Synthesis, Characterization, and Applications of Polyacrylamide Fluorinated-Chitosan Hydrogel Membranes

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ABSTRACT

A large range of synthetic/semisynthetic membrane materials today, including polymers, ceramics, metals, composites, and others, are accessible for various uses. The goal of this study was to fabricate polyacrylamide (PAAm) composite membranes incorporating internally linked cylindrical pores of fluorinated chitosan (F-chitosan) that would achieve high water flux, increased hydrophobicity, and adequate dimensional stability. Fluorination of chitosan was initially conducted, followed by the preparation of varying mass ratios of PAAm to F-chitosan membranes involving 0, 5, 10, 20, 50, and 75% F-chitosan hydrogels.

The membranes synthesized underwent multiple characterization procedures to evaluate their performances and behavior. Those characterizations included; contact angle and refractive index measurements, which revealed that the 10% and 20% F-chitosan membranes are the most polarizable and possess an amphiphilic nature. Fourier-Transform infrared (FT-IR) spectrophotometric analyses were performed, confirming fluorination and the combination of both polymers within the composite membranes. Swelling in different media was evaluated, from which the swelling kinetics were determined utilizing the Fickian diffusion model. This showed a non-Fickian swelling behavior for all membranes in different pH. Additionally, applications of the prepared hydrogels involving the flux of different media and diffusion of glucose in different pH were executed. The overall results concluded that the 10% F-chitosan membrane is the most reliable, having the ability to be exploited in future applications.

This study intended to design a low-cost, simple, and safe separation process for removing a small amount of substance, in this case glucose, from a feed stream to produce a purified product.

Keywords: Composite membrane, Chitosan, polyacrylamide Hydrogel, Swelling, Diffusion

1. INTRODUCTION

Different types of membranes have been exploited for decades in a wide variety of applications. Such membranes include those natural, synthetic, composite, porous, nonporous, asymmetric, isotropic, etc. Hydrogel membranes are a type of membranes which are selectively permeable. Polymer chains comprise the hydrogel matrix that serves as a selective barrier, allowing the passage of certain molecules while retaining and inhibiting the passage of others. Due to their semi-permeability, hydrophilicity, biocompatibility, flexibility, and many other significant properties, hydrogels are utilized in a wide range of applications (Martinez-Ruvalcaba et al. 2009- Barber and Kalorkoti 2020). Such applications primarily involve feed stream purification by molecular separation.

Hydrogel composite membranes are a type of membrane consisting of two materials. Organic compounds or monomers are typically combined with natural macromolecules or biopolymers to form a composite hydrogel membrane. The biopolymer is intended to serve as a porous material, provide support to the membrane, and enhance the membrane’s physical, mechanical, and chemical properties. This may provide remarkable potential for such membranes to be utilized in desired future applications (Pillai et al. 2009).

A wide variety of characteristics many biopolymers possess, including the natural polymers chitin and chitosan, render them valuable materials to be exploited for the synthesis of hydrogel composite membranes (Cheung et al. 2015). It is worth noting that a variety of biopolymers, primarily chitin, have an intractable structure. Due to that, chitin tends to be insoluble in water and common organic solvents (Pillai et al. 2009, Nagahama et al. 2008). That is where the idea of utilizing chitosan of similar properties yet less intractable structure to chitin stemmed from (Pillai et al. 2009).

Chitosan is a polysaccharide that forms fibrous cylindrical pore structures in a variety of applications, including membrane technology, biosensors, drug delivery systems, cosmetics, and a variety of biological uses (Cunha and Gandini (2010)- Nagahama et al. 2008). Those hydrophilic structures are modified with hydrophobic groups to produce amphiphilic materials, primarily essential when combined with synthetic polymers intending to fabricate polysaccharide-polymer composites.

Today, in addition to the natural materials used for the synthesis of membranes, a large range of synthetic membrane materials are accessible for various applications. Such materials include polymers (such as polysulfone, polyacrylonitrile, polyacrylamide), ceramics, metals, cellulose derivatives, composites, and others (Svec 2004).

Various studies have utilized free radical graft copolymerization of acrylamide and chitosan to synthesize hydrogel composite membranes to be utilized in intended applications (Martinez-Ruvalcaba et al. 2009, Ibrahim 2009, Pourjavadi and Mahdavinia 2006, Risbud and Bhonde 2000). These studies have concluded that hydrogels produced by a grafting reaction of a blend of materials is preferable to those acquired by using one of either material involved. This is due to the fact that grafting relatively enhances the mechanical strength thus swelling properties of the hydrogels synthesized. They have additionally deduced a proportional relationship of varying the concentration of any of the materials with the swelling capacity and swelling kinetics and parameters. Moreover, the studies confirmed the grafting reaction and identified the hydrogel’s structure by either FT-IR or SEM. They have also illustrated the pH-independency towards hydrogel swelling, and the effect of ionic strength on the swelling capacities.

As such, the presented study was designed to synthesize, evaluate, and elucidate the characteristics of hydrogel composite membranes of polyacrylamide (PAAm) integrated with modified fluorinated chitosan (F-Chitosan). Fluorination of chitosan was initially achieved, followed by the preparation of membranes of varying mass ratios of PAAm to F-Chitosan (0, 5, 10, 20, 50, 75% F-Chitosan membranes) by a free radical polymerization. Those membranes consist of a matrix of crosslinked polymeric chains of polyacrylamide, incorporating linear cylindrical pores of F-Chitosan biopolymer.

Characterization of the synthesized membranes was accomplished, where the swelling capacity in different media and deswelling performance were evaluated. In addition, the swelling kinetics of the membranes were investigated, classifying the membranes’ behavior based on Fickian diffusion model. Contact angle and refractive index measurements were also assessed utilizing a travelling microscope and refractometer respectively. The hydrogel matrices were analyzed spectrophotometrically utilizing Fourier-Transform Infrared spectroscopy (FT-IR) to confirm fluorination of chitosan and the incorporation of F-chitosan into the membranes. Additionally, the applicability of the membranes was tested by investigating their ability to withhold and allow proper flux of different media and diffusion of glucose in different pH (acidic, neutral, and basic).

This study intended to create novel polyacrylamide composite membranes with proper water flux, increased hydrophobicity, and good dimensional stability to achieve a great feed stream purification in different media.

2. Materials and Methods

2.1. Materials

All the chemicals and solvents were reagent grade and used as received without further purification. Chitosan (PXPARK); 48% hydrofluoric Acid (SIGMA-ALDRICH); potassium fluoride (GCC); acrylamide and N,N,N´,N´-tetramethylethylenediamine (ALDRICH); N,N´-methylenebisacrylamide and initiator ammonium persulfate (BDH); extra pure sodium hydroxide (LOBA Chemie); sodium chloride (BEIJING HUAGONGCHANG); 37% hydrochloric acid (GCC); potassium hydroxide (J.C.L.E); glucose (MERK); and finally distilled water.

2.2. Preparation of Fluorinated Chitosan (F-Chitosan)

F-chitosan was synthesized by suspending 10 g of chitosan into 100 ml H_2O in a plastic container. Then, the plastic container and its contents were left overnight to enhance the dispersion of the polysaccharide into water. The next day, 8.58 g of a stock solution of HF/KF were added to the chitosan suspension. The mixture was then stirred thoroughly by placing the container in a sonication bath at a temperature of ~ 70°C for 3 hrs and left overnight. The product (F-chitosan) was left to dry in the plastic container.

