

A Study of the Solubility and Mobility of Silver Ions in Chitosan and Fibroin Membranes

by

Xiaojia Li

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Chitosan and fibroin are biopolymers widely applied in wound healing and wastewater treatment with silver ions (Ag^+). The solubility and mobility of Ag^+ in these polymers are important parameters for designing and optimizing related applications, but they are seldom studied. This study investigates and compares the sorption and transport properties of Ag^+ in chitosan and fibroin membranes to reveal the unique interactions between these polymers and ions. The solubility and mobility of NaCl are also studied for comparison.

The sorption performance was evaluated through sorption uptake and sorption isotherms at different Ag^+ concentrations. The Ag^+ equilibrium uptake and solubility in chitosan membranes were higher than those in fibroin membranes. The sorption of Ag^+ in fibroin membranes followed the Freundlich isotherms, but neither the Langmuir nor the Freundlich isotherm applied to the sorption of Ag^+ in chitosan membranes due to strong Ag^+ -chitosan complexation interactions.

The permeance, permeability and diffusivity were studied through permeation/diffusion tests. The permeance, permeability and diffusivity of Ag^+ in chitosan membranes were found to be dependent on the Ag^+ concentration, while those values in fibroin membranes were relatively constant lower than those in chitosan, except the transient diffusivity coefficients and steady-state diffusivity coefficients. The transient diffusivity coefficients of Ag^+ in chitosan ranged from 0.7 to 7.1 $\mu\text{m/s}^2$, while those values in fibroin were in the range of 42.0 to 48.5 $\mu\text{m/s}^2$. The steady-diffusivity coefficients of Ag^+ were 2.7 to 31.7 $\mu\text{m/s}^2$ in chitosan and 32.8 to 49.9 $\mu\text{m/s}^2$ in fibroin. The diffusivity of Ag^+ in chitosan was further studied by desorption tests. The diffusivity coefficients obtained from different methods were compared to gain better understanding of the diffusion process. The formation of Ag^+ -chitosan complexes played an important role and it significantly affected solubility and mobility of Ag^+ in chitosan.

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Chapter 1

Introduction

1.1 Background

With the increasing demand for low-carbon economy and sustainable production, biopolymers are becoming appealing alternatives to synthetic polymers as they are biodegradable and can be obtained from a wide range of renewable sources. Chitosan is a derivative of the second most abundant polysaccharide, chitin, which supports the mechanical structure of crustaceans, insects, and the cell walls of fungi^[1]. Another abundant polymer, silk fibroin, is the inner core of silk that provides mechanical strength, taking about 72-81wt.% of silk^[2,3]. Silk can be obtained easily from silkworms and has been applied to various applications for thousands of years. Both chitosan and fibroin are biocompatible, biodegradable, renewable and versatile biopolymers that can adsorb metal ions. They have been applied and investigated in fields such as wastewater treatment, tissue engineering, drug delivery, wound healing, food packing, and biosensing^[4].

Silver is a heavy metal toxic to aquatic life at a concentration beyond certain levels, but also valued as a precious metal used in jewelry, silverware, electrical contacts, and conductors. Adsorption is widely used for silver recovery due to its simplicity in process design and operation. Low cost and environmental-friendly adsorbents are required for silver recycling and recovery^{[5][6]}. Studies have been done on chitosan and fibroin for their sorption capacity of silver ions^{[7][8]}. Silver is also currently used widely in many biomedical applications due to its antibacterial property. It is often applied to the human body together with biocompatible polymers such as fibroin and chitosan for wound healing^[9-11]. An emerging field for silver-ion application is carrier-facilitated transport for olefin/paraffin separation. Silver ions (Ag^+) act as carriers in polymer membranes to improve selectivity of the carried compound. Our lab have found chitosan as an effective base material for Ag^+ facilitated olefin/paraffin separation^[12]. While fibroin is considered as another candidate due to its ability to adsorb heavy metals and its similar functional groups as chitosan like amino groups ($-\text{NH}_2$) and hydroxyl groups ($-\text{OH}$).

To further develop these applications related to Ag^+ , the solubility and transport properties of silver ions in chitosan and fibroin should be studied in depth. The sorption capacity of Ag^+ in chitosan and fibroin is useful for the optimization of wastewater treatment and silver recovery systems. The solubility, permeability and diffusivity of Ag^+ are necessary fundamental data for the design of

controlled release of Ag^+ in wound healing. They are also significant for estimating and modeling of Ag^+ facilitated transport of olefin/paraffin separation. All these parameters are helpful for comparing the sorption and permeation behavior of different polymer materials at varying experimental conditions and providing guidance for choosing new materials.

1.2 Research Objectives

The goal of the present work was to study the solubility and mobility of Ag^+ in chitosan and fibroin membranes and compare the properties of the two biopolymers. All tests were conducted under room temperature at different AgNO_3 concentrations in the liquid phase. Through the sorption tests, the equilibrium sorption uptake of AgNO_3 and water were measured, resulting in the solubility (S) of AgNO_3 , and the ternary diagram in terms of mass fractions for AgNO_3 , water and polymer. Sorption isotherms were constructed by plotting the concentration of Ag^+ in the membrane and in the solution. The experimentally obtained equilibrium data were fitted into Langmuir and Freundlich models to provide information on the nature of sorbate-sorbent interactions^[13–15] and determine model parameters. The swelling performance was also evaluated to observe the change in membrane thickness before and after sorption equilibrium, which was closely related to the water uptake. Diffusivity (D), permeability (P) and permeance (P') of Ag^+ were investigated through the permeation test to describe its mobility in the two types of biopolymer membranes at different AgNO_3 concentrations. The diffusivity can be obtained from the time lag method, pseudo-steady state permeation rate, or the desorption data. These approaches were compared to acquire a deeper understanding for the diffusion process.

As far as the author knows, a study of Ag^+ mobility in chitosan membranes was done by Lin over a AgNO_3 concentration range of 0-1 M from 21-61 °C^[16]. However, prior work in the literature regarding Ag^+ mobility is rarely found. This study expanded the evaluated concentration range of AgNO_3 in chitosan and was the first study on mobility and solubility of Ag^+ in fibroin.

1.3 Outline of the Thesis

Chapter 1 briefly introduced the background, initiatives and background of the study. Chapter 2 presented a detailed literature review on chitosan, fibroin, their applications related to Ag^+ , and mathematical models applied in this work. Chapter 3 described the procedures for membrane preparation, sorption tests, permeation tests and diffusion tests. Chapter 4 analyzed the results for

these tests at varying AgNO_3 concentrations and compared the performance of chitosan and fibroin membranes. General conclusions from this study and recommendations for future studies were presented in Chapter 5.

Chapter 2

Literature Review

2.1 Chitosan

2.1.1 Structure

Chitosan is a natural polysaccharide that is obtained by the deacetylation of chitin. Chitin is a long chain linear polymer consisting of 2-acetamido-2-deoxy- β -D-glucose units connected through the β (1 $\rightarrow$ 4) linkage^[17]. It is insoluble in dilute acids and water because of the high intermolecular and intramolecular hydrogen bonding^[18].

Chitosan was first reported in 1895 when chitin was boiled in a concentrated potassium hydroxide solution^[19]. It is soluble in dilute organic acids such as formic, acetic, tartaric and citric acids. It is insoluble in water or alkaline solutions with pH higher than around 6.5^[20]. Chitosan can be defined as the sufficiently N-deacetylated product of chitin, with a degree of deacetylation being 50% or higher to form a soluble product^[21]. During the deacetylation process, the acetyl group in chitin is replaced by a hydrogen atom through the nucleophilic substitution reaction^[22]. Figure 1 shows the chemical structure of chitin and chitosan.

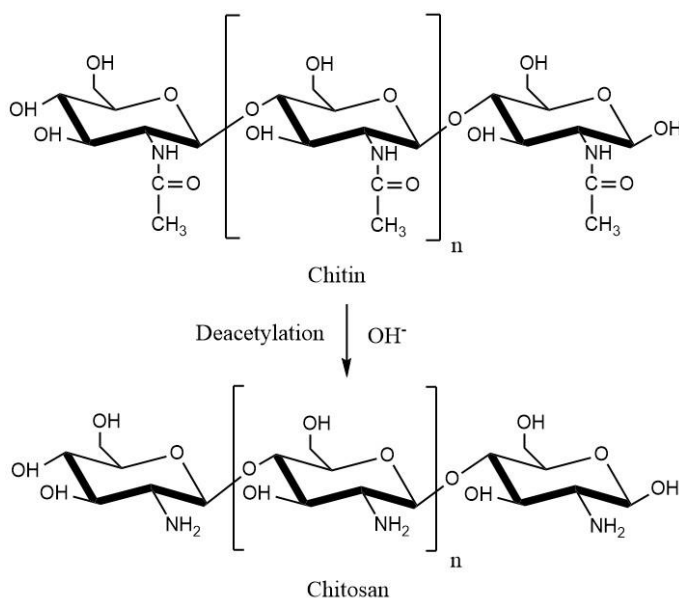


Figure 1 Chemical structure of chitin and chitosan^[23]

2.1.2 Sources and Manufacturing

Chitosan is mainly derived from waste shells of crustaceans such as crabs, prawns and shrimps from the food processing industry^[1]. The quantity of the raw materials depends highly on seasonality, and large quantities of chemicals are needed^[24]. Chitosan can also be collected as a byproduct of proteins extracted from insects for food/animal feed industries^[25], silkworm pupae from silk industry^[26], and cell walls of fungi during the fermentation process^[27,28]. The raw materials of these methods are not limited by season. Fungi-derived chitosan, though with higher production costs and smaller quantities, is free of allergenic animal source protein and its molecular weight and degree of deacetylation can be controlled^[29]. Insect rearing facilities are built worldwide, and the fertility of insects gives insect-derived chitosan the ability to compete with marine chitosan on the volume of production^[30]. The manufacture procedures from different sources^[1,30,31] are shown in Figure 2.

The traditional chemical extraction processes of chitin from crustaceans or insects are similar, including grinding, deproteination, demineralization, bleaching/discoloration and deacetylation. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are often reported as bases used for deproteination, while KOH is recommended by some literature because it removes proteins efficiently^[23,31,32], and the byproducts with potassium ions (K^+) are more environmentally friendly than sodium ions (Na^+) since potassium is an element improving plant growth used in fertilizers^[33–35]. In the demineralization step, sulfuric, hydrochloric, nitric, acetic, oxalic and formic acids can be used to break down calcium carbonate^[36]. The currently most preferred reagent for both insects and crustaceans is hydrochloric acid^[37], which converts calcium carbonate into calcium chloride and carbon dioxide. Depending on the species of the insect, the demineralization step is sometimes unnecessary^[38].

The fungi cell walls contain chitin/chitosan and glucan as main fungal skeletal polysaccharides. Demineralization is not needed for fungi extraction but deproteination is still necessary. Alkali soluble materials including proteins, lipids and some carbohydrates are removed usually using 1M NaOH at 60 – 120 °C for 0.5 – 12 h^[39]. Then acids (e.g. hydrochloric, lactic or acetic acid) are used to remove phosphates and other acid insoluble materials, typically 2%–10% acetic acid at 25–95 °C for 1–24 h. The acid soluble materials rich in chitosan are treated with alkali, usually NaOH, to raise the pH to 9–10 for chitosan precipitation^[39].

Discoloration/bleaching may be desired to remove natural pigments. Discoloration of fungi chitosan is achieved by centrifugation and washing with acetone and ethanol^[24,39]. Crustacean chitin can be bleached with sodium hypochlorite, potassium permanganate and oxalic acid or hydrogen peroxide^[40]. Insect chitin is often discolored by a mixture of methanol-chloroform or alcohol-chloroform^[38].

The resulting chitin is treated with alkaline (e.g. concentrated NaOH or KOH (40-45%)) at temperatures higher than 100 °C to break the N-acetyl linkage^[1,39,40]. The degree of deacetylation is generally a function of NaOH concentration, reaction time, temperature, density and molecular weight of the initial chitin polymer. Alkaline treatment of chitin consumes a large amount of energy and alkali solution, creating chitosan with broad degrees of deacetylation and molecular weight^[1]. Other more environmental-friendly methods are emerging recently such as enzymatic deacetylation^[41,42] and microwave-assisted extraction^[43,44].

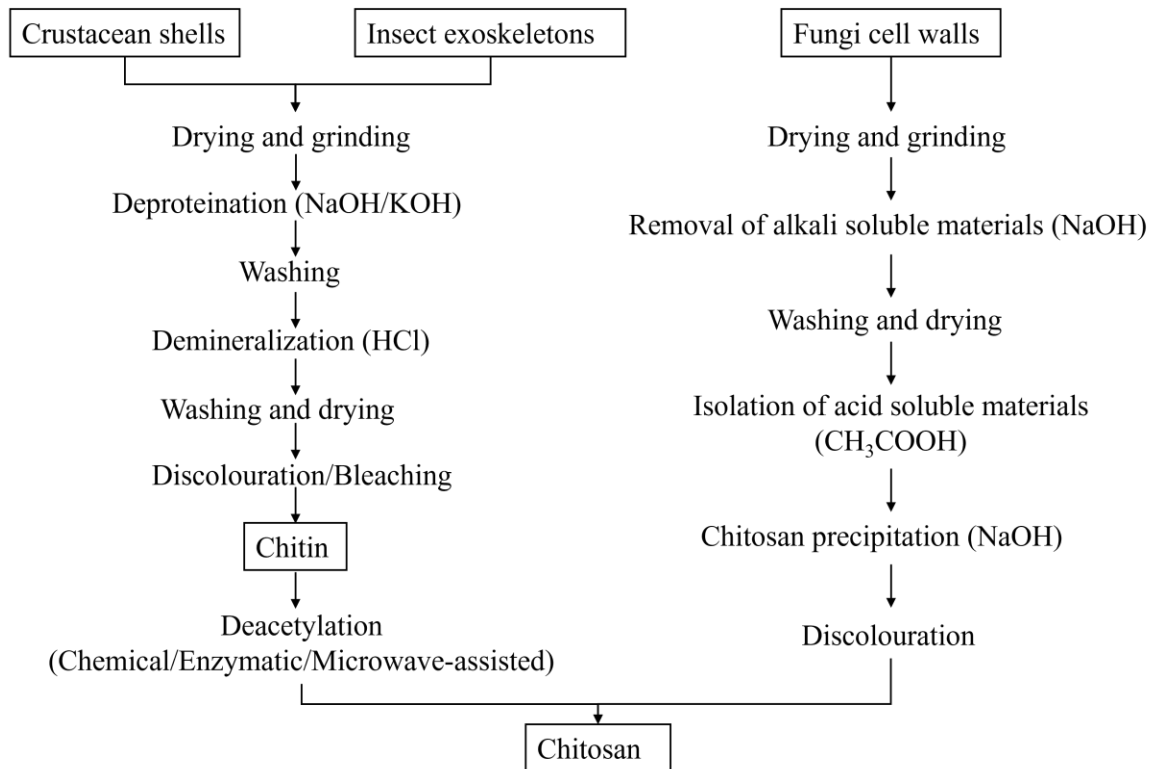


Figure 2 Sources and Manufacture processes of chitosan

2.1.3 Properties and Applications

Cationic property

Chitosan is a cationic polyelectrolyte that has versatile solubility. At $\text{pH} < 6.5$, the amine groups in chitosan are protonated, enabling it to be soluble in water and weak acids, and react with negatively charged compounds. Dissolved chitosan is easily processed into beads, cast into membranes, spun into fibers and nanofibers, and crosslinked to produce fibers and sponges^[45]. Since chitosan can bind anionic lipid and fat molecules, it is considered as a potential candidate for food packaging^[46], and used as a coagulant to remove solid suspension in juice or beer^[47]. Chitosan and its derivatives are also used as additives in cosmetics and personal care products, because of their adherence to hair and skin with negatively charged polysaccharides and proteins^[45,48]. In the medical industry, the negatively charged chitosan in acidic condition is a promising gene delivery vector in gene therapy, which interacts strongly with negatively charged mucosal surfaces or other macromolecules like genetic materials^[49].

Chelating property

With 6-7 wt.% of nitrogen in amino groups, chitosan is an effective chelating and complexing agent^[50] towards proteins, amino acids, cholesterol, fats^[50] and heavy metals (e.g. iron, copper, magnesium, silver, cadmium, mercury, lead, nickel, zinc, manganese, chromium and uranium)^[51,52]. It acts as a sorbent to remove contaminants in wastewater treatment. Chitosan nanoparticles are used as antimicrobial agents and plant protectors in medical and agriculture fields^[49,50], as they bind trace metals and prevent the production of toxins and microbial growth^[53,54].

Biological properties

Chitosan is a non-toxic, biodegradable, biocompatible and physiologically inert biopolymer. The degradation of chitosan by lysozyme results in oligosaccharide chains, which are mostly metabolized by the liver^[54]. These properties allow it to be applied in numerous fields. In the food industry, it is widely applied as nutritional ingredients, antimicrobial coating, anticholesterolemic dietary products, etc.^[55-57]. In the medical field, chitosan is commonly applied as excipients in drug delivery^[58], wound healing, tissue engineering, dentistry, biosensors, and many other applications^[45]. Chitosan can also be applied in agriculture for controlled release of fertilizers and biocides, seed coating and plant

protection from frost^[45,49,59]. In biotechnology, chitosan can be used as a support for enzymes mainly by crosslinking reactions, constituting the biological recognition elements in biosensors and other biodevices^[45].

In addition, chitosan is actively employed in aquaculture, ophthalmology, bio-imaging, veterinary medicine, textile and fiber industries, paper industry, chemistry, catalysis, chromatography, beverage industry, photography, sludge dewatering, biotechnology, and nanotechnology^[45].

