	3 light yellow	4-5 yellow	4-5 yellow	3-4 light yellow	4 yellow
Sulfuric acid	2 fade orange	3 light yellow	3 light yellow	3 light yellow	4 medium yellow	3 light yellow	3-4 light yellow

It is observed from the **Tables 3.39** to **3.46** that the colour fastness of undyed and modified (with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC) dyed washed fibres to spotting with acids such as sulphuric acid, acetic acid and tartaric acid is excellent in all cases. But in case of undyed and dyed modified fibres, strong acid such as sulphuric acid is used for spotting tests when a change in colour occurs. It is also observed that sulphuric acid is more effective to change the colour than acetic acid and tartaric acid because mineral acids (such as sulphuric acid, hydrochloric acid) are more reactive to fibres than organic acids e.g. acetic acid, tartaric acid. (Grey scale is used for assessing change in colour. International Standard, British Standards Institution).

3.19.4 Colour fastness to alkali spotting

Table 3.47: Colour fastness and change in colour to alkali spotting of Reactive Orange 14 dyed unspotted and spotted modified jute fibres with different alkalies.

Alkali used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
Sodium carbonate	4-5 orange	4-5 orange	5 orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange
Ammonia solution	2-3 light orange	3-4 medium orange	3-4 light orange	3-4 medium orange	3-4 medium orange	3-4 medium orange	3-4 medium orange
Ammonium carbonate	4 orange	4-5 orange	3-4 light orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange
Sodium hydroxide	2-3 fade yellow	3 light orange	3 light orange	3 light orange	3 light orange	3 light orange	3 light orange

Table 3.48: Colour fastness and change in colour to alkali spotting of Reactive Orange 14 dyed unspotted and spotted modified cotton fibres with different alkalies.

Alkali Used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange	5 deep orange
Sodium carbonate	4-5 yellow	3-4 medium yellow	3-4 medium yellow	3-4 medium yellow	4-5 yellow	3 light orange	4 orange
Ammonia solution	3 light orange	3 medium orange	3 medium orange	4 bright orange	3-4 medium orange	4 orange	3-4 light orange
Ammonium carbonate	3 light orange	4 medium orange	4 medium orange	4 bright orange	3-4 medium orange	3 light orange	4 orange
Sodium hydroxide	2-3 dull yellow	3 light orange	2-3 dull yellow	4-5 yellow	5 bright yellow	3 light orange	4-5 orange

Table 3.49: Colour fastness and change in colour to alkali spotting of Reactive Brown 10 dyed unspotted and spotted modified jute fibres with different alkalies.

Alkali used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 bright brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
Sodium carbonate	4-5 brown	5 bright brown	4-5 medium brown	5 bright brown	5 bright brown	4-5 brown	5 bright brown
Ammonia solution	3 light brown	4-5 medium brown	4 light brown	4-5 medium brown	4-5 brown	4-5 medium brown	4-5 medium brown
Ammonium carbonate	3-4 light brown	4-5 medium brown	3-4 light brown	4 light brown	4 medium brown	4 medium brown	4 medium brown
Sodium hydroxide	2 dull brown	3 light brown	2 dull brown	3 light brown	3 light brown	3 light brown	3 light brown

Table 3.50: Colour fastness and change in colour to alkali spotting of Reactive Brown 10 dyed unspotted and spotted modified cotton fibres with different alkalies.

Alkali used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 bright brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown	5 deep brown
Sodium carbonate	4-5 brown	4-5 brown	4-5 brown	5 deep brown	5 bright brown	5 bright brown	5 deep brown
Ammonia solution	4 brown	5 bright brown	5 bright brown	5 bright brown	5 bright brown	5 bright brown	5 bright brown
Ammonium carbonate	3-4 light brown	4-5 brown	3 light brown	4-5 brown	4-5 brown	4-5 brown	4-5 brown
Sodium hydroxide	3 brown shaded	3 light brown	3 brown shaded	3 light brown	3 light brown	3 light brown	3 light brown

Table 3.51: Colour fastness and change in colour to alkali spotting of Direct Orange 31 dyed unspotted and spotted modified jute fibres with different alkalies.

