



Preparation and characterisations of chitosan thin film coated on the soda-lime glass substrate

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Abstract

Chitosan is a biopolymer obtained from chitin, one of the most abundant and renewable material on Earth. Chitin is a primary component of cell walls in fungi, the exoskeletons of arthropods, such as crustaceans, e.g. crabs, lobsters and shrimps, and insects, the radulae of molluscs, cephalopod beaks, and the scales of fish and Lissamphibia's. Chitosan is a biodegradable natural polymer derived from the exoskeleton of crustaceans. Because of its biocompatibility and non-biototoxicity, chitosan is widely used in the fields of medicine and agriculture. With the latest technology and technological progress, different active functional groups can be connected by modification, surface modification, or other configurations with various physical, chemical, and biological properties. Measuring the thickness of thin films is strongly required in the display industry. In recent years, as the size of a pattern has become smaller, the substrate has become larger. Consequently, measuring the thickness of the thin film over a wide area with low spatial sampling size has become a key technique of manufacturing-yield management. Films prepared by natural polymers have received considerable attention, in recent years due to their biodegradable and environmentally friendly properties. In this work the film thickness of chitosan was prepared and characterized by measure the film thickness at different speed of spin . From the results it can be seen the film thickness is inverse preportional to the spin speed at constant time.

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Table of Contents

Abstract	1
Acknowledgements	2
CHAPTER ONE	6
1.1 Introduction.....	6
1.1.1 Chitosan	7
1.1.2 Chitosan resources	8
1.1.3 Chitosan production	9
1.1.4 Properties and modifications of chitosan biopolymers	10
1.2 Recent researches of chitosan biopolymers	14
1.3 Application of chitosan biopolymers in environmental protection.....	20
CHAPTER TWO	29
2-1 Materials and Methods	29
2.1.1 Materials	29
2.1.1.1 Chitosan	29
2.1.1.2 Soda-lime glass	30
2.1.1.3 Acetic Acid.....	30
2.1.2 Methods	31
2.2 Devices and equipments	31
2.3 Chitosan and silica particle film preparation	33
2.4 Mechanical Methods to Measure Thin Film Thickness.....	34
2.5 Principle of film thickness measurement by spectroscopic reflectometry.....	35
CHAPTER THREE	37
3.1 Callipration of chitosan film thickness	37
CHAPTER FOUR	41
CHAPTER FIVE	42
REFERENCES	43

Table of Tables

Table 1-1 The main properties of chitin and chitosan	- 7
Table 1-2 Experimental conditions and adsorption capacities of MChs for the removal of Cu(II) ions from aqueous solutions [43].	- 23 Table
2-1 Chitosan properties	- 29
Table 2-2 Thermophysical and optical properties of the soda lime glass	- 30
Table 2-3 Physical and chemical properties of acetic acid.	- 30
Table 3-1 calibration speed of chitosan film at 2% concentration	- 37

Table of Figures

Figure 1-1: Chitosan chemical structure. NH_2 group is shown in the chitosan chemical structure produced by using chem. Office.	8
Figure 1-2: Differents between fungal source and sea source chitosan	10
Figure 1-3: Chemical equation of chitosan preparation by base of hydrolysis of chitin-	10
Figure 1-4: The chemical method for chitosan pre from shrimp and crab shells.-	13
Figure 1-5: Structure (a) and polymeric forms (b) of chitosan	13
Figure 1-6: Various physical and chemical properles of chitosan [26]	14
Figure 1-7: Different modifications of chitosan biopolymers [62]. Modifications can be used to attach different functional groups and to regulate hydrophobic, cationic and anionic properties of the obtained derivatives of chitosan demonstrating unlimited potential for application in various fields of science	15
Figure 1-8: Application potential of chitosan. Unique properties of chitosan and its derivatives find the application in various fields of human activity	16
Figure 1-9: Applications of chitosan-based biomaterials in infection diseases. Chitosan biomaterials having good biocompatibility, bioactivity and biosafety, demonstrate great potential in the field of infection control [126].	19
Figure 1-10: Electro spun nanofibers [37] as a novel class of materials that can be used in various biomedical applications.	21
Figure 1-11: Adsorption process of heavy metals from water, soil, air to food chain and finally to human [40].	23
Figure 1-12: Structures of investigated divalent metal-CS complexes [43].	25
Figure 1-13: Mechanism of monolayer chemical adsorption of toxic metal ions on the surface of chitosan-based magnetic adsorbent [165]. Metal ions, marked by red circles,	

are gradually adsorbed on the surface of the magnetic adsorbent.	28
Figure 2-1: Electronic scale that used to wiegh the chitosan powderer	32
Figure 2-2: magnetic stirrer	32
Figure 2-3 Ultrasonic cleaner wich used to clean substrate Ifusid silica)	33
Figure 2-4. Spin coater	34
Figure 2-5 chematic diagram of interfernce thin film thickness	35
Figure 2-6 Principle of interfernce for two layers	36
Figure 3-1 Cured chitosan layer thickness with respect to the spincoating speed film-	37
Figure 3-2 Schematic of stress/strain creation within thin films.	39

CHAPTER ONE

BIOCOMBATBLE MATERIAL

1.1 Introduction

Chitin and its deacetylated derivative, chitosan, are a family of linear polysaccharides composed of varying amounts of (β 1 \rightarrow 4) linked residues of N-acetyl-2-amino-2-deoxyD-glucose (glucosamine, GlcN) and 2-amino-2-deoxy-Dglucose (N-acetyl-glucosamine, GlcNAc) residues. Chitosan is soluble in aqueous acidic media via primary amine protonation. In contrast, in chitin, the number of acetylated residues is high enough to prevent the polymer from dissolving in aqueous acidic media. Chitin is a very abundant biopolymer that can be found in the exoskeleton of crustacea, insect's cuticles, algae and in the cell wall of fungi. Chitosan is less frequent in nature occurring in some fungi (Mucoraceae). Historically, commercial chitosan samples were mainly produced from chemical deacetylation of chitin from crustacean sources. More recently, chitosan from fungi is gaining interest in the market, driven by vegan demands. Moreover, these samples are better controlled in terms of low viscosity and exhibit a very high deacetylation degree [1]. Production from insect cuticles is also gaining interest, driven by the increased interest in protein production from these sources. The interest in chitin and chitosan relies on the myriad biological and technological properties exhibited by these polymers (Table 1-1). However, these properties are tightly related to the physicochemical properties of the polymers (mainly molecular weight and acetylation degree) [2]. Therefore, when working with chitin and chitosan a good and completed polymer characterization is mandatory. Several methodologies have been described to characterize chitin, chitosan and chitooligosaccharides, a description of which is far from the objective of this paper—but for interested readers, we recommend publications

Table 1-1 The main properties of chitin and chitosan

Property/Activity	Reference
Mucoadhesive	[5,6]
Anti-inflammatory	[7]
Antioxidant	[8]
Antimicrobial	[9]
Antifungal	[10]
Antihyperglycemic	[11]
Antitumoral	[7–12]

1.1.1 Chitosan

Usually in nature chitosan can be found as chitin. There are many natural products produced from chitin [13], however, each one has a different amount of chitin. For example, the proportion of chitin in shrimp and crab is 58% and 85% respectively, while, it is about 20% and 60% respectively in mosquito and butterfly, as well as in some parts of animals contain chitin e.g. in hoofs and feet. Chitosan is derived from Chitin in the form of Deacetylation Degree (DD) [14], others use the degree of acetylation (DA) [15].

$$DA = 100 - DD$$

Deacetylation means removing an acetyl from chitin, by deacetylation, chitosans are considered as a chitin family [16]. The chitin becomes soluble in a dilute acid and is called chitosan when the deacetylation degree is over of 60% [13]. The deacetylation degree can be defined by [15]:

$$DD = 100 \frac{n_{GlcN}}{n_{GlcN} + n_{GlcAc}} \quad (1-1)$$

Where, n_{GlcN} is the average number of D-glucosamine units, and n_{GlcAc} is the average number of N-acetylglucosamine units. The chitosan is a copolymer of D-glucosamine and N-acetylglucosamine [17]. Therefore, from equation (1-1), the DD is a ratio between the D-glucosamine units and N-acetylglucosamine units.

Figure (1-1) shows the chemical structure of chitosan [17], it appears as a straight chain copolymer, therefore, it is a semi crystalline polymer in the solid state.

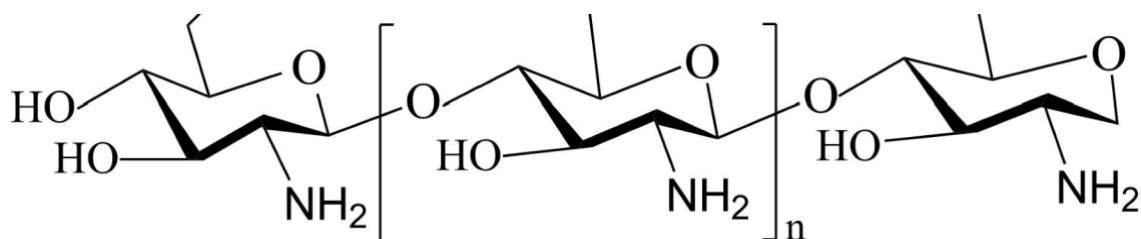


Figure 1-1 Chitosan chemical structure. NH₂ group is shown in the chitosan chemical structure produced by using chem. Office.

Figure (1-1) shows that the chitosan contains a NH₂ functional groups and these functional groups give chitosan their exclusive properties that are used in medical and pharmaceutical applications [16]. These unique properties such as biocompatibility, biodegradability and non-toxicity [18], which make it suitable for applications in the biomedical field. In addition, chitosan has the following chemical properties; linear polyamine, reactive amino groups, reactive hydroxyl groups available and chelates many transitional metal ions [18]. There are different mechanisms of structural degradation. For example, oxidative, hydrolytic, thermo-photo and ultrasonic degradation are responsive to chitosan. Moreover, chitosan has an active surface for the chemical reactions such as the photochemical reaction, this surface has considerable importance for these reactions because it has an NH₂ group [17] as has been mentioned before, it is a positive group. These groups give the chitosan films their special properties which allows chitosan to be suitable for many reactions including biological reactions that occur on the chitosan surface.

1.1.2 Chitosan resources

What is the differences between fungal source and sea source chitosan?

1. Fungal source is totally non-animal products.
2. Fungal source solve the problem of the sea food may cause allergy problem.
3. Fungal chitosan is also a good choice for vegetarian.

1.1.3 Chitosan production

Two methods are used to produce chitosan [308], chemical method and enzyme method. Figure (1-2) below shows the chemical equation to produce the chitosan by removing acetyls from chitin by base of hydrolysis of chitin. From this equation it can be observed that the function of NaOH concentration is playing an important role in the deacetylation processing as well as the time of reaction and temperature [17], and these factors affect the chitosan performance.