2.2 Fibroin

2.2.1 Structure

The silk thread from *Bombyx mori* silkworms consists of two parallel fibroin fibers wrapped in a layer of sericin^[3] that can be removed by the degumming process. Each fibroin fiber is composed of several microfibril bundles^[60]. In one microfibril, a disulfide bond bonds a heavy (H) chain (~390,000 Da) and a light (L) chain (~26,000 Da) at the C-terminus of the heavy chain, forming the H-L complex. Glycoprotein P25 (25,000 Da) is linked non-covalently to the H-L complex^[61]. The H-chain have both hydrophobic and hydrophilic regions. The hydrophobic units in H-chain are antiparallel β -sheet crystallites composed of repeating amino acid pattern of (GAGAGS) and dipeptide pattern of (G-AST). The hydrogen bonding in β -sheet crystallites is the main reason for the mechanical strength of fibroin^[62]. The L-chain containing non-repetitive units is hydrophilic and relatively elastic^[2,63–65]. Figure 3 is a schematic illustration of fibroin structure. The computational models of silk fibroin as a semi-crystalline polymer are still in the development stage^[60]. From the current literature, silk fibroin is recognized as a promising adsorbent for heavy metals^[61,63] due to the presence of amino (-NH₂) and carboxyl (-COOH) groups in the amino acid molecules^[66].

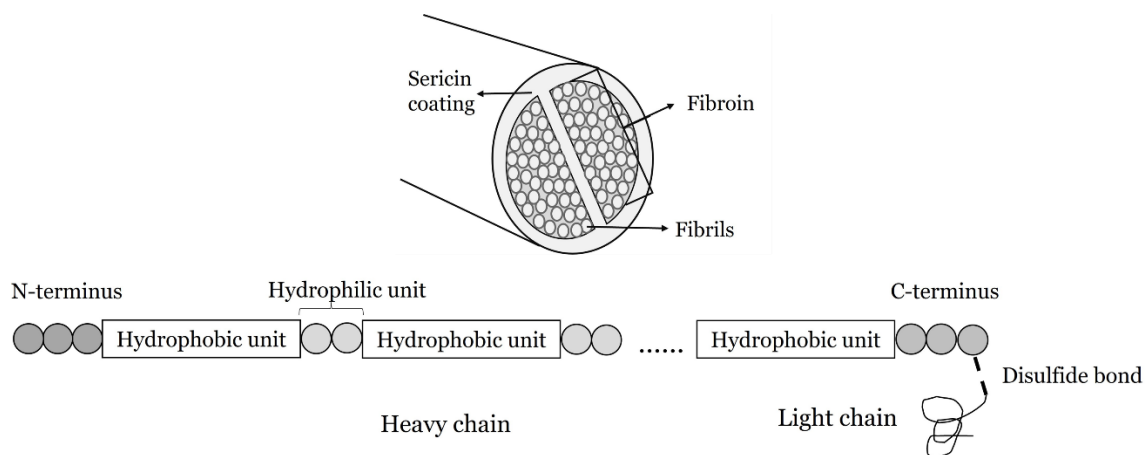


Figure 3 Schematic illustration of fibroin structure ^[61]

2.2.2 Source and Manufacturing

Bombyx mori (*B. mori*) silkworms are the main producer of silk worldwide^[3]. They produce silk threads from silk glands to construct cocoons. Sericin is usually removed to extract fibroin by the degumming process. Several ways of degumming are often used: water boiling degumming, soap solution degumming, alkali treatment, amine treatment, acid treatment, enzyme treatment, and microwave treatment^[15,61,67]. The simplest degumming method is to use water at high temperatures to remove sericin from fibroin. The cocoon shells are cut into pieces and boiled in water at 95-100 °C for different time periods. In this process, sericin dissolves in water and insoluble fibroin remains in the fiber form^[68]. Water degumming carried out at higher temperatures such as 120 °C under pressure is not widely adopted because silk fibroin may be damaged at high temperatures^[69]. Soap solutions with Marseille soap, sodium laurate, sodium myristate, sodium stearate, etc. are used for soap degumming at 92-98 °C for 2-4 hours at pH of 10.2-10.5^[70]. The alkali formed during soap hydrolysis reacts with sericin coating and forms soda salt that dissolves in water^[71]. Calcium and magnesium ions should be avoided in the solution to avoid insoluble metallic complex, which may harm the quality of fibroin. To solve this issue, surfactants are usually added to soften water^[72]. Alkali such as sodium carbonate, potassium carbonate and sodium bicarbonate are commonly used on both laboratory and industrial level for silk degumming. The pH is generally maintained at 9.5-10.5 to ensure degumming efficiency and quality. Buffers and detergents are often used together with alkali, since if alkali is used alone, the resultant fibroin will tend to be yellowish^[73]. Amine treatment of silk fiber occurs in alkaline pH. The main advantage of amine degumming is being less affected by the hardness of water than

alkaline treatment, but the degumming rate is relatively low^[74,75]. Some studies on acid degumming with lactic acid, tartaric acid, oxalic acid, citric acid, glacial acetic acid, succinic acid, malonic acid, and sulfuric acid are reported^[76], but even dilute acid may damage the structure of fibroin. As a result, acid treatment is not popular^[15]. Enzyme degumming processes with trypsin, papain, and proteases are carried out at moderate temperature (40-65 °C) and pH (7-9), so silk fibroin obtained by these methods is less likely to be structurally damaged. However, the mild condition is also a cause for uncomplete removal of hydrophobic impurities^[77].

In this work, water degumming at 95 °C with deionized water was used to obtain fibroin, to ensure the solubility and mobility of silver ions in fibroin were not affected by residuals such as alkaline or soap in the degumming process.

Fibroin fibers are fabricated as braided, knitted and non-woven matrices. Regenerated fibroin from fibroin solution can be processed into sponges, hydrogels, films, mats, microparticles, etc. for numerous applications^[68,78-83].

2.2.3 Properties and Applications

Adsorption properties

Silk fibroin can bind metal ions through free amine groups or cysteine residue in proteins^[84]. Studies have been conducted on adsorption of lead (Pb), chromium (Cr), copper (Cu) and cobalt (Co) in silk fibroin in both fiber and membrane forms. Fibroin is considered as a potential adsorbent for heavy metal recovery from wastewater^[15,85]. It can also be combined with other materials such as chitosan, keratin and cellulose acetate to form composite films for wastewater treatment^[61].

Mechanical properties

Naturally produced fibroin fiber, especially from *B. mori*, has attractive mechanical properties, with a Young's modulus around 10-17 GPa, ultimate strength of 300-740 MPa, and breaking strain of 4-26%^[86-89]. In the textile industry, silk fibroin surpasses many synthetic materials due to its lustrous appearance, soft texture, ease of dyeing and superior mechanical properties. Fibroin is widely used in tissue engineering. The versatile processability of fibroin provides templates of tissue regeneration that have similar mechanical properties as human tissues including ligament, tendon, cartilage, bone, skin, liver, trachea, nerve, cornea, eardrum, bladder, etc^[90-92]. In controlled drug delivery, the therapeutic agent can diffuse gradually through the semi-amorphous regions in the fibroin capsule. By

controlling the fraction of β -sheet crystallites, the release profile of drugs can be easily adjusted^[93–95]. Fibroin is also investigated for applications in optics and sensors due to its mechanical versatility, lightweight properties, and biocompatibility^[96–98].

Biological properties

Fibroin, as a naturally derived, biocompatible, biodegradable polymer enriched in proteins, can be degraded by enzymes into peptides and amino acids^[99]. These properties make it applicable to countless medical applications such as surgical suture, tissue engineering and drug delivery. Compared to chitosan, it degrades slower and has better mechanical strength^[100]. Sometimes chitosan and fibroin are combined to complement each other. For example, in soft tissue repair, silk fibroin improves the structural stability and permeability, while chitosan is responsible for antioxidant and antibacterial properties, and also improves the mucoadhesiveness of the soft tissue^[101–104]. In bone and cartilage regeneration, chitosan improves the swelling property, porosity, fiber diameter and antibacterial properties, while silk fibroin acts as a mechanical support and enhances resistance to degradation^[105,106].

2.3 Applications of Chitosan and Fibroin with Silver Ions

2.3.1 Wound Dressing

The use of broad-spectrum antibiotics has been increasing the chance of infection by antibiotic-resistant bacteria strains in combat trauma wounds^[107,108]. Ionic silver, as an alternative to traditional antibiotics, has the antimicrobial activity against a wide range of pathogens, with a much lower tendency to develop bacteria resistance^[109,110]. As biocompatible and biodegradable polymers found to enhance wound healing, chitosan and fibroin are combined with silver ions for wound healing applications. Chitosan membranes have been applied on wounds and slowly release antibiotics such as silver sulfadiazine (AgSD) as they swell^[111,112]. The diffusion rate of silver ions into the wounds can be tuned by varying the morphology of membranes and addition of other components^[113]. Fibroin nanofiber encasing silver nanoparticles has been reported to increase healing rate^[114–116]. Graphene oxide functionalized silk fibroin/PVA dressing material doped with Mg^{2+} and Ag^+ shows a high rate of re-epithelialization, with ions used to overcome aggregation of Ag and Mg nanoparticles^[117]. Fibroin and chitosan composite membranes are developed to combine the advantages of the two

polymers. The existence of chitosan improves hydrophilicity and antibacterial activity, while fibroin helps cell adhesion with its unique arginine-glycine-aspartic acid (RGD) sequences^[100,105,118,119].

2.3.2 Silver Recovery from Wastewater

Silver residuals from industrial wastes are toxic to aquatic life and pose potential risk on human health and the environment^[120]. On the other hand, silver is a valuable metal with increasing industrial need and limited sources^[121]. The conventional methods for silver recovery such as ion-exchange resin, chemical precipitation, membrane separation and oxidation are able to remove silver ions from wastewater, but they are not economical and effective for low concentrations^[8]. Novel materials with high adsorption capacity, stability, reusability, and ease of operation need to be developed. Chitosan and silk fibroin are investigated as naturally abundant, biodegradable and environmental-friendly biosorbents. Chelating resin with chitosan as a base material was reported to have high selectivity, high adsorption capacity and good stability over months^[122]. Chitosan can bind both cations and anions with pH adjustment and the binding behavior was comparable to that of commercial resins^[123] in the 1990s. A few studies have been focused on the fibroin adsorption performance of silver. Regenerated silk fibroin beads (rSFB) was reported to adsorb silver ions in AgNO_3 with a removal efficiency up to 98.82% in 90 min with a rSFB content of 5 mg/L. The high operability and shaping ability of chitosan and fibroin allow them to be ideal candidates for silver recovery applications.

2.3.3 Facilitated Transport for Olefin/Paraffin Separation

Olefin and paraffin produced from the petrochemical industry are conventionally separated by low-temperature and high-pressure distillation, which is a highly energy-intensive process due to similar volatilities of an olefin and its corresponding paraffin^[16]. Metal-based facilitated transport membranes have been studied as an alternative for olefin/paraffin separation since the 1980s^[124]. Silver ion can form reversible π -complexation with olefin, when the π electron cloud in olefin overlaps with the empty outermost orbital of Ag^+ (5s) to form a σ bond, and the backdonation of electron density from the 4d atomic orbital of Ag^+ to the vacant empty π^* -antibonding molecular orbital of the olefin results in a π bond^[125–128]. Olefin and paraffin can both transport through the membrane by the physical solution-diffusion mechanism, but Ag^+ only facilitates the transport of olefin by forming the π -complexation. As a result, the permeability of olefin is much higher than that of paraffin. Silver nitrate (AgNO_3) solution is mainly used to incorporate Ag^+ into membranes because of its relatively low cost and good stability compared to other solution of silver salts^[129]. Studies from our lab has

shown that chitosan, with its amino groups chelating Ag^+ and good hydrophilicity, is an effective base membrane material for Ag^+ facilitated olefin/paraffin separation^[130]. Fibroin membrane is also considered as a potential candidate because of its abundance in amino groups and hydroxyl groups.

2.4 Transport Theories through Membranes

2.4.1 Solution-Diffusion Mechanism

The chitosan membranes and fibroin membranes are dense and non-porous^[16,131], and the transport of ions in these membranes follows the solution-diffusion mechanism. Molecules are separated by the differences in their solubility and/or mobility in the membrane material^[132]. The most commonly accepted model illustrated in Figure 4 describes solute transport between the bulk of two solutions through the dense film^[133]. C_{1m} and C_{2m} are solute concentrations at the membrane surface on the feed (1) or downstream (2) side, respectively. C_{1b} and C_{2b} are solute concentrations in the bulk on the feed (1) or downstream (2) side, respectively. The solute first diffuses from the bulk solution to the membrane surface on the feed side. Then it is sorbed into the film and diffuses through the film under a concentration gradient. Finally on the downstream side, the solute is desorbed and diffuses to the bulk solution.

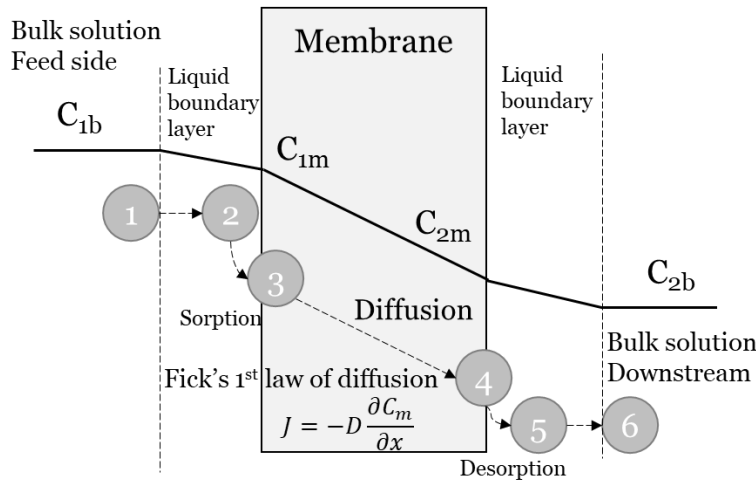


Figure 4 Schematic illustration of the solution-diffusion model

When the concentration gradient is large and the bulk solutions on both sides are well stirred, the effect of the boundary layers is assumed to be negligible. The overall transport resistance is due to the membrane, and the solute diffusion across the film is the rate-determining step.^[134]

2.4.2 Fick's Law of Diffusion

The Fick's law describes the diffusion of solute through a non-porous membrane, assuming that the solute does not chemically react with the membrane material. The Fick's first law states that the substance diffusion is driven by the concentration gradient at steady state:

$$J = -D \frac{dC_m}{dx} \quad (2.1)$$

where J is steady state permeation rate, or the rate of diffusion substance transfer per unit area, C_m is the concentration of diffusion substance in the membrane, x is the length normal to the membrane surface, and D is the diffusivity coefficient.

If the diffusion occurs effectively in only one direction in a homogeneous membrane and the diffusivity coefficient is a constant independent of concentration, according to mass balance, Fick's second law of diffusion states that:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} \quad (2.2)$$

Consider the membrane as a plane of thickness L, constant concentrations C_{1m} and C_{2m} are maintained at all points of the membrane surfaces $x = 0$ and $x = L$, respectively. At steady state, the permeation rate can be derived from Equation (2.1) as:

$$J = -D \frac{dC_m}{dx} = \frac{D(C_{1m} - C_{2m})}{L} \quad (2.3)$$

If the concentrations of the diffusing substance on both sides of the membrane surface are unknown, the permeation rate can be expressed as:

$$J = \frac{P(C_{1b} - C_{2b})}{L} = P'(C_{1b} - C_{2b}) \quad (2.4)$$

where C_{1b} and C_{2b} are the bulk concentrations on the feed and downstream sides, respectively, P is the permeability coefficient and P' is the permeance; both P and P' are based on the penetrant concentration across the membrane.

If the solubility (S) of the diffusing substance in the membrane is constant at equilibrium, a linear relationship between the bulk concentration and concentration at the membrane surface can be written as:

$$C_m = SC_b \quad (2.5)$$

From Equation (2.3) to (2.5), an equation for permeability coefficient (P), diffusivity coefficient (D) and solubility (S) can be derived:

$$P = SD \quad (2.6)$$

The diffusivity coefficient is a measure of the mobility of individual molecules within the membrane. The permeability coefficient is the intrinsic property of the material. It can be considered as the rate of diffusing substances transport across the membrane from the perspective outside of the membrane, shown as measurable changes in the concentrations of bulk solutions on both sides of the membrane^[16]. Solubility is also considered as a partition coefficient, which describes how the diffusing substances are distributed between the bulk solution and membrane phase. It is also a measure of the sorption capacity of the sorbate at equilibrium. By analogy, diffusivity is how fast a car is moving on a bridge, and solubility indicates how many cars are on the bridge, and permeability describes the total quantity of cars passed through the bridge over a certain amount of time. Permeance is the total quantity cars of passing through a unit length of a bridge over a certain amount of time.

2.4.3 The Time Lag Method for Determination of Diffusivity and Permeability

The time lag method allows the measurement of diffusivity and permeability directly from experiment data based on the solution-diffusion mechanism and Fick's law of diffusion^[135].

Consider the membrane as a plane of thickness L , whose surfaces at $x = 0$ and $x = L$, are kept at constant concentrations of C_{1m} and C_{2m} , respectively. A concentration gradient exists across the membrane, which is the main driving force for diffusion.

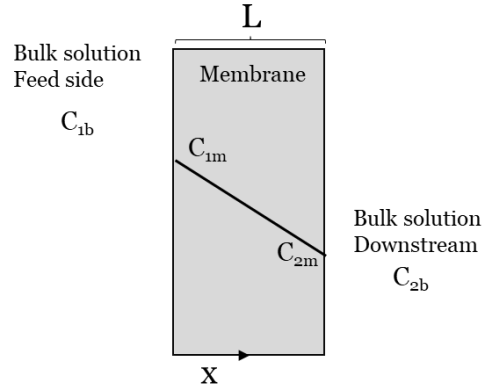


Figure 5 Concentration profile for solute transport across the membrane

The following assumptions are made:

- The diffusivity coefficient is a constant independent of diffusant concentration.
- The concentration of the diffusing substance on the downstream side is negligibly low ($C_{1b} \gg C_{2b}$, $C_{2b} \approx 0$).
- Initially, the membrane is free of any diffusing substance ($C_m = 0$ at $t = 0$).
- The diffusant is constantly removed from the membrane surface on the downstream side ($C_{2m} = 0$).