2.3. Preparation of Membranes

The F-chitosan membranes were prepared by dissolving F-chitosan in a chloroform and distilled water solvent mixture. The acrylamide (AAm) monomer and the crosslinker N,N'-

methylenebisacrylamide (MB) were then added. Several drops of the activator N,N,N',N'-tetramethylethylenediamine (TEMED) were also deposited once the mixture was sufficiently homogenous. The reaction mixture was then poured into a Petri dish and left for 24 hrs to allow the complete gelation thus formation of the membrane. The homogeneous reaction mixture was then left to stand overnight at room temperature (RT) after adding the initiator ammonium persulfate (APS).

Table 1 shows the mixing proportions of F-Chitosan and acrylamide for the preparation of 0% (PAAm), 5%, 10%, 20%, 50%, and 75% F-chitosan membranes.

Table 1 Amounts of Acrylamide & F-Chitosan used for Hydrogels' Preparation

F-Chitosan (%)	Acrylamide (g)	F-Chitosan (g)
0	2.50	-
5	2.38	0.13
10	2.25	0.25
20	2.00	0.50
50	1.25	1.25
75	0.63	1.88

2.4. Refractive Index

The refractive index was measured for each synthesized membrane utilizing an Abbe Refractometer from Bellingham + Stanley Limited. It was achieved through cutting a piece of a relatively swollen membrane and placing it on the refractometer. Through those measurements, the dielectric constant (ε), which reflects the ratio of the electric permittivity of the membrane to that of free space (Barber and Kalorkoti 2020) was determined by squaring the value of the refractive index (n) as indicated in equation (1).

$$\varepsilon = n^2 \qquad (1)$$

2.5. Contact Angle

The hydrophobicity of the membranes was examined through conducting contact angle measurements. The measurements were determined by a Travelling Microscope from Philip Harris Limited. A small piece of each membrane was placed onto a slit, adjusted and focused upon to read the scale that determines the angle created by a deposited drop of water.

2.6. Fourier Transform Infrared Spectroscopy – FT-IR

The samples were analyzed using a Thermo Nicolet 4100 FT-IR spectrometer at a wavelength range of 4000-400 cm^{-1}. The samples analyzed were initially prepared by removing all the water content from each membrane i.e. deswelling, followed by grinding a small amount of each. Afterwards, each dried ground piece was mixed and pressured with a potassium bromide solid salt carrier for further analysis in the FT-IR spectrophotometer.

2.7. Swelling

The swelling behavior of the dried membranes was observed in H_2O, 0.1 M HCl, 0.1 M NaOH, 0.1 M NaCl, and 100 g/ L (0.56 M) glucose solutions at room temperature over a period of 24 hrs. The completely dried pre-weighed membrane samples were placed in 100 ml of the above-mentioned solutions. Then, the swollen membranes were taken out at regular time intervals, wiped superficially with filter paper to remove surface water, weighed, and then placed in the same bath. The percentage swelling or mass swelling (S%) was determined using the following Equation (2) (Jayaramudu et al. 2019):

$$\%S = \frac{w_t - w_0}{w_0} * 100\% \qquad (2)$$

where (W_0) and (W_t) are the initial weight and weight at different time intervals, respectively.

2.8. Deswelling

The deswelling behavior of the water-filled membranes was measured by weighing them at predetermined intervals of heat exposure in an oven of a temperature of 110°C to measure the percentage of water lost. The moisture percentage was calculated using the following Equation (3):

$$\%DS = \frac{w_0 - w_t}{w_0} * 100\% \qquad (3)$$

where (W_0) and (W_t) are the initial weight and weight at different time intervals, respectively.

2.9. Flux

Flux tests were conducted for H_2O, 0.1 M HCl, 0.1 M KCl, 0.1 M KOH and 100 g/ L (0.56 M) glucose solutions using PAAm, 5%, 10%, 20%, and 50% F-chitosan composite membranes. The flux was evaluated based on the below Equation:

$$Flux\ (L/m^2.h) = \frac{V_p}{A * t} \qquad (4)$$

Where V_P is the volume of permeated water (L). A is beneficial membrane surface area (m^2), t is the time duration for collecting permeated water (h).

A membrane of an area about 3.46 cm^2 (diameter (r) = 10.5 mm) was installed into a diffusion cell, as depicted in **Figure 1**. In the cell, compartment (1) contained approximately 70 ml of one of the above-mentioned solutions, while compartment (2) was empty. Flux was observed by collecting the permeated solution in a 100 ml graduated cylinder, measuring the volume of the permeated glucose solution at different times.

Figure 1 Diffusion Cell - Flux

2.10. Diffusion

Diffusion tests were done for glucose dissolved in a buffer solution (pH = 4, 7, 10) using 5%, 10%, 20%, and 50% F-chitosan membranes.

A membrane of an area about 3.46 cm^2 (r = 10.5 mm) was installed into a diffusion cell. In the cell, compartment (1) contained approximately 70 ml 100 g/ L glucose dissolved in a buffer solution, while compartment (2) contained the buffer solution only, as shown in **Figure 2**. Diffusion of glucose was determined by the ACCU-CHEK Go device which measures the concentration of the diffused glucose at different times. The rate of diffusion $\frac{dn}{dt}$ (mol/sec), diffusion coefficient D (cm^2/sec), and permeability P (cm/sec) were calculated using Fick's first law (Ritger and Peppas 1987) using the following Equations:

$$D\ (cm^2/sec) = \frac{(dn/dt)}{A * (dC/dx)} \qquad (5)$$

$$P\ (cm/sec) = \frac{D}{x} \qquad (6)$$

$$dn/dt = P * A * (C_{in} - C_{out}) \qquad (7)$$

where; n: number of mol of solute transfer (mol), t: time (seconds), P: permeability constant for a particular molecule (cm/sec), A: surface area of the cell membrane (cm^2), C_1: initial concentration before diffusion (mol/cm^3), C_2: concentration of diffused solute (mol/cm^3), D: diffusion constant (cm^2/sec), L: membrane thickness (cm).

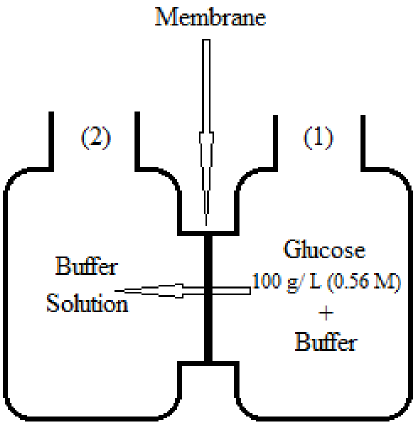

Figure 2 Diffusion Cell - Diffusion

3. RESULTS AND DISCUSSION

3.1. Synthesis of Fluorinated Chitosan (F-Chitosan)

The properties of the synthesized composite membranes are enhanced by decreasing the overall hydrophilicity of the membranes i.e. raising their hydrophobicity (Dalvi and Rossky 2010). The adjustment was achieved through allowing chitosan to undergo fluorination in the presence of a stock buffer solution of potassium fluoride and hydrofluoric acid.

The hydrophobicity is increased by the introduced fluorine intermolecular hydrogen bonding along with intramolecular covalent bonds illustrated in **Figure 3**. This increased hydrophobicity is expected to enhance the purification process of glucose solutions, where the large glucose molecules containing nonpolar structures would be retained by the membrane of a hydrophobic character while permeating relatively larger amounts of water. Therefore, this increased hydrophobicity may allow a bigger retention of solutes relative to that of the solvent, achieving an enhanced molecular separation hence a greater stream purification.

FT-IR analysis as well as contact angle measurements also confirm the incorporation of fluorine into chitosan (further discussed).

