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Physicochemical of microcrystalline cellulose from oil palm fronds as potential methylene blue adsorbents

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ABSTRACT

The present study sheds light on the physical and chemical characteristics of microcrystalline cellulose (MCC) isolated from oil palm fronds (OPF) pulps. It was found that the OPF MCC was identified as cellulose II polymorph, with higher crystallinity index than OPF α-cellulose (CrI_{OPFMCC}: 71% > $CrI_{OPF\alpha\text{-cellulose}}$: 47%). This indicates that the acid hydrolysis allows the production of cellulose that is highly crystalline. BET surface area of OPF MCC was found to be higher than OPF α-cellulose ($S_{BETOPFMCC}$: 5.64 $m^2\,g^{-1}$ > $S_{BETOPF\alpha\text{-cellulose}}$:$Q_a^0$ 2.04 $m^2\,g^{-1}$), which corroborates their potential as an adsorbent. In batch adsorption studies, it was observed that the experimental data fit well with Langmuir adsorption isotherm in comparison to Freundlich isotherm. The monolayer adsorption capacity (Q_a^0) of OPF MCC was found to be around 51.811 mg g^{-1} and the experimental data fitted well to pseudo-second-order kinetic model.

1. Introduction

The removal of textile dyes from wastewater has become an interesting topic for environmental chemists recently since it also considers the impact of these pollutants on the waters where they are discharged. Generally, the presence of textile dyes in waters can lead to problems related to flora and fauna development, occurrence of different by-products with carcinogenic effect formed by dyes degradation. The removal of these dyes is not always easy due to its complex structures, which make resistant to light, heat and biodegradation [1]. Some examples of wastewater treatment processes are ion exchange [2], chemical precipitation [3], chemical degradation [4], reverse osmosis [5], oxidation/chemical reduction [6], and adsorption [7].

Adsorption particularly stands out because of its high efficiency combined with low cost. It removes chemical pollutants, returning the natural transparency of the medium, and often enables reusing the reuse of the adsorbent. It is a process that is commonly reversible, where the regeneration of the adsorbent becomes possible, further cheapening the practice of this process, beside the use of natural waste in the trash [7,8]. The adsorption of natural low-cost adsorbents has been studied by many authors due to its effectiveness and environmental friendly; such example includes oil palm fronds [9], corn cob [10], sugarcane bagasse [11] and sawdust [12]. Currently, the utilization of cellulose based adsorbent has been studied by some authors [13–15] and it was revealed that cellulose can be recognized as an effective adsorbent for the decontamination of water.

Cellulose is a polydisperse polymer of high molecular weight and comprised long chains of D-glucose units joined together by β-1, 4-glucosidic bonds [16]. Cellulose has four different polymorphs, named cellulose I, II, III and IV. Cellulose II specifically is the crystalline form that appeared after re-crystallization or mercerisation with aqueous sodium hydroxide and it is thermodynamically the most stable crystalline form [17,18]. The dominant intra-chain hydrogen bond in cellulose II is O3-H–O5 which gives cellulose chain its rigid, linear shape. However the difference between cellulose I and cellulose II (Fig. 1) is that cellulose II has an anti-parallel packing and the inter-chain bonding is O6-H–O2 [19]. Even though crystalline cellulose is hydrophilic (due to the abundance of the

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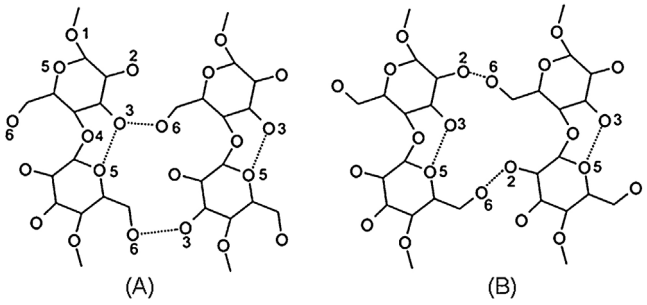

Fig. 1. The supramolecular structure of (A) cellulose I and (B) cellulose II [18].

hydroxyl groups) it does not dissolve in water [18]. Cellulose can be converted into smaller fragments, such as micro or nano sized cellulose and this have drawn intention for many researchers due to their prompt applications.

Microcrystalline cellulose (MCC) is a fine, white, odourless, crystalline powder and biodegradable material that can be isolated from α-cellulose. The isolation of microcrystalline cellulose particles can be done via mechanical treatments [20], biological treatments [21] and chemical treatments; for instance acid hydrolysis [22,23]. MCC has a high degree of crystallinity (as determined by X-Ray diffraction, XRD), typically from range 55 to 80% [24]. It was said that cellulose obtained from different origins and hydrolysis conditions would differ in their crystallinity, moisture content, surface area, porous structure, particle size and molecular weight [25,26]. Due to its excellent properties, MCC has generated much attention and interest during these few last decades in both academic and industrial fields. MCC has tremendous applications for examples as a direct compressor in development of tablets and soluble drugs in pharmaceutical field [27], a stabilizer, emulsifier in several dairy compounds [28], and a reinforcing agent in polymers [29]. So far, the isolation of MCC from oil palm biomass waste has only focus on empty fruit bunches (EFB) [22] and stalk and spikelet [30] without proper study especially from the other parts (like oil palm fronds and trunks).