A partial differential equation can be derived from the mass balance or Fick's law of diffusion as Equation (2.2). With the above initial condition and boundary conditions, the diffusant concentration inside the membrane C_m can be solved as a function of distance x and time t . The permeation rate J at time t can be written as:

$$J(x, t) = -D \frac{\partial C_m(x, t)}{\partial x} \quad (2.7)$$

By integrating Equation (2.7) over time, the amount of diffusant that has passed through the membrane over time, t , can be expressed as Equation (2.9)^[136]:

$$Q_t = \int_0^t J(x = L) dx \quad (2.8)$$

$$\frac{Q_t}{LC_{1m}} = \frac{Dt}{L^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right) \quad (2.9)$$

If time approaches infinity, Equation (2.9) can be written in a simpler form as the permeation rate approaches a pseudo-steady state:

$$Q_t = \frac{DC_{1m}}{L} \left(t - \frac{L^2}{6D} \right) \quad (2.10)$$

The plot of Q_t vs. t crosses the x-axis at τ by extrapolation, which is the “time lag” of diffusion:

$$\tau = \frac{L^2}{6D} \quad (2.11)$$

And thus,

$$D = \frac{L^2}{6\tau} \quad (2.12)$$

From Equation (2.12), we can get the transient diffusivity (D), which is the diffusivity at the transient period of diffusion before pseudo-steady state is reached.

When a pseudo-steady state is reached, the permeation flux can be calculated from the slope of Q_t vs. t graph. Permeance and permeability can be obtained from Equation (2.4). The diffusivity at steady state (D^*) can be derived from Equation (2.3).

The time-lag method is commonly applied for the study of gas permeation through dense polymers. It is rarely used directly for ionic diffusion. A study on Na^+ and Cl^- transport across polyimide films and du Pont Kapton films was conducted in a diffusion cell using ion-selective electrodes^[137]. The diffusion coefficients, permeability coefficients and partition coefficients were obtained by the time-lag analysis. However, discrepancies were observed possibly due to heterogeneities and contaminants in the film^[133]. In our lab, Lin has attempted to study the transport properties of silver ions through chitosan membranes directly by the time lag method at AgNO_3 feed concentrations less than 1 M, and the experimental results were considerably consistent^[16]. In this work, the same method and set-up were used to study the mobility of silver ions in chitosan and fibroin membranes in a wider range of concentrations from 0 to 9 M, since concentrated AgNO_3 solution is more applicable in industry such as carrier-facilitated transport of olefin^[138]. Also, the transport properties at higher Ag^+ concentrations might have different trends than those in lower concentrations due to the adsorption and reaction of silver ions in those materials.

2.4.4 Desorption Kinetics and Modelling

Another way to evaluate the diffusivity coefficients is by the desorption test proposed by Crank and Park^[136]. The membrane is modeled as a plane sheet of thickness, L . If the concentration of sorbate in the membrane is a constant, and the membrane is placed in a large water reservoir where the concentration of sorbate is initially zero, the Fick's second law of diffusion as shown in Equation (2.2) can be applied. A model shown in Equation (2.13) can be derived, where Q_t is the amount of sorbate diffusing out of the membrane at time t . The quantity Q_t can be determined experimentally from Equation (2.14), where V_m is the membrane volume, V_L is the solution volume in the reservoir, and C_t is the concentration of sorbate in the solution at time t . Q_e is the amount of sorbate diffusing out of the membrane during infinite time, which is also the sorbate concentration at sorption equilibrium, and D is the diffusivity of sorbate in the membrane,

$$\frac{Q_t}{Q_e} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-\frac{D(2n+1)^2 \pi^2 t^2}{L^2} \right] \quad (2.13)$$

$$Q_t = \frac{V_L C_t}{V_m} \quad (2.14)$$

This model assumes that the desorption is fully governed by diffusion and the diffusion coefficient is independent of sorbate concentration in the membrane. The diffusion coefficient is obtained by fitting the experiment data to the model. The data fitting can also be used to evaluate whether the desorption process is fully controlled by diffusion, or whether some interactions between the sorbate and the membrane materials affect the diffusion process^[139].

2.5 Equilibrium Models of Adsorption

The adsorption isotherm graphically represents the relationship between the amount of sorbate per unit weight of adsorbent and the content of a sorbate in a test medium at equilibrium^[140,141]. It also shows the distribution pattern of the adsorbate on the adsorption sites. The Langmuir and Freundlich isotherms are the most well-known isotherms describing sorption equilibrium.

2.5.1 The Langmuir Equation

Langmuir was the first to study adsorption on a plane surface from a kinetic perspective^[142,143]. The Langmuir model assumes that^[144]:

- Adsorption surface is structurally homogeneous and energetically identical.
- Each adsorption site can hold only one adsorbate molecule.
- Adsorption is only monolayer.
- Adsorbate are adsorbed at definite, localized sites.

At adsorption equilibrium, the rate of adsorption onto the surface and the rate of desorption from the surface are equal^[143,145]. The Langmuir equation can be written in the form below:

$$\theta = \frac{bC_e}{1 + bC_e} \quad (2.15)$$

where θ is a dimensionless parameter indicating the fractional coverage of adsorbate, C_e is the adsorbate concentration in the test medium at equilibrium, which in the case of this work, is the salt concentration in the liquid phase at equilibrium, and b is the affinity constant or Langmuir constant, as a measure of the affinity of an adsorbate molecule to the adsorbent surface. The Langmuir model only considers the force between the adsorbate and the adsorbent, ignoring other possible forces involved in adsorption, such as adsorbate-adsorbate interaction^[146].

The fractional coverage θ can be expressed as the amount of adsorption capacity at equilibrium q_e , divided by the maximum adsorption capacity, q_{max} :

$$\theta = \frac{q_e}{q_{max}} \quad (2.16)$$

Equation (2.15) can be rearranged as:

$$q_e = \frac{q_{max}bC_e}{1 + bC_e} \quad (2.17)$$

The model can also be written in a linearized form as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{q_{max}b} \quad (2.18)$$

If the experimental sorption data generate a plot of $\frac{C_e}{q_e}$ vs. C_e as a straight line, the validity of the Langmuir will be verified. Then the maximum adsorption capacity q_{max} and the affinity constant b can be determined from the slope $\frac{1}{q_{max}}$ and the intercept $\frac{1}{q_{max}b}$.

2.5.2 The Freundlich Equation

The Freundlich isotherm is an empirical model that can be written as a power function or in the logarithmic form^[143,147], where k is the Freundlich isotherm parameter indicating the sorption capacity and n is the heterogeneity factor indicating the sorption intensity. The type of isotherm is irreversible when $n = 0$, favorable when $0 < n < 1$ and unfavorable when $n > 1$ ^[147,148].

It is developed based on the following assumptions^[144,149]:

- The adsorbent surface is heterogeneous where the interaction between adsorbed molecules is considered.
- The adsorption is a multi-layer process and the amount of adsorbate per unit mass of adsorbent increases as adsorption proceeds.
- The adsorption energy decreases exponentially on completion of the sorption centers of the adsorbent.

$$q_e = kC_e^n \quad (2.19)$$

If the Freundlich model is valid for the sorption equilibrium data, the plot of $\log q_e$ vs. $\log C_e$ according to Equation (2.20) will be a straight line with an intercept $\log k$ and a slope n :

$$\log q_e = \log k + n \log C_e \quad (2.20)$$

The Langmuir and Freundlich isotherms have been expanded from surface adsorption to bulk sorption, which is the case for the present study.

Chapter 3

Experimental

3.1 Materials and Equipment

Chitosan flakes (Flonac N, molecular weight 100,000) were provided by Kyowa Technos Co. Ltd., Japan. Fibroin was extracted from cocoon shells of silkworm *Bombyx mori* by the degumming process. Sodium hydroxide (NaOH), silver nitrate (AgNO₃), acetic acid ($\geq 99.7\%$) and formic acid (98%) were purchased from Sigma Aldrich company. Deionized water was supplied by the chemical engineering department at University of Waterloo.

A micrometer supplied by Starrett Company was used to measure the membrane thickness. The vacuum environment was created by Isotemp vacuum oven model 281A from Thermo Fisher Scientific Inc., and the drying processes at certain temperatures were carried out in Precision Thelco oven model 16 from Precision Scientific company. The salt solution conductivity was measured with Oakton CON2700 conductivity meter in the permeation and desorption tests. A UV-Vis Spectrophotometer (Shimadzu UV mini-1240) was used to verify the removal of sericin in the degumming process. Whatman™ grade I filter paper with a diameter of 125 mm and pore size of 11 μm was used to filter fibroin particles from suspension.

3.2 Membrane Preparation

Both chitosan and fibroin membranes were prepared by the solution casting technique.

3.2.1 Chitosan Membrane

The synthesis method of chitosan membranes was similar to that used by Lin^[16]. The casting solution of chitosan membranes was composed of 1.5 wt.% chitosan, 2 wt.% of acetic acid and 96.5 wt.% of deionized water. Acetic acid was used to protonate the amino groups ($-\text{NH}_2$) into amine groups ($-\text{NH}_3^+$) in chitosan. The solution was stirred slowly until it became homogeneous, followed by filtration to remove insoluble impurities. The chitosan solution was cast onto a horizontally placed glass plate or a Petri dish. The membrane thickness was adjusted by changing the volume of the casting solution. The cast film of chitosan was air-dried until a constant weight was reached. The chitosan films were treated with 1 M NaOH solution for 24 h to convert the amine groups ($-\text{NH}_3^+$) back into the amino form ($-\text{NH}_2$) to make the membranes insoluble in water. After the alkaline

treatment with NaOH, the membranes were rinsed thoroughly with deionized water and cut into desired sizes. The membranes were dried under vacuum and the weight and thickness before and after drying were measured.

The membranes used for sorption tests were prepared from glass plates, cut into circles with diameters of 3.94 cm and stored at 70 °C to keep them dry. The membranes for permeation or desorption tests were prepared from Petri dishes, cut into circles with diameters of 5.25 cm, and stored in deionized water.

3.2.2 Fibroin Membrane

The previous work on heavy metal separation using fibroin as adsorbent by Farooq provides useful reference for the extraction of fibroin and fabrication of fibroin membranes^[15]. Fibroin was extracted from cocoon shells through the degumming process. The cocoon shells were cut into pieces of an average size of 1 cm × 1 cm, washed with deionized water to remove dust and impurities, and then dried in an oven at 80 °C until a constant weight was reached. 10 g of the dried pieces were heated in 2 L of deionized water at 95 °C for 8 h to separate fibroin from sericin. The solution with dissolved sericin was tested for sericin content with the UV-Vis Spectrophotometer after 8 h, at wavelength of 275 nm, and the concentration was verified by the calibration curve of sericin concentration vs. absorbance according to Farooq's work^[15]. The undissolved cocoon fiber was filtered out and heated in 2 L of fresh deionized water at 95 °C for 8 h again. This process was repeated for around 5 cycles (with 10 L deionized water in total) until no sericin was detected in the degumming water, which indicated all sericin was removed and the left fibrous part was filamentous fibroin. Water was separated from fibroin by a strainer. The fibroin was dried in the open atmosphere overnight and then placed into an oven at 70 °C for four days until constant weight. Finally, it was preserved in an airtight glass bottle for further use. Around 5 to 6 g of dry filamentous fibroin can be extracted from 10 g of dried cocoon shells.

18 g filamentous fibroin was dissolved completely in 100 ml of 9.5 M lithium bromide (LiBr) at 85 °C in 8 h. The strong ionic solution of LiBr can break the hydrogen bonding in the long fibroin chains^[150,151]. The LiBr solution with dissolved fibroin showed a reddish-brown color. It was filtered with a stainless-steel mesh screen (120 mesh) to remove insoluble impurities. The filtered fibroin solution was stored in a glass bottle at 4 °C as stock.

To separate LiBr from the solution, a novel method using ethanol to precipitate fibroin was applied^[152,153], instead of traditional time-consuming dialysis^[154–156]. 10 ml of the fibroin solution was added slowly drop by drop into 800 ml ethanol stirred at 300 rpm. The fibroin precipitated in ethanol was in the form of a white slurry. The fibroin in the mixture was allowed to settle for 8 h, after which ethanol and LiBr were decanted out of the container, leaving the concentrated fibroin slurry. In the previous work, ethanol and LiBr were removed from the slurry by washing with deionized water repeatedly, followed by gravity settlement of fibroin^[15]. This process was time-consuming, and it could take months to obtain only a few grams of fibroin paste. In this work, the concentrated fibroin slurry was rinsed with deionized water and centrifuged at 9000 rpm for 10 min repeatedly to separate fibroin from ethanol and LiBr. After one centrifugation cycle, the supernatant containing ethanol and LiBr was decanted. Deionized water was added to the centrifuge tube containing fibroin slurry to further dilute LiBr. The concentration of LiBr in the slurry was checked after each cycle with a conductivity meter. This process was repeated about 10 times to remove most of LiBr in the fibroin slurry. Note that when the conductivity of slurry dropped to around 10 $\mu\text{S}/\text{cm}$, more centrifugation cycles could no longer lower the conductivity. The slurry was allowed to settle overnight, during which time the conductivity would rise slightly because the aggregated long polymer chain of fibroin might slowly disentangle themselves. If this phenomenon occurred, centrifugation would be applied again, or deionized water would be added to lower the slurry conductivity. Finally, the resulting fibroin slurry (conductivity below 3 $\mu\text{S}/\text{cm}$) was filtered with a piece of filter paper (pore size 11 μm) to get fibroin paste.

32 g fibroin paste^[157] was dissolved in 100 ml 98% formic acid to obtain the casting solution for fibroin membranes. This was done in the fumehood because formic acid had a strong smell. Before casting, the solution was filtered with filter paper (pore size 11 μm) to remove any dust and impurities. The filtered solution was poured into a glass Petri-dish and dried in the air. The membrane thickness was controlled by changing the fibroin concentration in formic acid. After the first film formation, water was added into the glass Petri-dish to soak the membrane for 36 h to detach it from the glass. The film formed for the first time had poor mechanical strength because of water in the fibroin paste. Up to this stage, the membrane casting procedure followed the work by Farooq^[15]. To improve the mechanical strength, the film was dried at 70 °C for 24 h and then dissolved in 98 % formic acid again to make a 15 % (w/v) solution. This process excluded water in the fibroin paste from the casting solution. Now the casting solution in amber color (Figure 6) could produce fibroin

membranes with acceptable mechanical strength by drop casting. The 15 % (w/v) fibroin solution in formic acid resulted in a membrane thickness of $180 \pm 20 \mu\text{m}$, which was the thickness chosen for permeation test. Thinner membranes tended to develop cracks in AgNO_3 solution quickly (often less than 5 min) at concentrations higher than 2 M.



Figure 6 Casting solution for fibroin membranes

The membranes were stored at 70°C to keep them dry before sorption tests. The membranes for permeation tests were cropped into circles with diameters of 4.5 cm by a knife and stored in deionized water. The cutting should be done under water, keeping the membrane wet to avoid undesirable cracking.

3.3 Sorption Tests

The original dry membrane weight (m_0) and thickness (l_0) were first measured. The membrane was then immersed into 40 ml AgNO_3 solution of known concentrations ranging from 0 M to 9 M for 24 h until the sorption equilibrium was achieved. The membrane was removed from the solution, and after blotting the surface water, the membrane weight (m_w) was determined. This was the weight of the membrane with sorbed water and AgNO_3 . The wet membrane thickness (l_w) was measured with a micrometer after weight measurement. The wet membrane was then dried at 70°C in an oven to remove the sorbed water until a constant weight (m_d) was obtained, which was the weight of the dry membrane and sorbed AgNO_3 . The water uptake and AgNO_3 uptake in membrane were calculated on a mass basis.

AgNO_3 solution and membranes sorbed with AgNO_3 should be shielded from light since AgNO_3 oxidizes easily under light.

3.4 Permeation Tests

The method and setup of the permeation test was similar to those used by Lin^[16]. The permeation tests were conducted using the apparatus shown in Figure 7. The feed compartment and the receptor compartment were separated by a piece of wet membrane stored in deionized water. Before the experiment, the receptor compartment was filled with 1.5 L of deionized water. The membrane was placed at the opening of the feed compartment and sealed with a plastic ring to avoid solution leakage to the receptor compartment. The experiment began when 50 ml AgNO_3 solution of a known concentration was admitted into the feed compartment and in contact with the membrane. During the test, the solution on the feed side was stirred vigorously by a mechanical stirrer, and the solution on the receptor side was stirred by a magnetic stirrer to minimize the influence of bulk mass transfer. The concentration gradient across the membrane was the main driving force for AgNO_3 diffusion from the high-concentration feed solution to deionized water in the receptor. The solution conductivity in the receptor compartment was monitored and recorded as a function of time during the experiment by a conductivity meter linked to a computer. The data were logged every three seconds until a pseudo-steady state of permeation was reached. The conductivity data was stored in a software, CyberComm 2700, and was converted to AgNO_3 concentration through a pre-established calibration curve. During the entire test, the AgNO_3 concentration on the feed side was much higher than that on the receptor side, and the change in feed AgNO_3 concentration was negligible. The quantity of silver nitrate in the receptor compartment, Q_t , was plotted against time, and the time lag method was used to analyze the data.

