Effect of Sodium Hydroxide/Urea/Deionised Water Solution Ratio on the Solubility of Oil Palm Empty Fruit Bunches Extracted Biocellulose

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Biocellulose extracted from oil palm empty fruit bunches (OPEFB) is attracting increased research interest in versatile applications as an alternative material to synthetic cellulose. Normally, biocellulose needs to undergo dissolution prior its applications. Among all explored solvents to dissolve biocellulose, aqueous sodium hydroxide (NaOH)/urea solution is gaining increased attention. OPEFB biocellulose solubility in NaOH/urea/deionised (DI) water solution has not been fully studied by researchers. This study aimed to investigate the solubility of OPEFB biocellulose in NaOH/urea/DI water solution by manipulating the NaOH/urea/DI water solution ratio and weight percentage of OPEFB biocellulose. Results indicated that increasing the NaOH/urea/DI water solution ratio increased the solubility of OPEFB biocellulose. Further increased NaOH/urea/DI water solution ratio resulted in decreased solubility. Meanwhile, increased OPEFB biocellulose weight percentage decreased the solubility of OPEFB biocellulose in NaOH/urea/DI water solution. The highest solubility of 70.89±1.85% was exhibited by 7% NaOH/12% urea/81% DI water (w/w) solution and 1 w/v% OPEFB biocellulose. This study on OPEFB biocellulose solubility in NaOH/urea/DI water solution can promote cost-effective and wide utilisation of the abundantly available OPEFB for the synthesis of cellulose fibres, films, and hydrogels in the textile, packaging, and biomedical industries.

Keywords: oil palm empty fruit bunches; biocellulose; solubility; sodium hydroxide/urea/deionised water solution

I. INTRODUCTION

The increasing palm oil demand has contributed to the fast development of the palm-oil industry in Malaysia (Athirah et al., 2018). This phenomenon has resulted in increased biomass production during palm-oil processing (Teow et al., 2020). One of the major biomass produced from palm-oil processing is oil palm empty fruit bunches (OPEFB). Malaysia is estimated to produce around 7.78 million tonnes of OPEFB annually (Hamzah et al., 2019).

OPEFBs comprise 37%–46% biocellulose, 25%–33% hemicellulose, and 27%–32% lignin (Sudiyani et al., 2013).

The conventional practice of burning OPEFBs in boilers as a power source could lead to serious air pollution. Accordingly, awareness on the resources and solid-waste management in the palm-oil industry is raised (Haan et al., 2020). Nazir et al. (2013) successfully extracted a high percentage of biocellulose (64 w/w%) from OPEFBs, indicating the success of recovering biocellulose from agricultural biomass. The biodegradability, sustainability, high hydrophilicity, and availability of biocellulose in nature render it a favourable natural polymer for various applications, such as ion-battery synthesis (Faizi et al., 2017), biocellulose-membrane

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numerous solvents (Haan et al., 2020), and synthesis of biocellulose hydrogel (Salleh et al., 2019).

Biocellulose needs to undergo dissolution prior to its application. Numerous solvents have been explored to dissolve biocellulose. Among them, aqueous sodium hydroxide (NaOH)/urea solution is gaining increased attention owing to its simplicity, low toxicity, environment friendliness, and low cost (Yang et al., 2020; Zainal et al., 2020). However, the solubility of OPEFB biocellulose in NaOH/urea/deionised (DI) water solution has not yet been fully elucidated. The present study aimed to investigate the solubility of OPEFB biocellulose in NaOH/urea/DI water solution by adjusting the NaOH/urea/DI water solution ratio and weight percentage of OPEFB biocellulose. The optimum dissolution of biocellulose extracted from the abundantly available OPEFB in the environment-friendly NaOH/urea/DI water solution is important. It can promote more sustainable and cost-effective applications of OPEFB biocellulose.

II. MATERIALS AND METHODS

A. Materials

OPEFB samples were collected from the Tennamaram palm oil mill in Malaysia. NaOH and hydrogen peroxide (30 w/w%) were obtained from Classic Chemicals Sdn. Bhd., Malaysia. Formic acid (98–100, w/w%) was purchased from Thermo Fisher Scientific, USA. Ethanol (99.5, v/v%) was supplied by Sciensfield Expertise PLT, Malaysia. Urea was purchased from Merck KGaA, Germany.

