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Recovery of Rice Straw Cellulose on Pilot Scale for Fabrication of Aerogel for Oil/Water Separation

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Recently, bio-based materials that are both environmental-friendly and highly functional were synthesized from various waste and biomass. Rice straw, a by-product of paddy production, is abundant lignocellulosic biomass with high cellulose content. The utilization of this natural resource for high functional material often meets with difficulties due to a large amount of lignin and silica present in the material matrix. While rice straw has been employed for biofuel production on pilot scale, its use for cellulose recovery has only been performed in laboratory-scale equipment. Here we show a simple process to effectively recover cellulose from rice straw on a pilot scale, after which the extracted cellulose was used for the preparation of aerogel. The alkali pretreatment removed the majority of lignin and silica, yielding semi-product with cellulose content of 73 %, then the bleaching step with hydrogen peroxide further eliminated colored impurities to increase the cellulose content to 90 %. The obtained cellulose was then employed to fabricate cellulose aerogel with low density, high surface area, and porous structure, which showed a good performance in the separation of oil and water, with the maximum capacity reaching 21.7 g/g. The process is a promising solution for converting rice straw into a more valuable product for water treatment on a larger scale.

1. Introduction

Among the hazards that damage marine life, oil spills during production and transportation are considered one of the most severe. Oil leakages have caused significant loss of energy resources and threatened aquatic ecosystems as well as human health (Leng et al., 2021). Several synthetic materials and chemicals have been studied for the removal of oil from water, and one emerging trend in recent years is aerogel (Doshi et al., 2018). Due to its ultra-light density, high porosity, nontoxicity, biocompatibility, and biodegradability (Nguyen et al., 2021), aerogel presents itself as a potential material in catalysis, pollutant removal, thermal insulation, biomedicine, and many other fields (Liu et al., 2021). Aerogel can be prepared from various sources including silica, carbon, graphene, cellulose fiber, etc., in which cellulose aerogel has gained considerable attention as a bio-based and cost-effective type of material (Leng et al., 2021).

With the constantly growing population, it is essential to enhance the production of food crops, especially rice crop which accounts for nearly half of the world's energy need (Singh et al., 2021). With almost 1,600 billion m^2 of cultivated area and 770 Mt produced every year (FAO, 2018), the huge amount of leftover rice straw has also raised concerns about its environmental impacts. Only a small part is valorized for fuel, livestock feed, fertilizer, etc. (Goodman, 2020), while the remaining is usually open-burned in the field after harvest. The consequences of the extensive burning have attracted much attention of experts to discover a more effective route to utilize this abundant waste source for more valuable materials. Up to now, there have been several studies on pilot scale conversions of rice straw into glucose (Thanh et al., 2021), bioethanol using chemical (Le et al., 2022)

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and physicochemical method (Chen et al., 2013), or biogas through anaerobic digestion (Muhayodin et al., 2020).

Cellulose occupies a large proportion of rice straw mass (up to 44 %) and need to be isolated for further use (Paul and Dutta, 2018). To do so, various methods have been employed, including physical, chemical, physicochemical, and biological pretreatment (Chen et al., 2017). In the case of rice straw, due to the large amount of lignin and silica in the material matrix, chemical treatments have been used to effectively recover cellulose, which commonly involve alkali treatment, organic solvent extraction (Zhao et al., 2019), and/or prolonged chlorine bleaching (Jiang et al., 2013), in which the last two present as a barrier in scaling up the process.

Rice straw is an abundant cellulose-rich agricultural waste, and while the isolation and utilization of cellulose from rice straw have been widely studied for materials to remove organic solvent (Dilamian and Noroozi, 2021) or oil (Huynh et al., 2018), reports on a larger scale are still rare. This work aims to recover cellulose from rice straw on a pilot scale for the fabrication of aerogel. The facile and feasible process successfully yielded material with low density, high porosity, and good performance in separating oil from water.

2. Materials and methods

2.1 Materials

Rice straw was collected in An Giang Province, Vietnam. All the reagents, including sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), polyvinyl alcohol (PVA), and methyltrimethoxysilane (MTMS) were purchased from commercial suppliers and used without further purification.