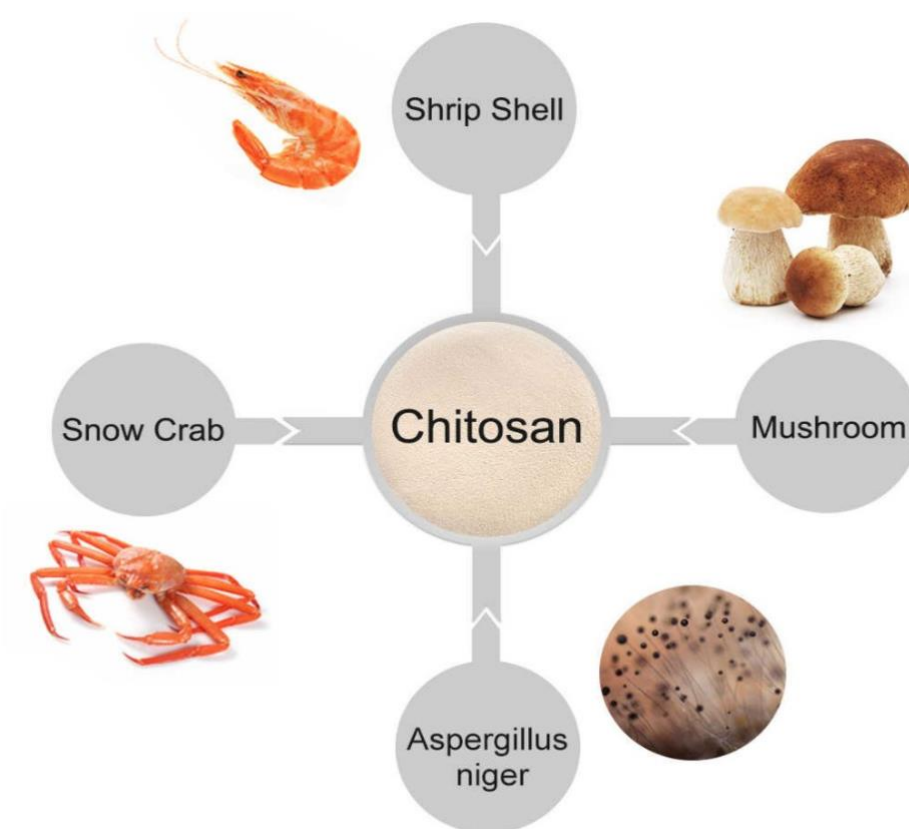


Figure 1-2 Differents between fungal source and sea source chitosan

Chemical methods have been used to prepare chitosan and it involves several methods; the Alkali fusion method, the concentrated alkali solution method, the alkali catalysis method and the hydrazine hydrate method [13]. The preparation

process to get the chitosan from shrimp and crab by chemical method is shown by figure (1-3).

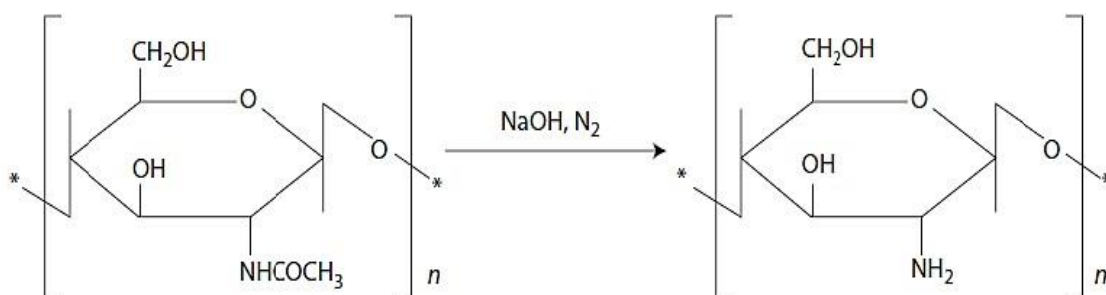


Figure 1-3 Chemical equation of chitosan preparation by base of hydrolysis of chitin

Three solvents can be used in the deacetylation process; acetone, ethanol and water [13]. The DD will be higher with acetone, and the chitosan will be yellowish and you can have difficulty in washing a product. However, using water as a medium of reaction will cause a low DD especially when the temperature reaches 80°C and washing the product will be hard. Consequently, for deacetylation, ethanol is considered as the best medium between them. After production processing chitosan has a solubility in different chemical materials. For example, an organic solvent, alkali, acid at a high concentration, chitosan is insoluble [17], while, Chitosan has a good solubility in water when the DD is 50%. In addition, chitosan becomes a modifiable polymer by reaction between the hydroxyl and the amino group [18-20]. Chitosan can accept a wide range of groups to offer a specific functionality, biological and physical properties. Different examples for reaction modifications [18]; acylation, hydrolysis, alkylation, acetylation. In the last few decades, several techniques have been developed to prepare chitosan microspheres, but the more recent one is spray drying[19-22]

1.1.4 Properties and modifications of chitosan biopolymers

Properties of chitosan biopolymers Chitosan is white odourless powder (or flakes) with different molecular weight (MW), degree of deacetylation (DD),

insoluble in water and organic solvents, soluble in dilute hydrochloric, formic and acetic acids. Melting point is approximately 290 °C [10]. Thus, the reason for the dissolution of chitosan in dilute hydrochloric acid is explained by the interaction of amino groups with hydrogen cations and converting it into a positively charged polyelectrolyte [13-18]. Cations in the composition damage hydrogen bonds among the chitosan molecules, and it leads to dissolving them in water. The solubility of chitosan depends on MW and DD. The higher the DD of chitosan, the higher the degree of protonation of amino groups in the molecule, and the easier it dissolves. The larger MW of chitosan, the large number of hydrogen bonds formed in its polymer chain, and more difficult it dissolves [23]. Solubility in water increases, biodegradability and biocompatibility enhance at partial removal of the acetyl groups (see figure 1-4) . DD and MW greatly determine many properties of chitosan, in particular, antimicrobial and antibiofilm activities, DD determines chitosan solubility and viscosity [24]. Therefore, at the application of chitosan biopolymers in practice (for example, as biomaterials, biopesticides, in drug delivery, immunology, etc.), it is necessary to have information about the main characteristics and control some parameters, such as the content of heavy metals, radionuclides, residual protein content, the presence of endotoxins, allergens bacteria and yeast, and other impurities [23,25]. Unlike other representatives of polysaccharides (cellulose, pectin, agar, dextran, etc.) chitosan possesses many important properties (Fig. 1-5), including non-toxicity, chelating activities, biocompatibility, biodegradability, adsorption capacities, film-forming ability, bacteriostatic action [25]. The antiviral, antibacterial activity of chitosan has been proven, the immunostimulating, adjuvant, adaptogenic, antihypoxic, cholestric, radioprotective, hemostatic effects of chitosan and its derivatives have been confirmed [26]. The antibacterial effect of chitosan is explained by the interaction of its positively charged amino groups with negatively charged phosphoryl groups of phospholipids of the bacterial cell wall, changes in metabolism, which leads to cell death [24]. It is known that chitosan is capable of interacting with nucleic acids, which, in turn, leads to the disturbance of synthesis of vital proteins and enzymes, and damaging the structure and function of the bacterial cell [27]. The

fungicidal properties of chitosan are described by identical mechanisms [28]. The analgesic effect of chitosan has been established due to its ability to absorb bradykinin. Chitosan sulfate, the structural analogue of chitosan, is similar in structure to the heparin— natural blood anticoagulant; the possibility of a synergistic effect of chitosan allows to create the drugs with anticoagulant and anti-sclerotic action . Furthermore, sulfated chitosan is a natural antioxidant, which absorbs hydroxyl and superoxide anion radicals, and can be a substrate for creating drugs and biologically active additives as well [28]. Chitosan can be used for treatment of diabetes because it increases insulin levels [29]. Possibility of using as a polymer matrix for the delivery and dosage release of drugs and anti-allergic properties of chitosan are proven [Application of chitosan in immunotherapy is proposed as an antitumor agent that suppresses the growth of tumor cells, pathogens, stimulates humoral and cellular immunity, for gene therapy with the aim of targeted delivery of genetic material [26]. Chitosan has wound healing properties, stimulates the formation of granulation tissue and the activity of fibroblast proliferation [30] and suppresses fibrosis [25]. Chitosan and its derivatives can be used to create biodegradable carriers of pharmaceuticals in the form of films, which provides the prolonging effect of their action [28].

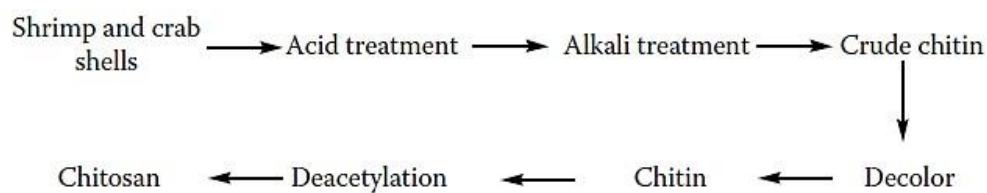


Figure 1-4 The chemical method for chitosan preparation from shrimp and crab shells.

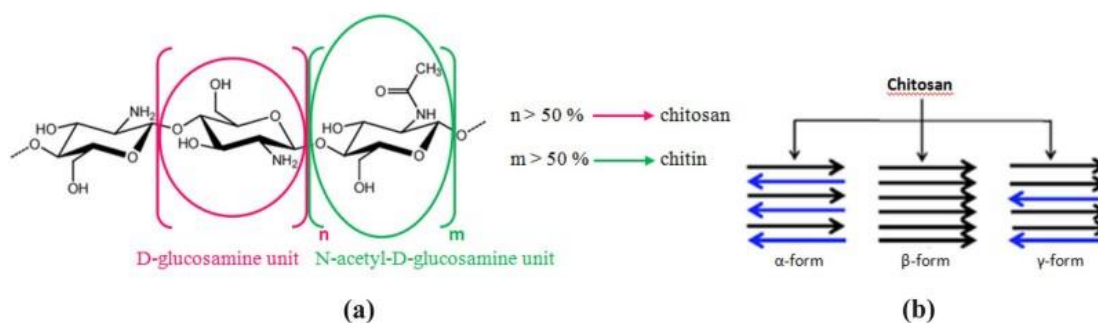


Figure 1-5 Structure (a) and polymeric forms (b) of chitosan

Modifications of chitosan biopolymers In order to improve the solubility, rheological properties, thermal stability, and oxidation resistance, chitosan is subjected to chemical modifications (Fig. 1-6). Amino groups, hydroxyl groups at C3 and C6 positions are the active groups in the chemical structure of chitosan. As a rule, the NH₂-amino group is more reactive than the C6-OH primary hydroxyl group (due to the free rotation), and the primary hydroxyl group is more reactive than the C3-OH secondary hydroxyl group. Chemical modification of chitosan could be carried out on amino, hydroxyl, or both amino and hydroxyl groups to form N-, O- or N,O-modified chitosan derivatives [31]. Etherification, esterification, crosslinking, graft copolymerization and O-acetylation are reactions carried out on hydroxyl groups, while acetylation, quaternization, Schiff's base reaction and grafting are carried out on amino groups [32].