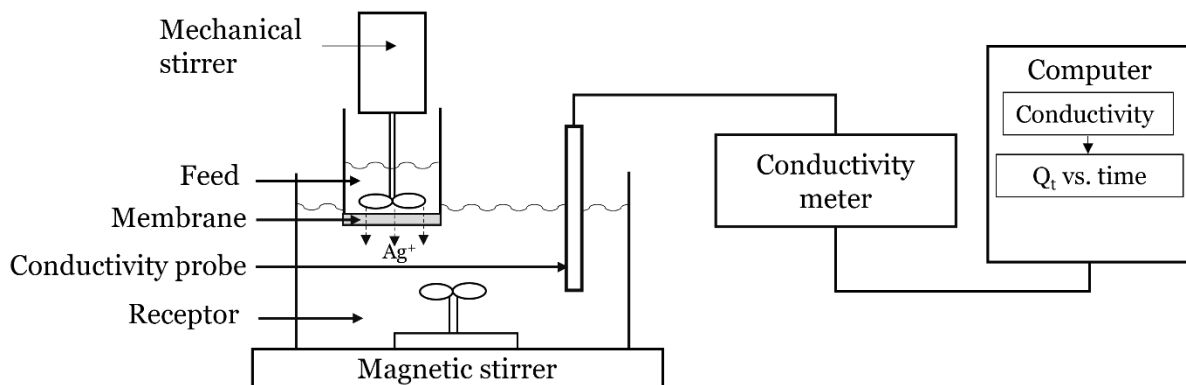


Figure 7 Schematic illustration for permeation test setup

3.5 Desorption Tests

The diffusivity coefficient can also be evaluated by the desorption test. The chitosan membrane was first immersed in AgNO₃ solution until sorption equilibrium. The wet membrane with sorbed AgNO₃ was placed into a reservoir with 1.5 L deionized water for diffusion of silver ions from the membrane to water. The solution in the reservoir was rigorously stirred to ensure homogeneity. The change in conductivity of solution in the reservoir was monitored for a short period of time to obtain the desorption kinetic data, which were compared with the model shown in Equation (2.13), taking $m = 10$. The diffusivity was estimated by minimizing the sum of squared errors (SSE) between the experimental data and model prediction, using the ‘solver’ function in Excel.

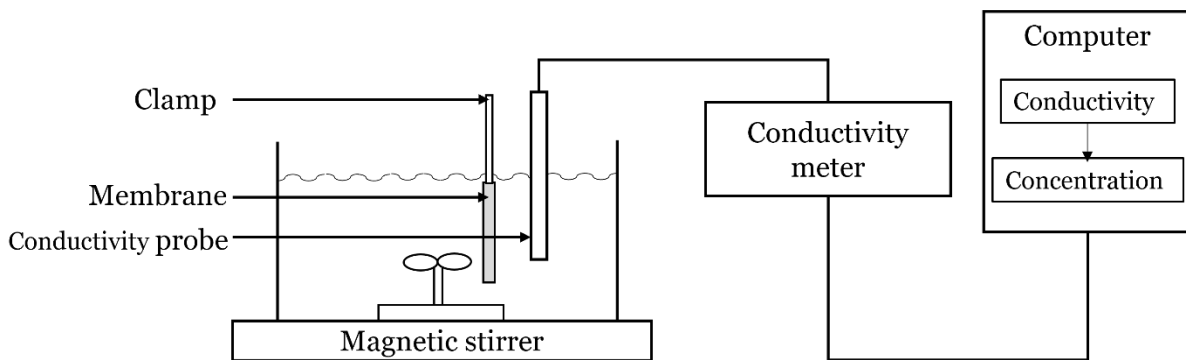


Figure 8 Schematic illustration for desorption test setup

The same permeation and desorption measurement procedures were used for evaluating permeability and diffusivity of Ag⁺ in chitosan and fibroin membranes. When deemed necessary, the

experiment were also carried out for NaCl to reveal the unique Ag^+ /chitosan and/or Ag^+ /fibroin interactions as compared to weakly interactive Na^+ /chitosan and Na^+ /fibroin systems.

Chapter 4

Results and Discussion

4.1 Sorption test

4.1.1 Sorption Uptake and Solubility

Figure 9 shows the AgNO_3 uptake in chitosan and silk fibroin membranes at sorption equilibrium on a mass basis at AgNO_3 concentrations from 0 to 9 M. The sorption uptake of NaCl in chitosan membranes was tested from 0 to 4.5 M for comparison. The fibroin membrane tended to crack in AgNO_3 solutions higher than 3 M, but the samples were still capable for measurements in sorption tests. The average experimental error was less than 8 %, mainly caused by the uncertainty in membrane thickness measurement and water blotting of the wet membrane.

The highest concentrations of salts tested were close to their solubility limit in water. The salt uptake (per unit mass of dry polymer) was calculated by Equations (4.1) and (4.2), where m_0 is the mass of dry polymer membrane (g), and m_{salt} is the mass of salt uptake at equilibrium, m_d is the total mass of dry polymer membrane and salt uptake.

$$m_d = m_0 + m_{\text{salt}} \quad (4.1)$$

$$\text{Salt uptake} = \frac{m_d - m_0}{m_0} \quad (4.2)$$

Chitosan sorbed more AgNO_3 than NaCl at a given salt concentration, because AgNO_3 can be both physically and chemically sorbed by chitosan, while NaCl can only be physically adsorbed. The sorption capacity of chitosan was much higher than that of fibroin at the same AgNO_3 concentration on a mass basis.

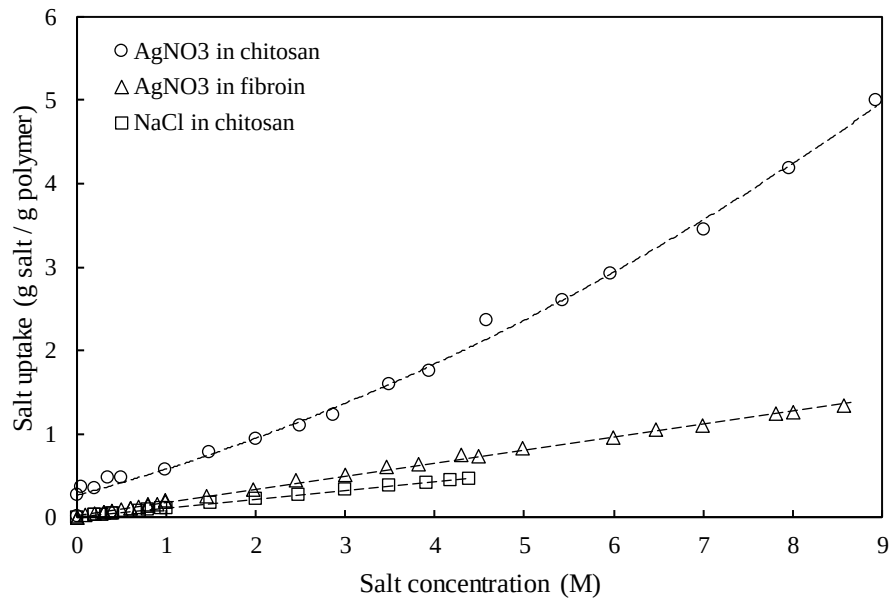


Figure 9 Effects of salt concentration on sorption uptake of salts in chitosan and fibroin membranes at sorption equilibrium. Temperature, 25 °C.

Figure 10 and 11 demonstrate the water uptake (per g dry polymer) and degree of membrane swelling of the same set of membrane samples and salt solutions corresponding to Figure 9, respectively. Water uptake can be calculated using Equation (4.3) where m_w is total mass of polymer, water and salt at equilibrium.

$$\text{Water uptake} = \frac{m_w - m_d}{m_0} \quad (4.3)$$

The water uptake of chitosan with AgNO₃ showed a decreasing trend at low AgNO₃ concentrations and then increased at higher concentrations. The water uptake in chitosan membranes with NaCl decreased continuously with NaCl concentration. Chitosan in NaCl solution overall sorbed more water than when it was in AgNO₃ solution.

Fibroin absorbed more water as the AgNO₃ concentration increased. Overall, its water sorption capacity was much lower than that of chitosan. Chitosan is known as a hydrophilic polymer, and fibroin is less hydrophilic than chitosan.

By looking at the three sets of data, a hypothesis is proposed for the change of trend in water uptake in chitosan and fibroin: Ag⁺ and water are always competing with each other during the

sorption process. At low AgNO_3 concentrations, both chemical adsorption and physical adsorption of Ag^+ happen in chitosan. The sorption of Ag^+ dominates, and water uptake decreases. When the chemical binding sites of chitosan are all filled at equilibrium at a certain AgNO_3 concentration, additional AgNO_3 will only physically adsorb in chitosan, which causes an increase in polarity of the salt-water-polymer complex. The sorption of water begins to dominate, and the water uptake thus shows an increasing trend at higher concentrations. On the other hand, the water uptake of chitosan decreases as the NaCl concentration increases because more NaCl are physically adsorbed and less sites are left for water sorption. The water uptake in fibroin increases with the salt concentration because fibroin is relatively hydrophobic, and the salts sorbed in fibroin will help to take additional water. At low Ag^+ concentration, water does not compete with Ag^+ to bind fibroin as much as in the case of chitosan, and Ag^+ is not chemically adsorbed in fibroin, and thus there is no change of trend in water uptake of fibroin. The water uptake of fibroin in AgNO_3 solution increases with AgNO_3 concentration due to increasing polarity.

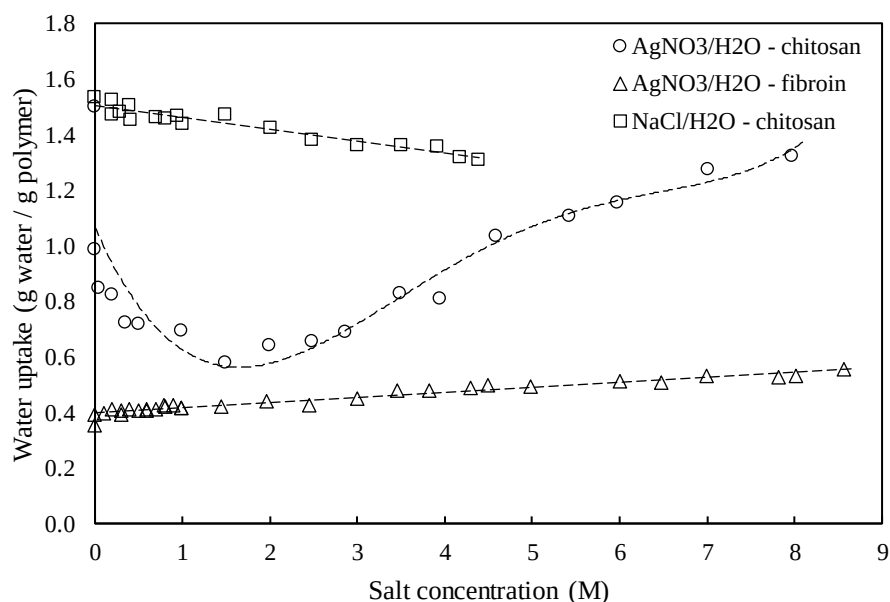


Figure 10 Effects of salt concentration on sorption uptake of H_2O in chitosan and fibroin membranes at sorption equilibrium. Temperature, 25 °C.

The degree of membrane swelling is expressed as the swelling ratio, R , the ratio of wet membrane thickness, l_w , at sorption equilibrium to the initial dry membrane thickness, l_0 , before sorption, as shown in Equation (4.4):

$$R = \frac{l_w}{l_0} = \frac{\text{wet thickness}}{\text{dry thickness}} \quad (4.4)$$

The swelling ratio was evaluated for chitosan membranes in AgNO_3 solution, chitosan membranes in NaCl solution and fibroin membranes in AgNO_3 solution at different salt concentrations. The effects of salt concentration on the swelling ratio of the membranes are shown in Figure 11.

The membrane swelling of chitosan with AgNO_3 followed the same trend as water uptake, which decreased slightly and then increased at higher AgNO_3 concentrations. The swelling of chitosan membrane is affected by the competing sorption of water and Ag^+ . At low AgNO_3 concentrations, water content inside chitosan contributes more to swelling^[16]. As the concentration of AgNO_3 increases, i.e., more AgNO_3 is competing with water, the water content in the chitosan membrane decreases. Thus, the degree of membrane swelling decreases. When the AgNO_3 concentration is sufficiently high, the chitosan polymer will sorb enough silver salts to be polar. Therefore, the water uptake begins to increase with AgNO_3 concentration due to the rising ionic strength of silver salt sorbed in chitosan. The degree of membrane swelling increases as well.

When chitosan was immersed in $\text{NaCl}/\text{H}_2\text{O}$ solutions, with an increase in the NaCl concentration, less water was adsorbed into the chitosan membrane as the water concentration decreased. However, the swelling of chitosan membrane with NaCl showed a minor increasing trend at higher NaCl concentrations. The reason might be that the effect of NaCl sorption on the swelling is more significant than the effect of water sorption, and the water uptake is much higher than NaCl uptake. The swelling ratios in NaCl solution were generally higher than those in AgNO_3 solution because NaCl is less adsorbed in chitosan than AgNO_3 and more water is sorbed in chitosan membranes with NaCl .

The fibroin membrane swelled more as the AgNO_3 concentration increased, and the trend was the same as water uptake in fibroin. Since the overall water uptake of fibroin is less than that of chitosan (Figure 10), the overall degree of swelling of fibroin is lower than that of chitosan.

Based on the swelling ratio, the actual membrane thickness was used for calculation of diffusivity and permeability. The actual volume of the membranes in the sorption tests can also be estimated with the actual wet membrane thickness. In the following, the sorption uptake of salts on a mol per volume basis will be calculated (Figure 12), and these data will be used to calculate such quantities as solubility, permeability and diffusivity for dimensional consistencies. The solubility, or partition coefficient, is the ratio of salt concentration in the membrane phase to salt concentration in the solution phase as shown in Figure 13. The units of solubility here are [mol salt/m³ polymer] and [mol salt/m³ solution]. It is clear that the solubility of AgNO₃ in chitosan is not constant, while the solubility of AgNO₃ in fibroin and the solubility of NaCl in chitosan are largely constant over the experimental concentration range. The values of solubility are shown in Table 1. From Figure 13, we can see that the overall AgNO₃ solubility of chitosan is higher than that of NaCl in chitosan at a given molar salt concentration, and it is also higher than that of AgNO₃ in fibroin. The results are consistent with the sorption uptake on the mass basis (Figure 9), as expected.

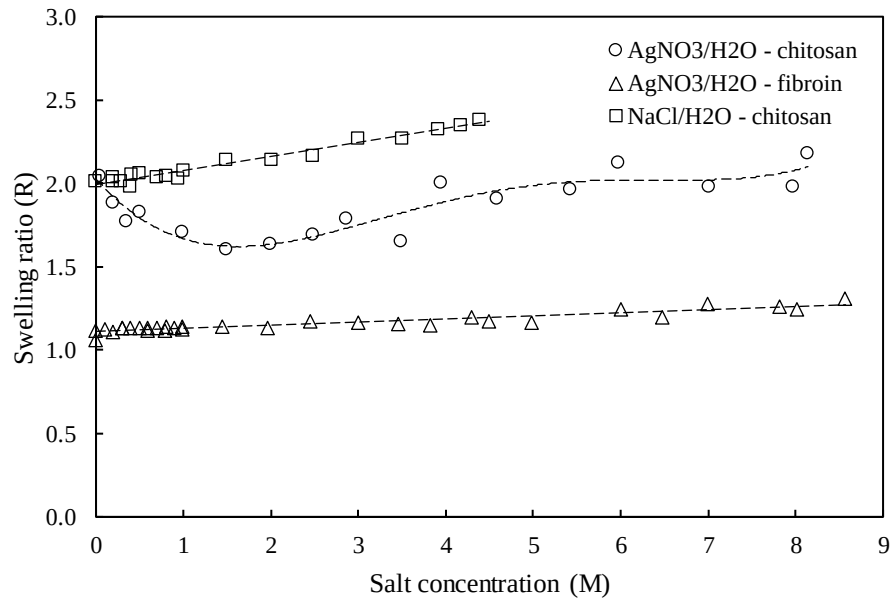


Figure 11 Effects of salt concentration on the swelling ratio (R) of chitosan and fibroin membranes at sorption equilibrium. $R = \text{wet membrane thickness at sorption equilibrium} / \text{original membrane thickness before sorption}$. Temperature, 25 °C.

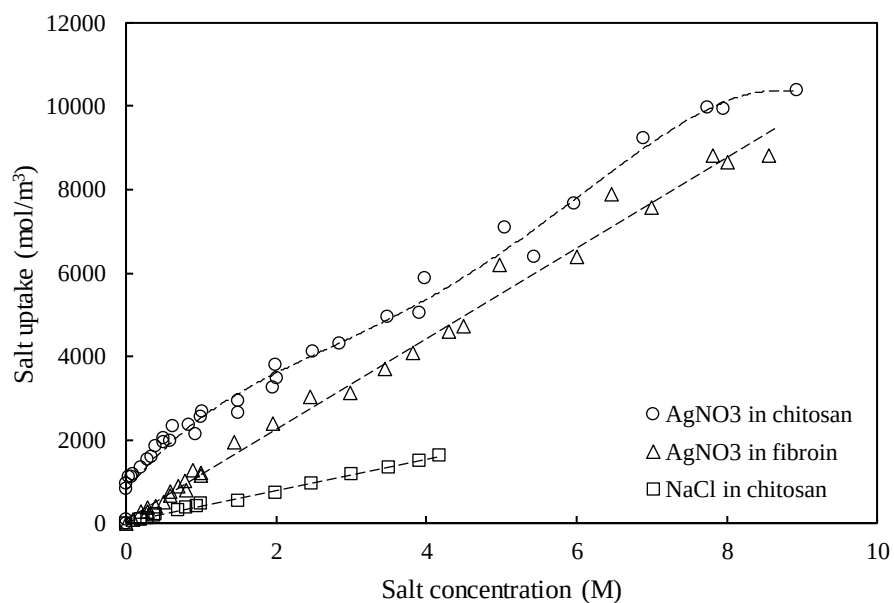


Figure 12 Effects of concentration on sorption uptake of salts in polymer membranes (mol/volume basis) at sorption equilibrium. Temperature, 25 °C.

