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Characterization of Microcrystalline Cellulose Isolated from Paper Sludge

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Abstract
The large amount of paper sludge generated from wastepaper industries emphasizes the importance of developing green waste management. The study aimed to characterize microcrystalline cellulose from paper sludge using different acid concentrations. The properties of chemical composition, morphological, thermal, reflectance, and crystallinity index were accessed. The disappearance of peaks in FTIR was related to the removal of amorphous structure. SEM confirmed the reduction in diameter with the decomposed temperature of 266°C. 3.0 M reflects the highest UVB at 28% and UVA at 39% due to the highest crystallinity index of 31%, which is possible for reinforcement application in film packaging.

Keywords: Paper sludge, microcrystalline cellulose, wastepaper, acid hydrolysis

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1.0 Introduction

Microcrystalline cellulose (MCC) is an odorless and white powdered micro cellulose. Because of its mechanical strength, biodegradability, biocompatibility, wide surface area, and compressibility, MCC is used in pharmaceuticals, cosmeceuticals, foods, and textiles. It is used as a diluent in tablets, as a suspending agent and viscosity modifier in suspensions and emulsifiers, and as a water adsorbent in creams and pastes. Wood fiber is the most prevalent industrial source of MCC. Renewable resources that can be utilized to manufacture MCC include coir fiber (Gichuki et al., 2022), oil palm empty fruit bunches (Krishnan et al., 2022), cotton fibers (Do et al., 2022), nata de coco (Nurhadi et al., 2022), birch wood (Tarabanko et al., 2022), flax (Tkachenko et al., 2022), sunflower seed waste (Akatan et al., 2022), and Lagenaria siceraria fruit (Asif et al., 2022). The physical properties of cellulose and MCC are taken from different plants, and their parts vary in water absorbability, polymerization, porosity, and crystallinity (Asif et al., 2022).
The most popular methods of preparing MCC via cellulose hydrolysis are acid hydrolysis, enzymatic hydrolysis, and microbial hydrolysis. Strong acid hydrolysis, for example, removes amorphous portions from cellulose fibers, resulting in micro- or nano-sized fibers. Cellulose has both crystalline and amorphous areas. Microcrystalline cellulose is the crystalline particles released when acid hydrolysis removes the amorphous region. In the acid hydrolysis process, a strong acid solution, such as sulfuric acid (Tang et al., 2021) or hydrochloric acid, is utilized (Mamat Razali et al., 2021). Tawalbeh et al. (2021) extracted crystalline cellulose from sludge using hydrochloric acid and discovered a significant percentage of fiber containing crystalline cellulose. Du et al. (2020) converted paper sludge to cellulose nanofibrils and cellulose nanopaper using formic acid hydrolysis followed by microfluidization, which demonstrated excellent thermal stability, crystallinity index, surface functionality, and a high yield of more than 75 wt %. This approach provides a simple technique that is fast and efficient, and eco-friendly, potentially lowering waste treatment expenses (Wibowo et al., 2018). This study produced MCC from wastewater treatment plant paper sludge comprising lignocellulosic materials.

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Paper sludge may contain up to 40-80% cellulose, which is very promising for MCC synthesis. Malaysian mill solid waste production climbed from 16 200 tons per day in 2001 to 19 100 tonnes per day in 2005, averaging 0.8 kg per capita per day. Malaysia's paper sector produces approximately 30% of the country's paper sludge, increasing at a pace of roughly 4% per year (Daud et al., 2018). In Malaysia, 67 paper mills generate more than 50 tonnes of paper per day, 19 of which are small paper manufacturing firms in Sipitang, Sabah, that employ wood fiber and integrated pulp (Sabah Forest Industries). Malaysia's pulp and paper industry primarily depends on crucial fiber, mainly virgin pulp, with recycled paper serving as a feedstock supply (Abdullah et al., 2016). Some researchers, such as Du (2020), Adu (2021), and Glinska (2020), have employed paper sludge as a raw material for cellulose preparation (Du et al., 2020), (Adu et al., 2021), (Glińska et al., 2020).

Herein, the feasibility study of the utilization of hydrochloric acid for producing MCC from paper sludge is studied. In the present work, we examined the chemical composition, morphology, thermal, reflectance, and crystallinity properties of untreated and treated paper sludge by using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermal gravimetric analyzer (TGA), Ultraviolet-Visible Infrared Spectroscopy (UV-Vis), and X-ray diffraction (XRD).