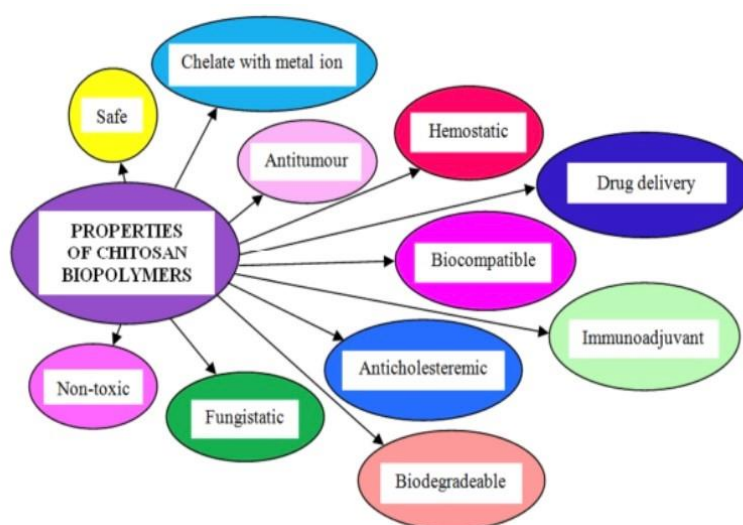


Figure 1-6 Various physical and chemical properties of chitosan [26]

1.2 Recent researches of chitosan biopolymers

The presence of amino and hydroxyl groups in chitosan opens the great opportunities for many industrial and biomedical applications. Use of chitosan biopolymers is uninterruptedly growing in such fields as medicine, pharmaceutical research, paper, textile, agriculture and food industries, cosmetology, tissue engineering, ecology, biotechnology, wastewater treatment (Fig. 1-7). Chitosan-based materials have also found application in veterinary medicine, medical nutrition, production of dietary supplements, biopesticides, biosensors, chromatographic materials [33]. The use of chitosan has been described in direct tablet compression, as tablet disintegrant, for the production of controlled release dosage form or for the improvement of drug dissolution [25,32]. Application of chitosan biopolymers in biomedical practice Recent applications are in ophthalmic, nasal, sublingual, buccal, periodontal, gastrointestinal, colon-specific, vaginal, mucosal-vaccine and gene carrier fields. Chitosan, being an adsorbable and nontoxic polymer, is favored in drug delivery because of antiulcer and antacid properties, which help in preventing drug irritation. During the last years the use of chitosan composite-based scaffolds as a biomaterial has been reported for tissue engineering due to the cationic nature and ability to form interconnected porous structures. Chitosan with other biomaterials such as hydroxyapatite, bioactive glass ceramic are used for bone repair and reconstruction to form a carbonated apatite layer to enhance the mechanical properties [33]. Owing to unique properties (toughness, biocompatibility, oxygen permeability) chitosan-based biomaterials in the form of fibers, mats, sponges have been used for burn treatment and wound dressings [28,33]. Influence of chitosan biomaterials on the synthesis of collagen for wound healing was studied [34]. Chitosan has been modified by authors [31] for using as a dressing material for treatment of wounds and burns. It was found that dressing materials based on chitosan and its modified forms, having haemostatic and analgesic properties, and also possessing properties of high strength, nontoxicity, good water absorption capacity and biocompatibility, together with other polymers (both synthetic and natural) accelerate the process of wound contraction and healing [35]. Researches carried out in the field of infectious

diseases show the effectiveness of the use of chitosan in this area. Systems developed on the base of chitosan with different properties have been proposed [34]. It has been shown that these systems reduce the side effects of drugs and increase the effectiveness of treatment.

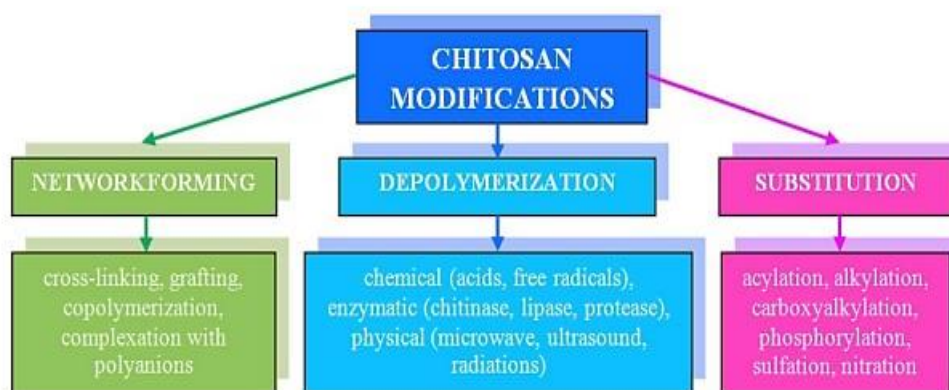


Figure 1-7 Different modifications of chitosan biopolymers [62]. Modifications can be used to attach different functional groups and to regulate hydrophobic, cationic and anionic properties of the obtained derivatives of chitosan demonstrating unlimited potential for application in various fields of science

Taking account the current situation in the world with COVID-19 and other viruses, chitosan is also active in the form of a vaccine system, for example, it can deliver antibodies to the nasal mucosa and load gene drugs that prevent or disrupt the replication of viral DNA/RNA, and deliver them to infected cells. Further work on the development of systems is proposed that will be widely used in clinical practice, in particular, for the treatment of infectious diseases (Fig. 1-8). From year to year, the spread of dangerous pathogenic bacteria is very serious for all mankind and that requires the creation of new materials for the treatment of bacterial infections. Thus, antibacterial and antibiotic properties of the chitosan biomaterial with grafted ferulic acid (CFA) against *Listeria monocytogenes* (LM), *Pseudomonas aeruginosa* (PA), and *Staphylococcus aureus* (SA) were studied [30,35]. It was found that CFA exhibits bactericidal action against LM and SA and bacteriostatic action against PA within 24 h of incubation. In dependence on the

concentration it suppresses the viability of pathogenic bacteria, which was associated with a change in membrane properties.

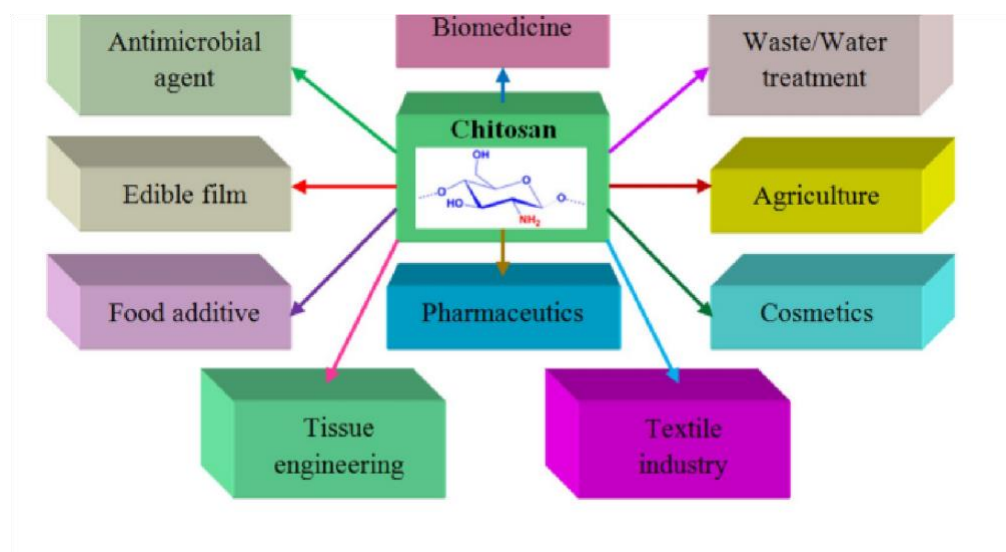


Figure 1-8 Application potential of chitosan. Unique properties of chitosan and its derivatives find the application in various fields of human activity

Silver nanoparticles functionalized with chitosan (CSAgNP) using ethanolic buds extract of *Syzygium aromaticum* have been studied by authors of the given research [35]. Decrease in the level of fibrinogen was observed, platelet aggregation was decreased at relatively high concentrations of CS-AgNP. It has been shown, that due to the stable nature, antibacterial, anticoagulant, antiplatelet and thrombolytic activity, CS-AgNP can be used as effective antibacterial agents and anticoagulants with low toxicity in the biomedical field. The antibacterial efficacy of chitosan has been confirmed as a drug for pulpctomy of infectious teeth. Chitosan can play an important role in preventive dentistry as an agent to prevent dental diseases (caries, periodontitis), an ingredient in dentifrices (toothpaste, chewing gum) having antibacterial effects, increasing salivary secretion, dental adhesives, etc. [36]. Blend hydrogels based on poly(vinyl alcohol) and carboxymethylated chitosan were prepared by electron beam irradiation at room temperature. The antibacterial activity of the hydrogels was studied by optical density method. It was found that the hydrogels exhibited satisfying antibacterial activity against *E.coli*. and can be widely used in the field of biomedicine and pharmacy . A new antifungal denture base material was proposed by modifying polymethyl

methacrylate (PMMA) with chitosan salt (chitosan hydrochloride (CS-HCl) or chitosan glutamate (CS-G)) [25,37]. When studying its properties in vitro, the analyses carried out showed that, despite the antifungal effect of CS salts in solution, modification of the PMMA polymer with these CS salts does not improve the antifungal, antibiofilm and antiadhesive properties of the base material of PMMA dentures. Possible applications of biomaterials based on chitosan, antibiotics and antifungal drugs, considering the factors and mechanisms of the antimicrobial and antifungal action of chitosan, and also clarifying the question of the genetic response of microorganisms to chitosan are described [38]. It was established that there are electrostatic interactions between positively charged chitosan and negatively charged cell surface of the microorganism (teichoic acid in gram-positive bacteria, lipopolysaccharide (LPS) in gramnegative bacteria and phosphorylated mannosyl in fungi). In addition, chitosan chelates environmental ions and nutrients which are necessary for the survival of bacteria. It was found that low-molecular-weight chitosan and oligo-chitosan exhibit an extracellular antifungal action, inhibit mitochondrial activity and ATP production, and are also able to penetrate the cell wall, inhibiting DNA/RNA and protein synthesis. The research indicates that despite the fact that chitosan exhibits a high antimicrobial effect, its use on a large scale is limited by some of its properties, such as low solubility in water, lack of a certain molecular weight and purity. Nanoparticles based on chitosan and its modified forms are widely tested as drug carriers in ophthalmology for the treatment of bacterial and viral infections, glaucoma, age-related macular degeneration and diabetic retinopathy. Authors summarize recent advances in chitosan-based nanotherapy for drug delivery to the eye and the problems that arise during this process [37]. It has been shown that a high degree of crosslinking in chitosan nanoparticles allows to increase drug retention and facilitates penetration into the eyes. The following research describes in detail the recent developments of chitosan blends with an emphasis on electrospun nanofibers, which represent a new class of biomaterials, in the field of biomedical applications (drug delivery, wound healing, tissue engineering, biosensing, regenerative medicine) (Fig. 1-9) [38]. A new method (electrospinning) for the

production of chitosan nanofibers with a large surface area and porosity was considered [39]. Specialists working with this material can optimize the properties of these fibers and expand their range of applications. Thus, it is indicated that the development of complex organ structures will be achieved by the method of electrospinning in combination with 3D printing technology, three-dimensional scaffolds will be designed, integrated with growth factors and cells with high viability. It is noted that despite the fact that specialists were able to simulate the structure and morphology of natural tissue, these studies need further clinical trials until they can be reliably applied in medical practice.