B. Dissolution of OPEFB Biocellulose

The biocellulose-extraction process was adapted from the study of Nazir et al. (2013) and modified. OPEFB was initially washed with 1 w/v% detergent until the rinse water turned colourless. The washed OPEFB was then dried at 100±2 °C until constant weight was obtained. The dried OPEFB was cut, passed through a 1.18 mm-opening mesh sieve, and dewaxed using 70 v/v% ethanol in a soxhlet extraction apparatus for 6 h at 78±2°C. The OPEFB fibres were then washed with DI water and dried at 100±2°C. NaOH solution (3 w/v%) was added to the dewaxed OPEFB fibres, which were heated to 121 °C for 1 h for delignification. Acid treatment was then started by soaking 10 g of delignified OPEFB fibres in 200 mL of 20 v/v% formic acid and 10 v/v% hydrogen peroxide mixture. The mixture was heated to 85 °C for 2 h. Finally, light-yellow OPEFB biocellulose fibres were bleached by suspending in 10 v/v% hydrogen peroxide (pH 9) at 60 °C for 90 min. The OPEFB biocellulose fibres were then rinsed with DI water until neutral pH was obtained and dried in an oven at 60±2 °C.

An aqueous solution containing NaOH/urea/DI water at different weight ratios was prepared as the solvent for OPEFB biocellulose dissolution. Different weight/volume percentages of OPEFB biocellulose was added into 100 mL of NaOH/urea/DI water solution and dispersed through continuous stirring at 300 rpm for 5 min. The mixture was then stored under refrigeration at -12 °C for 15 h. After thawing the frozen mixture at room temperature and stirred extensively at 1500 rpm for 30 min (Teow, Ming & Mohammad, 2018), the mixture was centrifuged at 10 000 rpm for 5 min to remove undissolved OPEFB biocellulose. The dissolved OPEFB biocellulose (supernatant) was separated from the mixture using a pipette. The undissolved OPEFB biocellulose (precipitate) was rinsed several times with DI water until neutral pH was obtained. Subsequently, the undissolved OPEFB biocellulose was collected, dried in an oven at 60 °C for 24 h, and weighed. The solubility of OPEFB biocellulose was calculated using Equation (1), and the actual concentration of dissolved OPEFB biocellulose was calculated using Equation (2) (Salleh et al., 2019). The percentages of NaOH, urea, DI water, and OPEFB biocellulose manipulated adjusted in this study were set based on one-factor-at-once and are summarised in Table 1.

Solubility of OPEFB biocellulose (%) = \[ \frac{W_o - W}{W_o} \times 100 \% \] (1)

where \( W_o \) was the initial weight of OPEFB biocellulose before dissolution (g), and \( W \) is the weight of undissolved OPEFB biocellulose (g).

Actual concentration of dissolved OPEFB biocellulose \( \frac{R}{mL} \) = \[ \frac{\text{Solubility of OPEFB biocellulose}}{100} \times \frac{W_o}{V_s} \] (2)

where \( V_s \) is the volume of NaOH/urea/DI water solution (mL).
III. RESULTS AND DISCUSSION