2.0 Method

The Paper sludge used in this research was obtained from Pascorp Paper Industry, Bentong, Pahang, Malaysia. The wet paper sludge was oven dried, grinded, crushed, sieved, and stored in the chiller in powder. All chemicals used for the extraction of MCC were purchased from Merck.

20 ml of rehydrated sludge refluxed into 10 mL tetrakis (hydroxymethyl) phosphonium chloride ionic liquid and then vigorously agitated for 24 h at 100°C to isolate the cellulose. 10 ml methanol and 5 ml hexane were added and centrifuged for 10 mins at 3500 rpm until the organic and aqueous phases became transparent. The bleaching treatment was performed by adding 8% hydrogen peroxide agitated for 24 h at room temperature and was then ultrasonicated into 0.1 M hydrochloric acid at 60°C for five h. The resulting solution was cooled and washed with distilled water. The procedure will be repeated for various hydrochloric acid molarities, and the names of the corresponding samples were 1.0 M, 2.0 M, 3.0 M, and 4.0 M, respectively.

The isolated microcrystalline cellulose (MCC) was characterized by the FTIR (Perkin-Elmer spectrum 1650), morphology (phenom XL Benchtop Scanning Electron Microscope (BSEM), thermal property (TGA Q500 V20.13), UV-vis reflectance (Varian Cary 5000), and crystallinity index (X'pertPro, PANalytical, and X'pert Pro Highscore software).

3.0 Result and discussions

3.1 Chemical composition

FTIR spectroscopy was used to examine changes in chemical composition brought on by the series of treatments, including ionic liquid treatment and bleaching of the cellulose. Figure 1 illustrates the two leading absorbance bands that were prominent in the six samples: the first at lower wavelengths (800-1800 cm^{-1}) and the latter at higher wavelengths (2800-3500 cm^{-1}) (Burhani et al., 2022). The differences between the FTIR spectra of the untreated and treated paper sludge suggest distinct chemical compositions. O-H stretching and bending vibrations caused by hydrogen-bonded hydroxyl (OH) groups in cellulose are accountable for the peaks at 3290 cm^{-1}, 3066 cm^{-1}, 3000 cm^{-1}, and 2918 cm^{-1} regions (Burhani et al., 2022). Peak attributed to CH_2 and CH_3 of lignin at 1425 cm^{-1} (Burhani et al., 2022) subsidies. Two peaks emerged after chemical treatment at 1380 cm^{-1} (Yu et al., 2021) and 1453 cm^{-1} (Mohammad et al., 2020), attributed to the CH_2 bending motion in cellulose. In contrast, the peak attribute to hemicellulose and cellulose appears at 1176 cm^{-1} (Hasanin et al., 2021). A new peak also formed after chemical treatment at 895 cm^{-1} points to cellulose (Vasu et al., 2021), while a rise at 868 cm^{-1} indicates the amorphous phase of raw paper sludge disappeared after chemical treatments (Vilarinho et al., 2021).

