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Microwave assisted acetylation of cellulose isolated from the banana pseudo-stem

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Cellulose acetate (CA) is an ester derivative of cellulose with a wide range of industrial applications as coatings, cigarette filters, textile fibers, filtration membranes, photo films, composites, and medical and pharmaceutical products.[1] Annually, a few tons of banana pseudo-stems are left behind in the plantation soil as an agro waste in Sri Lanka. Therefore, this study was performed to develop efficient and environmentally friendly methods to isolate cellulose from the banana pseudo-stem (Pisang Awak-species 'seeni kesel'), which is an agro waste in Sri Lanka, and to synthesize CA using the isolated cellulose.

Cellulose was isolated using microwave (MW) irradiation in the dewaxing step and the % yield (W/W) was compared with that of the conventional method[2] which involves dewaxing by Soxhlet extraction for six hours. The crystallinity index of the isolated cellulose was determined using X-ray Diffraction. CA was synthesized using the isolated cellulose in the presence of iodine as the catalyst1 and the reaction conditions (reaction temperature, MW power and reaction time) were optimized. The degree of substitution (DS) of CA was determined using a back titration method.[3] Isolated cellulose and the CA were characterized by FT-IR spectroscopy.

The % yield (W/W) of cellulose (19.7%) obtained using MW irradiation in the dewaxing step at optimum reaction conditions (300 W, 60 ^{o}C, 5 minutes) was higher than that of the conventional method (8.35%), indicating that the Soxhlet extraction in the dewaxing step can be successfully replaced with the MW irradiation. The FT-IR spectroscopic data summarized in Table 1 indicate that the cellulose isolation was successful.

The crystallinity index of the isolated cellulose was high (73%), indicating that the isolated cellulose is in high quality, high rigidity and thus, suitable for industrial applications.

The best % yield (W/W) of CA synthesized using the cellulose isolated from the banana pseudo-stem was 97.8% with DS of 2.87 at the optimum reaction conditions (500 W, 50 ^{o}C for 25 minutes with 1.27 eq of iodine). The three characteristic peaks for CA at 1737 cm^{-1}, 1368 cm^{-1} and 1236 cm^{-1} corresponding to C=O stretching of ester, C-H stretching in –O(C=O)-CH_3 and C-O stretching of acetyl group, respectively indicate that the acetylation of the isolated cellulose was successful. The results obtained from this study indicate that CA can be successfully synthesized with a high yield using the cellulose isolated from the banana pseudo-stem in the presence of iodine as the catalyst. This CA synthesis makes the banana pseudo-stem which is an agro waste into a value-added product. The high percentage of crystallinity index of cellulose indicates an ordered and compact structure which results in high material strength and can be applied in improving the mechanical properties of composite materials.[4] The use of MW irradiation makes the process more efficient by reducing the reaction time and environmentally friendly with lesser use of solvents. The successful use of an agro waste in Sri Lanka into industry makes the process more economical and environmental friendly.

Keywords

cellulose, cellulose acetate, banana pseudo-stem, microwave irradiation, iodine catalyst.

Table 1: The comparison of the FT-IR spectroscopic data obtained for commercial cellulose and the isolated cellulose

Spectrum	-OH stretching/ (cm^{-1})	-C-H stretching/ (cm^{-1})	H-O-H bending of absorbed water / (cm^{-1})	-C-O stretching/ (cm^{-1})	C-O-C pyranose ring skeletal vibration/ (cm^{-1})
Commercial cellulose	3336	2900	1643	1160	1053
Isolated cellulose (Soxhlet extraction)	3338	2902	1635	1158	1053
Isolated cellulose (MW irradiation)	3335	2899	1644	1158	1056

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Synthesis and characterization of novel zinc ditriazine complexes

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Triazine derivatives have gained considerable attention due to their biological properties. Here we have focused on the synthesis and spectroscopic characterization of novel Zinc complexes bearing derivatives of 1,2,4-Ditriazine ligands (R = Me, Et, Py). Although the ditriazine scaffold was synthesized more than five decades ago,[1] only a few reports exist on their metal complexes[2,3] and Zn(II) complexes of ditriazine are relatively unexplored. Three novel Zn(II) complexes [$Zn(Me_4dt)Cl_2$] (**C1**), [$Zn(Et_4dt)Cl_2$] (**C2**) and [$Zn(Py_4dt)$ Cl2] (**C3**) of three selected ditriazine derivatives [Me_4dt= Bis-3,3'-(5,6-dimethyl-1,2,4-triazine) (**L1**), Et_4dt= Bis-3,3'-(5,6-diethyl-1,2,4-triazine) (**L2**), Py_4dt= Bis-3,3'-(5,6-dipyridyl-1,2,4-triazine) (**L3**)] were obtained by the reaction of $ZnCl_2$ with each ligand (1:1). Since higher melting point is a characteristic feature of a metal complex, melting points of all three complexes were determined (**C1**: 182-184 °C, **C2**: 220-221 °C, **C3**: >300 °C) and found to be are much higher than that of the corresponding ligands (**L1**: 91-93 °C, **L2**: 118-120 °C, **L3**: 256-258 °C).

These complexes were characterized by UV-visible, FT-IR and ^{1}H NMR spectroscopy. In UV-visible spectra, two peaks were observed for the ligands (**L1**: 240 nm, 256 nm, **L2**: 240 nm, 257 nm, **L3**: 226 nm, 302 nm) vs. one for the corresponding complexes (**C1**: 236 nm, **C2**: 240 nm, **C3**: 297 nm). FTIR spectra of the complexes are different from those of the ligands and the wavenumber of C=N of the ligands decreased from 1674.08 υ / cm^{-1} (L1), 1527.51 υ / cm^{-1} (L2), 1581.51 υ / cm^{-1} (L3) to 1623.94 υ / cm^{-1} (C1), 1504.36 υ / cm^{-1} (C2), 1573.79 υ / cm^{-1} (C3), respectively confirming that nitrogen attributable to C=N is coordinated to zinc metal *via* lone pair donation. ^{1}H NMR spectra recorded for above methyl and ethyl zinc(II) complexes do not show considerable shifts in comparison to their corresponding ligands and may be due to metal coordinating with the solvent. It is suggested to record the ^{1}H NMR again in non-coordinating solvent such as CD_2Cl_2. Surprisingly in the case of Py_4dt, its corresponding zinc(II) complex showed large downfield thus providing proof that the metal complex has been formed.

Keywords

1,2,4-ditriazine, Zn(II) ditriazine complexes, spectroscopy methods, melting points.

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