2.2 Cellulose recovery and enrichment from rice straw

A pilot-scale reactor with the capacity of 100 L was employed to isolate cellulose from rice straw. A total of 5 kg of dried, grinded rice straw was pretreated with a 1 wt% solution of NaOH, solid-to-liquid ratio of 1/20 (g/mL) at 80 °C in 120 min. Pretreated rice straw was subsequently treated with NaOH 6 wt%, solid-to-liquid ratio of 1/25 at 80 °C in 90 min under constant stirring at 150 rpm. The obtained solid was filtered and washed until reaching neutral pH. After that, the rice straw was dried and bleached using a solution containing 10 wt% of H_2O_2 and 0.25 wt% of NaOH, solid-to-liquid ratio of 1/20 (g/mL). The bleaching was carried out at 80 °C in 45 min under constant stirring (150 rpm). Afterwards, the solid was filtered and washed until reaching neutral pH, then dried to yield white cellulosic material.

2.3 Cellulose aerogel preparation

Bleached rice straw fiber was used to fabricate cellulose aerogel. The fiber was dispersed in a 0.2 wt% PVA solution with the solid/liquid ratio of 1/50 (w/w). The mixture was sonicated for 15 min, followed by incubation at 80 °C for 3 h. The sample was then frozen at -5 °C for 24 h before undergone freeze-drying process to form rice straw cellulose aerogel. After that, the freeze-dried samples were placed in a box containing an open vial of MTMS inside. The box was tightly capped and incubated in an oven at 80 °C for 8 h. Finally, the samples were put under vacuum to remove excess MTMS.

2.4 Analysis techniques

Crystallinity of the samples was determined through X-ray diffraction (XRD) patterns, which were collected using D8 Advance Bruker powder diffractometer with Cu-Kα1 radiation (λ = 1.5418 Å), operated with a Ni filter at 40 kV and 40 mA, scanning range 2θ = 5 – 80° and step size 0.02°. Fourier transform infrared spectroscopy (FTIR) results were recorded on a Bruker Alpha II spectrometer at a resolution of 4 cm^{-1} in the 4000 – 500 cm^{-1} range. Morphology of the aerogel sample was captured by scanning electron microscopy (SEM) using a Hitachi S-4800 at an accelerating voltage of 10 kV. The density of the aerogel (ρ_a, mg/cm^3) was determined by dividing the mass by the volume of the sample, in which the mass and the volume were measured with an analytical balance (resolution of 0.1 mg) and a digital caliper (resolution of 0.01 mm). The aerogel porosity (P, %) was calculated according to Eq(1):

$$\text{Porosity}(\%) = \left[1 - \frac{\rho_a}{\rho_s}\right] \times 100 \tag{1}$$

where ρ_a is the density of aerogel, and ρ_s denotes the bulk density of the composite as given by Eq(2):

$$\rho_a = \frac{1}{\frac{w_{cellulose}}{\rho_{cellulose}} + \frac{w_{PVA}}{\rho_{PVA}}} \tag{2}$$

where $w_{cellulose}$ and w_{PVA} are weight fraction of cellulose and PVA. The bulk density of PVA (ρ_{PVA}) is assumed as 1.19 g/cm^3, while that of cellulose ($\rho_{cellulose}$) is taken as 1.6 mg/cm^3 (Dilamian and Noroozi, 2021).

2.5 Oil adsorption study

Oil adsorption experiments were conducted at room temperature. The adsorption capacity of the prepared aerogel was determined using Eq(3), where Q (g/g) is the maximum trapping capacity, m_1 (g) is the dry weight of aerogel sample before adsorption, and m_2 (g) is the final weight of the sample after adsorption experiment.