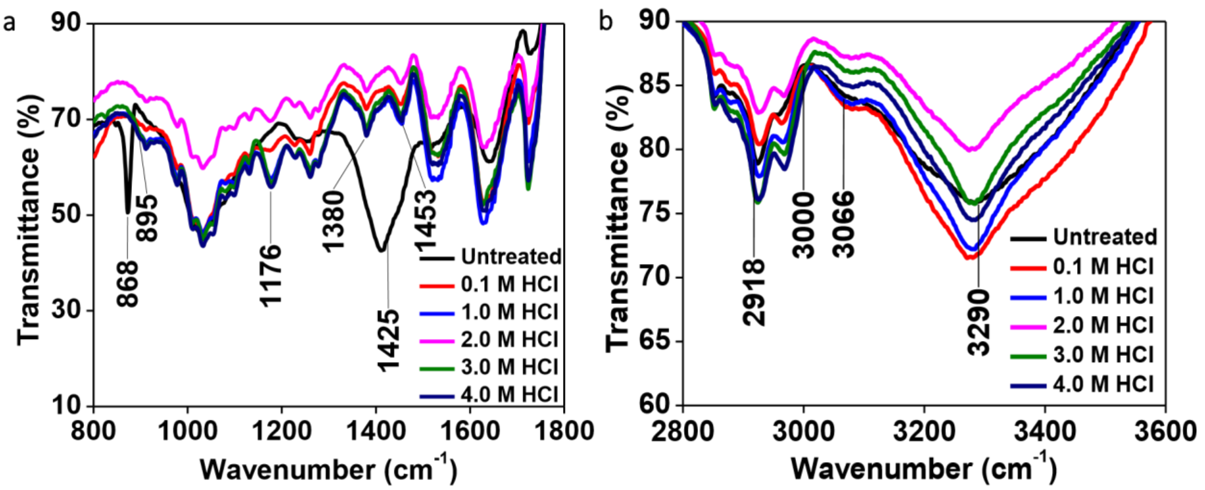

Fig. 1: FTIR spectra of untreated and treated (0.1 M, 1.0 M, 2.0 M, 3.0 M, and 4.0 M) paper sludge in different wavelength ranges, (a) 800-1800 cm^{-1}; (b) 2800-3500 cm^{-1}

3.2 Morphology analysis

A scanning electron microscope was used to examine the surface micromorphology of raw paper sludge and hydrochloric acid-treated paper sludge at different concentrations (SEM). The morphologies of raw paper sludge, 0.1 MCC, 1.0 MCC, 2.0 MCC, 3.0 MCC, and 4.0 MCC, are shown in figure 2. Untreated paper sludge has surface impurities (Dhote et al., 2021). The shape of the treated paper sludge is smaller and asymmetrical after hydrochloric acid treatment. The cellulose diameters of the 0.1 MCC, 1.0 MCC, 2.0 MCC, 3.0 MCC, and 4.0 MCC samples were 68, 58, 51, 40, 30, and 43 μm, respectively. The diameter of the cellulose will influence the bonding side of cellulose reinforcement.