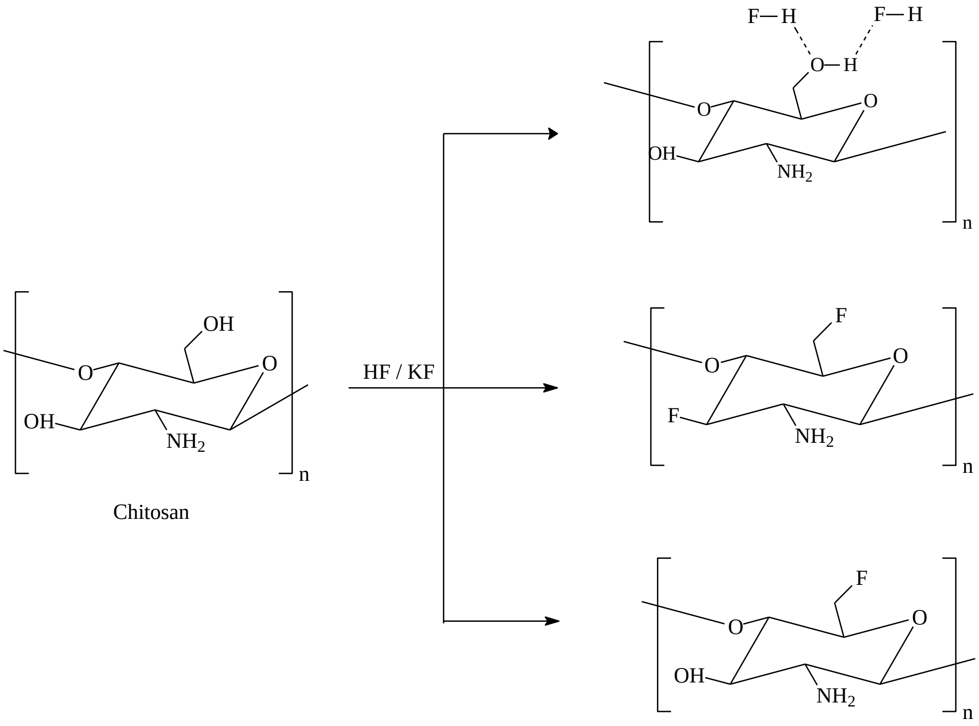

Figure 3 Fluorination Reaction & the Possible Products of F-Chitosan

3.2. Synthesis of PAAm Composite Membranes Containing 5%, 10%, 20%, 50%, and 75% F-Chitosan.

Polyacrylamide hydrogel composite membranes incorporating varying mass ratios of F-chitosan were synthesized by a free radical polymerization reaction illustrated in **Figure 4**. Due to the concentration difference between F-chitosan to acrylamide, the resulting membranes would have varied permeability, mechanical stability, swelling capacity, and other distinct properties summarized in **Table 2**.

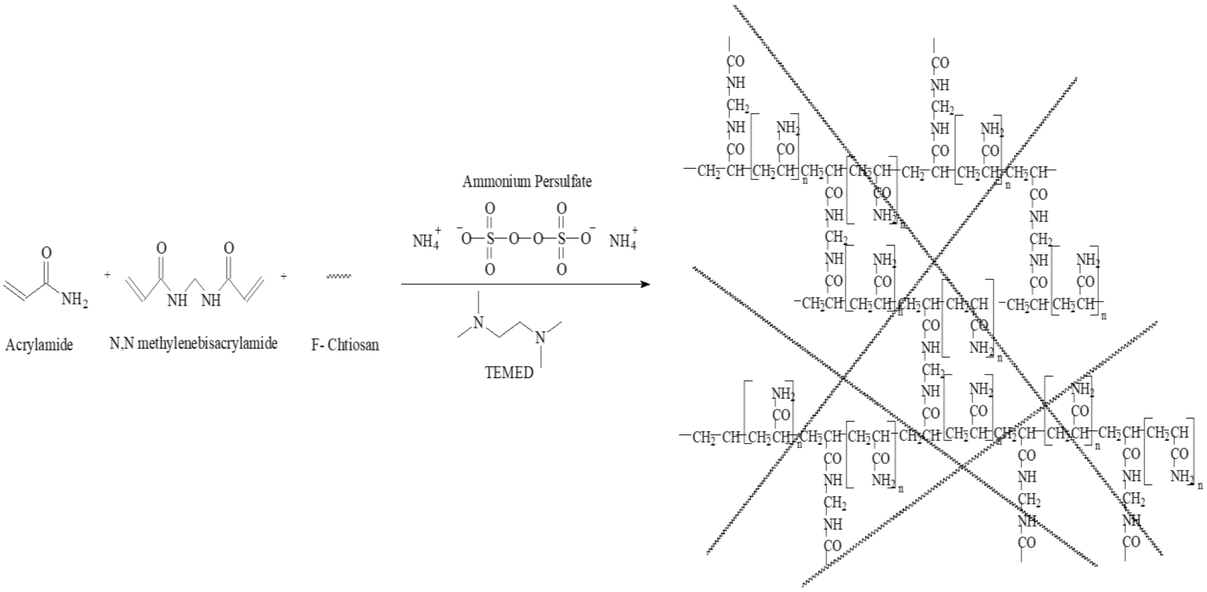

Figure 4 Free Radical Addition Polymerization Reaction for the Synthesis of the Hydrogels

Table 2 Color, Integrity, and Decomposition Temperature of the Hydrogels Prepared

F-chitosan Concentration (%)	Membrane Color	Membrane Integrity	Decomposition Temperature (^{0} C)
0	Transparent	Integrous	278-330
5	White	Integrous	299-322
10	White	Integrous	301-325
20	White	Integrous	303-328
50	Creamy	Moderately integrous	291-328
75	Creamy	Non-integrous	273-300

Referring to **Table 2** along with **Figure 5** below, it can be noticed that the membranes tend to have their color darkened and their integrity decreased with the increase of F-chitosan concentration. This is explained by the lesser amount of PAAm that forms the intact matrix, and the higher amount of the randomly distributed F-chitosan cylindrical pores. Those pores render the membranes denser thus darker in color yet less intact, resulting in substantial fragility hence less integrity.