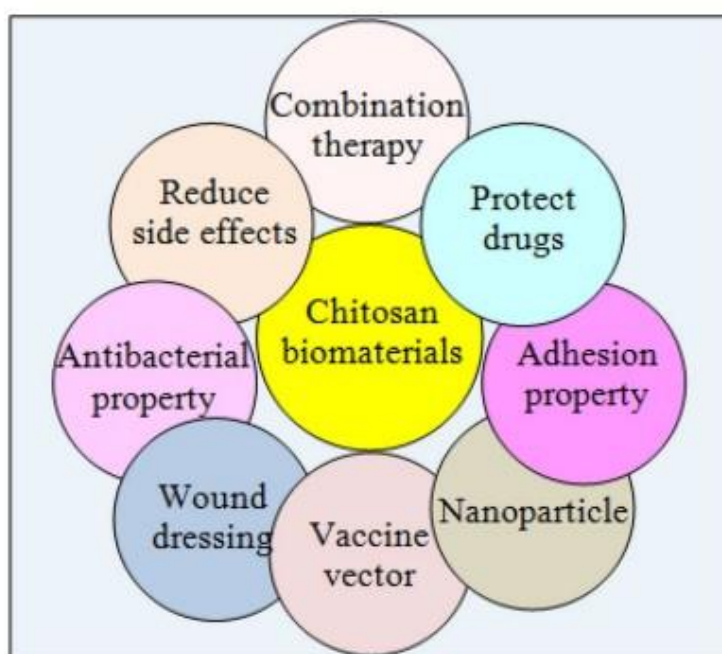


Figure 1-9 Applications of chitosan-based biomaterials in infection diseases. Chitosan biomaterials having good biocompatibility, bioactivity and biosafety, demonstrate great potential in the field of infection control [126].

Chitosan-g-poly(acrylic acid)/ attapulgit /sodium alginate composites were synthesized as drug delivery matrices [39]. It was found that the composite hydrogels displayed high pH-sensitivity. The cumulative release ratios of diclofenac sodium from the hydrogel were 3.76% at pH=2.1 and 100% at pH=6.8 within 24 h, respectively. It has been noted that such pH-sensitive polymeric materials can be offered for the development of new controlled drug delivery

systems. Hydrogels based on different ratios of chitosan and sodium alginate were synthesized by gamma irradiation in the presence of glutaraldehyde, as a cross-linking agent. It was found that these blend hydrogels exhibited high water swelling and showed high thermal stability. Also, pH responsive release character of ketoprofen drug was studied in this research [138]. The recent developments in chitosan delivery systems for the treatment of brain tumors and neurodegenerative diseases are presented [38,39]. It has been found that chitosan nanoparticles improve therapeutic efficacy in various brain diseases due to their biocompatibility, biodegradability, low toxicity, controlled release, mucoadhesiveness and effective absorption by nasal mucosa and tumor cells. Chitosan nanoparticles are also often used as carriers for the delivery of therapeutic agents, successfully increasing their concentration in the brain, and when administered intranasally chitosan nanoparticles are commonly used to deliver drugs to the brain and can increase nasal residence time and absorption by the nasal mucosa. It is known that chitosan composites are widely used in medical practice (treatment of burns, artificial kidneys, blood anticoagulation and bone, tendon or blood vessel engineering), and also developed for use in biosensors, packaging, separation processes, food or agricultural industries, and catalytic processes. It is planned to create modulated three-dimensional structures of chitosan using cross-linking processes that improve its use in various fields of medicine, as well as the development of porous catalysts based on chitosan in order to increase the efficiency of catalytic processes by increasing the number of available active sites [37]. The presence of electron-donating amino and hydroxyl groups allows to use chitosan biopolymers in the separation and purification of biologically active compounds (nucleic acids and products of their hydrolysis, steroids, amino acids). Recent studies have indicated usage of chitosan-based compounds as effective materials to inhibit biofilm formation and attenuate of virulence properties by various pathogenic bacteria [40]

1.3 Application of chitosan biopolymers in environmental protection

Environmental pollution with heavy toxic metals is dangerous for all living organisms. Currently, methods (such as bioadsorption, solvent extraction, remediation by plants and microbial communities, green separation by hydrogel polymers, immobilization, and others) are being developed for the extraction of heavy metals from soil and wastewater. Taking into account the ingestion of heavy metals by humans with food and to prevent serious risks to human health, development of effective methods for removal of heavy toxic metals and to eliminate the toxicity of these metals in air, soil, and water is of great importance. The food chain of the adsorption process of heavy toxic metals by humans is shown in Fig. 1-10 . In work [41] it was shown that chitosan hydrolysates obtained by hydrolysis of high-molecular-weight chitosan by the fenton reaction can be used as potent agents that block or form tight complexes with fine dust in the air, containing some solid particles and unknown species of microorganisms. This data can be used in the future for the production of various dust-proof masks and filters for the purpose of human healthcare. Nanomaterials prepared on the basis of chitosan and its modified forms together with carbon nanotubes have been used as bacterial disinfectors of various pollutants in the field of water purification [40,41]. The use of these materials compared to ozonation, chlorination and other disinfection methods has demonstrated the absence of treatment by-products. In the future, the authors plan to develop materials with increased stability and low toxicity, and pay special attention to the design of nanomaterials, which affects the properties and efficiency of the material, in order to eliminate undesired adsorption of biomolecules and increase antibacterial activity. A promising direction for application of chitosan biopolymers is the sphere of environmental protection, for development of drugs with radioprotective properties, sorbents for the isolation of radionuclides . Chitosan can also be used as a flocculant for water treatment, surfactants and membranes in ultrafiltration, reverse osmosis and evaporation, purification of industrial effluents containing heavy metal ions [41].

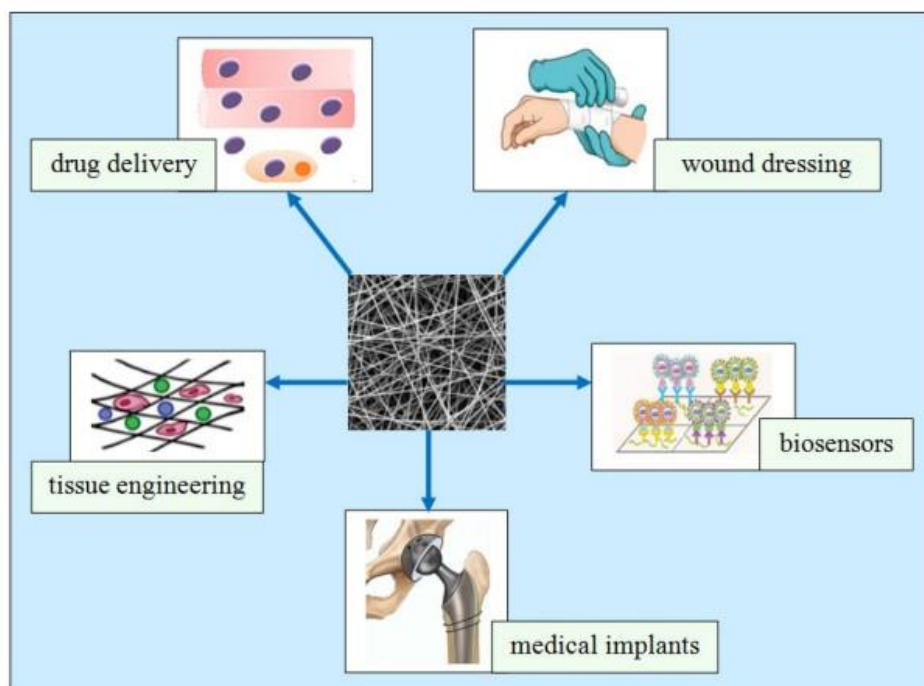


Figure 1-10 Electro spun nanofibers [37] as a novel class of materials that can be used in various biomedical applications.

Chitosan is capable of forming complexes with transition metals [42]. The heavy metal complexes are formed as a result of donation of a nonbonding pair of nitrogen or oxygen electrons on the $-NH_2$ and/or $-OH$ groups, respectively, to a heavy metal ion. Chitosan granules obtained by cross-linking chitosan with tripolyphosphate have significant adsorption properties towards the metal ions and could be effectively used in wastewater treatment [41]. The nature of the cation is very important in the mechanism of interaction; the affinity of chitosan for cations absorbed on film shows selectivity in the following order [43]: One of the important applications of chitosan biopolymers is connected with their ability to bind heavy and toxic metal ions. The adsorption capacity values of modified chitosans (MChs) for metal ions removal were reported by Zhang et al. [40]. It has been noted that adsorption process depends not only on adsorbent structure (modifications of chitosan) but also on conditions of the process (pH, temperature, adsorbent dosage, contact time, co-existing ions). The following results for $Cu(II)$ ions adsorption were observed on various MChs (Table 1-2). Authors of research [41] developed monodisperse microspheres of chitosan by the microfluidic method and carried out experiments to study the adsorption characteristics to remove

copper ions from waste water. The adsorption mechanism was developed based on various adsorption kinetics and isotherms models. The research results showed a high adsorption capacity (75.52 mg/g) and a readsorption efficiency of 74% after 5 cycles. The adsorption capacity in the presence of other competing ions was also studied by the density functional theory (DFT) analysis. It was shown that the most energetically favorable structure of the studied metal complexes is the central model, where metal ions are coordinately bound to several amino groups (Fig.1-11). Pb(II) imprinted magnetic biosorbent was prepared by means of lead ion imprinting technology and cross-linking reactions between chitosan, Fe₃O₄ and *Serratia marcescens* in order to remove of Pb²⁺ ions. The influence of solution pH, adsorbent dosage, selectivity of sorption and desorption processes were studied on the adsorption of lead ion. Kinetics and thermodynamics of adsorption process were investigated and adsorbent was studied by XRD, VSM, SEM, EDS, FTIR, XPS and BET analyses. It has been established that nitrogen of amino group and oxygen of hydroxyl group in Pb(II) imprinted magnetic biosorbent were coordination atoms [40,43]. A method of heavy metal ions removal by bioadsorption with hybrid 3D printing technology was proposed [44]. For this purpose, 3D chitosan composite of a monolithic structure of reusable application was prepared, which showed high efficiency in contrast to conventional biosorbents.