$$Q = \frac{m_2 - m_1}{m_1} \tag{3}$$

3. Results and discussion

3.1 Cellulose recovery from rice straw

The appearances of raw rice straw and samples after chemical treatment steps in Figure 1 show that the color of the fiber lightened gradually, which proves the effectiveness of these steps in liberating rice straw from lignin and other impurities. The alkali treatment removed the majority of lignin and a part of hemicellulose, then the chlorine-free bleaching step attacked the colored matters, which turned the fiber from light brown to white. The material obtained after bleaching was analyzed using NREL procedure (Sluiter et al., 2008) and the result showed that cellulose content was over 90 %. The chemical structure of the cellulose obtained was analyzed using FTIR (Figure 2a). All the spectra showed bands at 3,300 cm^{-1}, corresponding to the stretching of O-H, and 2,900 cm^{-1}, signalling C-H bonds of the cellulose. The band at around 1,600 cm^{-1}, corresponding to the vibrational stretch C=O in hemicellulose, while the one at around 1,500 cm^{-1} demonstrates the presence of lignin (aromatic C=C vibrational stretch) (Huynh et al., 2018). These bands are more visible in raw rice straw and sample after 1st alkalization than in those after 2nd alkalization and bleaching, which confirmed the successful removal of the majority of hemicellulose and lignin from raw rice straw.

Raw rice straw　After 1st alkali treatment　After 2nd alkali treatment　After bleaching

Figure 1: Rice straw appearance after chemical treatments

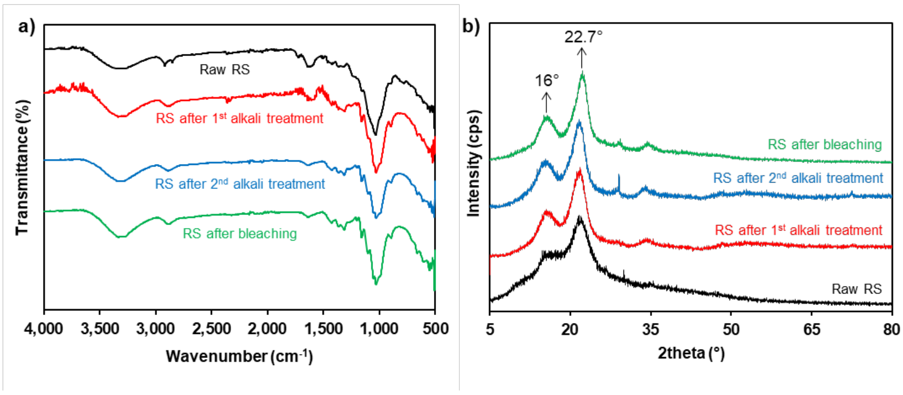

Figure 2: (a) FTIR spectra, and (b) XRD patterns of raw rice straw and samples after treatments

XRD analyses were performed to explore the crystalline structure of the samples at different treatment stages, with the patterns obtained in Figure 2b. All the patterns exhibit peaks at 2θ=16° and 22.7°, which are characteristic for cellulose (1 1 0) and (2 0 0) crystal planes (Jiang and Hsieh, 2013). The patterns of samples after treatments shows more intense and narrow signals, while those of raw rice straw are broader and less defined, a clear indication of lower crystallinity. The degree of crystallinity of the sample was also determined using crystallinity index (CrI), calculated using a previously suggested method (Segal et al., 1959). The CrI of rice straw was enhanced with chemical treatments, from 46.7 % in raw rice straw to 69.8 % in bleached sample (Table 1). These results were in agreement with previous studies and confirmed the effectiveness of the pilot-scale process in isolating cellulose from rice straw with a capacity of 1.1 kg per batch.

Table 1: Crystallinity index of raw rice straw and treated samples

Sample	Crystallinity index (CrI)
Raw rice straw	46.7 %
After 1st alkali treatment	62.6 %
After 2nd alkali treatment	64.4 %
After bleaching	69.8 %