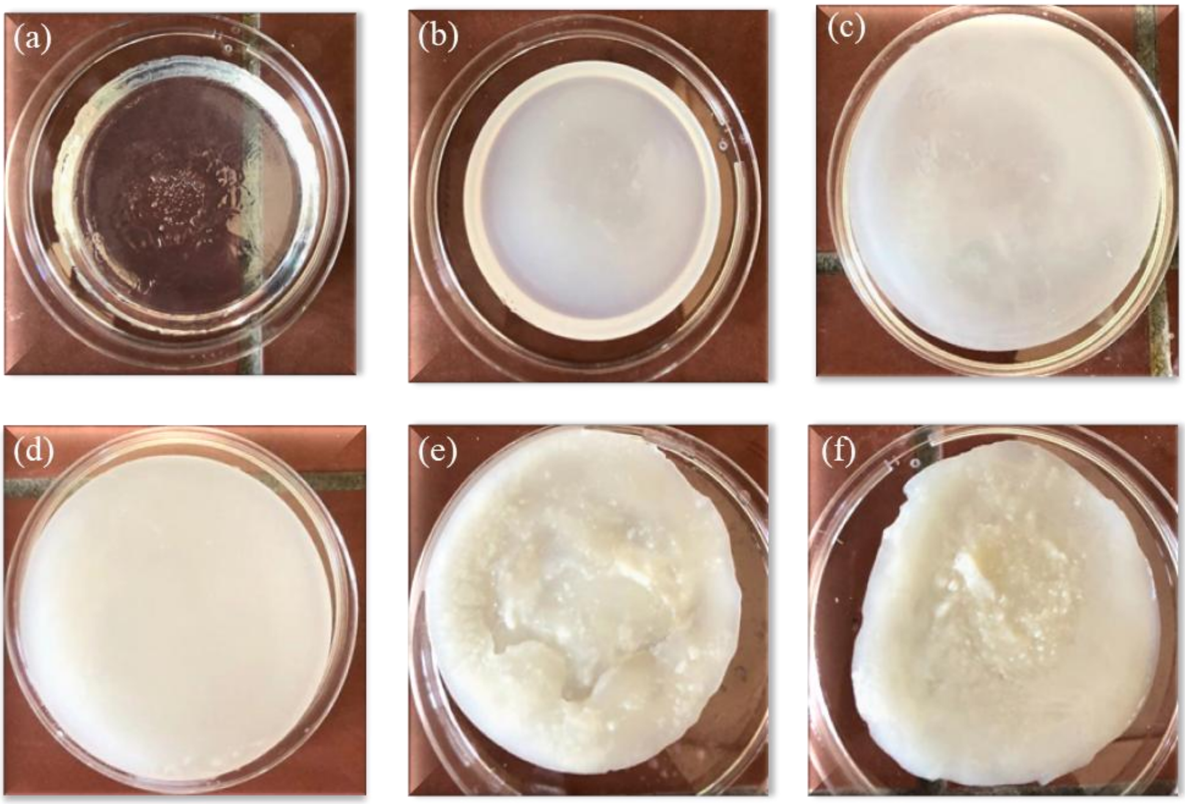

Figure 5 (a) PAAm membrane (b) 5% F-Chitosan membrane (c) 10% F-Chitosan membrane (d) 20% F-Chitosan membrane (e) 50% F-Chitosan membrane (f) 75% F-Chitosan membrane.

3.3. Refractive Index of the Prepared Membranes (n).

A refractometer was used to characterize the composite membranes, which measures the refractive index (n) through light refraction. The index of refraction is a measurement of how light passes through a material. It is determined by the material's ability to scatter light and, in most cases, its density. When the membranes are swollen, they become translucent, their refractive index is then measured.

The results obtained from measuring the refractive index of all membranes are considerably similar according to **Table 3**. However, closely examining the results in **Figure 6**, it appears that the RI values increase with the increase of F-chitosan concentration up to the 10% and 20% F-chitosan membranes. The initial increase in RI values is due to the increase of F-chitosan content where the cylindrical pores occupy more space within the membrane, inhibiting the passage of light, resulting in higher RI values. Afterwards, the values appear to decrease where the 75% F-chitosan membrane shows the least RI value. This is because the lower concentration of PAAm forms a less intact matrix with an increased fragility due to the F-chitosan cylindrical pores introduced. This fragility provides more room, pores, or cracks within the membrane through which light may readily pass through, resulting in decreased refractive index values.

Table 3 Refractive Index and Dielectric Constant of Membranes

F-Chitosan (%)	Refractive index (n)	Dielectric constant (ε)
0	1.387	1.924
5	1.391	1.935
10	1.393	1.940
20	1.394	1.943
50	1.376	1.893
75	1.372	1.882

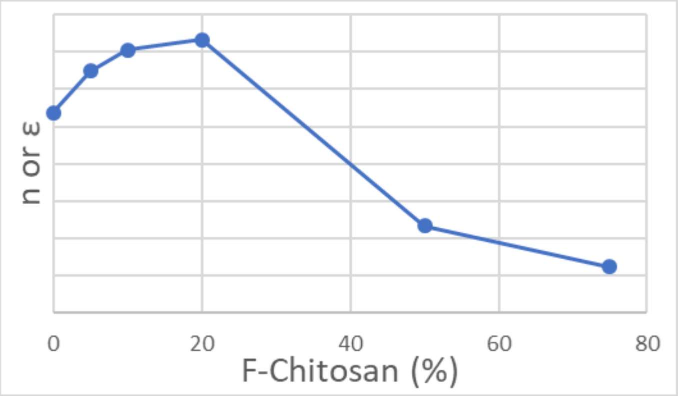

Figure 6 Refractive Index / Dielectric Constant of Membranes

Dielectric constant is a constant of proportionality between the incident electric field (electromagnetic waves) and the polarization of the matter. Higher (lower) dielectric constants result in more orientation of dipoles and larger (smaller) polarization for a fixed applied external electric field. The values of the dielectric constants are calculated (The dielectric constant (ε) = n^2) and summarized in **Table 3**. As shown, the membranes containing a low percentage of F- chitosan have higher refractive index values and, subsequently, a higher dielectric property. That indicates that those membranes have higher polarizability and more charge on the surface. Therefore, they are more affected by external polarizing forces (Barber and Kalorkoti 2020). F^- group is a polarization group; its presence results in an increase in the refractive index values as compared to (OH) group. This provides information on the capability of such membranes to purify mixtures containing electric charges or ionic species in future applications.

3.4. Characterization of the Membranes Using FTIR Spectroscopy

The FTIR spectra of the prepared membranes were compared with each other to observe the noticeable differences between them, depicted in **Figure 7** and **Table 4**. When comparing the spectrum of polyacrylamide membrane with the spectra of the membranes with different F-chitosan ratios, it is noticed that pure F-chitosan displays bands that correspond to C-F and H-F bonds at 3781 and 1251 cm^{-1} respectively, while pure chitosan does not. This indicates that fluorination did take place, inter- and intramolecular bonds with fluoride were introduced into the matrices, and fluorine was incorporated into chitosan. However, since pure PAAm demonstrates no fluoride-containing peaks, it indicates that the presence of fluorine within the hydrogels had originated from F-chitosan.

Table 4 Wavenumber of Certain Signals of the Materials FT-IR Analyzed

Material	**Wavenumber cm^{-1}**		
	C-F	H-F	C=O
Pure Chitosan	-	-	-
Pure F-Chitosan	1251	3781	-
Pure PAAm	-	-	1669
Membranes	Observed	Observed	Observed