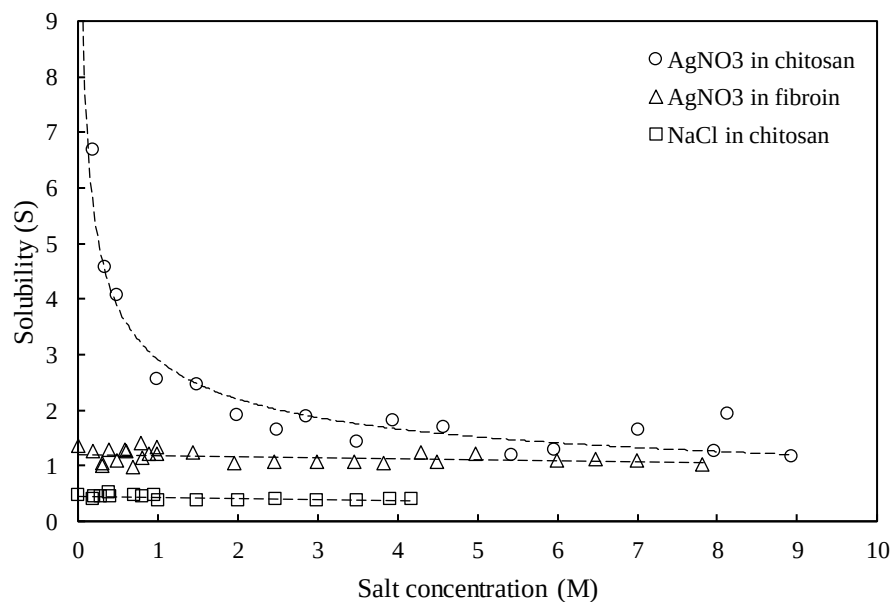


Figure 13 Effects of salt concentration on solubility (S) of salts in polymer membranes defined as [mol salt/m³ polymer]/[mol salt/m³ solution]. Temperature, 25 °C.

Figure 14 - 16 show the changes of mass fractions of polymer, water, and salt in the membrane with changing salt concentration. The overall change of water and AgNO_3 mass fractions over the tested AgNO_3 concentration range in the fibroin membranes were smaller than those in the chitosan membranes. In chitosan membranes, the mass fraction of AgNO_3 exceeded that of water at around 1.3 M AgNO_3 (Figure 14), which was also the concentration at which the changes in water uptake (Figure 10) and degree of membrane swelling (Figure 11) began to change in a different manner. For chitosan immersed in NaCl solution, the mass fraction of water was always much higher than that of NaCl (Figure 16). The overall mass fractions of salt increased and mass fractions of water decreased with an increase in the salt concentration.

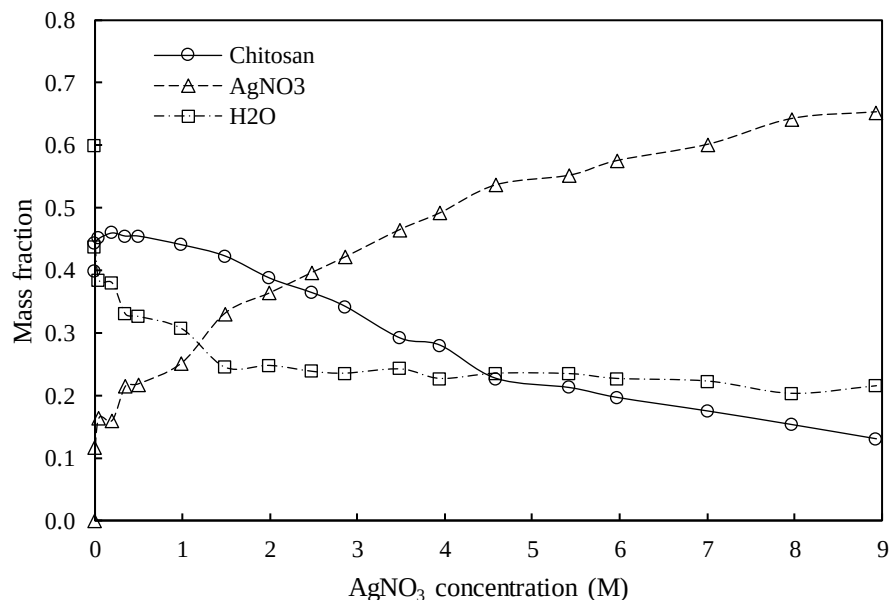


Figure 14 Effects of AgNO_3 concentration on the mass fraction of chitosan, H_2O and AgNO_3 in chitosan membranes at sorption equilibrium. Temperature, 25 °C.

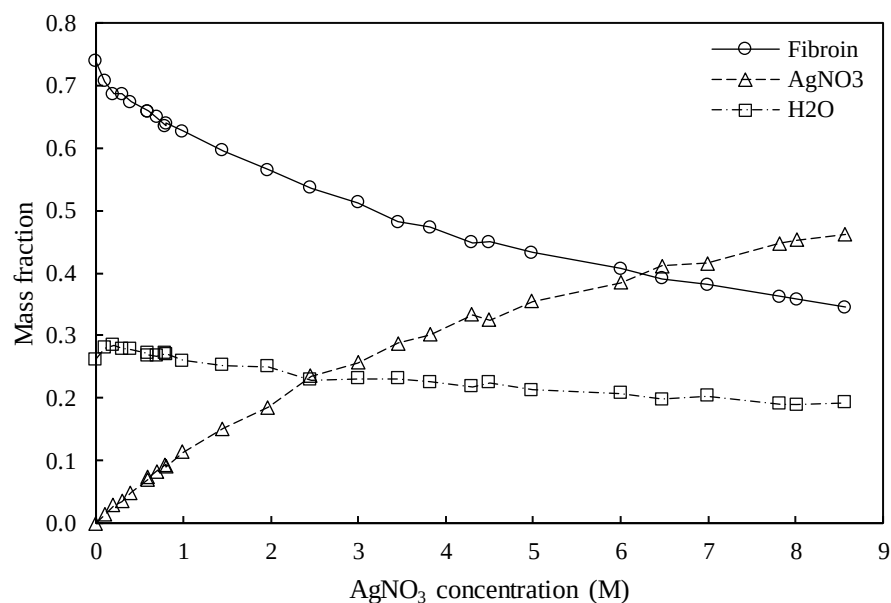


Figure 15 Effects of AgNO₃ concentration on the mass fraction of fibroin, H₂O and AgNO₃ in fibroin membranes at sorption equilibrium. Temperature, 25 °C.

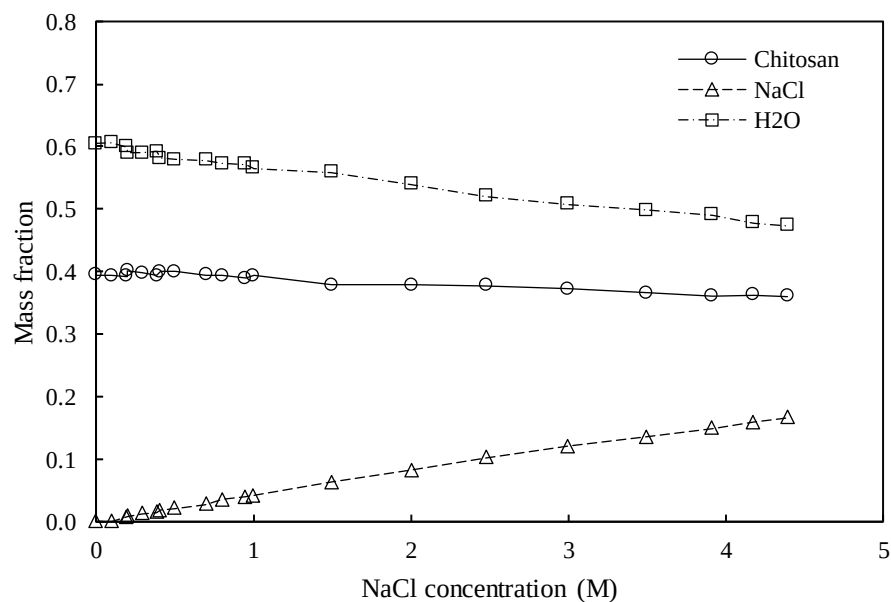


Figure 16 Effects of NaCl concentration on the mass fraction of chitosan, H₂O and NaCl in chitosan membranes at sorption equilibrium. Temperature, 25 °C.

The data from Figure 14 and 15 are transformed into ternary diagrams, shown in Figure 17 and Figure 18, respectively. The horizontal axis for the ternary diagram is the mass fraction of AgNO_3 , and the corresponding molar concentration of AgNO_3 is also shown for easy reference. The axis on the left from top to bottom shows the water mass fraction from 0 to 1, and the axis on the right from bottom to top presents the water mass fraction from 0 to 1.

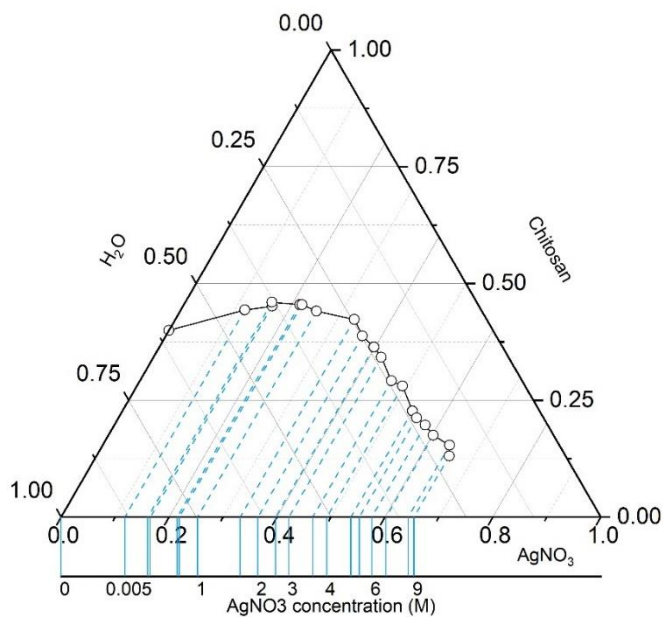


Figure 17 Ternary diagram of AgNO_3 , H_2O and chitosan at sorption equilibrium. Temperature, 25 °C.

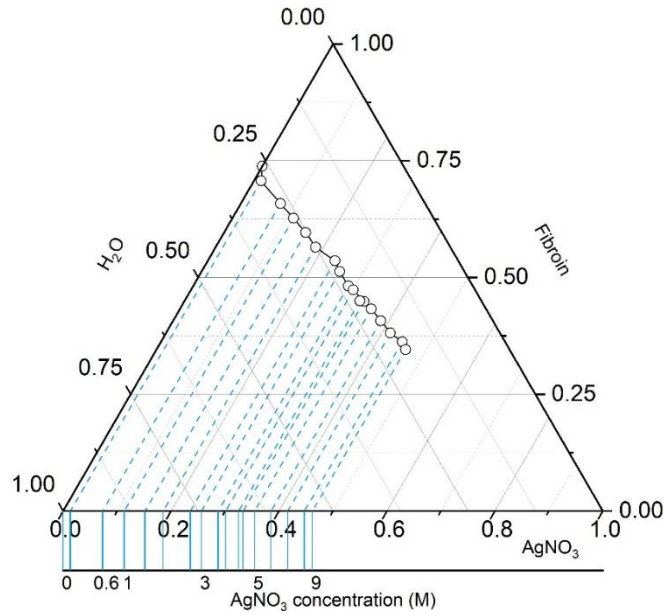


Figure 18 Ternary diagram of AgNO₃, H₂O and fibroin at sorption equilibrium. Temperature, 25 °C.

4.1.2 Sorption Isotherms

Figure 19 shows q_e vs. C_e for the equilibrium sorption uptake of AgNO₃ in chitosan and fibroin membranes. The NaCl sorption uptake in chitosan membranes at equilibrium was also tested for comparison. The sorption capacity of the adsorbate in the polymer at equilibrium, q_e (g salt/g membrane) is calculated by:

$$q_e = \frac{m_d - m_0}{m_0} \quad (4.5)$$

The concentration of salt in liquid phase at equilibrium C_e (g salt/L) is:

$$C_e = C_0 - \frac{q_e m_0}{V} \quad (4.6)$$

where m_0 is the dry membrane weight before sorption, m_d is the total of dry membrane weight and salt uptake, C_0 is the initial salt concentration in the solution, and V is the volume of salt solution in the sorption test.

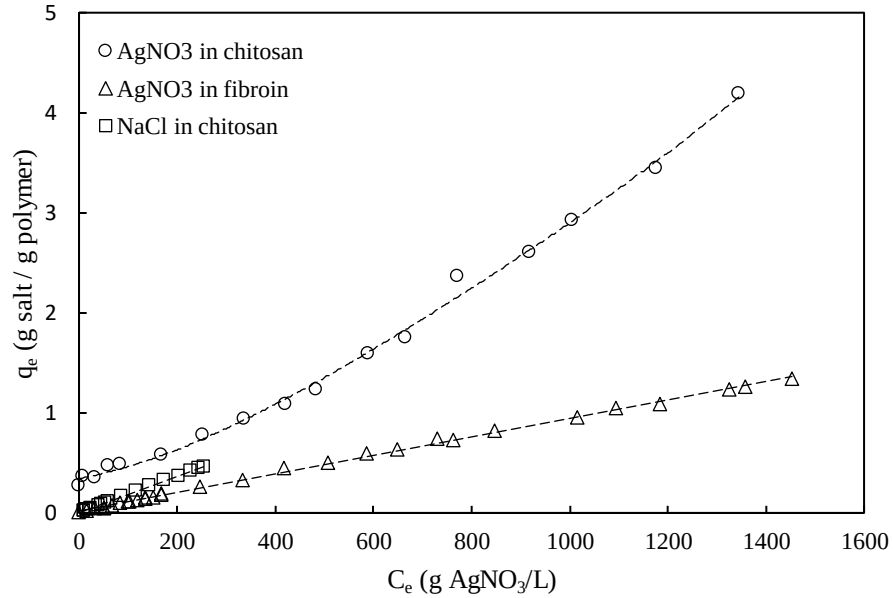


Figure 19 Adsorption isotherms of salts in chitosan and fibroin membranes. Temperature, 25 °C.

Fitting the data to the Langmuir isotherms showed no clear trend, and thus the Langmuir model does not appear to be suitable for describing the sorption uptake for the systems studied here.

To test the applicability of the Freundlich model, Equation (2.20) was used to fit the experimental data. A plot of q_e vs. C_e is plotted on a logarithmic scale in Figure 20. The Freundlich isotherm of AgNO₃ in chitosan has a rather poor linearity. Neither the Langmuir nor the Freundlich model can describe the sorption of AgNO₃ in chitosan membranes. The sorption of NaCl in chitosan and AgNO₃ in fibroin membranes appear to follow the Freundlich model better. The values of the Freundlich isotherm parameters, k , and the heterogeneity factors, n , were estimated, as shown in Table 1. k indicates the sorption capacity and n indicates the sorption intensity. The sorption intensity of AgNO₃ in fibroin is less than 1, so the isotherm is favorable, while the sorption intensity of NaCl in chitosan is 1.005, so the isotherm is slightly unfavorable.

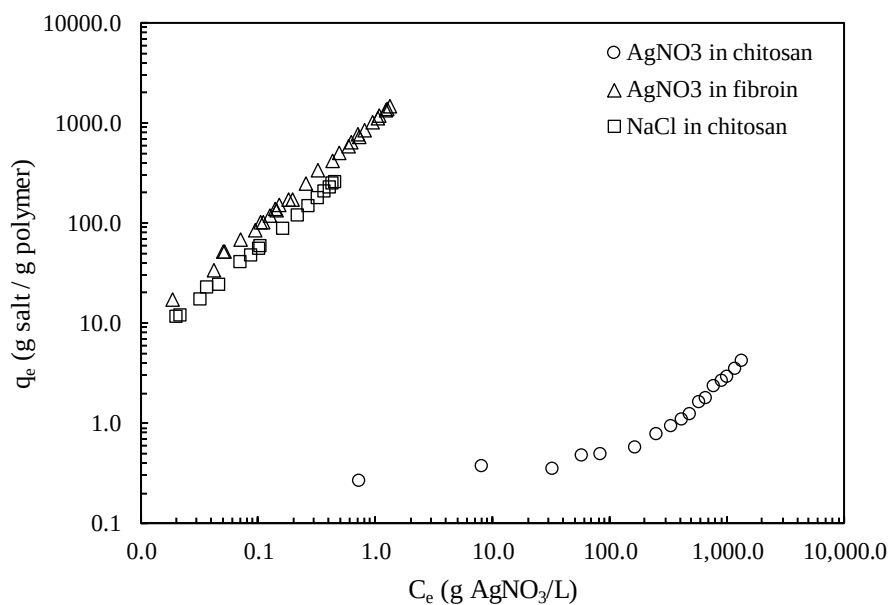


Figure 20 Adsorption isotherms of salts in chitosan and fibroin membranes according to the Freundlich equation. Temperature, 25 °C.

Table 1 Solubility and isotherm model parameters from sorption of salts in the polymer membranes.

		AgNO ₃ in chitosan	AgNO ₃ in fibroin	NaCl in chitosan	Unit
Solubility		Not constant	1.10	0.39	$\frac{mol\ salt/m^3\ polymer}{mol\ salt/m^3\ solution}$
Freundlich equation	k	N/A	1.33×10^{-3}	1.79×10^{-3}	$\frac{g\ salt}{g\ polymer} / \left(\frac{g\ salt}{L} \right)^n$
	n	N/A	0.953	1.005	N/A
	R ²	N/A	0.9866	0.9982	N/A

4.2 Permeation test

In the permeation test, salt ions diffused from the high-concentration feed compartment to the low-concentration receptor compartment through the membrane driven by the concentration gradient. The salt concentration in the receptor compartment was measured with a conductivity meter connected to a computer. The conductivity data was transformed into concentration (C_t), which was then used to determine the total amount of salt in the solution as a function of time ($Q_t = C_t V$). The calibration curves are shown in Appendix A. The average experimental error in this test was less than 8 %, which was possibly caused by inaccurate reading of the conductivity meter at low salt concentrations, diffusion in the bulk solution, and uncertainty in extrapolation of the time lag.