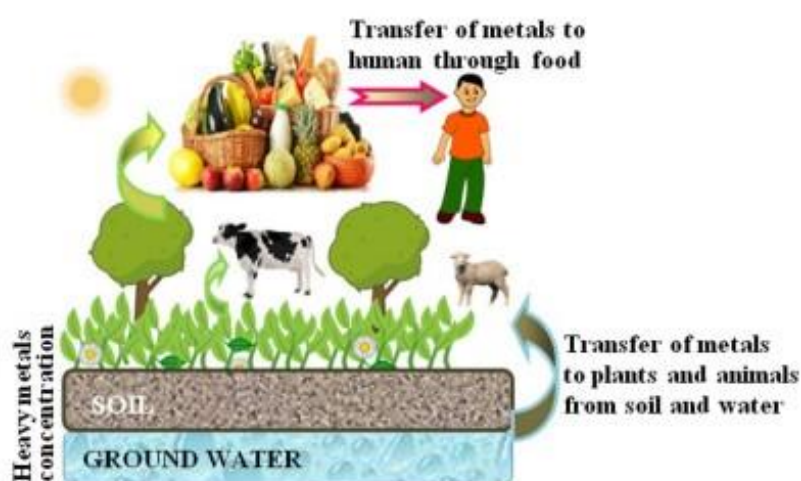


Figure 1-11 Adsorption process of heavy metals from water, soil, air to food chain and finally to human [40].

Table 1-2 Experimental conditions and adsorption capacities of MChs for the removal of Cu(II) ions from aqueous solutions [43].

Modified chitosan	Characterization methods	Amount of Cu(II) mg/g	Optimum conditions		
			pH	T(K)	contact time(min)
Chitosan/sulphydryl-functionalized graphene oxide composite	FTIR, TG, SEM, XRD	425.00	2.0	293	30
	FTIR, SEM, NEXAFS	413.20	6.0	298	15
Carbonaceous sulfur-containing chitosan-Fe(III)	FTIR	192.57	4.5	298	500
Chitosan/poly(vinyl amine) composite beads	FTIR, XRD	132.50	5.0	303	90
Epichlorohydrin o-crosslinked maleic acyl chitosan adsorbent	FTIR, EDS, TGA, DSC	130.72	6.0	298	180
	FTIR, SEM	126.00	6.0	303	0
Chitosan-epichlorohydrin-triphosphate adsorbent	SEM, FTIR, TGA, XRD	124.00	5.0	303	300
					120
Cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base resin	FTIR, 13C-NMR, DSC, SEM	88.07	5.0	303	
			6.5	298	360
8-Hydroxyquinoline-2-carboxaldehyde chitosan	XRD, TEM, FTIR, zeta potential	43.47	5.0	323	500
Chitosan-modified MnFe ₂ O ₄ nanoparticles		20.10	5.5	313	144
Epichlorohydrin cross-linked xanthate chitosan	FTIR, 13C-NMR, XPS		5.5		0
Chitosan/poly(vinyl) alcohol thin adsorbent	FTIR, SEM.	1.34		298	240

membranes modified with amino functionalized

Permeability

The adsorption capacity of this material was about 13.7 mg/g at T=25 °C and pH=5.5. The analyses performed showed that the –NH₂ and –OH functional groups of chitosan are actively involved in the adsorption process, which indicates the possibility of this sorbent using to remove numerous metal ions from different solutions.

In work [162] recent data on removal of lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) by chitosan-based magnetic adsorbents from various aqueous solutions are presented. It has been shown that these adsorbents have a high adsorptive capacity towards toxic metals and can be reused in consecutive adsorption–desorption cycles. Langmuir isotherm model confirms good monolayer capacity values of 341.7 mg/g for lead, 152 mg/g for mercury, 321.9 mg/g for cadmium and 65.5 mg/g for arsenic (Fig. 1-12). Removal of cadmium ions from waste water was studied using polypropylene/sisal fiber/ banana fiber (PP/SF/BF) and chitosan/sisal fiber/banana fiber (CS/SF/BF) composite materials as adsorbents. It has been established that sorption capacity of CS/SF/BF composite (419 mg/g) is higher than PP/SF/BF composite (304 mg/

g), and permits multilayer adsorption. The carried out tests have shown that adsorption process was best satisfied with the Freundlich isotherm [44]. Modified chitosan-based nanocomposites (MCS/GOPEI) were prepared for removal toxic heavy metals and organic compounds from environmental water. The results of research showed that sorption process was characterized by pseudo-second-order kinetic and Langmuir isotherm model. High adsorptive capacities of these samples for arsenic, mercury ions, congo red, amaranth (220.26, 124.84, 162.07, 93.81 mg/g, respectively) were presented and the possibility of re-using these nanocomposites as promising adsorbents was shown [43]. Preparation of graphene oxide/ chitosan (GO/CS) composites as new promising sorbent materials for removal of heavy metal ions, dyes and other organic molecules from aquatic environment is presented in paper [45].

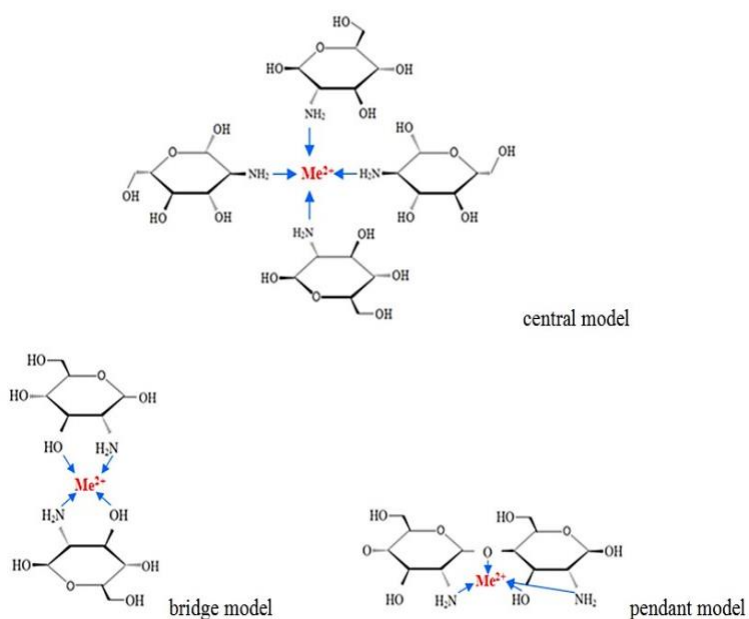


Figure 1-12 Structures of investigated divalent metal-CS complexes [43].

Sorption of copper (II), cobalt (II) and iron (III) ions, using chitosan composite sponges prepared by ice-segregation procedure, was studied for purification of waste water [45]. It has been determined that iron (III) ions were mainly adsorbed from two-component mixtures with cobalt (II) ions at pH=4, whereas copper (II) ions were removed from two-component mixtures with cobalt (II) ions at pH =6. Carried out experiments showed high chemical stability and reusability of these

sponges in sorption– desorption processes. Nitrogenenriched chitosan-based activated carbon biosorbent was prepared for separation of Cr(VI) and Pb(II) ions from contaminated water. Thermodynamic parameters have been studied, and kinetics of adsorption of these metal ions is well-fitted by a pseudo-second-order model. High efficiency, availability, recyclability, and cost effectiveness make it possible to use this biosorbent for wastewater treatment [43]. Magnetic phosphorylated chitosan composite (P-MCS) as an adsorbent for Co(II) ions was prepared by authors [46]. Adsorption capacity for Co(II) was equal to 46.1 mg/g. Adsorption isotherms and kinetic models of these ions well fitted the Langmuir model and the pseudo-second-order model, respectively. The carried out experiments have shown dependence of Co(II) adsorption process on surface chelation between functional groups and metal ions, and possibility of use P-MCS for treatment of wastewater. In order to eliminate the limitations in the use of chitosan as an adsorbent for the removal of heavy metals, such modifications as cross-linking, grafting, and the use of magnetic chitosan (modified with Fe₃O₄) were carried out [45,46]. It was suggested in further studies to focus attention on: issues of regeneration and desorption; replacing glutaraldehyde and epichlorohydrin as crosslinking agents with less toxic ones; the use of an adsorbent that does not depend on pH; the use of various optimization tools (for example, the response surface methodology) and other issues in order to use chitosan on an industrial scale. New class of crystalline porous composite consisting of metal ions and multidentate organic ligands is metal organic framework (MOF), which showed an appreciable capability in wastewater treatment for the removal of heavy metal ions. Functionalization of chitosan with ionic liquids (new class of salts with combination of organic and inorganic ions and with very unique and novel properties) was found to have increased adsorption capacity. They are immobilized on a solid support or they chemically react due to their high reactivity in adsorption process. Analyses carried out in work [46] showed that introduction of ionic liquids in chitosan improves thermal stability and heavy metal uptake properties. Chitosan conjugated magnetite nanoparticle (CH-MNP) as an effective adsorbent was synthesized for the removal of Pb(II) ions by means of controlled coprecipitation

technique and studied by response surface methodology (RSM) for optimization of process parameters [45]. Optimum value of pH, adsorbent concentration and contact time were obtained as 5.1, 1.04 g/L, and 59.9 min, respectively. Adsorption isotherm data were correlated well with the Langmuir adsorption isotherm model, and the equilibrium data followed the pseudosecond-order kinetics and intraparticle diffusion kinetic model. New EDTA modified γ -MnO₂/chitosan/Fe₃O₄ nanocomposite was produced for the removal of heavy ions from aqueous solutions. Experiments data have been shown high adsorption capacities for Pb(II) and Zn(II) (310.4 and 136 mg/g, respectively). Results of thermodynamic tests ($\Delta G^\circ < 0$, and $\Delta S^\circ > 0$) showed that the nature of adsorption by this nanocomposite for Pb(II) and Zn(II) ions is spontaneous and endothermic, and is favored at higher temperatures [47]. Adsorption and removal of chromium (VI) ions from aqueous solutions, using chitosan hydrogel crosslinked with polyacrylic acid and N, N'-methylenebisacrylamide, has been studied in paper [46]. Evaluation of adsorption mechanism was carried out using Langmuir, Freundlich, Redlich-Peterson, and Sips nonlinear isotherms. The removal of chromium (VI) at pH 4.5 and an initial metal concentration of 100 mg/L was 94.72%. It was proposed to use chitosan hydrogel as an economical and environmentally friendly adsorbent of heavy metal ions for water and wastewater treatment. A new efficient method of adsorption and removal of heavy metal ions with electric field-driven from wastewater has been proposed [48]. A composite adsorbent based on chitosan (CS) and sodium phytate (SP) deposited on a polyethylene glycol terephthalate (PET) material was used and placed near the cathode in a pair of titanium plate electrodes. Experiments have shown that the rate of copper ions removal adsorbed on the CS-SP/PET adsorbent increased from 56 to 88% for 10 mg Cu (II) solution per liter when the applied voltage was from 0 to 1.2 V (energy consumption was economical). The adsorption mechanism was correlated to the Langmuir isotherm model and the kinetic equation of the pseudo-second order. Chitosan and silica gel-based composite was prepared with the purpose to study the adsorption of heavy metal ions in various solutions [48]. This composite was studied by FTIR and SEM–EDS methods in order to obtain information about the presence of active sites and surface