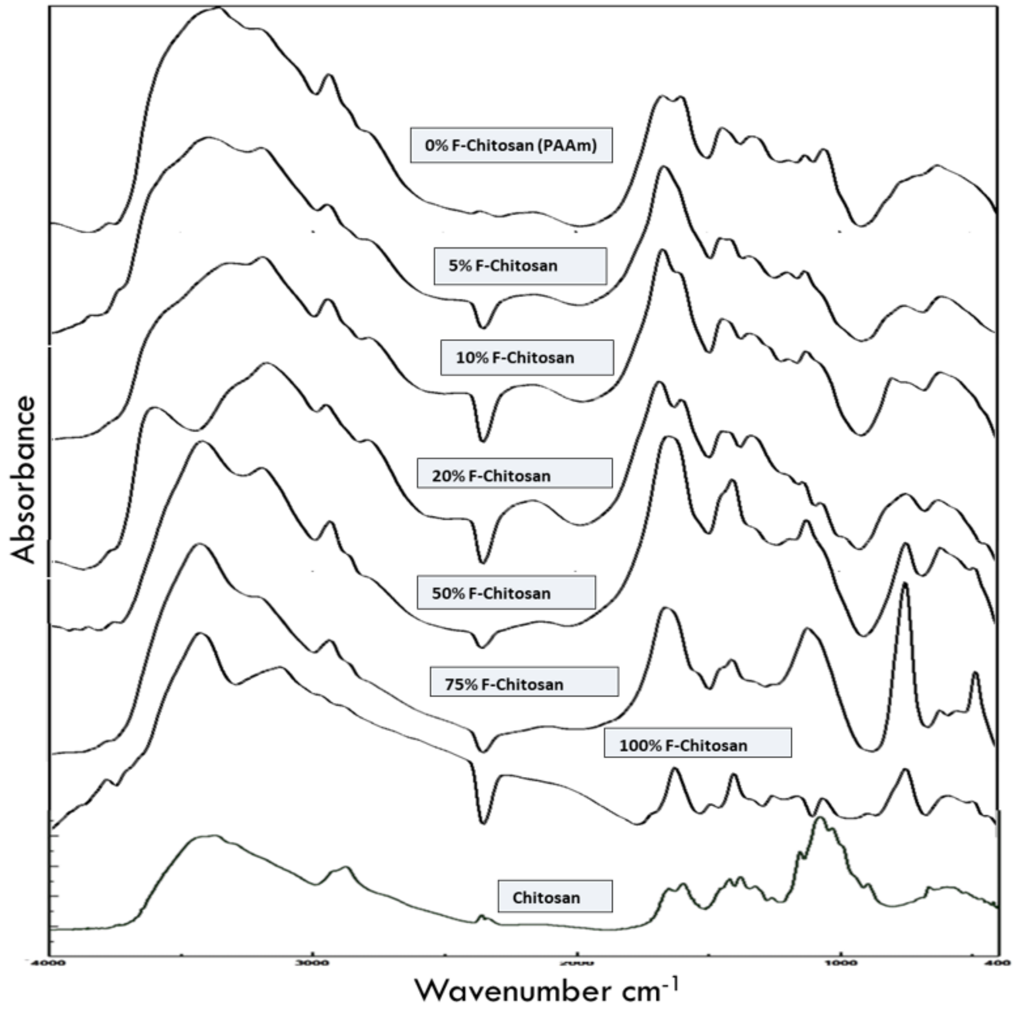

Figure 7 FT-IR Spectrum for All Membranes, Pure Chitosan & Pure F-Chitosan

Moreover, all membranes prepared display a band at a range of 1680-1653 cm^{-1}, reflecting the presence of a carbonyl group within their structure. In the meantime, pure chitosan and F-chitosan show no such peaks, indicating the lack of the carbonyl group. This result means that the carbonyl group present in the membranes originates from polyacrylamide rather than F-chitosan with a corresponding signal displayed at 1669 cm^{-1}.

3.5. Contact Angle

Contact angle is a term used to describe the angle created by a droplet of a liquid when it gets in contact with a solid surface. It is typically referred to as the wetting angle for it reflects and measures the wettability of the solid surface achieved by the liquid deposited and the resulting inter- and intra-molecular forces (Childress and Brant 2000). The values of contact angle were measured using a Traveling Microscope. **Table 5** gives information on the surface hydrophobicity of the synthesized membranes, indicating their performance. It may also show the effect of fluorination previously conducted (Kertész et al. 2014).

Table 5 Contact Angle and Corresponding Nature of Each Membrane

F-Chitosan (%)	Contact Angle (^{0})	Nature
0	56.31	Amphiphilic
5	63.43	Amphiphilic
10	71.57	Amphiphilic
20	63.43	Amphiphilic
50	47.49	Amphiphilic
75	37.57	Hydrophilic

* $\theta < 45^o$: hydrophilic, $45^o < \theta < 90^o$: amphiphilic, $\theta > 90^o$: hydrophobic.

The 10% F-chitosan membrane possesses the highest hydrophobicity value of 71.57^o among the other membranes, even though it contains hydrophilic groups. After that, the hydrophobicity decreases gradually with the increase of the F-chitosan percentage until it reaches its minimum value, 35.57^o, for the 75% F-chitosan membrane. The initial increase can be explained by the increase of F-chitosan's concentration as more fluorinated species are introduced into the membrane, resulting in a higher hydrophobicity thus higher contact angle. This ensures that fluorination did take place and had influenced and enhanced the hydrophobicity. In the meantime, the following decrease in the contact angle is elucidated by the further increase in F-chitosan's concentration and the resulting fragility.

In all cases, these polymers can be described as hydrophobic/hydrophilic (amphiphilic) with the hydrophobic constituent originating from the (C-C) group of the backbone. As deduced, fluorination did not take place on every monomer, and fluorine was primarily introduced in the form of hydrogen bonding, contributing to a lower expected hydrophobicity and fluorination effect.

3.6. Swelling Behavior

The study of the swelling behavior of membranes in neutral, acidic, basic, salt, and sugar solutions offers good information about the stability of membranes in aqueous media and their capacity to incorporate water. The swelling behavior of the membranes-hydrogels depends on the chemical structure of the polymers and the environmental conditions. When a membrane (hydrogel) is brought into contact with water, water diffuses into the membrane, causing it to swell. Diffusion involves migration of water into preexisting or dynamically formed spaces between membrane chains.

The effect of H_2O (neutral medium), NaOH solution (basic medium), HCl solution (acid medium), NaCl (salt solution), and 100 g/ L (0.56 M) glucose solutions (pH 4, 7, and 10) on the swelling behavior of the six different membranes (PAAm, 5%, 10%, 20%, 50%, 75% F-chitosan membranes), was studied at room temperature. The percentage swelling of all the different membranes has been depicted in **Table 6** and **Figure 8**.

Table 4 Equilibrium Swelling Percentage of All Membranes in Different Media

F-Chitosan (%)	**Swelling (%)**						
	Distilled H_2O	0.1M HCl (pH=4)	0.1M NaOH (pH=10)	0.1M NaCl	0.56M Glucose (pH=4)	0.56M Glucose (pH=7)	0.56M Glucose (pH=10)
0	698.7	884.8	2878.9	965.4	520.0	469.0	568.9
5	568.7	824.4	3145.3	789.8	707.3	355.9	512.0
10	998.3	**1035.6**	3232.0	889.2	767.1	577.8	564.1
20	1105.8	933.8	1977.6	981.3	628.2	413.1	624.9
50	905.4	850.0	2457.5	889.3	677.0	447.8	650.0
75	487.5	828.9	941.5	574.0	445.5	306.1	632.7

In the swelling experiments, all the membranes showed similar swelling behavior. Swelling capabilities of the membranes are increased with time, however at equilibrium, they show variable swelling percentages. The 75% F-chitosan membrane was relatively the least to swell in all media compared to the rest of the membranes. That is due to the fragility and non-integrity of such a membrane. Whereas, the 10% and 20% F-chitosan membranes appeared to have relatively the highest swelling percentages in all media compared to the rest of the membranes. That is because those membranes contained appropriate amounts of chitosan; not too high to contribute to the deterioration of the membranes and not too low to incorporate a diminished amount of chitosan's cylindrical pores leading to reduced retention of solvents. The remaining 0, 5, and 50% membranes showed swelling capacities that fall in between those achieved by the rest of the membranes discussed.