Alkali used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
Sodium carbonate	3 light orange	4 medium orange	4-5 medium orange	4-5 medium orange	4-5 medium orange	4-5 medium orange	4-5 medium orange
Ammonia solution	3 light orange	4-5 medium orange	4 medium orange	4 medium orange	4 medium orange	4-5 medium orange	4-5 medium orange
Ammonium carbonate	3 light orange	4 medium orange	3 light orange	3-4 light orange	4-5 medium orange	4 medium orange	4 medium orange
Sodium hydroxide	3 fade orange	3-4 fade increased	3-4 fade increased	3-4 fade increased	3-4 fade increased	3-4 fade increased	3-4 fade increased

Table 3.52: Colour fastness and change in colour to alkali spotting of Direct Orange 31 dyed unspotted and spotted modified cotton fibres with different alkalies.

Alkali used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange	5 bright orange
Sodium carbonate	4 orange	4-5 orange	4 medium orange	4-5 orange	4-5 orange	4-5 orange	4-5 orange
Ammonia solution	4 orange	3-4 light orange	4 medium orange	4-5 orange	4-5 orange	3-4 light orange	3-4 medium orange
Ammonium carbonate	3-4 light orange	4 medium orange	4 light orange	4-5 orange	4-5 orange	4 medium orange	4 medium orange
Sodium hydroxide	3 light orange	4 medium orange	3 light orange	4 medium orange	4 medium orange	4 medium orange	4 medium orange

Table 3.53: Colour fastness and change in colour to alkali spotting of Direct Yellow 29 dyed unspotted and spotted modified jute fibres with different alkalies.

Alkali used	Fastness grade and colour of jute fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
Sodium carbonate	3-4 light yellow	4-5 medium yellow	4 medium yellow	4-5 medium yellow	4-5 yellow shaded	4-5 medium yellow	4-5 medium yellow
Ammonia solution	3-4 light yellow	4 medium yellow	3-4 light yellow	4 medium yellow	4 yellow shaded	4 medium yellow	4 medium yellow
Ammonium carbonate	3-4 light yellow	4 medium yellow	3-4 light yellow	4-5 medium yellow	4-5 medium yellow	4 medium yellow	4 medium yellow
Sodium hydroxide	3 fade yellow	3-4 light yellow	3 fade yellow	3-4 light yellow	3-4 light yellow	3-4 light yellow	3-4 light yellow

Table 3.54: Colour fastness and change in colour to alkali spotting of Direct Yellow 29 dyed unspotted and spotted modified cotton fibres with different alkalies.

Alkali used	Fastness grade and colour of cotton fibre						
	Bleached	Chitosan modified	NOCh modified	CMCh modified	CMCh-g-AA modified	HTAChC modified	NMA-HTAChC modified
Unspotted	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow	5 deep yellow
Sodium carbonate	4 yellow	4-5 yellow	3-4 light yellow	4-5 yellow	4-5 yellow	4-5 yellow	4-5 yellow
Ammonia solution	4 yellow	4 yellow	3-4 light yellow	4-5 yellow	4-5 yellow	4 yellow	4 yellow
Ammonium carbonate	4 yellow	4 yellow	3-4 light yellow	4-5 yellow	4-5 yellow	4 yellow	4 yellow
Sodium hydroxide	3-4 fade yellow	4 yellow	4 fade shaded	4 yellow	4 yellow	4 yellow	4 yellow

It is observed from the **Table 3.47** to **3.54** that the colour fastness of undyed washed and modified (with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC) fibres and their dyed fibres to spotting with alkalis, such as, sodium carbonate, sodium hydroxide ammonium carbonate and ammonium hydroxide is satisfactory in most of the cases, but in some cases, it gives unsatisfactory results by changing colour. It is evident that sodium hydroxide is more effective to change in colour than sodium carbonate, ammonium carbonate and ammonium hydroxide. Here NaOH is stronger than Na_2CO_3, $(NH_4)_2CO_3$ and NH_4OH. So sodium hydroxide is more effective to change in colour of dyed washed and modified fibres.

Chapter 4
CONCLUSION

Huge amount of prawn shell wastes are deposited on prawn processing industry and sea food processing areas which have virtually no use. Prawn shell wastes as raw material can easily be collected with almost low cost and can convert into value added products. Chitosan is a deacetylated product of chitin which is successfully converted into its water soluble fibre-reactive functional derivatives, especially NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC which overcame the drawbacks of chitosan, such as limited solubility, low fibre reactivity and poor laundering durability when applied on cellulosic jute and cotton fibres. Keeping in mind the valuable inherent properties and potentiality, the aim of present study was focused on the applications of chitosan and its fibre-reactive derivatives in textile processing.