morphology. The study of the adsorption process by this material showed the maximum percentage of removal of Cu (89.78%), Pb (96.9%) and Ni (69.33%) at pH=5, Hg (92.78%) at pH=6 with adsorbent mass of 1.5 g, temperature 30 °C and 120 min contact time. Adsorption of Pb is best satisfied to pseudo-first order, whereas pseudo-second order is best fitted to the adsorption of Cu, Ni and Hg. Obtained values of change in enthalpy testify to the effect that both physical and chemical adsorption occur in this process. A highly adsorptive cross-linked carboxymethyl chitosan (CMC)/2,3- dimethoxybenzaldehyde Schiff base complex was synthesized for removal of heavy metals such as lead (II) and cadmium (II) ions from aqueous solutions and characterized using FTIR, XRD and SEM analysis [47]. It was confirmed that adsorption follows the Freundlich model and the pseudo-second order kinetic model. The cross-linked Schiff base has been found to be an effective, environmentally friendly and inexpensive adsorbent. Development of a new economical and environmentally friendly chitosan nanoadsorbent has been proposed for water purification [45,47]. Use of inorganic nanomaterials, agricultural waste, adsorbents based on polymer nanocomposites for removing of heavy metal ions such as Hg (II), Cu (II), Cr (VI), Zn (II), Co (II), Cd (II), Pb (II) from wastewater has been studied. Experiments have shown that polymer-based materials have a strong chelating ability towards heavy metal ions, fast adsorption kinetics, and are well regenerated due to the synergistic effect of polymers and various nanofillers present in nanocomposites. Hydrogels based on different ratios of carboxymethyl cellulose (CMC) and carboxymethyl chitosan (CMCh) and prepared by γ irradiation showed high adsorption capacities for Pb and Au ions. It has been established that the effective sorption of these metal ions occurred with amino groups of the hydrogel with (CMC/CMCh) composition of 75/25 or 50/50. (see fig 1-13) Properties of the obtained hydrogels (gel fraction, swelling ratio, gel strength) were also studied [49]. Carboxymethylated chitosan hydrogels were obtained by γ -ray irradiation crosslinking method. Kinetic studies of sorption process were carried out with a purpose to determine favourable conditions for the adsorption of Fe(III) ions on these hydrogels and showed that maximum uptake of Fe(III) ions was equal to 18.5 mg/g at pH =4.7 [184]. Favorable adsorption

behavior was explained due to the coordination of Fe(III) ions with amino, hydroxyl and carboxyl groups in the structures of the proposed hydrogels.

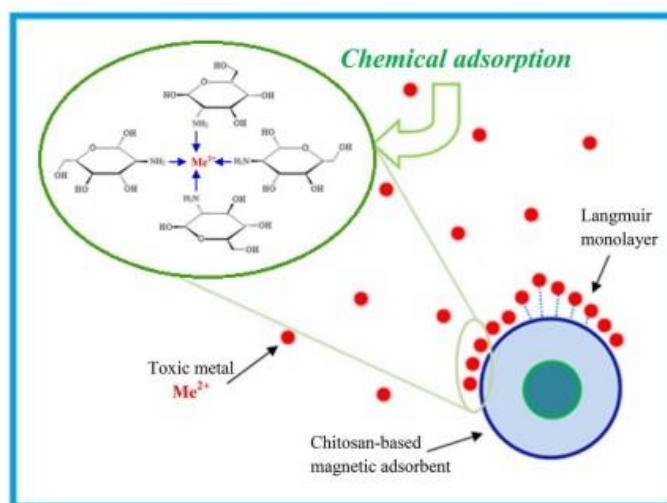


Figure 1-13 Mechanism of monolayer chemical adsorption of toxic metal ions on the surface of chitosan-based magnetic adsorbent [165]. Metal ions, marked by red circles, are gradually adsorbed on the surface of the magnetic adsorbent.

CHAPTER TWO

EXPERIMENTAL METHODOLOGIES

2-1 Materials and Methods

2.1.1 Materials

Chitosan, (extracted and purified from crab shell, deacetylation $\geq 85\%$ and Mw of ca. 370 kDa) was purchased from Sigma-Aldrich (Merck), Algés, Portugal. Acetic acid and lactic acid were acquired from Panreac Química S.L.U., Barcelona, Spain, and citric acid from Merck, Algés, Portugal. For microbiological tests, Mueller Hinton broth was purchase from Sigma-Aldrich (Merck), Algés, Portugal. All chemicals were used as received without any further purification.

2.1.1.1 Chitosan

Table 2-1 Chitosan properties

Physical properties	
. Appearance	Off-white powder .
Powder fineness	Finer than 120 mesh
size	
. Degradation temperature	250 °C.
. Powder Boiling Point	115.5 °C.
Chemical propertis	
. Degree of deacetylation	> 90.0%
. Solubility of 1% chitosan in 1% acetic acid	> 99.0%
. Viscosity	150–200 mPa s
. Moisture content	< 10.0%
. Ash content	< 1.0%
Mechanical properties at 25°C	
. Hardness	0.044±0.002
. Compressibility	0.132±0.007
. Adhesiveness	0.121±0.028 .
Cohesiveness	1.008±0.024 .
Elasticity	0.896±0.112

2.1.1.2 Soda-lime glass

Table 2-2 Thermophysical and optical properties of the soda lime glass

Property	value
Thermal conductivity	0.94 W/(m K)
Specific heat	0.88 kJ/(kg K)
Coefficient of linear expansion	$8.3 \times 10^{-6} \text{ }^\circ\text{C}$
Refractive index	1.58 cm ⁻¹ (at 355 nm)
Absorption coefficient	1.54 (at 355 nm)
Transmittance	0.85 (at 355 nm)
Hardness	5.37 GPa
Elasticity Modulus ratio 0.22	72 GPa Poisson's
Transition temperature	560°C
Refractive Index	1.52
Bulk density	2.49 g/cm ³
Thermal expansion coefficient	$8.5 \times 10^{-6} \text{ K}^{-1}$

2.1.1.3 Acetic Acid

Table 2-3 Physical and chemical properties of acetic acid.

Subject	Description
Formula Molecule	C ₂ H ₄ O ₂
Molecular Weight	60.05 g/mol
Appearance	Colourless liquid or crystals
Odor	Irritating odor of vinegar
Boiling Point	118.1°C
Melting Point	16.7°C
Acidity (pK _a)	4.76
Solubility in water	Fully miscible
Density	1.049 g/cm ³ , liquid

2.1.2 Methods

2.1.2.1 Preparation of Chitosan Solutions and Films

Chitosan, medium molecular weight, was dissolved in acidic aqueous solutions, using acetic, lactic and citric acid at different concentrations, ranging from 2.0 to 10.0 wt. %, by stirring the mixtures until a homogeneous solution is obtained. After complete dissolution, chitosan solutions were centrifuged at 3600 rpm (ca. $2200\times g$) for 10 min to remove any residual undissolved polymer. Fifteen grams of each solution was then cast in a plastic Petri dish with a diameter of 90 mm and dried in the oven at 50 °C overnight.

2.2 Devices and equipments

Figure.2-1 bellow shows the electronic scale that use in lab to wieght the 2mg from chitosan poweder. Figure 2.2 shows the a magnetic stirrer is a device widely used in laboratories and consists of a rotating magnet or a stationary electromagnet that creates a rotating magnetic field. This device is used to make a stir bar,immerse in a liquid,quickly spin or stirring or mixing a solution, for example.



Figure 2-1. Electronic scale that used to wiegh the chitosan powede



Figure 2-2 magnetic stirrer

Ultrasonic cleaning uses cavitation bubbles induced by high frequency pressure (sound) waves to agitate a liquid. The agitation produces high forces on contaminants adhering to substrates like metals, plastics, glass, rubber, and ceramics. After cutting the sodalime glass for square samples (20 cmX20 cm) the ionised water was used to clean sodalime glass substrate and placed in Ultrasonic cleaner for 10 mins finally dried the samples substrate see figure 2-3.



Figure 2-3 Ultrasonic cleaner used to clean substrate (fused silica)

2.3 Chitosan and silica particle film preparation

The Chitosan and the solution used in these experiments were purchased from (Sigma-Aldrich, Chitosan-448869, 0.1M acetic acid). To achieve a 2% concentration, the chitosan solution was prepared by dissolving 0.2 mg chitosan in 10 mL acetic acid. Chitosan films were produced by spin coating the chitosan solution (Oscilla) onto soda-lime glass microscope slides, (Thermo Scientific). To identify the spin speed for samples having thicknesses in the range 300 nm to 10 μm , a calibration curve was made. Before carrying out the laser ablation experiments, the samples were left to dry for one day.



Figure 2-4 Spin coater

2.4 Mechanical Methods to Measure Thin Film Thickness

Stylus profilometry and interferometry are two mechanical methods used to measure film thickness. Both methods require the presence of a groove or step between the surface of the film and the substrate. The grooves are produced either by masking portions of the substrate or by removing parts of the deposited film. In addition, interferometry requires a highly reflective surface to obtain interference fringes. In both methods, the film thickness is measured at a specific point. As a result, the uniformity of the film is a critical parameter that determines the accuracy of thickness. Reflectometry measures the intensity of reflected light as a function of wavelength. This method helps obtain spectra for single- and multi-layered thin films. The thickness of a small spot on the substrate can be measured via reflectometry using a microscope. The intensity of the reflected light as a function of wavelength can have a complex shape in the spectra depending on the film's RI, thickness, and other properties. Evaluating the spectra requires powerful software to extract the desired information.

2.5 Principle of film thickness measurement by spectroscopic reflectometry.

When a light beam is incident on a transparent film, a portion of the beam gets reflected at the surface, but the remaining portion goes through and hits the boundary with the substrate underneath. A portion of this remaining beam gets reflected there and goes back towards the surface of the film. When the two reflected beams - one from the surface and the other from the boundary - meet, they cause interference. This is thin film interference. In reality, what actually happens is much more complex. Some portion of the reflected beam from the boundary does not go through the surface. It gets reflected by the film surface and goes back towards the boundary. It gets reflected by the boundary again, and the same phenomenon is repeated many times. Thin film interference is produced by the superposition of multiple beams see fig 2-5 below:

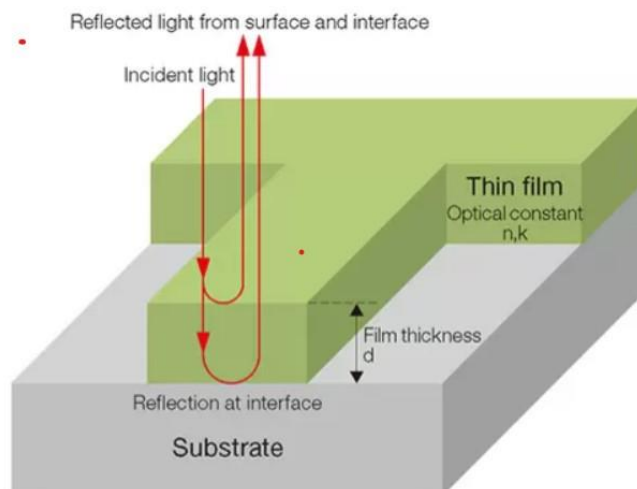


Figure 2-5 schematic diagram of interference thin film thickness

The thickness of a single-layer film can be measured easily using a spectrophotometer. Note, however, that this is possible only for film thickness in a range of approximately 0.3 to 60 μm , and that the refractive index of the film material is required for measurement.