A. Effect of NaOH/Urea/DI Water Ratio

Figure 1 shows the solubility of OPEFB biocellulose at different NaOH/urea/DI water ratios. Generally, the solubility of OPEFB biocellulose increased with increased NaOH and urea percentage in NaOH/urea/DI water solution. The solubility of OPEFB biocellulose increased with the use of 2 w/w% NaOH (SN2) to 7 w/w% NaOH (SN7). However, it decreased with further increased NaOH percentage in NaOH/urea/DI water solution. This finding was probably due to the concentration-dependent size of NaOH–DI water hydrates. At lower NaOH percentage, NaOH–DI water hydrates have large hydrodynamic diameters (Medronho & Lindman, 2014). Crystalline biocellulose chains were densely packed, with an intersheet distance of about 10 Å and a crystallite diameter of only 5 nm (Zhang et al., 2010). NaOH molecules broke the inter- and intra-hydrogen bonds among the biocellulose molecules and destroyed the long-range order of biocellulose crystals to form a biocellulose molecular solution through swelling and activating the biocellulose (Zhang et al., 2010). Thus, at low NaOH percentage (SN2 and SN4), the hydrodynamic diameter of NaOH–DI water hydrates was too large to penetrate the crystalline region of biocellulose, so the solubility of OPEFB biocellulose decreased. Moreover, the amount of NaOH was insufficient to dissolve biocellulose at low NaOH percentage (Zhang et al., 2010). Low NaOH percentage resulted in an insufficient number of alkali ions (Na⁺). The function of Na⁺ was to bring water molecules into biocellulose to cleave hydrogen bonding among biocellulose chains, resulting in biocellulose swelling (Kuo & Hong, 2005). Consequently, low NaOH percentage led to poor swelling, thereby decreasing the solubility of OPEFB biocellulose. Among the different ratios of NaOH/urea/DI water solution, 7% NaOH/12% urea/81% DI water (w/w) solution and 1 w/v% OPEFB biocellulose exhibited the highest solubility of 70.89±1.85%. At higher NaOH percentage (SN10 and SN12), the concentration of Na⁺ was too high, so the hydration of Na⁺ was low because of the insufficient water molecules (Kuo & Hong, 2005). The hydration of the low amount of ions decreased the frequency of hydrogen-bonding cleaving, resulting in poor swelling of biocellulose. Thus, the solubility of the OPEFB biocellulose decreased.

Meanwhile, OPEFB biocellulose solubility increased with increased urea percentage in NaOH/urea/DI water solution from 2 w/w% urea (SU2) to 12 w/w% urea (SU12). The dissolution of biocellulose in NaOH/urea/DI water solution occurred through the formation of a biocellulose–NaOH–urea inclusion complex (IC), where NaOH and urea surrounded the biocellulose chains in a hydrate layer to form a wormlike structure (Huber et al., 2016). Urea in biocellulose–NaOH–urea aqueous solution existed in two forms, namely, hydrates associated with the IC and free hydrates. Both forms existed in equilibrium with each other. A higher percentage of urea resulted in excess urea free hydrates, which displaced the equilibrium toward the inclusion of urea in IC, thereby strengthening the shielding of biocellulose chains (Huber et al., 2016). The formation of IC minimised the intermolecular biocellulose interactions, leading to increased OPEFB biocellulose stability.

<table>
<thead>
<tr>
<th>Solution</th>
<th>NaOH (w/w%)</th>
<th>Urea (w/w%)</th>
<th>DI water (w/w%)</th>
<th>OPEFB biocellulose (w/v%)</th>
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<tbody>
<tr>
<td>SN2</td>
<td>2</td>
<td>12</td>
<td>86</td>
<td>1</td>
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<tr>
<td>SN4</td>
<td>4</td>
<td>12</td>
<td>84</td>
<td>1</td>
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<tr>
<td>SN7</td>
<td>7</td>
<td>12</td>
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<td>1</td>
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<td>SN10</td>
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<td>12</td>
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<td>1</td>
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<tr>
<td>SN12</td>
<td>12</td>
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<td>SU2</td>
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<td>2</td>
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<td>1</td>
</tr>
<tr>
<td>SU4</td>
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<td>SU7</td>
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<td>83</td>
<td>1</td>
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<tr>
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<td>81</td>
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<tr>
<td>SC4</td>
<td>7</td>
<td>12</td>
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</table>
4

Figure 1. Solubility of OPEFB biocellulose at different NaOH/urea/DI water ratios

