CHAPTER I

CELLULOSE SHEET

FOR

SUBSTRATE AND SUPERSTRATE

1. METHODS OF ISOLATION OF CELLULOSE

The isolation of cellulose from its natural sources is carried out using a variety of methods. In this section, some of the most common methods of isolation of cellulose have been discussed.

1.1. CHEMICAL PULPING METHOD

The chemical pulping method is one of the most commonly used methods for the isolation of cellulose from wood. This method involves the use of chemicals to break down the lignin and hemicelluloses present in wood, leaving behind the cellulose fibers. The most commonly used chemicals for this process are Sodium Hydroxide (NaOH) and Sodium Sulfide (Na_2S). The process begins with the preparation of wood chips, which are then immersed in a solution of NaOH and Na_2S. This mixture is heated to a high temperature and pressure, which breaks down the lignin and hemicelluloses present in the wood. The resulting product is known as pulp, which is then washed and bleached to remove any impurities (Abe & Yano 2009, Wei et al. 2020). The final product is a pure form of cellulose.

1.2. MECHANICAL PULPING METHOD

The mechanical pulping method is another method that is commonly used for the isolation of cellulose from wood. This method involves the use of mechanical force to separate the cellulose fibers from the wood. The most commonly used equipment for this process is a refiner, which is a machine that uses a series of rotating discs to grind the wood chips into a pulp, which is then washed and screened to remove any impurities (Klemm et al. 2011, Sousa et al. (2021). The cellulose obtained is of good purity.

1.3. ACID HYDROLYSIS METHOD

The acid hydrolysis method is a process that is used to hydrolyze the cellulose fibers in plant material using acid. This method is commonly used for the isolation of cellulose from agricultural waste products such as corn husks, sugarcane bagasse and rice straw Phanthong et al. 2016, Mohamed et al. 2021).

The process begins with the preparation of the plant material, which is then treated with a dilute acid solution. The mixture is heated to a high temperature and pressure, which breaks down the cellulose fibers into individual glucose molecules. The resulting product is known as hydrolyzed cellulose, which can be further purified to obtain a pure form of cellulose (Fatah et al. 2014, Corrêa et al. 2019).

1.4. ENZYMATIC HYDROLYSIS METHOD

The enzymatic hydrolysis method is a process that is used to hydrolyze the cellulose fibers in plant material using enzymes. This method is also commonly used for the isolation of cellulose from agricultural waste products such as corn husks, sugarcane bagasse, and rice straw (Betlej et al. 2022).

The plant material is treated with a mixture of enzymes. The enzymes break down the cellulose fibers into individual glucose molecules. The resulting product is known as hydrolyzed cellulose, which can be further purified to obtain a pure form of cellulose.

1.5. Alkali Treatment Method

The alkali treatment method is a process that is used to isolate cellulose from natural sources such as cotton, flax, and hemp (Mwaikambo & Ansell 2002, Sawpan et al. 2011). This method involves the use of an alkali solution to break down the non-cellulosic components of the plant material, leaving behind the cellulose fibers.

The plant material is generally treated with an alkali solution such as sodium hydroxide (NaOH). The mixture is heated to a high temperature, which breaks down the non-cellulosic components of the plant material (Števulová et al. 2014, Peetla et al. (2006). The resulting product is known as alkali cellulose, which can be further purified to obtain a pure form of cellulose.

1.6. Ionic Liquid Method

The ionic liquid method is a process that is used to dissolve cellulose in an ionic liquid, which is a salt in a liquid state at room temperature. This method is commonly used for the isolation of cellulose from natural sources such as cotton, flax, and hemp.

One of the commonly used ionic liquid is 1-butyl-3-methylimidazolium chloride. The raw material is dissolved in the ionic liquid, which isolates the cellulose fibers (Ouajai & Shanks 2005, Han et al. 2022). The resulting product is known as dissolved cellulose, which can be further purified to obtain a pure form of cellulose (Haule et al. 2014).

1.7. Steam Explosion Method

The steam explosion method is a process that is used to break down the lignocellulosic components of plant material using steam and pressure. This method is also used for the isolation of cellulose from agricultural waste products.

The process begins with the preparation of the plant material, which is then treated with steam at a high temperature and pressure. The steam causes the lingo-cellulosic components of the plant material to break down, leaving behind the cellulose fibers. (Yang et al. 2018) The resulting product is known as steam exploded cellulose. It is purified to obtain a pure form of cellulose.

1.8. Bacterial Cellulose Production Method

This method involves the use of bacteria such as Gluconacetobacterxylinus, which produces cellulose as a byproduct of their metabolism (Lin & Catchmark 2015).