First, I will explain the principle of film-thickness measurement relative to reflection measurement. When light strikes the film at a certain angle, there is interference between light reflected from the incident surface (A) and light reflected from the opposite surface (B), as shown in Fig.2.6

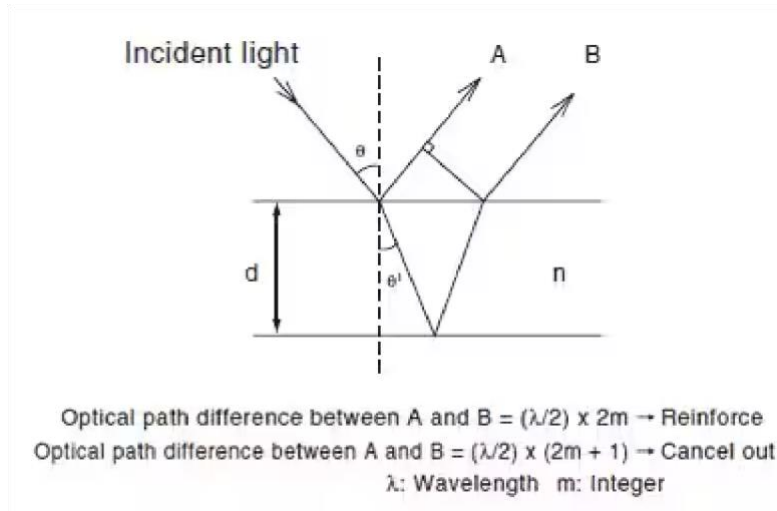


Figure 2-6 Principle of interference for two layers

Counting the number of peaks (or valleys) in the interference spectrum within a certain wavelength range makes it possible to calculate the film thickness using equation (2-1).

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2 \theta}} \times \frac{1}{\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)} \text{-----2-1}$$

Here, "d" is the film thickness, " Δm " is the number of peaks in the wavelength range used for calculation, "n" is the refractive index, " θ " is the angle of incidence with respect to the sample, and " λ_1 " and " λ_2 " are the start and end wavelengths in the wavelength range used for calculation.

CHAPTER THREE

RESULTS AND DISCUSSION

In this section the results of all experiments were carried out using the 5CB LC doped chitosan material and will be presented and discussed at a later point

3.1 Calliprariion of chitosan film thickness

Spin coating is the simplest method for fabricating a film on a substrate. Thinresist layers for photolithography are coated with this technique. The spincoating process starts with the dilution of the material to be deposited in a solvent. The solution is subsequently dispensed on the substrate surface. The wafer is then spun at a high speed. The thickness of the film is determined by the spinning speed, surface tension, and viscosity of the solution. The solvent is removed partly during the spinning process due to evaporation and partly by subsequent baking at elevated temperatures. Spin coating results in a relatively planar surface.

Table 3-1 calibration speed of chitosan film at 2% concentration

Spin speed (rpm)	Thickness (nm)
500	2000
1000	1300
2000	700
3000	400
4000	300
5000	200

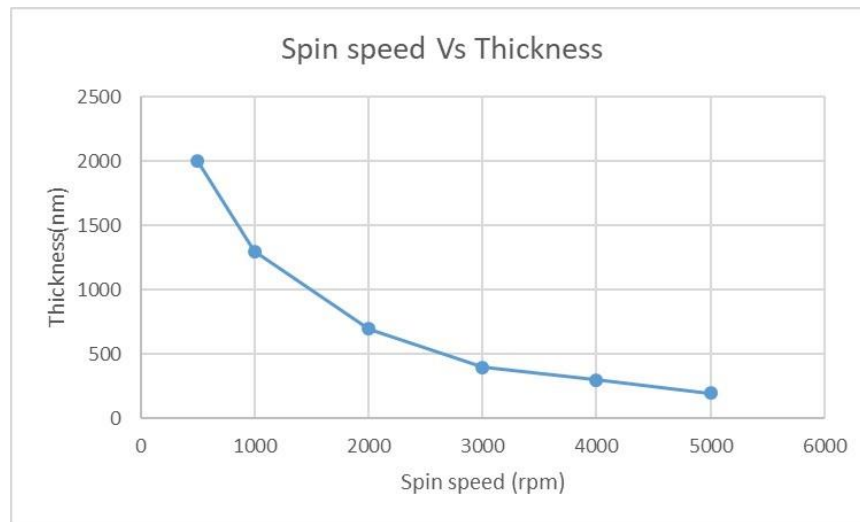


Figure 3-1 Cured chitosan layer thickness with respect to the spincoating speed film

The exact thickness of a film will depend upon the material concentration and solvent evaporation rate (which in turn depends upon the solvent viscosity, vapour pressure, temperature and local humidity) .

From this one or more data points, the spin thickness curve can be calculated - usually with a good degree of accuracy. The spin speed can then be adjusted to give the desired film thickness.

This process is to ensure that the approximate thickness of the chitosan layer can be determined. The relationship of the cured chitosan layer thickness with respect to the spin coating speed is as shown in Figure3-1 . The result shows consistency on the cured chitosan layer thickness from five measurements conducted. As a results the film thickness is invers preportional to the spin speed at constant time. The minimumm film thickness appered at 5000 rpm while the maximum thickness appeared at 500 rpm. Film thickness significantly affects coating quality and costs. Measuring it, and knowing which gauge to use, should be routine for all coaters. Coating thickness plays an important role in product quality, process control and cost control, and it can be measured with many different instruments.

Different and complex chemical reaction occur during the deposition process depending on the technique employed and deposition parameters, such as substrate temperature, deposition rate, pressure, and alignment of vapor stream with substrate, which give rise to a variety of microstructures. The resulting microstructure in turn defines the physical and chemical properties of the film, which means that an appropriate management of these variables is essential to obtain tailored film properties.

Thin films, due to their versatility to provide tailored properties, have found application in a number of sectors going from simple coatings for wear and corrosion protection, to more advanced applications such as antireflective coatings, microelectronics, photovoltaics, etc. Although these material structures have been selected due to exclusively their functional properties, they must be able to provide a reliable service operation with a proper mechanical and chemical resistance during the lifetime. These films, during deposition and operation, are prone to develop large stresses that might cause deformation and eventually mechanical failure, and therefore, it is essential to understand the microstructural processes involved in such effects to attempt to mitigate through the control of microstructure during the fabrication. Unlike bulk structures where the mechanical properties do not show a clear dependence on the sample size, in reduced structures like these, these properties are strongly affected by the resulting microstructure giving rise to a different behavior as compared to their bulk counterparts.

Let us assume a thin film deposited on relative tick substrate as illustrated in Figure 1. If strain by any means were produced on the film, it would change its dimensions relative to the substrate where it is deposited to maintain the equilibrium. If, hypothetically, the film were not adhered to the substrate, it would be visible the change in dimensions, for example, when the strain has expanded the original dimensions of the film, as shown in part b of Figure 1. The action of matching again the expanded film into the substrate entails the application of a deformation to force the film to adopt the substrate dimensions as shown in part c, giving rise to the generation of stress within the film. The stored stress naturally tends to be

released to reach equilibrium, but depending on the degree of the substrate stiffness, part of this strain can be absorbed if the substrate is compliant which is reflected in a bending produced in the film/ substrate system, or can remain entirely in the film if the substrate has a high stiffness.

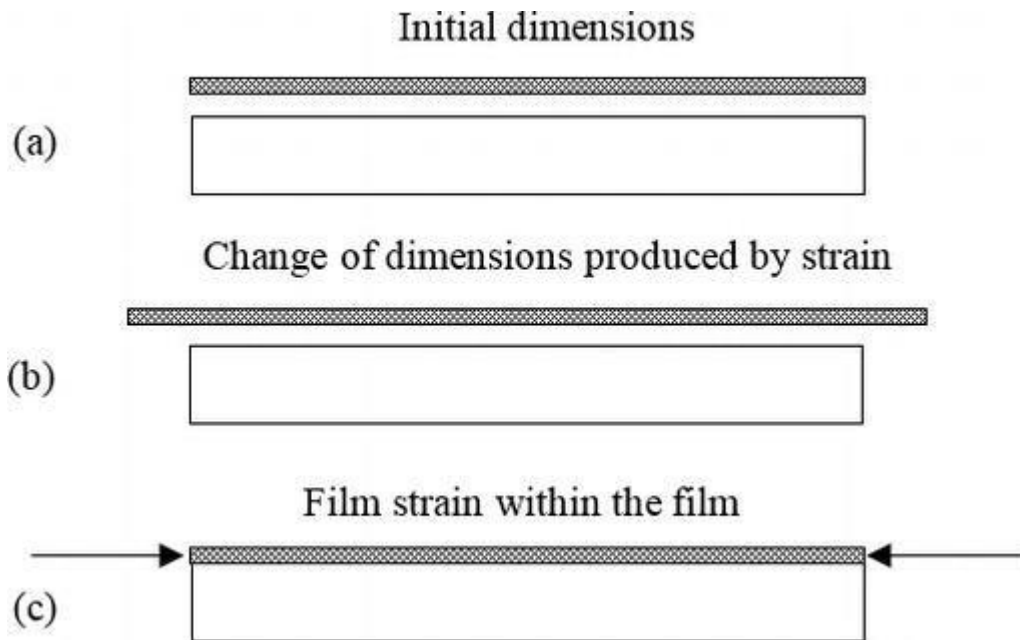


Figure 3-2 Schematic of stress/strain creation within thin films.

There are several techniques available for thin film characterization, but their accuracy strongly depends on the depositing material, substrate material, and film thickness. In most cases, two or more techniques are complementary used to access the required information with high precision. Regardless of the progress in thin film technology, important challenges remain to be tackled, including the accurate prediction of film properties based on the final microstructure, more advanced characterization techniques in the biomedicine field, and sophisticated models for data analysis.

CHAPTER FOUR

CONCLUSIONS

Physical and mechanical properties of chitosan films can be controlled by choosing appropriate molecular weight of chitosan and solvent system. Film prepared from 2g chitosan in acetic acid to make 2% concentration showed thickness of 2000 nm which was high value at lower spin speed (500 rpm), As a results the film thickness is inversly proportional to the spin speed.

In summary, calibration curve between spin speed and chitosan film thickness is done and it is so important to use as refernce for making the required thickness at the specified speed of spin. hin film is utilized across a wide range of industries including semiconductors, microelectronics, display technologies, and of course optical elements; this technology has enabled many of the technological breakthroughs taken for granted in modern times. While the end application of thin films can vary widely, what remains consistent is the need for precise control over the thickness of each layer during the epitaxial growth process.