B. Effect of OPEFB Biocellulose Weight Ratio

Given that 7% NaOH/12% urea/81% DI water (w/w) exhibited the highest OPEFB biocellulose solubility of 70.89±1.85%, effect of OPEFB biocellulose weight ratio was studied at this constant NaOH/urea/DI water ratio. Figure 2 shows the solubility of OPEFB biocellulose and actual concentration of dissolved OPEFB biocellulose at different OPEFB biocellulose weight ratios. The solubility of OPEFB biocellulose decreased with increased initial OPEFB biocellulose percentage in NaOH/urea/DI water solution. Low-percentage OPEFB biocellulose in NaOH/urea/DI water solution was more efficient for mixing as it facilitated the contact between NaOH/urea/DI water solution and OPEFB biocellulose, thereby allowing a higher percentage of OPEFB biocellulose to dissolve. Additionally, the self-aggregation of OPEFB biocellulose at a high initial percentage of OPEFB biocellulose may have caused the low solubility. This observation has been made by Kaco et al. (2014), who found that the solubility of biocellulose derived from kenaf core powder in NaOH/urea/DI water solution decreases with increased biocellulose weight percentage.

Meanwhile, the actual concentration of dissolved OPEFB biocellulose increased with increased initial OPEFB biocellulose percentage from 1 w/v% to 3 w/v% and achieved a plateau after 3 w/v%. This finding could be due to the limited capacity of NaOH/urea/DI water solution for dissolving cellulose. When the maximum dissolution capacity of NaOH/urea/DI water solution was reached, the excess OPEFB biocellulose added into NaOH/urea/DI water solution did not dissolve, causing a plateau trend for the actual concentration of dissolved OPEFB biocellulose.

OPEFB biocellulose was not completely dissolved in NaOH/urea/DI water solution possibly because of the high molecular weight and degree of polymerisation (DP) of OPEFB biocellulose. This feature can affect the penetration of NaOH/urea/DI water solution into OPEFB biocellulose resulting in partial solubility and producing undissolved OPEFB biocellulose (Baharin et al., 2018). The high molecular weight of OPEFB biocellulose molecules corresponds with a large excluded volume that promotes intermolecular interaction and thus suppresses its solubility (Guo et al., 2017). Conversely, a high DP resulted in a network of fibres held together through hydrogen bonds forming long-chain segments. Thus, OPEFB biocellulose with high DP was strong and resisted dissolution (Ni et al., 2015). The solubility of OPEFB biocellulose ranging from 44.12±3.03% to 70.89±1.85% has been found to be higher than that of OPEFB biocellulose at 54.52±0.50% (Salleh et al., 2019). Salleh et al. (2019) used OPEFB cellulose and 7% NaOH/12% urea/81% DI water (w/w) solvents at -12 °C refrigeration, which is comparable to the solvent and temperature in the current study. Our higher OPEFB-biocellulose solubility than that in literature supported the successful dissolution of the maximum percentage of OPEFB biocellulose in NaOH/urea/DI water solution in the current study.

Figure 2. Solubility of OPEFB biocellulose and actual concentration of dissolved OPEFB biocellulose at different OPEFB biocellulose weight ratios
IV. CONCLUSION

The dissolution of OPEFB biocellulose in different NaOH/urea/DI water solution ratios and weight percentages of OPEFB biocellulose was investigated. At different NaOH/urea/DI water solution ratios, 7% NaOH/12% urea/81% DI water (w/w) solution and 1 w/v% OPEFB biocellulose exhibited the highest solubility of 70.89 ± 1.85%. However, OPEFB biocellulose solubility decreased at higher NaOH percentage (SN10 and SN12). Meanwhile, the solubility of OPEFB biocellulose decreased with increased initial OPEFB biocellulose percentage in NaOH/urea/DI water solution. The low-percentage OPEFB biocellulose in NaOH/urea/DI water solution was more efficient for mixing and facilitated the contact between NaOH/urea/DI water solution and OPEFB biocellulose, thereby allowing a higher percentage of OPEFB biocellulose to be dissolved. The optimum dissolution of 1 w/v% biocellulose extracted from the abundantly available OPEFB in the environment-friendly 7% NaOH/12% urea/81% DI water (w/w) solution can promote more sustainable and cost-effective applications of OPEFB biocellulose. Further study on the solubility of OPEFB biocellulose using different solvents is suggested.

V. ACKNOWLEDGEMENT

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VI. REFERENCES