Figure 21 is a typical plot showing the salt quantity Q_t (mol) in the receptor compartment at three-second intervals. Diffusion happened through a chitosan membrane of 26 μm thick with an initial AgNO_3 concentration in the feed compartment of 0.8 M.

The deionized water obtained from the lab had an initial conductivity of 0 - 3 $\mu\text{S}/\text{cm}$ and this has been considered in converting the conductivity data into salt concentration.

During the transient permeation state, the time lag τ in Figure 21 is estimated by extrapolating the pseudo-steady state, or simply called 'steady state' permeation data to the time axis. The transient diffusion coefficient (D) can be calculated from Equation (2.11) with the value of τ . The region with a constant slope is the region for pseudo-steady state permeation when the permeation rate is constant, as in Equation (2.10). At the pseudo-steady state, the permeation rate (J) is calculated by dividing the slope by the membrane area. The permeance P' is obtained by Equation (2.4), assuming the salt concentration in the receptor compartment C_{2b} is much less than C_{1b} in the feed compartment. This condition was met because the solution volume in the receptor (1.5 L) was much larger than that in the feed (50 ml) and the data was recorded for a short period of time. Permeability (P) is the product of permeance and membrane thickness during the pseudo-steady state. The diffusivity coefficient at pseudo-steady state (D^*) is calculated by Equation (2.3), where C_{1m} and C_{2m} are the salt concentrations at the membrane surfaces on the feed and receptor side respectively. C_{1m} and C_{2m} in the membrane at the corresponding concentration of the bulk solution, C_{1b} and C_{2b} , can be obtained from salt solubility (S) in the sorption tests, as shown in Table 1. In the case for AgNO_3 in chitosan membranes, the solubility is not constant, and the solubility values are estimated by interpolation from Figure 12.

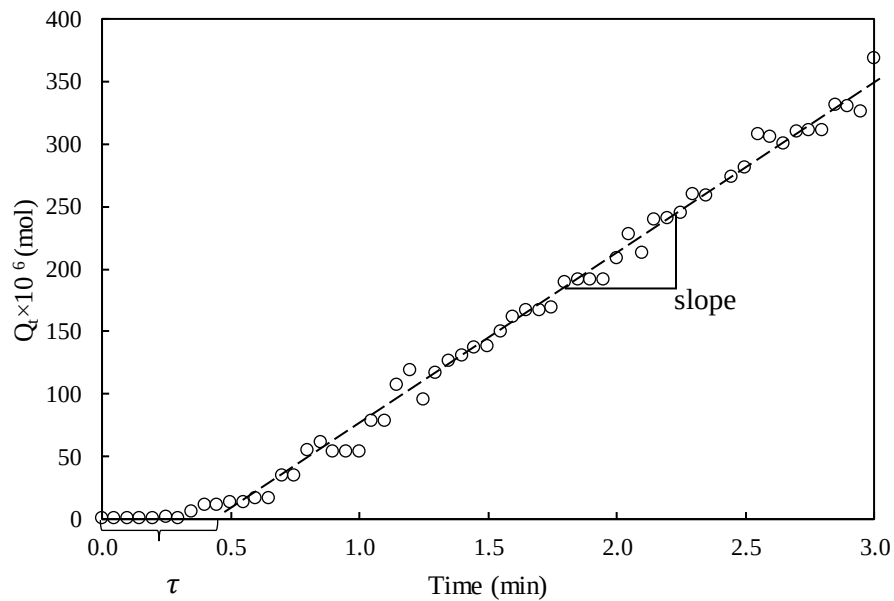


Figure 21 Time dependency of AgNO_3 quantity in the receptor solution for diffusion of 0.8 M AgNO_3 through a 26 μm chitosan membrane. τ is the time lag.

As shown by the sorption data in Figure 11, the membrane thickness varies with salt concentration due to swelling. In the calculation for diffusivity and permeability, the membrane thicknesses differ between the transient state and the pseudo-steady state at different salt concentrations. As shown in Figure 22, the salt concentration at any point in the membrane changes with time. The membrane used for permeation test was swollen by water completely because it was stored in deionized water for at least 24 h. When the permeation test started, the membrane surface on the feed side first contacted with salt ions. The receptor side was deionized water with negligible salt concentration. The concentration profile was a curve along the membrane thickness, with the highest salt concentration on the feed side and lowest salt concentration on the receptor side that gradually increased over time. As the pseudo-steady state of permeation was reached, the concentration profile became linear across the membrane thickness.

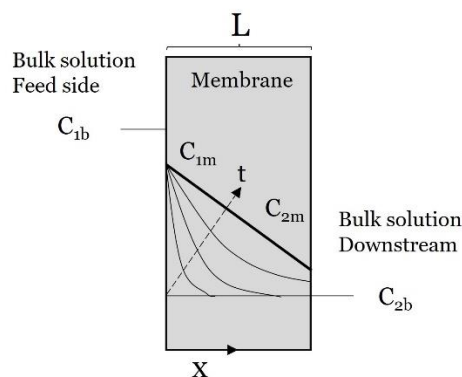


Figure 22 Schematic of concentration profile for permeation across the membrane varying with time

The swelling ratio (R) from the sorption test is the ratio of wet membrane thickness to the dry thickness at sorption equilibrium at a certain salt concentration. Linear functions that relates R with different salt concentrations could be established for NaCl in chitosan and AgNO_3 in fibroin for the estimation of wet membrane thickness at sorption equilibrium, and R at a certain AgNO_3 concentration in chitosan membrane was estimated by interpolation.

During transient permeation, only a trace amount of salt ions entered the membrane. The membrane thickness chosen for transient diffusivity calculation in Equation (2.12) is therefore the wet membrane thickness at sorption equilibrium when salt concentration is zero, obtained by multiplying the dry membrane thickness by R at zero concentration. For diffusivity and permeability at pseudo-steady state calculated from Equation (2.3) and Equation (2.4), membrane thickness is adjusted by the original dry membrane thickness multiplying the average of R values at zero salt concentration and R values at the salt concentration on the feed side^[16].

Figure 23 shows that steady state permeation rate increased linearly with feed salt concentration for all three sets of tests. As the concentration difference between the feed solution and the receptor solution becomes larger, the driving force for permeation goes up. The large difference in permeation rate of AgNO_3 through chitosan and fibroin may be caused by the low solubility of AgNO_3 in fibroin and different membrane thickness used. The chitosan membranes used in the tests were around $26 \mu\text{m}$ thick, but the fibroin membranes were $184 \mu\text{m}$ thick on average. This thickness was chosen because thinner fibroin membrane was fragile in AgNO_3 solution with concentrations greater than 3 M and could develop cracks easily (often within 5 min). The chosen thickness allowed the fibroin membrane to remain stable in 4 M AgNO_3 solution for more than 5 min .

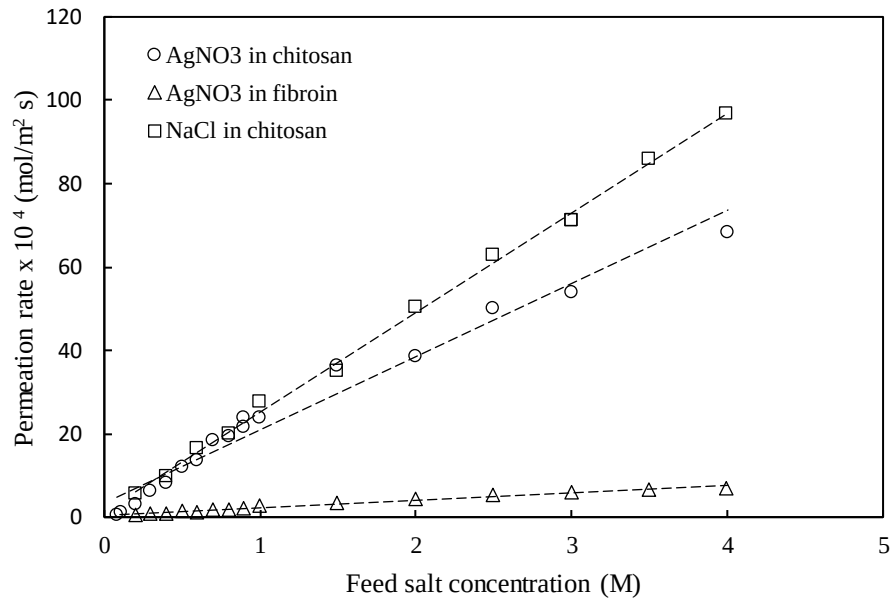


Figure 23 Effects of feed salt concentration on the permeation rate of ions through chitosan membranes ($l_{0,avg} = 26 \mu\text{m}$) and fibroin membranes ($l_{0,avg} = 184 \mu\text{m}$).

Figure 24 - 27 show the permeance (P'), permeability (P), transient diffusivity (D) and steady state diffusivity (D^*) with changing salt concentrations, respectively. The permeability, permeance and diffusivity of NaCl in chitosan and AgNO₃ in fibroin varied only slightly over the salt concentration ranges. The permeability coefficient and permeance for AgNO₃ in chitosan increased with salt concentration initially at low salt concentrations, and then began to decrease to approach constant values when the salt concentration was high enough. The diffusivity coefficients from the time lag method and pseudo-steady state of permeation increased from 0 to 1 M and then reached constant values.

These results are consistent with Lin's work for salt concentration less than 1 M. In both studies, the permeance, permeability, transient diffusivity and steady state diffusivity at 1 M were around $25 \times 10^{-4} \text{ mol}/(\text{s} \cdot \text{m}^2 \cdot \text{mol}/\text{m}^3)$, $10 \times 10^{-8} (\text{mol} \cdot \text{m})/(\text{s} \cdot \text{m}^2 \cdot \text{mol}/\text{m}^3)$, $10 \times 10^{-8} \text{ cm}^2/\text{s}$ and $35 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively^[16]. The effects of feed concentration on the transport properties of AgNO₃ in chitosan higher than 1 M, NaCl in chitosan and AgNO₃ in fibroin from 0 to 9 M have not been found in literature.

Overall, the permeance and permeability of NaCl in chitosan are the highest due to its high diffusivity at pseudo-steady state, and those of AgNO₃ in fibroin are the lowest. However, the values of transient diffusivity of AgNO₃ in fibroin are the highest, and those of AgNO₃ in chitosan are the lowest. The chelation of Ag⁺ in chitosan apparently plays an important role for this difference. The values of steady-state diffusivity for NaCl in chitosan are the highest, while at concentrations higher than 2 M, those values for AgNO₃ in fibroin and in chitosan are very close.

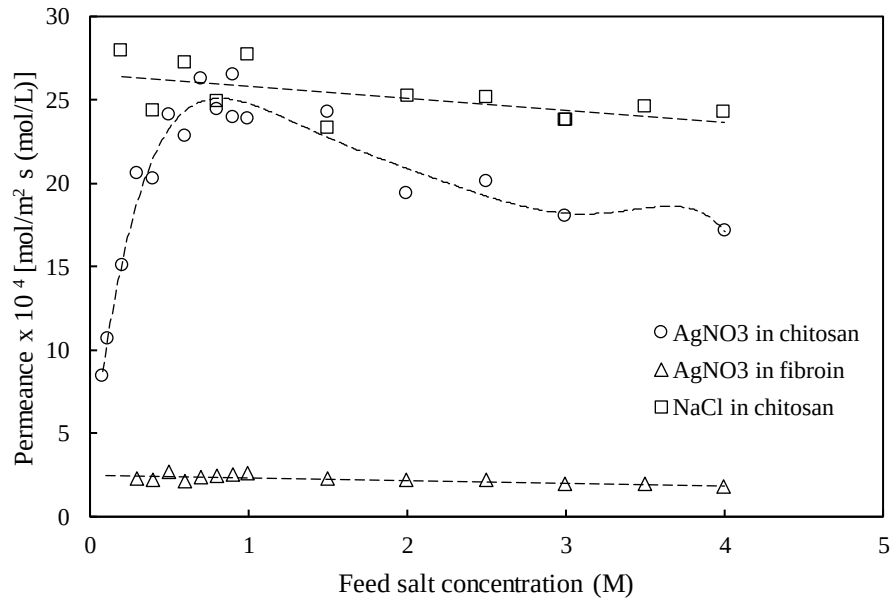


Figure 24 Effects of feed salt concentration on the permeance of ions in chitosan membranes ($l_{0,avg} = 26 \mu\text{m}$) and fibroin membranes ($l_{0,avg} = 184 \mu\text{m}$).

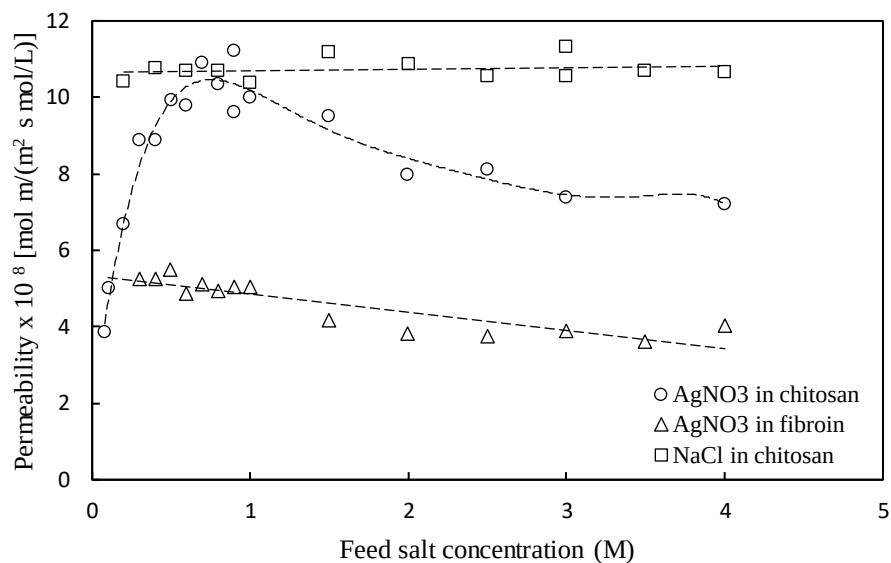


Figure 25 Effects of feed salt concentration on the permeability of ions in chitosan membranes ($l_{0,avg} = 26 \mu\text{m}$) and fibroin membranes ($l_{0,avg} = 184 \mu\text{m}$).

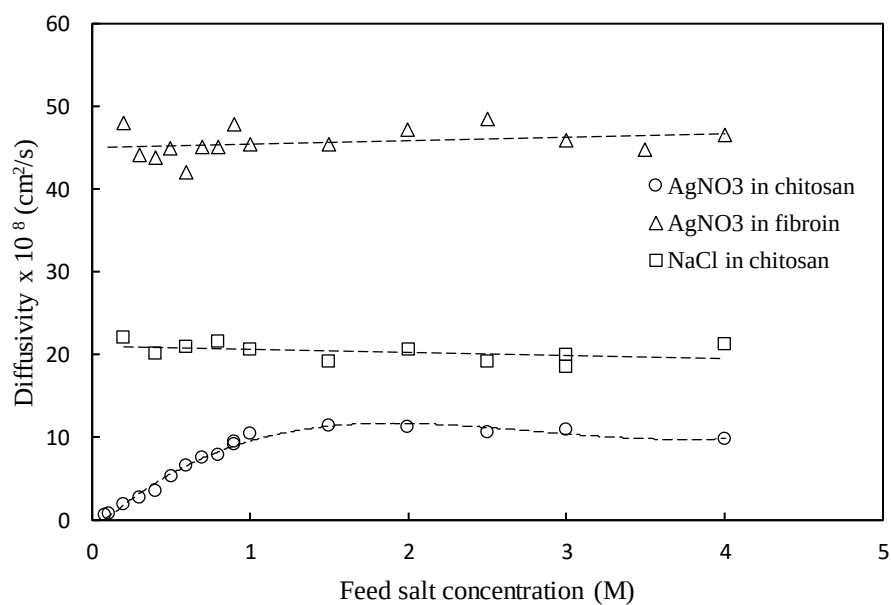


Figure 26 Effects of feed salt concentration on the diffusivity coefficient of ions in chitosan membranes ($l_{0,avg} = 26 \mu\text{m}$) and fibroin membranes ($l_{0,avg} = 184 \mu\text{m}$). The diffusivity coefficient is evaluated from the time lag for transient permeation.

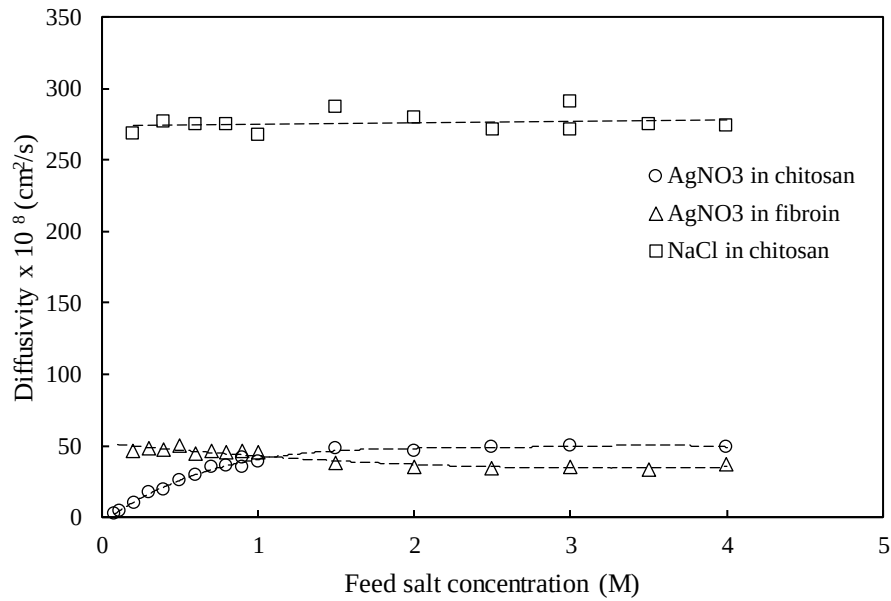


Figure 27 Effects of feed salt concentration on the diffusivity coefficient of ions in chitosan membranes ($l_{0,avg} = 26 \mu\text{m}$) and fibroin membranes ($l_{0,avg} = 184 \mu\text{m}$). The diffusivity coefficient is evaluated from the pseudo-steady state permeation rate.