Additionally, the utilization of OPF as adsorbent for heavy metal ions in waste water has been reported recently [9], but until now no researcher has propose the applicability of microcrystalline cellulose from OPF as dye adsorbent. Therefore, the aim of the present study is to study the physicochemical of MCC prepared from the Kraft-treated OPF pulp and their ability to adsorb dyes. The isolated α- cellulose and MCC were characterized using Fourier Transform Infrared Spectroscopy (FTIR), cross polarization magic angle spinning nuclear magnetic resonance (CP/MAS ^{13}C NMR) and X-ray diffraction (XRD) spectroscopy, gel permeation chromatography (GPC), thermal behaviour, N_2-adsorption desorption and scanning electron microscopy (SEM). The ability of OPF MCC as a potential methylene blue dye adsorbent was studied via batch adsorption method. Understanding the physicochemical properties of MCC extracted from OPF biomass would help find and optimize proper applications for MCC.

2. Materials and methods

2.1. Materials

The oil palm fronds (OPF) were obtained from the Valdor Palm Oil Mill near Sungai Bakap plantation (Seberang Prai, Malaysia) in mid 2014. The composition (% w/w) of the OPF according to TAPPI T203 om-09 and laboratory analytical procedure (LAP) method is cellulose 35.73 ± 1.34%, hemicelluloses 28.39 ± 1.34% and Klason lignin 24.62 ± 1.17% on a dry weight basis. It also contains sugars such as glucans 56.30 ± 3.20%, xylans 16.80 ± 0.60%, arabinans 0.90 ± 0.10%, mannans 0.90 ± 0.01% and galactans 0.40 ± 0.01%. The OPF leaves were removed and the strands were chipped into small pieces. After sun dried for 3 days, the chips were then ground to a 1–3 mm size using Wiley mill and the fiber was further dried in an oven at 50 °C for 24 h. The OPF biomass was first subjected to Soxhlet extraction with ethanol/toluene (2:1, v/v) for 6 h before use.

All chemical reagents used in this study were purchased from Sigma Aldrich, Merck, QRec (Malaysia) and VWR (France) and used as received. Dried matter contents were determined using a moisture balance, KERN MRS 120-3 Infra-red moisture analyzer (drying at 105 °C to constant weight). The effective dry matter content of raw OPF biomass was ~89%.

2.2. Kraft pulping and bleaching

Kraft pulping process was carried out in a 4 L rotary digester. For Kraft pulping, a 20% of active alkali and 30% of sulfidity was used (with solid biomass to liquid ratio of 1:8). The time of maximum cooking temperature (170 °C) was set for 3 h (severity factor: S_0 = ~3.64). The pressure for Kraft pulping was around 12–14 bar. The pulp was washed and separated by screening through a sieve and the black liquor was discarded.

Holocellulose was isolated from the untreated feedstock by repeatedly treating with a mixture of acetic acid and sodium hypochlorite until the sample had a very low Klason lignin content (<1%). For this purpose oven dried weight of 1.5 g of Kraft-treated OPF pulp was placed in 125 mL deionized water with the addition of 1 mL of glacial acetic acid and 1 g sodium chlorite. The reaction mixture was heated at 70 °C for 2 h with constant stirring [31]. The holocellulose was further filtered and washed with distilled water.

Around 4 g of dried holocellulose was stirred with 200 mL of 17.5% (wt) NaOH for 30 min at room temperature. After 30 min, 200 mL of distilled water were added into the solution and the mixture was stirred for 30 min at room temperature (28 ± 2 °C). The α-cellulose was further filtered and washed with 1% acetic acid and excess distilled water.

2.3. Microcrystalline cellulose preparation

The acid hydrolysis was performed using a method described by Chauchan et al. [32] and Hanna et al. [20] with slight modification. The α-cellulose of OPF from mercerization process was further treated with 2 M HCl. The ratio of solid to liquor (1:30, w/v) was applied. The mixture was stirred for 30 min at 105 °C. The microcrystalline cellulose was further filtered and washed with distilled water, followed by 5% (wt) NH_4OH and excess distilled water.

2.4. Characterization of cellulose

Fourier Transform Infrared (FTIR) spectra of commercial MCC (Sigma Alderich), OPF MCC and α- cellulose were carried out by Perkin Elmer System 2000 spectrometer using the KBr method. The spectra were recorded in transmittance band mode in the range of 4000–400 cm^{-1}. The spectra were recorded for 32 scans per sample.

Solid-state 13C cross polarization nuclear magnetic resonance (CP/MAS NMR) was carried out using a Bruker Avance 400 MHz spectrometer, operating at a frequency of 76.46 MHz with external reference standards of tetramethylsilane. The samples were pressed into cylindrical zirconia rotors and spun at magic angle at 7 kHz. The spectra were acquired using a spectra width of 30 kHz, a single pulse length of 6 μs, a recycled delay of 3 s, acquisition time of 0.04 s, contact time of 3 ms. The spectra were recorded for 4000 scans. ^{13}C data were processed offline using XWinNMR processing software.