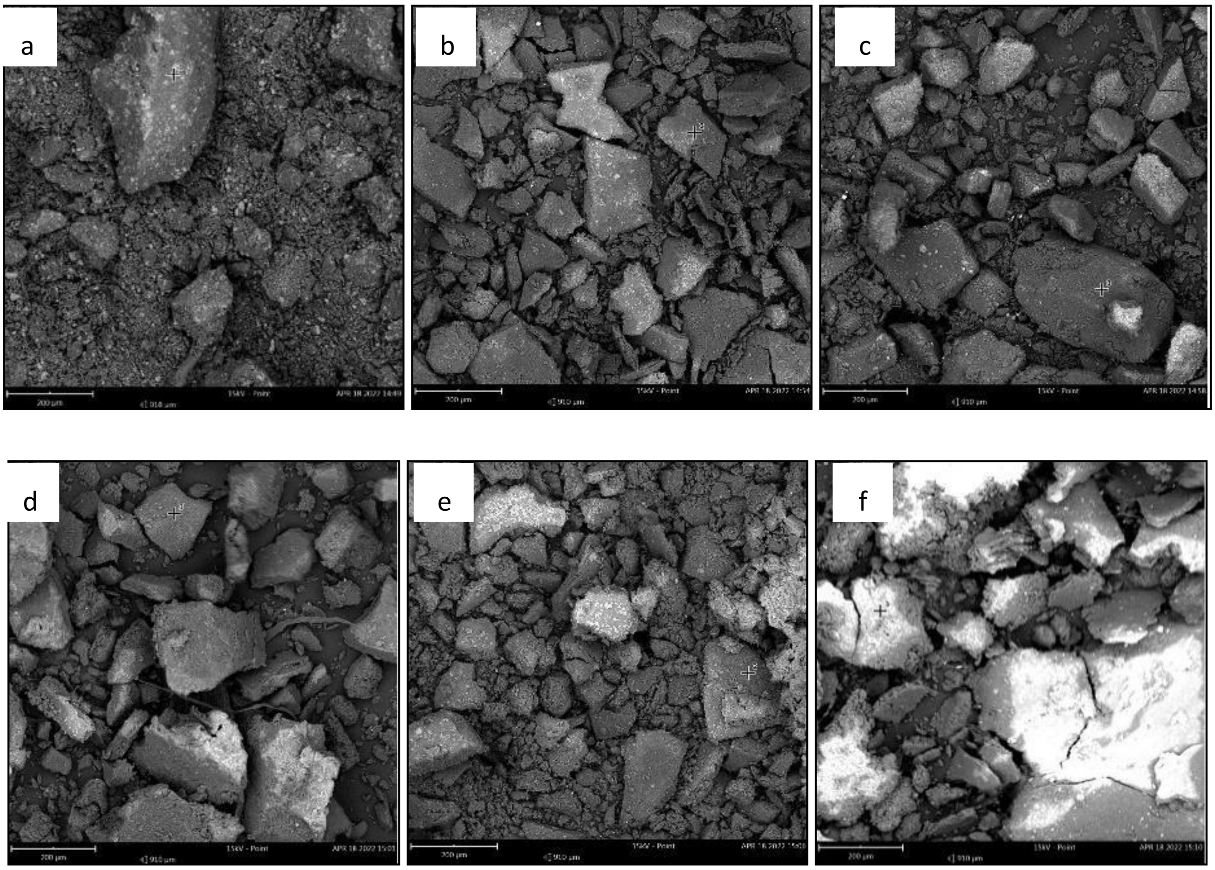

Fig. 2: SEM images of (a) raw paper sludge, (b) 0.1 MCC, (c) 1.0 MCC, (d) 2.0 MCC, (e) 3.0 MCC, (f) 4.0 MCC

3.3 Thermal stability analysis

The thermal weight loss temperature of treated paper sludge, as can be shown in figure 3, is around 266°C. The slight weight loss that occurs before the temperature reaches 266°C is primarily caused by the evaporation of moisture trapped by the surface. In contrast, the raw paper sludge's thermal weight loss temperature is around 233°C, and there is significant thermal weight loss under 233°C. The oxidation level affects the treated paper sludge's thermal performance. Furthermore, raw paper sludge drops intensively at high temperatures, which harms its thermal properties.

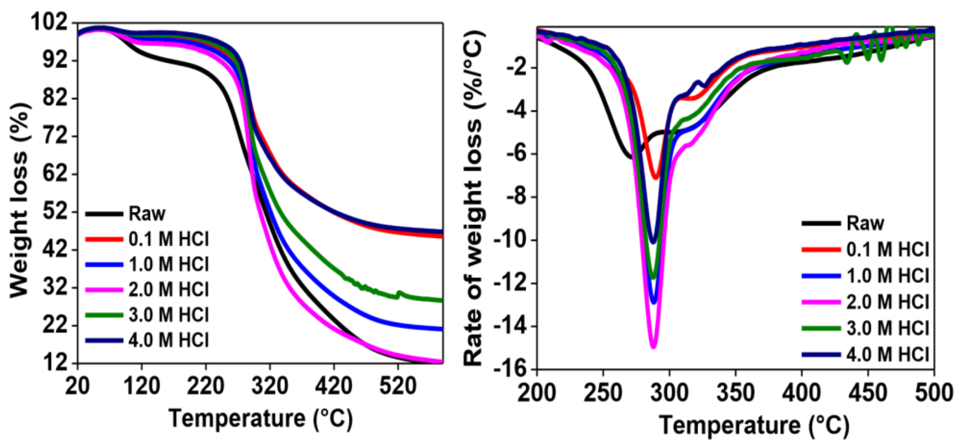

Fig. 3: The TG/DTG curves for pyrolysis of untreated and treated paper sludge obtained at different hydrochloric acid concentrations

3.4 Reflectance analysis

The thermal weight loss temperature of treated paper sludge, as can be shown in figure 3, is around 266°C. The slight weight loss that occurs before the temperature reaches 266°C is primarily caused by the evaporation of moisture trapped by the surface. In contrast, the raw paper sludge's thermal weight loss temperature is around 233°C, and there is significant thermal weight loss under 233°C. The oxidation level affects the treated paper sludge's thermal performance. Furthermore, raw paper sludge drops intensively at high temperatures, which harms its thermal properties.