The bacteria is cultivated in a nutrient-rich medium containing glucose (Lupaşcu et al. 2022). The bacteria produce cellulose as they metabolize the glucose, which forms a gel-like substance. (Santoso et al. 2020) The resulting product is known as bacterial cellulose. It needs further purification (Tang et al. 2020).

In conclusion, the isolation of cellulose from natural sources is an important process that is carried out using a variety of methods. The choice of method depends on the source of cellulose and the intended application. Chemical and mechanical pulping methods are commonly used for the isolation of cellulose from wood, while acid and enzymatic hydrolysis methods are used for the isolation of cellulose from agricultural waste products. The alkali treatment method is used for the isolation of cellulose from natural sources such as cotton, flax, and hemp, while the ionic liquid method is used for the isolation of cellulose from a variety of sources. The steam explosion method is also used for the isolation of cellulose from agricultural waste products. Each method has its advantages and disadvantages, and the choice of method depends on factors such as cost, scalability, and efficiency.

It is important to note that the isolation of cellulose is not a one-step process, and typically involves several steps of purification to obtain a pure form of cellulose.

As research continues to advance, new methods for the isolation of cellulose may be developed, which could further improve the efficiency and sustainability of the process.

In the present work, a combination of Alkali treatment and Acid Hydrolysis has been used.

2. FORMATION OF SUBSTRATES

2.1. ISOLATION OF CELLULOSE SHEET

Agricultural remnants were collected from local farms and were washed thoroughly to remove dirt and other impurities. It must me noted that amount of water used in washing process was around 30 liter which was obtained back after distillation and was successfully used in further process. Clean residues were boiled in 5% w/w NaOH solution for 4 hours. The amount of solution to be taken completely depends on the amount of residues i.e., the residues must be completely soaked in alkali solution. In our case, after a series of experiments, when the entire process was finalized, we took 5 kg of agricultural remnants for which 30 liter of solution was prepared. Reflux system was setup in order to avoid loss of water. After the process a sticky mess of substance was obtained. This obtained product was washed with water through, till the decolored water pours out of the material. Around 110 liter of water was used. The water used for the preparation of alkali solution and washing was the one obtained from previous step also. Again, the water was distilled and it was assured that it can be used for further processes. Product obtained, was then dried completely and passed through a regular domestic sieve to obtain a powder. This powder weighed around 3.2 kgs. Powder was then soaked in 10 liter sodium hypochlorite solution for bleaching overnight under constant stirring. Next day smooth white slurry was obtained which was filtered, washed water and methanol and dried. Dried slurry was again crushed to powder. Second bleaching process was carried out with 30% solution of hydrogen peroxide for three hours followed by washing, drying and crushing to powder. This powder would be further referred to as cellulose powder (CP). Absolutely fine, crystalline white CP in different amount was then hydrolyzed in refrigerated 15%v/v H_2SO_4 100 ml solution for 4 hours. The above process basically defibrillates all the cellulosic substance. Solvent exchange was done with methanol and then with DMAc for 3 hours. Saturated solution of 8% w/w LiCl/DMAc solution was prepared. Dispersed CP in DMAc was dissolved in this solution to form an absolute viscous gel. The gel was then centrifuged for 10 mins at 1100 rpm for degasification. Obtained gel was poured in specially designed acrylic plates of 10 cm x 10 cm and allowed to rest overnight. Casted films were regrated in water and dried in normal conditions over night.

Flow Chart of the entire Process

Dry agricultural remnants from local farms and were washed thoroughly with water

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Clean residues were boiled in 5% w/w NaOH solution for 4 hours

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Digested samples were treated with SDS for 3 hours

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The dried residues were bleached with sodium hypochlorite over night

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Bleached product was washed with water followed with methanol and dried

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Second bleaching process was carried out in Hydrogen peroxide for 3 hours

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Final bleached sample was hydrolysed 15% v/v for 4 hours

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Solvent exchange was done with methanol and then with N,N-dimethylactamide each for at least 3 hours

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Obtained sample was dissolved in 8% w/w LiCl/DMAc solution to form a fine viscous gel.

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The gel was centrifuged for 10 mins and 1100 rpm for degasification

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The gel in proper amount was poured in specially designed acrylic plates of 10 x 10 cm^2 area and allowed to rest over night

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Casted films were regenerated in water and dried over night at normal room conditions

Figure 10: (a) Raw Agricultural Residues, (b) Pulp obtained after bleaching treatment, (c) Dried crystalline powder after hydrolysis, (d) Wet transparent Sheet obtained after regeneration, (e) Dried sheet cut in 10 cm x 10 cm, (f) Sheet after ITO Sputtering.