Thin films technology has historically been used in a wide range applications going from decorative purposes in its early stage, evolving for optical purposes latter on, and an almost endless range of applications with the appearance of advanced deposition techniques, supported by the rapid development of vacuum technology and electrical power. Overall, thin films are used to enhance the properties of bulk materials by depositing a layer with the desired physical and chemical characteristics to improve their functionality.

CHAPTER FIVE

FUTURE WORKS

Thin-film technology has been used in many applications, including electronic and semiconductor devices such as micro-electromechanical systems (MEMS) and light-emitting diodes (LEDs), photovoltaic solar cells, optical coatings, manufacturing thin-film batteries, increasing the cost efficiency of photovoltaic systems, resisting chemical degradation, and manufacturing antireflective, reflective, and self-cleaning glass. Nowadays researchers are showing great attention towards the natural polymer or biopolymer based materials such as chitin, chitosan and cellulose. Major reason after this growing interest are the desired properties possessed by such biopolymers including biodegradability, biocompatibility, nontoxicity, antimicrobial features. Production of chitosan based biofilms have been reported in many articles along with their possible applications in several fields such biomedical, food preservation etc.

The modification of chitosan film depend upon the nature of application where they are supposed to be applied. Nowadays researcher are focusing more on the production chitosan active food packaging with good barrier, antioxidant and antimicrobial properties. These modification can be achieved by introducing certain active compounds such as plant extracts, essential oils and fruit extracts. Beside its application in food industry, chitosan films can be used as anti-biofilm drug carrier for wound healing where a prolonged release can be achieved. Keeping all these present applications in mind it can be concluded that still these chitosan films can be modified and enriched further for expanding its application areas. In the field of biomedical these films can be used as coating materials for all the appliances which are using in high temperature areas. This chitosan coating will help in protection of such valuable appliances due to its high thermal stability. But for such applications boosting of physicochemical properties is still needed. In future this can be achieved by incorporating several different compounds.

REFERENCES

1. Ghormade, V.; Pathan, E.K.; Deshpande, M.V. Can fungi compete with marine sources for chitosan production? *Int. J. Biol. Macromol.* 2017, 104, 1415–1421.
2. Aranaz, I.; Mengíbar, M.; Harris, R.; Paños, I.; Miralles, B.; Acosta, N.; Galed, G.; Heras, A. Functional characterization of chitin and chitosan. *Curr. Chem. Biol.* 2009, 3, 203–230.
3. Rinaudo, M. Chitin and chitosan: Properties and applications. *Prog. Polym. Sci.* 2006, 31, 603–632. [CrossRef] *Polymers* 2021, 13, 3256 20 of 27.
4. Group F. CHITOSAN-BASED HYDROGELS. 2012.
5. Rinaudo M. Chitin and chitosan: Properties and applications. *Prog Polym Sci* 2006;31:603–32. doi:10.1016/j.progpolymsci.2006.06.001.
6. Czechowska-biskup R, Jarosińska D, Rokita B, Ulański P, Rosiak JM. Determination of Degree of Deacetylation of Chitosan - Comparison of Methods. *Prog Chem Appl Chitin Its Deriv* 2012;XVII:5–20.
7. Aranaz I, Mengíbar M, Harris R, Paños I, Miralles B, Acosta N, et al. Functional Characterization of Chitin and Chitosan. *Curr Chem Biol* 2009;3:203–30. doi:10.2174/187231309788166415.
8. Alvarenga ES De. Characterization and Properties of Chitosan. *Biotechnol Biopolym* 2011:91–108.
9. Dutta PK, Duta J, Tripathi VS. Chitin and Chitosan: Chemistry, properties and applications. *J Sci Ind Res (India)* 2004;63:20–31. doi:10.1002/chin.200727270.
10. Draget KI. Alginates. 2009.

11. Burke, A. and Hasirci N. *Biomaterials: From Molecules to Engineered Tissues*. 2004.
12. Kurita K. Controlled functionalization of the polysaccharide chitin. *Prog Polym Sci* 2001;26:1921–71. doi:10.1016/S0079-6700(01)00007-7.
13. liveira BF, Santana MH a, Re MI. Spray-dried chitosan microspheres cross-linked with D,L-glyceraldehyde as a potential drug delivery system: Preparation and characterization. *Brazilian J Chem Eng* 2005;22:353–60.
14. Zargar V, Asghari M, Dashti A (2015) A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives, and applications. *ChemBioEng Rev* 2(3):204–226. <https://doi.org/10.1002/cben.201400025>
15. Perinelli DR, Fagioli L, Campana R, Lam JKW, Bafone W, Palmieri GF, Casettari L, Bonacucina G (2018) Chitosan-based nanosystems and their exploited antimicrobial activity. *Eur J Pharm Sci* 117:8–20. <https://doi.org/10.1016/j.ejps.2018.01.046>
16. Richter T, Gulich M, Richter K (2012) Quality control and good manufacturing practice (GMP) for chitosan-based biopharmaceutical products, Chitosan-based biopharmaceutical delivery, targeting and polymer therapeutics / Eds. B. Sarmento, J. Neves, John Wiley & Sons 503–542
17. Ahmed S, Ikram S (2015) Chitosan & Its Derivatives: A review in recent innovations. *Int J Pharm Sci Res* 6(22):14–30.
18. Chung YC, Chen CY (2008) Antibacterial characteristics and activity of acid-soluble chitosan. *Bioresour Technol* 99(8):2806–2814.
19. Leuba JL, Stossel P (1986) Chitosan and other polyamines: antifungal activity and interaction with biological membranes. *Chitin in Nature and Technology*. Plenum Press, New York, pp 215–221
20. Prabu K, Natarajan E (2013) Antihyperglycemic effect of chitosan of podophthalmus vigil in streptozotocin induced diabetic rats. *Int J Pharm*

21. Alemdaroglu C, Degim Z, Çelebi N, Zor F, Öztürk S, Erdoğan D (2006) An investigation on burn wound healing in rats with chitosan gel formulation containing epidermal growth factor. *Burns* 32(3):319–327.
22. Azmy EA, Hashem HE, Mohamed EA, Negm NA (2019) Synthesis, characterization, swelling and antimicrobial efficacies of chemically modified chitosan biopolymer. *J Mol Liq* 284:748–754. <https://doi.org/10.1016/j.molliq.2019.04.054>
23. Wang K, Liu Q (2014) Chemical structure analyses of phosphorylated chitosan. *Carbohydr Res* 386:48–56. <https://doi.org/10.1016/j.carres.2013.12.021>
24. Mutreja R, Thakur A, Goyal A (2020) Chitin and chitosan: current status and future opportunities. in: *Handbook of Chitin and Chitosan*. Chapter 13:401–417.
25. Kojima K, Okamoto Y, Kojima K, Miyatake K, Fujise H, Shigemasa Y et al (2004) Effects of chitin and chitosan on collagen synthesis in wound healing. *J Vet Med Sci* 66:1595–1598. <https://doi.org/10.1292/jvms.66.1595>
26. Nowroozi N, Faraji S, Nouralishahi A, Shahrousvand M (2021) Biological and structural properties of graphene oxide/ curcumin nanocomposite incorporated chitosan as a scaffold for wound healing application. *Life Sci* 264:118640. <https://doi.org/10.1016/j.lfs.2020.118640>
27. Morin-Crini N, Lichtfouse E, Torri G, Crini G (2019) Applications of chitosan in food, pharmaceuticals, medicine, cosmetics, agriculture, textiles, pulp and paper, biotechnology, and environmental chemistry. *Environ Chem Lett* 17:1667–1692. <https://doi.org/10.1007/s10311-019-00904-x>

28. Ke C, Deng F, Chuang C, Lin C (2021) Antimicrobial actions and applications of chitosan. *Polymers* 13:904. <https://doi.org/10.3390/polym13060904>
- 29.38. Vichare R, Garner I, Paulson RJ, Tzekov R, Sahiner N, Panguluri SK, Mohapatra S, Mohapatra SS, Ayyala R, Sneed KB, Biswal MR (2020) Biofabrication of chitosan-based nanomedicines and its potential use for translational ophthalmic applications.
30. Yu Sh, Xu X, Feng J, Liu M, Hu K (2019) Chitosan and chitosan coating nanoparticles for the treatment of brain disease. *Int J Pharm* 560:282–293.
31. Mahl CRA, Taketa TB, Rocha-Neto JBM, Almeida WP, Beppu MM (2020) Copper ion uptake by chitosan in the presence of amyloid- β and histidine. *Appl Biochem Biotechnol* 190(3):949–965. <https://doi.org/10.1007/s12010-019-03120-z>
32. Kassem A, Ayoub GM, Malaeb L (2019) Antibacterial activity of chitosan nano-composites and carbon nanotubes: a review. *Sci Total Environ* 668:566–576. <https://doi.org/10.1016/j.scitotenv.2019.02.446>
33. Muzzarelli RAA (1973) Natural Chelating Polymers: Alginic acid. Chitin and Chitosan, Pergamon Press, Oxford, UK 55:254p
34. Rhazi M, Desbrie`res J, Tolaimate A, Rinaudo M, Vottero P, Alagui A et al (2002) Influence of the nature of the metal ions on the complexation with chitosan. *Eur Polym J* 38:1523–1530. [https://doi.org/10.1016/S0014-3057\(02\)00026-5](https://doi.org/10.1016/S0014-3057(02)00026-5)
35. Zhang D, Xiao J, Guo Q, Yang J (2019) 3D-printed highly porous and reusable chitosan monoliths for Cu (II) removal. *J Mater Sci* 54:6728–6741. <https://doi.org/10.1007/s10853-019-03332-y>

36. Croitoru A, Fikai A, Fikai D, Trusca R, Dolete G, Andronescu E, Turculeț SC (2020) Chitosan/graphene oxide nanocomposite membranes as adsorbents with applications in water purification. *Materials* 13:1687.
37. Yuan D, Zhang W, Cui J, He L, Wang J, Yan C, Kou Y, Li J (2020) Facile fabrication of magnetic phosphorylated chitosan for the removal of Co(II) in water treatment: separation properties and adsorption mechanisms. *Environ Sci Pollut Res* 27:2588–2598.
38. Panahandeh A, Parvareh A, Moraveji MK (2021) Synthesis and characterization of γ -MnO₂/chitosan/Fe₃O₄ cross-linked with EDTA and the study of its efficiency for the elimination of zinc(II) and lead(II) from wastewater. *Environ Sci Pollut Res* 28:9235–9254.
39. Joshi S, Srivastava RK (2019) Adsorptive removal of lead (Pb), copper (Cu), nickel (Ni) and mercury (Hg) ions from water using chitosan silica gel composite. *Environ Monit Assess* 191(10):615. <https://doi.org/10.1007/s10661-019-7777-5>
40. Hiroki A, Tran HT, Nagasawa N, Yagi T, Tamada M (2009) Metal adsorption of carboxymethyl cellulose/carboxymethyl chitosan blend hydrogels prepared by Gamma irradiation. *Radiat Phys Chem* 78:1076–1080.