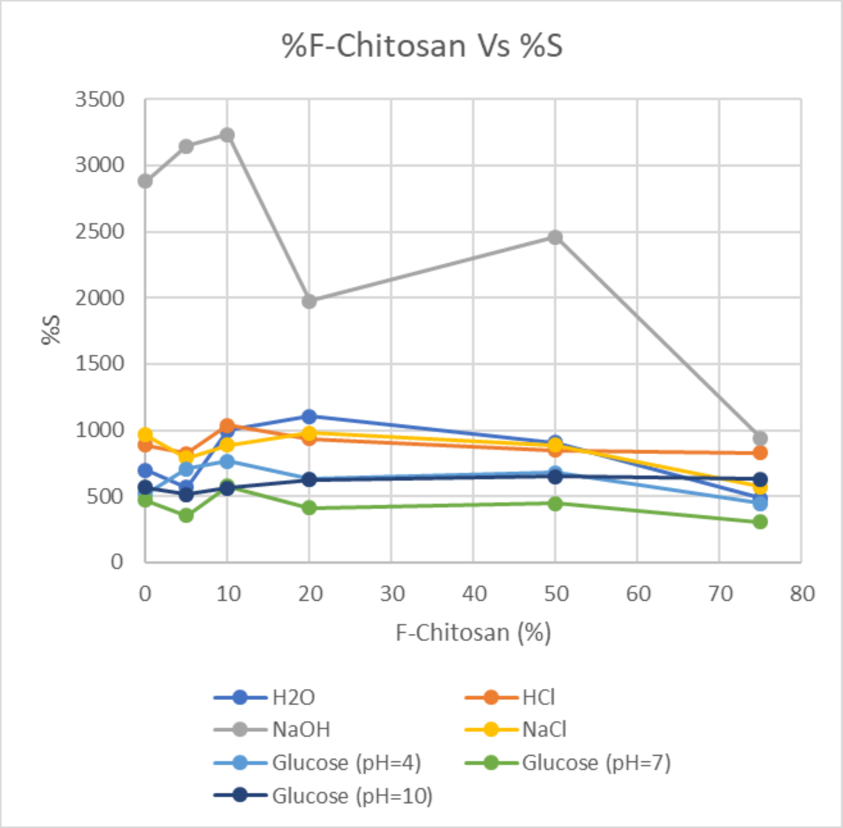

Figure 8 Equilibrium Swelling Percentage of the Membranes in Different Media

Swelling of the membranes in 0.1 M NaOH solution results in super gels that have the highest percentage swelling values than in any other solution used (super swelling). That is due to the amide group in acrylamide becoming more prone to hydrolysis under basic conditions, causing the acrylamide (-$CONH_2$) to transform into acrylic acid (-COOH). The carboxylate group of the acrylic acid becomes ionized, and the mutual ionic repulsion between these groups causes the molecule to adopt a greatly expanded configuration. This opens up the polymer matrix and leads to a higher swelling. It is also observed that the 10% F-chitosan membrane showed the highest swelling percentage followed by the 5% then the PAAm membranes. That means those membranes have bigger spaces between their chains than the remaining membranes.

Swelling in HCl solution is not as significant as that achieved in NaOH solution. In an acidic medium, the amide group in acrylamide is not very prone to hydrolysis at room temperature, but rather causes the protonation of the main functional groups comprising the matrix. Chitosan is majorly alkaline for having a primary amino group in its structure. The amino group would get protonated when placed in acidic media (NH_3^+) (Martinez-Ruvalcaba et al. 2009). Polyacrylamide follows that same line as chitosan as its amide groups also get protonated in an acid. This renders the polymers polyelectrolytes carrying a positive charge. The negative chloride ions are retained by mutual ion attractions thus increasing the crosslinking density of the network and providing moderate flexibility. This slightly limits the retention of the solvent within the matrix, which may stand to reason why swelling in acid is relatively greater than that in neutral media and lower than that in basic media.

In H_2O, it is observed that the 20% F-chitosan membrane showed the highest swelling percentage followed by the 10% then the 50% F-chitosan membranes. That means those membranes have bigger spaces between their chains than the remaining membranes. Distilled water allowed the membranes to swell without ionic interference that may restrict or elasticize the membrane resulting in a moderate / decreased swelling capacity compared to the other media used.

It is noticed from the swelling experiments in 0.1 M NaCl solution that the 20% F-chitosan membrane showed the highest swelling percentage followed by the 0% then the 10% and 50% F-chitosan membranes. That is due to the fact that the NaCl solution used was dilute (0.1 M), thus a small amount of salt can break the strong association between zwitterionic monomers by shielding the positive and negative charges, causing the network expansion and hence increasing the percentage swelling. In other words, the increase in ionic strength or the attraction between the polymeric hydrogels and the ions formed cause a bigger flexibility or expansion of the hydrogel matrix, resulting in an increased retention or swelling capacity compared to swelling in neutral distilled water (Jagadish and Roy 2017).

The swelling capacity of the hydrogels in 100g/L (0.56M) glucose buffer solutions of pH values of 4, 7, and 10 appears to be the lowest compared to the rest of the media used. This is due to the presence of relatively large glucose molecules that had been retained by the hydrogels, causing blockages within the pores. These blockages inhibited relatively higher amounts of water to be retained. That explains why the glucose solution of a pH of 10 did not achieve a great swelling as that of sodium hydroxide.

3.7. Swelling Kinetics

Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years because of the important applications of swellable polymers in fields of biomedical, pharmaceutical, environmental, and agricultural engineering. The swelling mechanism of the membranes was determined using the following Equation (Markovic and Naba 2004):

$$ln\ (M_t / M_{eq}) = n\ ln\ t + ln\ k \qquad (8)$$

where; M_t and M_{eq} are water uptake at time t and after the passage of 24 hrs, respectively, k is the swelling constant, and n is the swelling exponent (min^{-1}).

In the swelling process, two concurrent events may take place, namely the gel matrix relaxes its structure allowing water/solvent to diffuse in (relaxation – swelling) or the diffusing solvent compels the structure to relax (swelling – relaxation). The first process is called non-Fickian swelling, whereas the second is known as Fickian process (Martinez-Ruvalcaba et al 2009, Svec 2004). For cylindrical shaped-pores, n = (0.00 - 0.50) and corresponds to Fickian diffusion, whereas n = (0.50 – 1.0) indicates that diffusion is non-Fickian. For the membranes (PAAm, 5%, 10%, 20%, 50%, and 75% F-chitosan membranes), ln (M_t / M_{eq}) versus ln t plots were drawn using the kinetics of swelling in 100 g/ L glucose solutions (pH 4, 7, and 10). The swelling exponent n was calculated at 25°C and the type of behavior (Fickian/non-Fickian) are listed in **Table 7**.

Most of the prepared membranes exhibit non-Fickian behavior, however, the Fickian behavior appears in the 75% F-chitosan membrane. It is also evident that the six membranes have similar n values, which means that the swelling kinetics of the different membranes are very similar. Thus, the addition of F-chitosan does not generally alter the swelling kinetics of the membranes except for the 75% F-chitosan membrane, where the rate of swelling exceeds that of relaxation.

Table 5 "n" Value of all Membranes in Glucose Solutions of Different pH

F-Chitosan (%)	**n**		
	Glucose (pH=4)	Glucose (pH=7)	Glucose (pH=10)
0	0.50	0.59	0.48
	Non-Fickian	Non-Fickian	Fickian
5	0.61	0.54	0.59
	Non-Fickian	Non-Fickian	Non-Fickian
10	0.65	0.59	0.58
	Non-Fickian	Non-Fickian	Non-Fickian
20	0.59	0.58	0.59
	Non-Fickian	Non-Fickian	Non-Fickian
50	0.65	0.61	0.72
	Non-Fickian	Non-Fickian	Non-Fickian
75	0.29	0.38	0.33
	Fickian	Fickian	Fickian

3.8. Deswelling Behavior

The successive deswelling behavior of the six different membranes (PAAm, 5%, 10%, 20%, 50%, and 75% F-chitosan membranes) is shown in **Figure 9** as a function of the percentage of moisture lost (Moisture%) versus time. It can be noticed that the moisture loss increases as F-chitosan percentage increases. This means that the 75% F-chitosan membrane achieved the highest moisture loss percentage, while the PAAm membrane showed the lowest. That is because a higher F-chitosan percentage reflects a higher quantity of F-chitosan cylindrical pores introduced, providing more room for a larger water amount to evaporate through. In the meantime, the 10% membrane shows considerably little deswelling with time. That is due to the appropriate ratio of polyacrylamide to F-chitosan that provides substantially intact integrous networks or matrices that restrict the deswelling performance.