Chitosan (Ch) and its said derivatives were successfully synthesized by deacetylation of chitin, reductive amination of chitosan, carboxymethylation of chitosan, graft copolymerization of CMCh, quarternization of chitosan and acrylamidomethylation of HTAChC respectively at ambient condition which were also optimized.

The synthesized products were used as modifiers to cellulosic (jute and cotton) fibres in an optimized condition. From this investigation it is clear that absorption of dye has significantly increased due to the treatment of jute and cotton fibres with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC. Here chitosan and its derivatives acted as the bridges between the fibre surfaces and dye molecules, resulting in higher dye absorption for the dyestuffs. Fastness of the dyed sample had also been investigated through colour fastness to washing, acid, alkali and sunlight. Here treated fibres showed better colour fastness than untreated fibres.

On the basis of results obtained from our investigations the following conclusion may be drawn:

- Yield of chitin, chitosan and its derivatives depends on reaction conditions. Where demineralization, deproteinization, deacetylation, reductive amination, etherification, carboxymethylation, grafting etc. were involved.

- Difference among the FTIR peaks indicated the difference among the prepared chitin, chitosan and its different derivatives.
- Order of thermal behavior by TGA is as follows: chitosan modified > CMCh modified > unmodified > NOCh modified > HTAChC modified > CMCh-g-AA modified, NMA-HTAChC modified and chitosan modified > unmodified > HTAChC modified > NOCh modified > NMA-HTAChC modified > CMCh modified > CMCh-g-AA modified for jute and cotton fibres respectively.
- Order of crystallinity by XRD is as follows: chitosan modified > NOCh modified > CMCh modified > CMCh-g-AA modified > HTAChC modified > and NMA-HTAChC modified cellulosic jute and cotton fibres.
- Modification of jute and cotton fibres was confirmed by different instrumental techniques, namely FTIR, SEM, XRD, TGA, DTA and DTG and also uniformity assured by SEM.
- Swelling resistance, colour fastness and tensile strength of modified jute and cotton fibres were improved but incase of moisture absorbancy HTAChC and NMA-HTAChC modified fibres showed higher results whereas chitosan, NOCh, CMCh, CMCh-g-AA modified fibres showed lower results compared to unmodified fibres.
- Enhancement of dyeability was approved by the dye exhaustion percentage.

From the processing and useful characteristics of cellulosic fibres modified with chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC as compared with conventional modifiers have shown considerable advantages. Therefore, these chitosan derivatives are suitable for the economical fibres production as a replacement for synthetic modifiers like PVA and poly-acrylate.

The production of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC from prawn shell wastes can be considered as feasible alternatives and generative products for textile sector in Bangladesh. From all the investigations it can be concluded that the NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC can be successfully used as textile finish for the cellulosic jute and cotton fibres, as a good modifying agents thus will help to manage prawn shell waste and to save the environment from pollution and among these NMA-HTAChC appears to be better than the others.

4.1 Future Work or Suggestions

Dedicating myself as a man of devotion to my country, I have tried my level best to bring out some fruitful results which will help upcoming researchers to get an access to perform further research work on my products in this or different fields. I would like to invite researchers and industrialists to watch it at a glance so that you will be able to make use of it by getting the information's listed below:

1. Prawn shell wastes has been used here as raw materials for the production of chitin, chitosan and water soluble fibre-reactive functional derivatives of chitosan, such as N-octyl chitosan (NOCh), carboxymethyl chitosan (CMCh), carboxymethyl chitosan-g-acrylic acid (CMCh-g-AA), N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (NMA-HTAChC) which is indigenous cheap and can easily be collected with almost free of cost.

2. Some of the chemicals or reagents can be recovered and reused easily which makes the process lucrative to make the production of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC economically feasible and low cost.

3. Although many researchers were reported chitosan and its some derivatives use in drug delivery system and which were prepared from different sources and imported by means of huge foreign currencies but no chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC production plants from prawn shell wastes have been planned to be established in Bangladesh as an alternative ecofriendly modifier or textile finishing agents in place of chemical modifier.

4. Industrialists would find themselves advantageous and free of red eyes of law due to green environment by the social workers as they can be assured by knowing this the production and use of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC in textile sectors are environmental friendly.

5. Dyeability enhancer and betterment of fastness grade is another beauty of chitosan, NOCh, CMCh, CMCh-g-AA, HTAChC and NMA-HTAChC as a bridge in between jute, cotton and dye under consideration of modified and unmodified fibres.

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2. **Islam, Md. M.**, Sultana, M. S. Mondal, Md. I. H., Dyeing Effect on Chitosan Treated Jute Fibre.