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### Synthesis of cellulose sulfate by enhancing cellulose swelling using microwave energy

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Cellulose sulfate (CS) has many industrial applications. In traditional CS synthesis, swelling of cellulose was performed using a large amount of solvents and conventional heating for 10 to 12 hours. The objective of this study was to develop a method for synthesis of CS using chlorosulfonic acid (CSA) as the sulfation agent while enhancing cellulose swelling using microwave energy. The developed CS synthesis method can be divided into four stages; swelling, sulfation, neutralization and purification. Swelling was accomplished within 1 minute at 300 W microwave power while minimizing the solvent usage. Pyridine:formamide (1:1.2 v/v) was identified as the best solvent system for the swelling of cellulose. Use of microwave irradiation on sulfation is not advisable due to formation of char. CSA was added into the reaction mixture in an ice bath and kept 12 – 15 hours at 4°C. Neutralization was done using NaOH and the optimum concentration was identified as 1 mol dm<sup>-3</sup>. Cooling the reaction mixture while neutralizing enhanced the final yield up to 43%. Instead of the dialysis, crude CS was dissolved in distilled water (15.0 mL), and centrifuged to remove unreacted cellulose. Warming of the solution while dissolving crude CS further enhanced the yield. Finally the CS in the supernatant was precipitated by adding two volumes of ethanol. The maximum yield of 46% was achieved under optimized conditions (swelling at 300 W for 1 minute, 1 mol dm<sup>-3</sup> NaOH for neutralization, optimum cooling and warming at -12 °C and 60 °C, respectively) whereas the yield was 34% when the conventional swelling was performed. Products were characterized using ATR-FTIR spectroscopy and the S=O stretching peaks were observed between 1225-1235 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of CS shows the anomeric protons at 5.75 ppm and all other protons between 3.5 – 5.5 ppm. The mass spectrum (Electrospray ionization) gave a major peak at m/z 851, which corresponds to the sulfated glucose dimer unit with average degree of substitution 2.5. The resultant CS contains five –SO<sub>3</sub>Na groups having molecular formula C<sub>12</sub>H<sub>16</sub>O<sub>26</sub>S<sub>5</sub>Na<sub>5</sub> (Calculated: 851.51384; experimental: 851.3958). In conclusion, CS was successfully synthesized using a modified method by enhancing the swelling of cellulose using microwave energy. Optimized conditions can be successfully applied to convert agricultural wastes into value-added products in future.

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