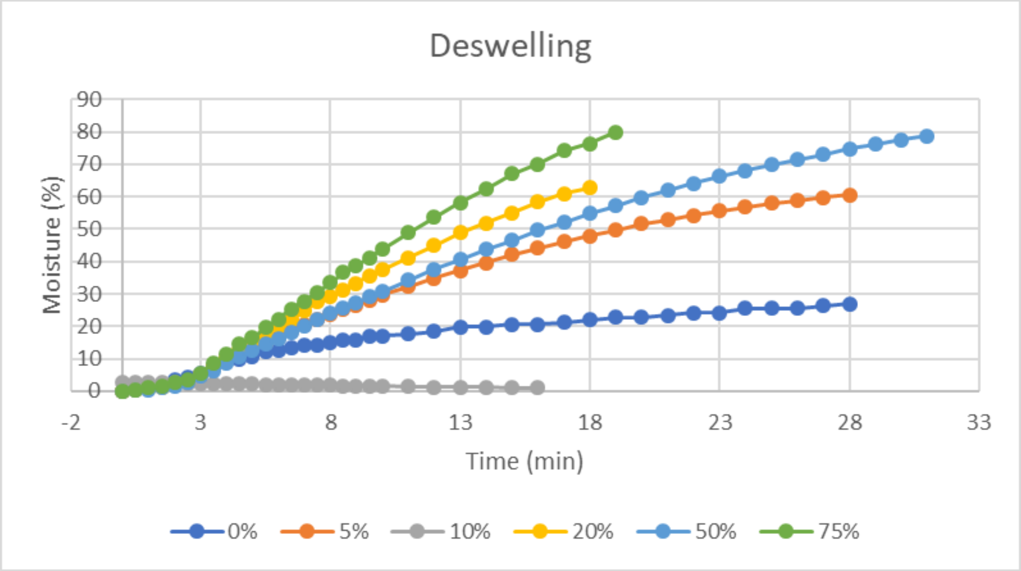

Figure 9 Time versus Moisture Loss Percentage; Deswelling

The deswelling process shows more or less linear behavior. The nonlinear curve line shown at the beginning is due to water entrapped at the surface. In other words, water molecules are buried at different depths in the structure of the membrane.

3.9. Flux through the Prepared Composite Membranes

Membrane flux, in simple words, is the process in which liquid flows through a specific area of a membrane over a certain period of time. In other words, it is a fluid's flowing rate; the amount of fluid that passes across an area of a membrane over a time period. It is necessary to determine the flux of each membrane to be able to distinguish their permeability and the extent to which each allows permeation prior to fouling (Pal 2020). Attempts were made to check the flux properties of the obtained membranes (PAAm, 5%, 10%, 20%, and 50% F-chitosan membranes) across a diffusion cell. The 75% F-chitosan membrane was ineligible in the flux studies because it is very brittle. The results have shown that those membranes can be classified as permeable, semi-permeable, or impermeable.

The impermeable behavior shows that these membranes are composed of dense network structures that can swell but does not offer a good transport media for the solution. This shows the retention properties of these membranes are sufficiently high to prevent passage of solutions. In such cases, external pressure can be utilized to improve the transport properties.

In general, transport occurs through internal connected pores. Since F-chitosan is a linear macromolecule, such pores are expected to be cylindrical in nature. Therefore, the transport is expected to increase with increasing F-chitosan percentage. However, PAAm, 5%, and 20% F-chitosan membranes showed impermeable behavior. The 0% and 5% membranes are substantially integrous due to the high percentage of crosslinked intact polyacrylamide, inhibiting the ability to permeate the chosen solvents, thus providing negligible flux and rendering them impermeable. The 20% membrane also permeated negligible amounts of solvents due to its higher ability of retaining substantial amounts of the solvent rather than permeating it.

As a result, merely the 10% and 50% membranes were able to provide proper flux data as the ratio of acrylamide to F-chitosan and the resulting mechanical stability seemed to be appropriate to retain and permeate reasonable amounts of solvents concurrently. **Table 8** shows the flux of H_2O, 0.1 M HCl, 0.1 M KCl, 0.1 M KOH, and 100 g/ L glucose solutions of these two membranes.

Table 8 Flux and Permeating Properties of 10% and 50% F-Chitosan Membranes in Different Media

F-Chitosan (%)	**Flux (L/m^2.hr)**				
	H_2O	0.1M HCl	0.1M KOH	0.1M NaCl	0.56M Glucose
10	5.68	45.97	**78.28**	67.44	73.78
	Semipermeable				
50	**2438.58**	1210.28	161.85	540.30	827.22
	Permeable				

Table 8 illustrates that the flux achieved by the 50% membrane is substantially greater than that achieved by the 10% membrane in all media. This draws the conclusion that the 10% membrane is semipermeable, while the 50% membrane is permeable. Those findings are elucidated by the greater number of F-chitosan cylindrical pores introduced into the 50% membrane, allowing the passage of higher amounts of fluid across.

Comparing the flux of the different media used, it appears that the 10% membrane permeates KOH the most, while the 50% membrane allows the passage of water the most by a flux value of about 78 and 2439 L/m^2.hr, respectively. That is due to the fact that the swelling percentage maximizes in basic media due to the formation of polyacrylate anions as previously discussed. This extensive swelling provides more room for more fluid to readily pass through. Since the 10% membrane contains much higher amounts of polyacrylamide than the 50% membrane, it permeates the base the most, while the latter of a much lower PAAm content permeates water the most where flux would not be influenced by external ionic conditions.

3.10. Diffusion of Glucose through the Prepared Composite Membranes

Simple diffusion results from the random net motion and flow of molecules across a membrane from a region of higher solute concentration to that of lower concentration. The diffusion rate (dn/dt) reflects the change in the number of molecules/moles within a diffusion cell over a certain period of time. It is affected by the nature and properties of the membrane used, the diffusing molecule, and the type of surrounding solution. Thus, the diffusion rates of glucose through those membranes were examined at pH of 4, 7, and 10.

Since the 75% membrane was sufficiently fragile to prevent flux thus characterized as inapplicable, it was also not able to tolerate diffusion. Additionally, no diffusion of glucose was observed through the PAAm and 5% F-chitosan membranes in any of the pH buffer solutions since both are impermeable. It was also observed that the 50% F-chitosan membrane is not applicable for diffusion applications as it disintegrates due to the pressure built by both solutions in the two compartments of the diffusion cell. Therefore, merely the 10% and 20% membranes were tested for their diffusion applicability.

Table 9 Diffusion Coefficient of 10% & 20% F-Chitosan Membranes in Different pH

pH	**D (cm^2s^{-1})**	
	10%	20%
4	$7.25*10^{-8} – 1.32*10^{-7}$	$7.56*10^{-9} – 2.39*10^{-6}$
7	$1.21*10^{-8} – 1.75*10^{-7}$	$3.27*10^{-8} – 6.75*10^{-8}$
10	$4.39 *10^{-8}– 9.27*10^{-8}$	$9.17*10^{-8} – 1.02*10^{-6}$

To begin with, the free diffusion of glucose i.e. the free flow of glucose without the presence of a barrier corresponds to a diffusion coefficient of $0.6x10^{-5} – 2x10^{-5}$ cm^2s^{-1} (Smith 2004). As can be noticed from **Table 9**, the diffusion coefficient of both the 10% and 20% membranes in all media is lower than that of free diffusion. This is a crucial observation as it reflects the fact that the diffusion of glucose was interrupted by the presence of a membrane barrier, indicating that the membrane is capable of resisting or inhibiting glucose diffusion.