4.3 Desorption test

The desorption test was conducted to further evaluate the diffusion of AgNO_3 in chitosan membranes. Figure 28 shows the desorption data as a function of time for chitosan membranes that have reached sorption equilibrium at different AgNO_3 concentrations. Q_t is the amount of sorbate diffusing out of the membrane during time t and Q_e is the amount of sorbate diffusing out of the membrane during infinite time, which is also the sorbate concentration at sorption equilibrium obtained from sorption tests. The diffusivity is not constant over the tested concentration range. Otherwise, the experimental data for different AgNO_3 concentrations would overlap.

Figure 29 illustrates an example of the comparison of experimental data and modeling result of a desorption test with an AgNO_3 concentration of 0.98 M according to Equation (2.13) and (2.14). The experimental data does not fit the model very well. Only the early-stage experiment data were used for fitting, and the long-time data did not fit well because the model itself is valid for a short time period. In addition, the model only considers diffusion process in the membrane, but in the experiment silver ions diffused in the membrane and entered the solution, where the conductivity was

measured. Even vigorous stirring was present in the solution, the diffusion process still could include bulk diffusion in the solution, which contributes to longer diffusion time and distance. Furthermore, the model does not account for the possible chitosan- Ag^+ complexes formation and deformation.

The final results for diffusivity coefficients obtained from modeling as a function of AgNO_3 concentrations are presented in Figure 30. The diffusivity showed an increasing trend with the AgNO_3 concentration. The model assumes that desorption is fully governed by diffusion and the diffusion coefficient is independent of sorbate concentration in the membrane, but actually this is not the case. The interaction between chitosan and silver ions definitely affects the transport process.

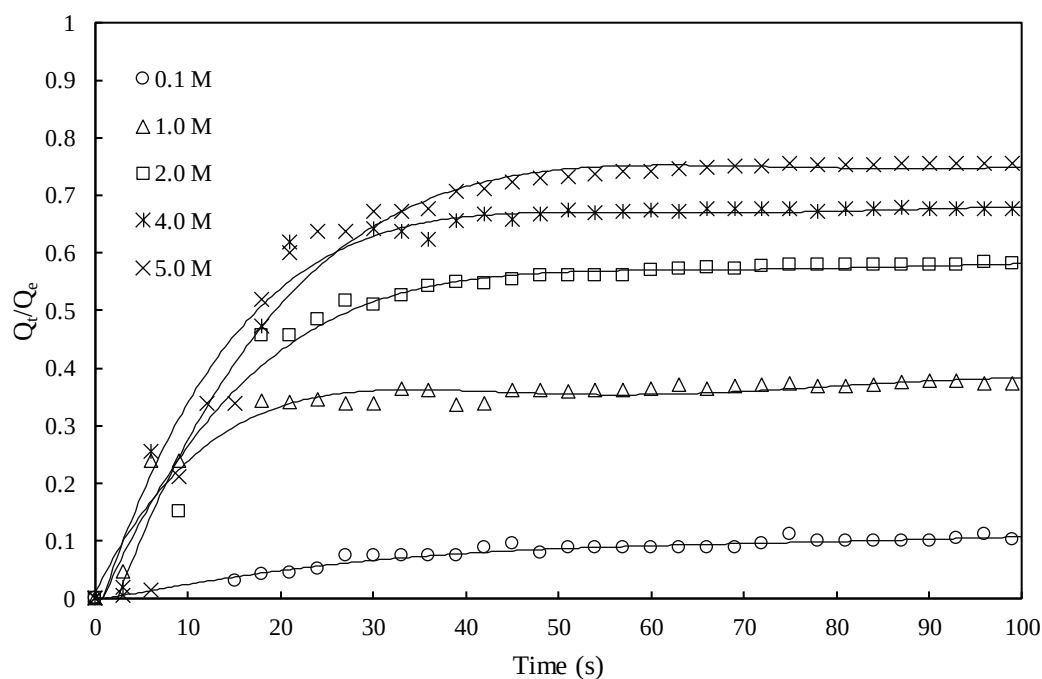


Figure 28 Experimental desorption data of AgNO_3 in chitosan membranes that have reached sorption equilibrium at different AgNO_3 concentrations.

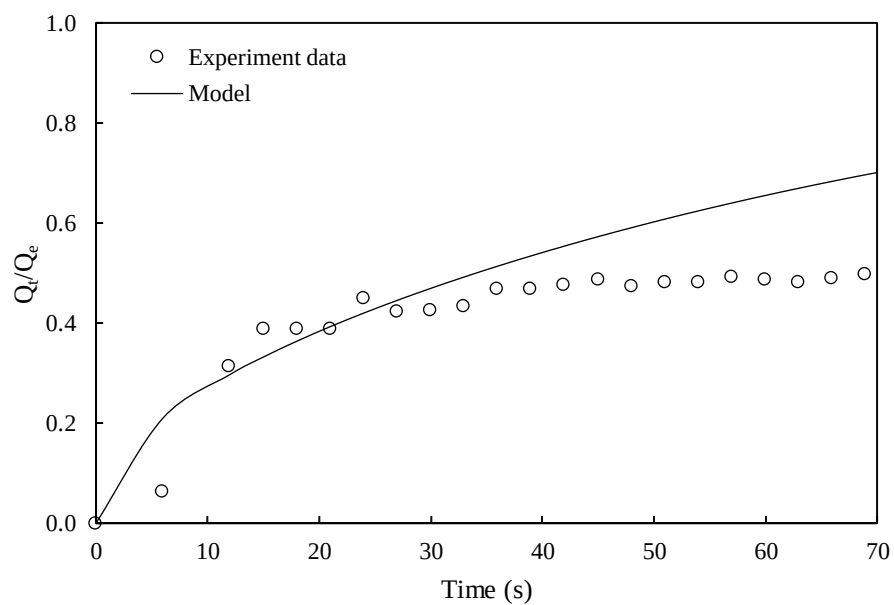


Figure 29 Modelling of desorption of AgNO_3 through a 26 μm chitosan membrane reached sorption equilibrium in 0.98 M AgNO_3 solution

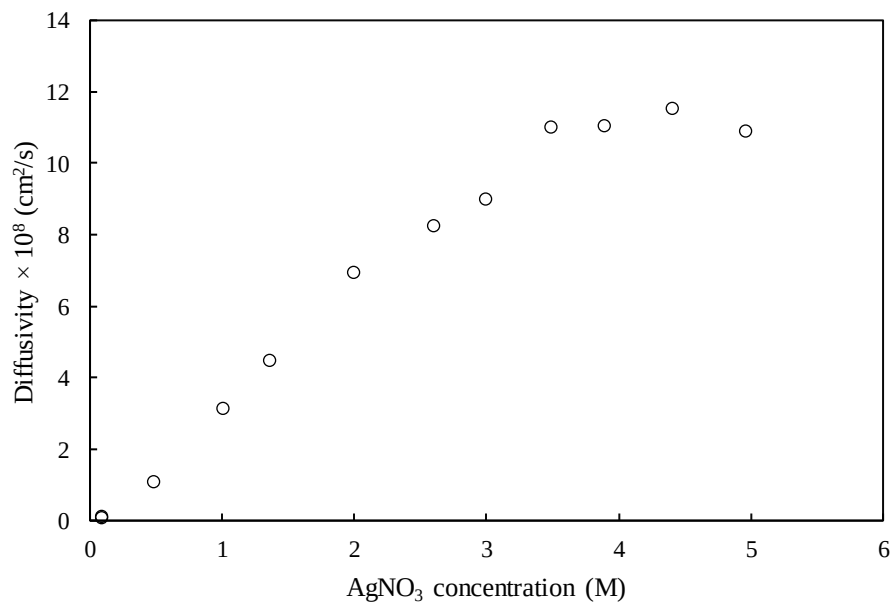


Figure 30 Effect of feed AgNO_3 concentration on the diffusivity coefficient of Ag^+ through chitosan membranes. The diffusivity coefficient is evaluated from the desorption test.

4.4 Diffusivity from Different methods

Figure 31-33 compare diffusivity coefficients obtained from different methods for AgNO₃ in chitosan, NaCl in chitosan, and AgNO₃ in fibroin respectively. Since the permeance is the permeation flux normalized by the concentration difference across the membrane and the concentration on the receptor side is assumed to be 0, the constant slope of permeation rate vs. feed concentration can be utilized to represent the permeance. Thus, the permeance can be seen as a constant independent of feed concentration. If the wet membrane thicknesses over the experiment concentration range are approximately constant, the permeability obtained from the product of permeance and wet membrane thickness will also be constant. The estimations for constant permeance and permeability coefficients are shown in Table 2. For NaCl in chitosan and AgNO₃ in fibroin, the solubility values are approximately constant. Therefore, another estimation for diffusivity coefficients can be obtained by Equation (2.6), as shown in Table 2, together with diffusivity coefficients obtained through other methods for comparison. The diffusivity coefficients from Equation (2.6) are close to those from pseudo-steady state, as expected. They are the ‘averages’ of diffusivity at pseudo-steady state.

For AgNO₃ in chitosan membrane, the diffusivity determined by the time lag method and pseudo-steady state method have a similar trend, while the diffusivity coefficients during the transient permeation are lower than that from the pseudo-steady state method. One of the reasons for this is that the Ag⁺ concentration is very low during the transient state permeation. Also, the time lag method detects the diffusivity coefficient at the transient state, during which the chelating sites of Ag⁺ were not filled and some Ag⁺ in contact with chitosan might form chitosan-Ag⁺ complexes, reducing the mobility of Ag⁺. At steady state, chelating sites became saturated with Ag⁺ and no more chitosan-Ag⁺ complexes were formed, and Ag⁺ complexes would diffuse in the membrane. The diffusivity coefficients determined by the desorption test verify that the diffusivity is not constant over the salt concentration range studied. Also, these values are obtained from modeling using the early-stage desorption data, so it is expected that they are close to the values from the time lag method since both methods measure the diffusivity at the early stage of transient state permeation.

For NaCl diffusion through chitosan membranes, the diffusivity coefficients determined by the time lag method and steady state method are almost constant, while the diffusivity coefficients at transient state (~20 μm²/s) are lower than those from the steady state method (~300 μm²/s). The difference in the diffusivity measured with these two methods for NaCl diffusion is much larger than

that for AgNO_3 diffusion in chitosan membranes (~ 10 to $\sim 50 \mu\text{m}^2/\text{s}$). The large difference in the case of NaCl is partly because time lag method detects the diffusivity coefficient at the transient state, during which some empty sites on chitosan may be available for physical adsorption, reducing the mobility of Na^+ . At pseudo-steady state, chitosan becomes saturated with Na^+ , and Na^+ diffuses through the membrane readily. The different diffusivity coefficients from time lag method and steady state for AgNO_3 in chitosan are caused by both chemical and physical adsorption. The mobility hinderance effect of Ag^+ -chitosan chelation and physical adsorption of Ag^+ appears to be much more significant than the effect of physical adsorption of NaCl on chitosan.

In the case of AgNO_3 diffusion in fibroin, the diffusivity coefficients during transient state and pseudo-steady state are close at low AgNO_3 concentrations, and the diffusivity during transient state is higher than that in the pseudo-steady state at higher AgNO_3 concentrations. This could be due to the low sensitivity and stability of the conductivity probe at low salt concentration. A minor concentration change in the receptor at low concentrations could not be detected as accurately as at high concentrations, and the results at low AgNO_3 concentrations may have greater experimental error in the measurements. Uncertainties from the time lag method could also contribute to this because the time lag was obtained by extrapolation. If diffusion of Ag^+ at pseudo-steady state was really lower, factors other than the sorption of Ag^+ might affect the diffusion, such as morphology change induced by sorption of Ag^+ . The reason for fibroin membrane cracking could be the breaking of hydrogen bonding at high salt concentrations.

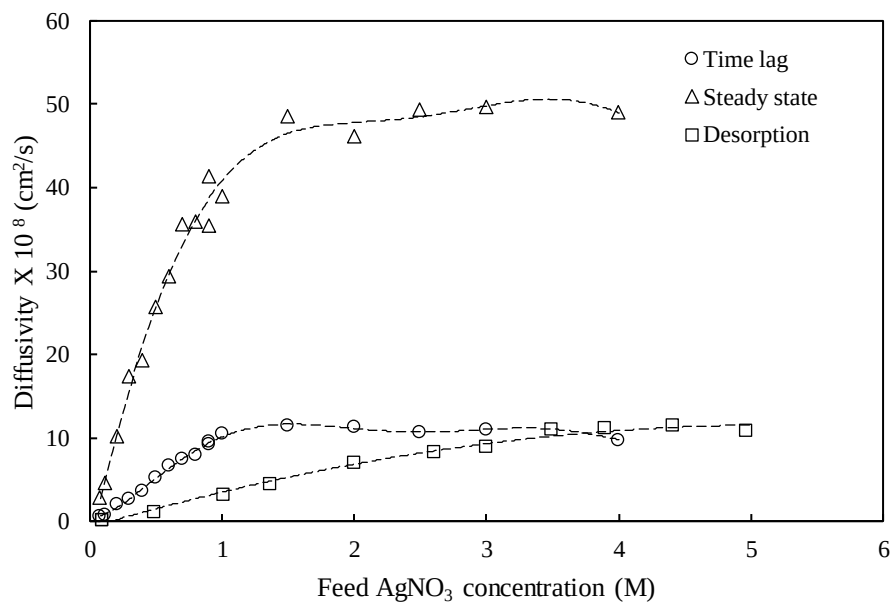


Figure 31 Comparison of diffusivity coefficients determined by time lag, steady state, and desorption at different AgNO₃ feed concentrations through chitosan membranes ($l_{0,avg} = 26 \mu\text{m}$).

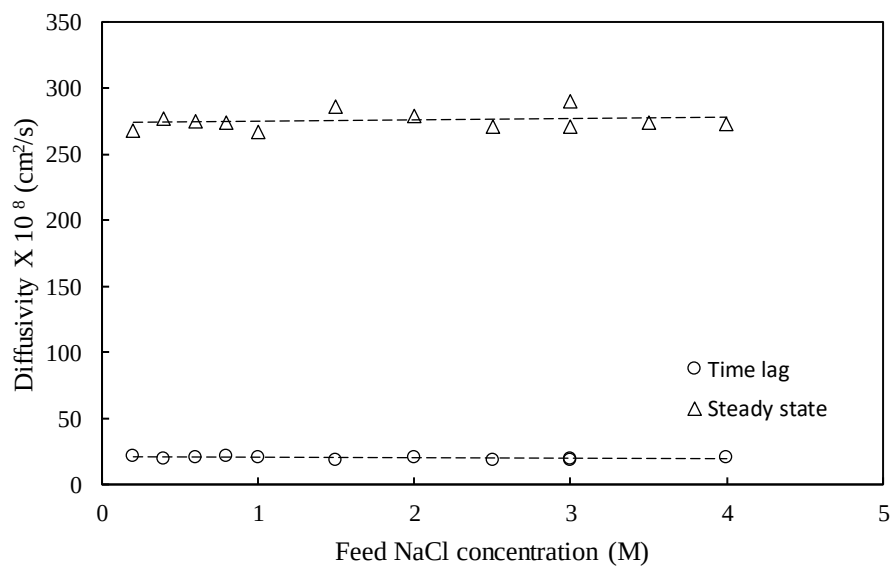


Figure 32 Comparison of diffusivity coefficients determined by time lag and steady state at different NaCl feed concentrations through chitosan membranes ($l_0 = 26 \mu\text{m}$).

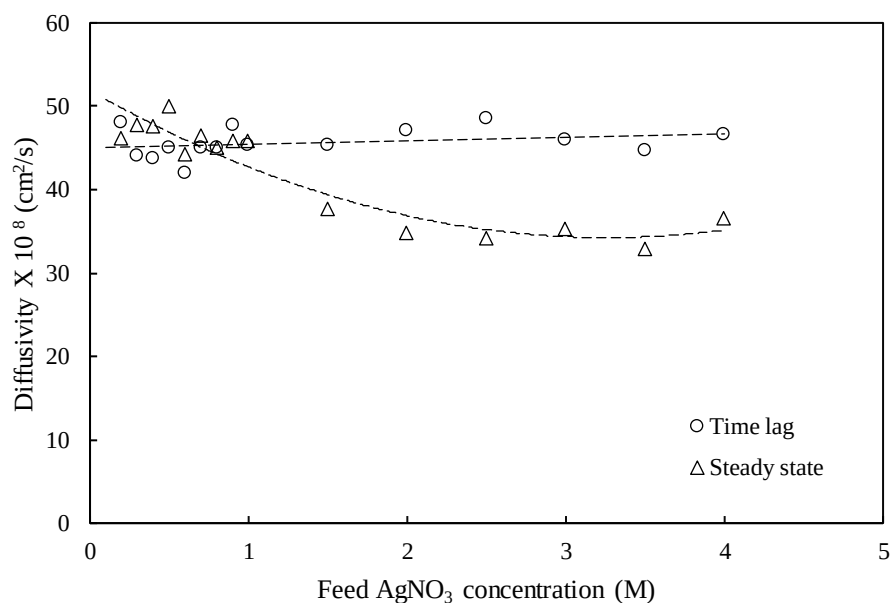


Figure 33 Comparison of diffusivity coefficients determined by time lag and steady state at different AgNO₃ feed concentrations through fibroin membranes ($l_{0,avg} = 184 \mu\text{m}$)

Table 2 Summary of transport properties for salts in different polymer membranes

Transport property		AgNO ₃ in fibroin	AgNO ₃ in chitosan	NaCl in chitosan	Unit
Permeance		2.0×10^{-6}	1.9×10^{-6}	2.4×10^{-6}	$\frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \frac{\text{mol}}{\text{m}^3}}$
Permeability		4.0×10^{-11}	8.1×10^{-11}	10.2×10^{-11}	$\frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \frac{\text{mol}}{\text{m}^3}}$
Diffusivity	Time lag	42.0~48.5	0.6~7.7	18.5~22.1	$\frac{\mu\text{m}^2}{\text{s}}$
	Steady state	32.8~50.0	2.7~31.7	267.2~290.7	
	D=P/S	36.7	N/A	262.8	
	Desorption	N/A	0.1~11.5	N/A	

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The solubility of Ag^+ in chitosan membranes is dependent on AgNO_3 concentration, and it is generally higher than that in fibroin membranes. The solubility values of AgNO_3 in fibroin and NaCl in chitosan were $1.10 (\text{mol AgNO}_3 / \text{m}^3 \text{ fibroin}) / (\text{mol AgNO}_3 / \text{m}^3 \text{ solution})$ and $0.39 (\text{mol NaCl} / \text{m}^3 \text{ chitosan}) / (\text{mol NaCl} / \text{m}^3 \text{ solution})$, respectively, independent of the salt concentrations. The water uptake and degree of membrane swelling for Ag^+ sorption in chitosan decreased with an increase in AgNO_3 concentration initially, and then began to increase with AgNO_3 concentration when the AgNO_3 concentration was sufficiently high.