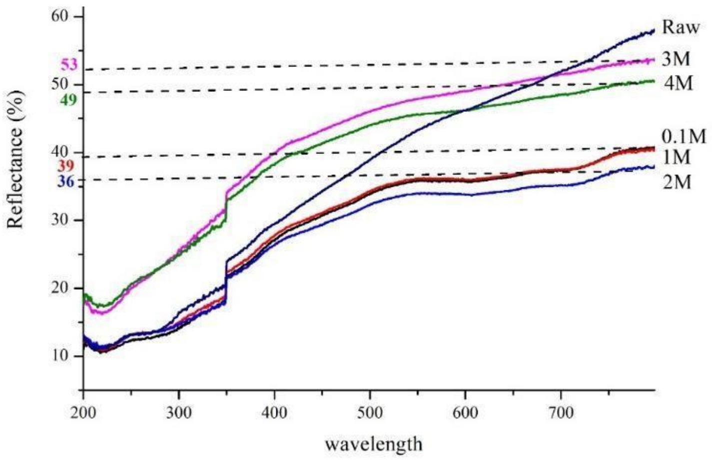

Fig. 4: UV-vis reflectance curves of untreated and HCl treated (0.1 M, 1.0 M, 2.0 M, 3.0 M, and 4.0 M) paper sludge

3.5 Crystallinity analysis

Figure 5 depicts the XRD curve and crystallinity index for untreated and treated paper sludge samples. XRD spectra of hydrolyzed paper sludge with various concentrations of hydrochloric acid show standard cellulose spectra at 2θ=18° and 21°. Compared to the diffraction patterns of treated paper sludge, the XRD pattern of raw paper sludge has no prominent peak. The concentration of HCl in the hydrolysis process influenced cellulose crystallinity. At 3 M of HCl concentration, the crystallinity index reached 31%, the highest value. According to Mamat Razali et al. (2021), acid hydrolysis increases the accessibility of cellulose's amorphous components to hydronium ions, which leads to the hydrolytic cleavage of glycosidic connections and the release of individual crystallites. The lateral attachment of elementary monocrystals could produce a structure resembling a monolayer. This will increase the crystallinity of cellulose, as well as its strength, rigidity, and stiffness.

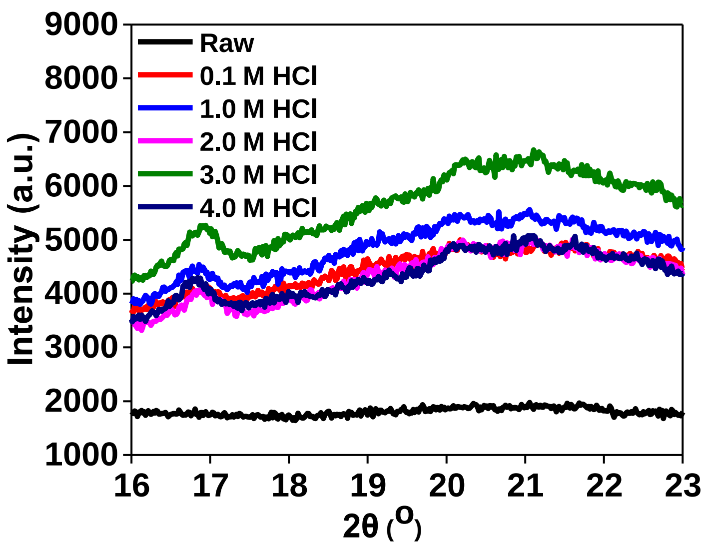

Fig. 5: The XRD patterns of hydrolyzed paper sludge using various concentrations of HCl (0.1, 1.0, 2.0, 3.0, and 4.0 M)

4.0 Conclusion

In conclusion, the isolation of microcrystalline cellulose from paper sludge has been successfully performed. FTIR spectra of untreated and treated paper sludge showed some differences that confirmed the removal of the amorphous phase at 868 cm^{-1} and the presence of cellulose at 895 cm^{-1}, 1176 cm^{-1}, 1380 cm^{-1}, and 1453 cm^{-1}. SEM results demonstrate that treated paper sludge has fewer impurities and a size reduction to 30μm for 3.0 M HCl. Thermal degradation results show that treated samples have better thermal properties at 266°C than untreated samples at 233°C. 3.0 M reflects the highest UVB at 28% and UVA at 39% due to the strong monolayer of crystallites proven by the highest crystallinity index, 30.63 %. Findings in this work demonstrate that paper sludge has the potential for a cellulose source for reinforcement application.

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Paper Contribution to Eco-Materials and Products Field of Study

This paper contributes to the knowledge of possible application of paper sludge from wastewater treatment for greener waste management in relation to the eco-materials and products field of study.

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