3. Results and Discussions

Variable amount of CP obtained after second bleaching process was taken and dissolved in saturated solution of LiCl/DMAc and following were the results. It must be noted that coefficient of viscosity (η) was measured at room temperature (at the time of measurement RT=32°C). Thickness of the film was calculated using digital micrometer screw gauge having least count of 1μm after the film was dried completely. Thickness measurements were done by taking average of 10 readings measured at different area of the film. Transparency was observed using UV-Vis Analysis. UV-Vis analysis was performed by taking that area of the film that was found to have highest thickness.

3.1. Transparency | Viscosity

Cellulose concentration (C) (g/ml)	Gel Coefficient of Viscosity (η) (Poise P)	Thickness (T) (μm)	Transparency (%)
0.1	7.81	36	96
0.12	8.14	46	97
0.14	8.32	53	95
0.16	8.49	65	96
0.18	8.62	72	94
0.20	8.91	86	94
0.22	**9.26**	**97**	**93**
0.24	9.49	107	92
0.26	9.77	113	90
0.28	10.01	127	88
0.30	10.38	134	88

Gel with 0.22 g/ml concentration was found to have coefficient of viscosity of 9.26 Poise. Films resulted in thickness of 97 μm with transparency of 93 %. This was chosen gel for casting of films in bulk and getting it processed for coating of conducting layer. It must be taken in consideration that any of the obtained films could be washed with water, ethanol, acetone and other solvents used for cleaning of substrates of solar cells.

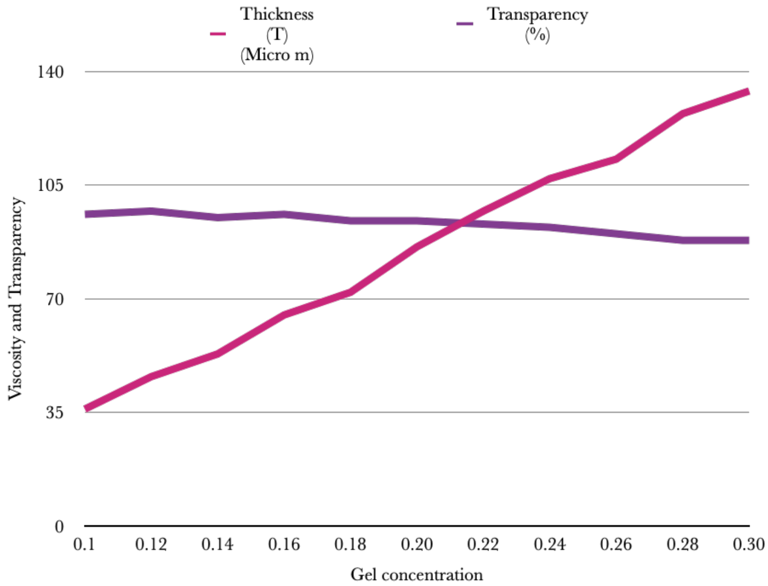

Figure 10: Variation in Thickness and Transparency with Gel Concentration

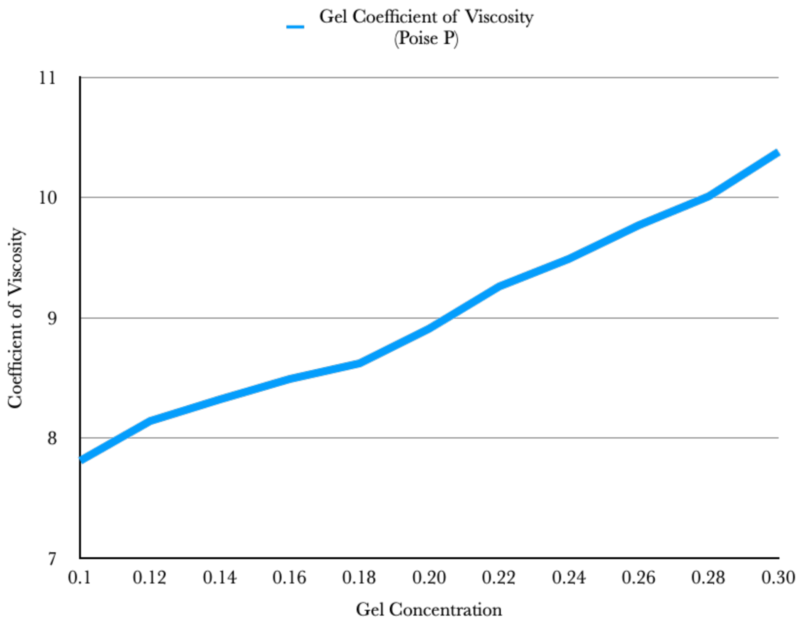

Figure 11: Variation in Coefficient of Viscosity with Gel Concentration