Neither Langmuir nor the Freundlich isotherm applies to sorption of Ag^+ in chitosan membranes. The Freundlich isotherm appears to be able to describe Ag^+ sorption in fibroin and Na^+ sorption in chitosan.

The permeance, permeability and diffusivity of Ag^+ in chitosan are dependent on AgNO_3 concentration due to the chelation interaction between Ag^+ and chitosan, while the transport parameters for Ag^+ in fibroin and Na^+ in chitosan are relatively constant. Ag^+ has a higher permeance and permeability Ag^+ in chitosan than in fibroin, but the diffusivity for transient permeation of Ag^+ in fibroin is much higher than in chitosan. The difference in the diffusivity coefficients from the time lag method and steady state permeation are mainly caused by the chelation and/or physical adsorption of ions in polymer membranes.

The desorption test verifies that the diffusivity of Ag^+ in chitosan is dependent on AgNO_3 concentration. The diffusivity obtained in desorption tests is close to that obtained from the time lag method since both measurement methods estimate diffusivity within a short period of time after the diffusion measurement is initiated.

5.2 Recommendations

The following recommendations are made to further evaluate transport properties of Ag^+ in chitosan and fibroin membranes.

- (1) Further studies can be done to evaluate the water uptake, diffusivity, permeability and permeance of Ag^+ in chitosan, taking account of the strong Ag^+ -chitosan chelating interactions, The model for diffusivity as a function of Ag^+ concentration can be developed.
- (2) The reason for fibroin membrane cracking at high Ag^+ concentrations should be investigated by observing the morphology change and sorption mechanism of Ag^+ in fibroin.
- (3) To improve the mechanical stability of fibroin membranes in AgNO_3 solutions, more efficient and effective synthesis methods should be developed. Other materials may be combined with fibroin to form composite membranes for improved mechanical and chemical stabilities.

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Appendices

Appendix A Calibration Curves

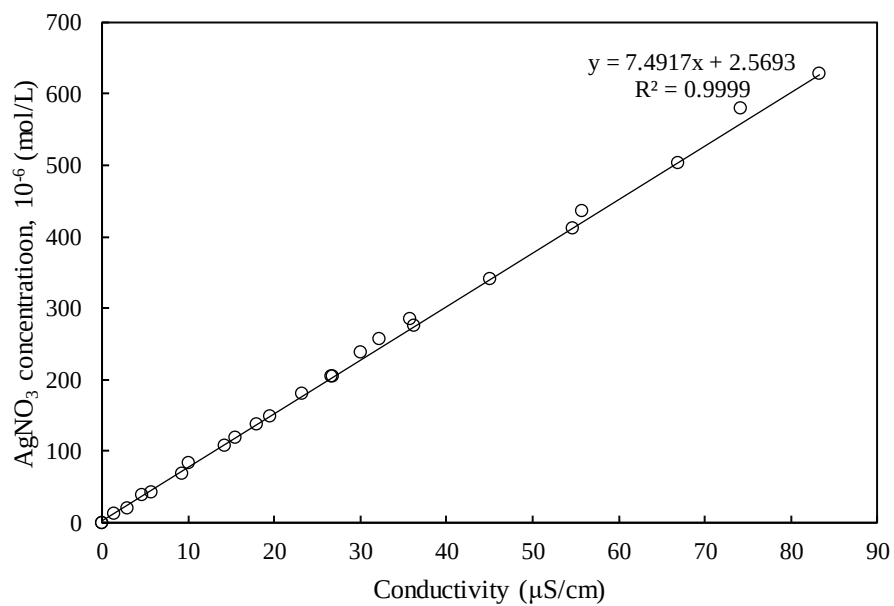


Figure A.1 Calibration curve used for AgNO₃ permeation tests

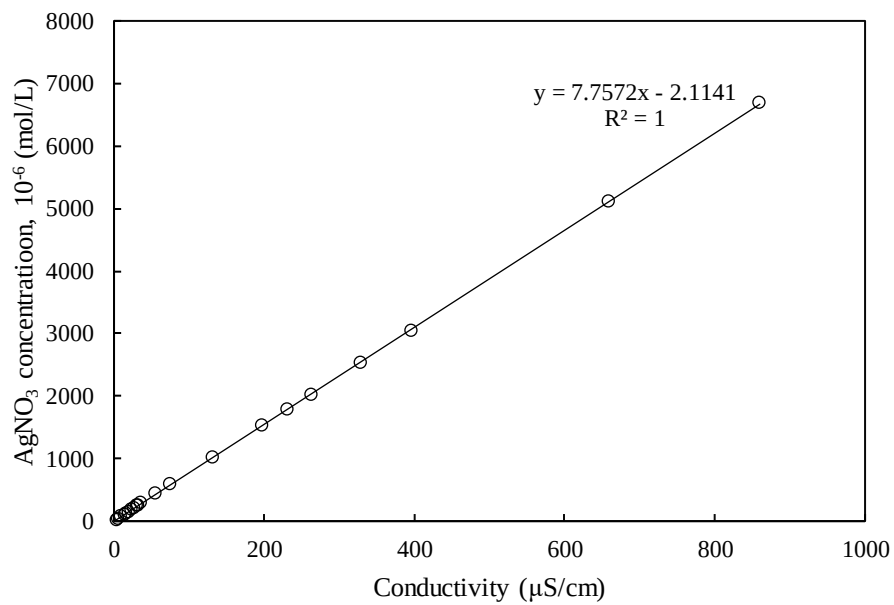


Figure A.2 AgNO_3 Concentration vs. conductivity for conductivity up to $860 \mu\text{S/cm}$

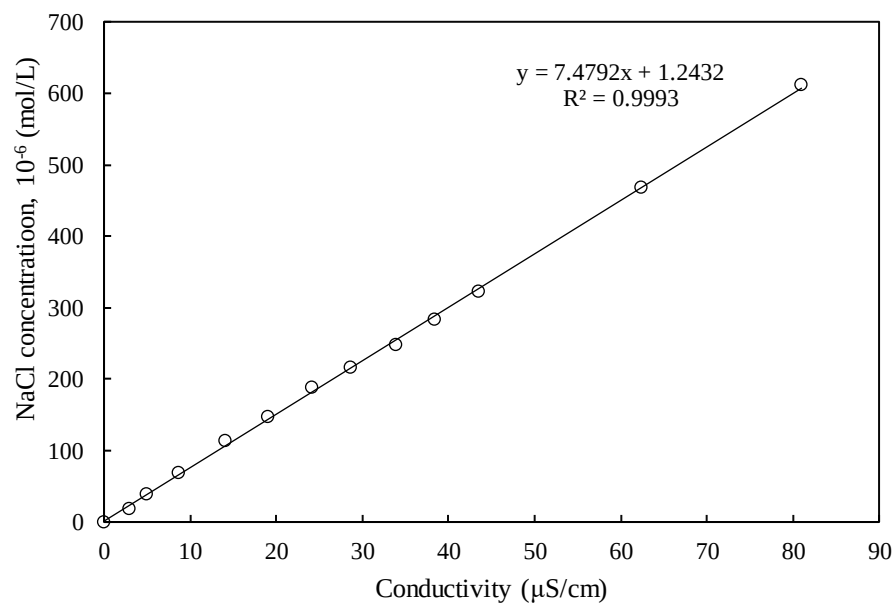


Figure A.3 Calibration curve used for NaCl permeation tests

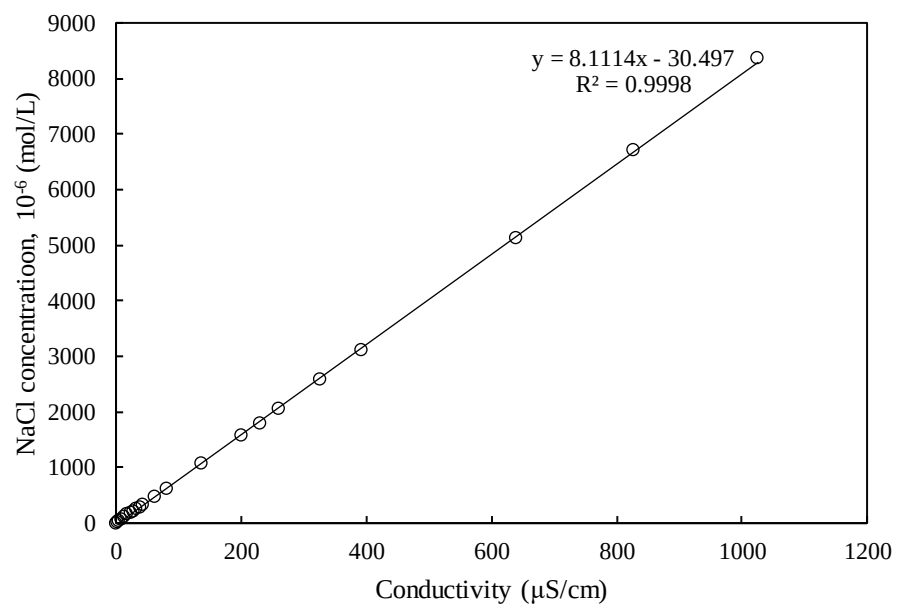


Figure A.4 NaCl concentration vs. conductivity for conductivity up to 1025 μS/cm

Appendix B

Sample Calculations

Sample Calculation for Sorption Test

Diameter of the chitosan membrane = 39.4 mm

Area of the membrane: $A = 1.22 \times 10^{-3} \text{ m}^2$

Volume of the AgNO_3 solution $V = 0.04 \text{ L}$

AgNO_3 concentration: $C_0 = 2.0 \text{ M}$

Original weight of dry membrane before sorption: $m_0 = 0.033 \text{ g}$

Wet weight of membrane at sorption equilibrium: $m_w = 0.086 \text{ g}$

Dry weight of membrane after sorption test: $m_d = 0.065 \text{ g}$

Original dry membrane thickness before sorption: $l_0 = 24.34 \text{ }\mu\text{m}$

Wet thickness of membrane at sorption equilibrium: $l_w = 39.79 \text{ }\mu\text{m}$

Molecular weight of AgNO_3 : $\text{MW}_{\text{AgNO}_3} = 169.87 \text{ g/mol}$

$$H_2O \text{ uptake} = \frac{m_w - m_d}{m_0} = \frac{0.086 - 0.065}{0.033} = 0.640 \frac{\text{g } H_2O}{\text{g chitosan}}$$

$$AgNO_3 \text{ uptake} = \frac{m_d - m_0}{m_0} = \frac{0.065 - 0.033}{0.033} = 0.940 \frac{\text{g } AgNO_3}{\text{g chitosan}}$$

$$Swelling \text{ ratio} = \frac{l_w}{l_0} = \frac{39.79}{24.34} = 1.63$$

$$AgNO_3 \text{ uptake} \left(\frac{\text{mol}}{\text{m}^3} \right) = \frac{m_d - m_0}{\text{MW}_{AgNO_3}} \div (A \cdot l_w)$$

$$AgNO_3 \text{ uptake} \left(\frac{\text{mol}}{\text{m}^3} \right) = \frac{0.065 - 0.033 \text{ g}}{169.87 \frac{\text{g}}{\text{mol}}} \div (1.22 \times 10^{-3} \cdot 39.79 \times 10^{-6} \text{ m}^3)$$

$$AgNO_3 \text{ uptake} \left(\frac{\text{mol}}{\text{m}^3} \right) = 3802 \frac{\text{mol } AgNO_3}{\text{m}^3 \text{ chitosan}}$$

$$AgNO_3 \text{ solubility in chitosan} = \frac{3802 \frac{mol AgNO_3}{m^3 chitosan}}{2 \frac{mol}{L} \cdot \frac{1000 L}{m^3}} = 1.90 \frac{mol AgNO_3 / m^3 chitosan}{mol AgNO_3 / m^3 solution}$$

Parameters for sorption isotherm:

q_e = amount of $AgNO_3$ adsorbed by chitosan at equilibrium

C_e = concentration of $AgNO_3$ in the liquid phase at equilibrium

$$q_e = \frac{m_d - m_0}{m_0} = \frac{0.065 - 0.033}{0.033} = 0.940 \frac{g AgNO_3}{g chitosan}$$

$$C_0 = 2 \frac{mol}{L} \times 169.87 \frac{g}{mol} = 339.74 \frac{g}{L}$$

$$C_e = C_0 - \frac{q_e m_0}{V} = 339.74 \frac{g}{L} - \frac{0.94 \times 0.033 g}{0.04 L} = 338.20 \frac{g}{L}$$

Sample Calculation for Permeation Test

Assumptions:

- The diffusivity coefficient is a constant independent of diffusant concentration.
- The concentration of the diffusing substance on the downstream side is negligibly low ($C_{1b} \gg C_{2b}$, $C_{2b} \approx 0$).
- Initially the membrane is free of any diffusing substance ($C_m = 0$ at $t = 0$).
- The diffusant is constantly removed from the membrane surface on the downstream side ($C_{2m} = 0$).

For $AgNO_3$ in chitosan membranes:

Original membrane thickness: $l_0 = 26.19 \mu m$

Area of membrane: $A = 1.081 \times 10^{-3} m^2$

Volume of receptor compartment: $V_L = 1.5 L$

Feed concentration of $AgNO_3$: $C_{1b} = 0.08 M$

Slope of AgNO₃ concentration in the receptor compartment vs. time: $\frac{\Delta C_{2b}}{\Delta t} = 4.86 \times 10^{-8} \frac{\text{mol}}{\text{L} \cdot \text{s}}$

Time lag from the x-axis intercept: $\tau = 434.86 \text{ s}$

At transient state, AgNO₃ concentration inside the membrane is assumed to be zero.

$$R = 1.5515$$

Actual membrane thickness:

$$l = l_0 R = 40.64 \mu\text{m}$$

Diffusivity coefficient from the time lag method:

$$D = \frac{l^2}{6\tau} = 0.633 \frac{\mu\text{m}^2}{\text{s}} = 0.633 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$$

Permeation rate:

$$J = \frac{\Delta C_{2b}}{\Delta t} \times \frac{V_L}{A} = 6.74 \times 10^{-5} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} = 0.674 \times 10^{-4} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

Permeance ($C_{1b} \gg C_{2b}$):

$$P' = \frac{J}{C_{1b} - C_{2b}} = \frac{J}{C_{1b}} = 8.42 \times 10^{-4} \frac{\text{mol}}{\text{m}^2 \cdot \text{s} \cdot \frac{\text{mol}}{\text{L}}}$$

At pseudo-steady state:

$$\text{Swelling ratio} = \frac{1}{2} [1.5515 + (-0.2533C_{1b} + 1.9599)] = 1.745$$

Actual membrane thickness:

$$l_{ss} = l_0 R_{ss} = 45.72 \mu\text{m}$$

Permeability:

$$P = P' l_{ss} = 3.85 \times 10^{-8} \frac{\text{mol} \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \frac{\text{mol}}{\text{L}}}$$

Diffusivity coefficient from the steady state permeation rate ($C_{2m} = 0 \text{ M}$):

At $C_{1b} = 0.08 \text{ M}$,

$$\Delta C_m = C_{1m} - C_{2m} = C_{1m} = SC_{1b} = 1124.77 \frac{\text{mol}/\text{m}^3}{\text{mol}/\text{m}^3} \times 0.08 \frac{\text{mol}}{\text{L}} = 124.23 \frac{\text{mol AgNO}_3}{\text{m}^3 \text{ chitosan}}$$

Solubility (S) here is by interpolation from Figure 12.

$$D^* = \frac{Jl_{ss}}{C_{1m} - C_{2m}} = 2.74 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$$

For AgNO₃ in fibroin membranes:

D can also be calculated from D=P/S when S is a constant.

If P, P' are constants independent of concentration for AgNO₃ in fibroin:

$$\text{Slope of flux vs. concentration} = P' = 1.975 \times 10^{-4} \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \frac{\text{mol}}{\text{L}}} = 1.975 \times 10^{-7} \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \frac{\text{mol}}{\text{m}^3}}$$

$$P = P'l_w = 1.975 \times 10^{-7} \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \frac{\text{mol}}{\text{m}^3}} \times 2.039 \times 10^{-4} \text{m} = 4.025 \times 10^{-11} \frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \frac{\text{mol}}{\text{m}^3}}$$

$$S = 1.101 \frac{\text{mol AgNO}_3/\text{m}^3 \text{ fibroin}}{\text{mol AgNO}_3/\text{m}^3 \text{ solution}}$$

$$D = \frac{P}{S} = 3.655 \times 10^{-11} \frac{\text{m}^2}{\text{s}} = 36.555 \frac{\mu\text{m}^2}{\text{s}}$$