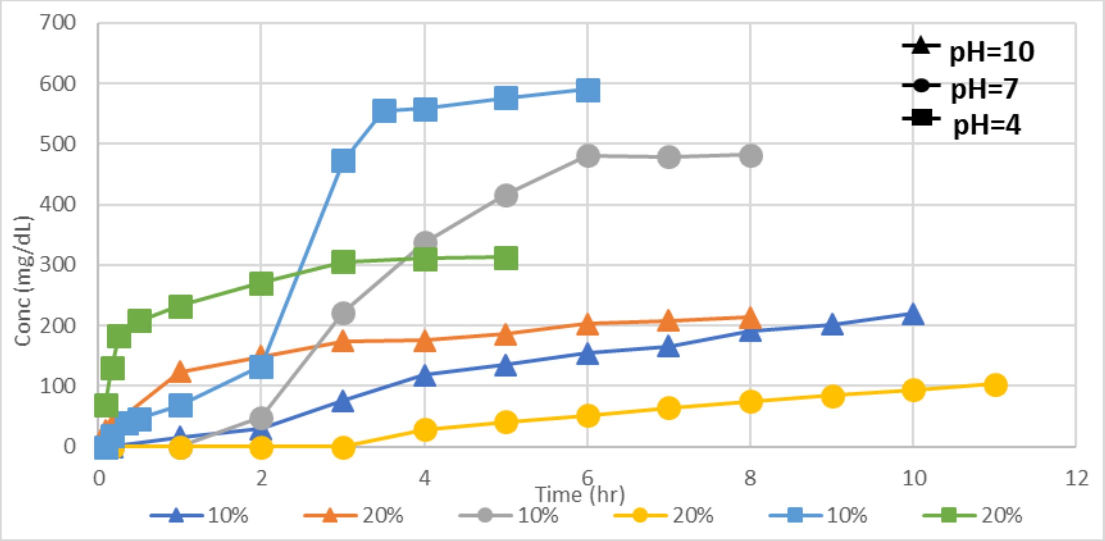

Figure 10 Time versus Diffusant Concentration across the 10% and 20% F-Chitosan Membranes in Different pH

The diffusion of glucose through the 10% and 20% F-chitosan membranes in pH 4, 7, and 10 buffer solutions was followed by measuring the concentration of the diffused glucose as a function of time. **Figure 10** shows the measured concentrations versus time. Based on this figure and comparing the nature of the media used, it may be noticed that the diffusion rate in acidic media is higher than that in neutral media and even alkaline media. That is reasoned by the swelling percentage that appears to maximize in alkaline media. Thus, it requires the membrane more time to initially retain the solvent then allow the diffusion of the solution. Therefore, glucose concentration in alkaline media after diffusion tends to be lower than in acidic or neutral media. Not to mention, both the membranes and glucose become protonated in acidic media, inducing repulsive forces that cause the membrane to expel protonated glucose molecules thus diffusing into the second compartment at a faster rate and providing a higher glucose concentration.

Comparing both membranes in each media, it is observed that the 10% membrane in acidic media initially achieves little diffusion until it experiences a sharp increase followed by a plateau, resulting in a higher diffusant concentration at 6 hrs. That is attributed to the lower chitosan concentration in the 10% membrane which reduces the crosslinking density, providing sufficient room for the solution to diffuse through after it had achieved proper retention with time.

Additionally, despite the fact that the 20% membrane achieves a higher yet somewhat similar swelling percentage as that of the 10% membrane in neutral media, it had still begun to diffuse the solution at about 4 hrs, unlike the 10% membrane that initiated diffusion at roughly 2 hrs. That reflects the longer time required by the 20% membrane to initially achieve proper retention and then allow diffusion, achieving a lower diffusion rate.

Considering the basic media used, it appears that the 20% membrane achieved a fairly higher diffusion rate until 8 hrs where the diffusion rate of both membranes seemed to be highly similar. The greater diffusion rate of the 20% membrane is attributed to the lower swelling percentage compared to the 10% membrane, as evident in **Figure 8**. Due to that substantial difference in swelling, the 10% membrane would require more time for the retention of the solvent first then allow diffusion, achieving a lower diffusion rate. Not to mention, this extensive swelling compared to the 20% membrane results in a bigger expansion thus longer pathway for the diffusant to pass across, contributing to a lower diffusion rate. Ultimately, both membranes appear to achieve similar diffusion rates.

4. CONCLUSION

Hydrogels have been widely exploited in the scientific field due to the many significant properties they possess. They have been utilized in pharmaceutical, biomedical, agricultural, and many other applications, primarily molecular separation processes, and drug delivery systems (Yazdi 2020, Nicoletta et al. 2015).

In this study, varying mass ratios of PAAm to F-Chitosan were fabricated including; 0, 5, 10, 20, 50, and 75% F-Chitosan membranes. That was achieved after the fluorination of chitosan. The F-chitosan formed is linear in shape, forming cylindrical pores within the polyacrylamide membrane matrix. FT-IR analyses and contact angle measurements confirmed the fluorination and incorporation of both materials. Those characterizations also confirmed that fluorination was primarily attained by hydrogen bonding. The results revealed an amphiphilic nature of almost all membranes, with the 10% membrane being the most amphiphilic.

Refractive index measurements and the corresponding dielectric constant evaluations showed that the 10% and 20% membranes contained the highest amount of electric charge on their surface, rendering them most susceptible to polarizing effects such as an electric field. That is necessary for their possible future applications in the purification processes of mixtures containing ionic species.

The swelling percentage was found to be highest in basic media due to amide hydrolysis and the resulting formation of polyacrylate anions that form electrostatic repulsions, causing further expansion. On the other hand, HCl and NaCl salt solutions resulted in lower swelling percentages due to the mutual ion attachment that results in the formation of flexible bonds that increase the overall flexibility of the membrane. This allows those media to achieve proper swelling capacities, yet lower than that observed in basic media. The neutral medium showed moderate swelling as it would be merely influenced by the ratio of PAAm to F-Chitosan.

The swelling kinetics of the membranes were evaluated utilizing Fick’s diffusion model. All membranes except for the 75% membrane showed a Non-Fickian (relaxation controlled) behavior. It was inferred that the pH of the media and the increase of F-Chitosan concentration do not influence the diffusion behavior of the membranes.

The deswelling performance was examined, where the results showed that the deswelling degree increases with the increase of F-Chitosan concentration. That is reasoned by the fragility of the membranes as F-Chitosan content increased, allowing an easier evaporation through the resulting non-integrous matrices. The 10% membrane seems to be the exception, reflecting the appropriate PAAm to F-Chitosan ratio that resulted in a sufficiently integrous membrane to restrict the deswelling performance.

Flux application of the membranes has shown that the 75% F-Chitosan is inapplicable, while the 0%, 5%, and 20% membranes are impermeable. The 10% membrane appeared to be semipermeable, while the 50% showed great permeability. This is explained by the increase of F-chitosan content that increases the space within the networks through which fluids may readily pass through.

The diffusion of glucose solutions of different pH values (4, 7, and 10) was conducted. Primarily the 10% and 20% F-Chitosan membranes allowed proper diffusion. The diffusion seemed to be highest in acidic media, deducing that glucose diffuses as $[\text{Glu-H}]^+$. On the other hand, diffusion was lowest in basic media. This is because of the swelling capacity that tends to maximize in such media, allowing the membrane to require more time to retain the solution and then allow diffusion.

It can be concluded that the 10% F-chitosan membrane is the most reliable and applicable with the most significant properties. It contains the appropriate PAAm to F-Chitosan ratio that creates an integrous intact semi-permeable membrane of proper flux and diffusion of glucose in different media. It displays an amphiphilic nature with high electric polarizability. It achieves the highest swelling and lowest deswelling degrees with a Non-Fickian behavior. This reliability can be exploited for substantial future applications in a variety of scientific fields.

5. RECOMMENDATIONS FOR FUTURE WORK

Future studies should concentrate on further developing the 10% F-Chitosan membrane and fine-tuning its more desirable characteristics. Furthermore, it is recommended to employ said composite membrane in separation technologies in the Bethlehem region to establish an economical, simple, and safe approach for purifying water in the Palestinian territories.

ACHNOWLEDGMENTS

This research was financially supported by the Internal Research Grant (IRG) maintained by the Deanship of Research-Bethlehem University.

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