3.2 Cellulose aerogel preparation and its oil adsorption performance

The aerogel samples were prepared using rice straw-derived cellulose and PVA as crosslinkers (Figure 3a), with its formation mechanism described in Figure 4a according to previous studies (Thai et al., 2020). The morphology of the cellulose aerogel was captured by SEM (Figure 3b), revealing a 3D network with pores distributing throughout its structure. The aerogel also displayed low density of 0.0286 g/cm^3 and high porosity of 98 %, facilitating its application in adsorption experiments. Figure 3c shows the hydrophobicity of the aerogel with high water contact angle of 140° after modified with MTMS using chemical vapor deposition method. The mechanism for this modification (Figure 4b) has been well described in previous literature (Rong et al., 2021). Particularly, the silanol groups (generated from MTMS under the presence of moisture) react with the hydroxyl groups of PVA and cellulose. Subsequently, the deposition of MTMS on the sample surface acts as a hydrophobic shield for the aerogel by forming polysiloxane layers with water-resistant Si-CH_3 groups and stable Si-O-Si bonds (Tran et al., 2020).

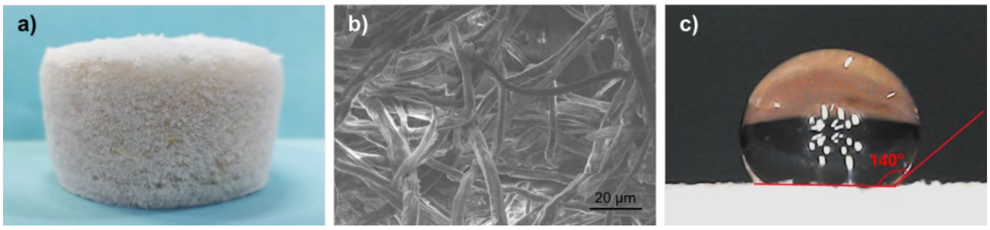

Figure 3: (a) Picture of freeze-dried rice straw cellulose aerogel, (b) SEM image of aerogel sample, and (c) water contact angle of MTMS-coated sample

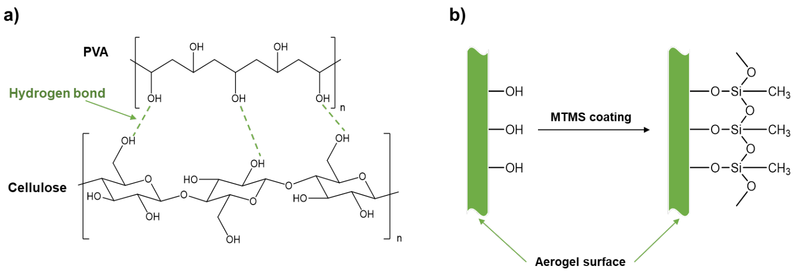

Figure 4: (a) PVA-cellulose formation mechanism, and (b) MTMS coating mechanism

To investigate the ability to separate oil from water of rice straw cellulose aerogel, experiments with aerogel submerged in engine oil/water mixture were carried out. As can be seen from Figure 5a, the hydrophobic and porous structure of the aerogel sample facilitated the effective adsorption of oil in aqueous environment. According to the results obtained in Figure 5b, the maximum capacities for 5W-30, 10W-40 engine oil, and n-hexadecane were 20.7, 20.9, and 21.7 g/g, relatively. It can be seen that the adsorption occurred rapidly with the equilibrium achieved after 30 s for engine oils and 5 s for n-hexadecane. The differences might be explained by the viscosity, as n-hexadecane has significantly lower viscosity compared to engine oils, and higher viscosity resulted in harder diffusion of oil into aerogel pores, which also explained for the faster uptake of n-hexadecane (with significantly lower viscosity compared to engine oils). The reusability of the prepared aerogel samples was also tested. After each cycle, the sample was hand-pressed to release as much adsorbed oil as possible, then submerged in oil for another 5-min cycle. The results in Figure 5c shows that there was a significant drop in adsorption capacity after the first use, which was likely due to the structure collapse caused by external force. Works to increase the compressive strength and flexibility of aerogel will be mentioned in our future study. This is to improve the reusability of the material as the material should be able to restore its original shape after being pressed to release the adsorbed oil.

Compared to previous studies on laboratory scale to obtain rice straw aerogel (Tran et al., 2020) or rice straw cellulose aerogel (Huynh et al., 2018), the pilot-scale cellulose isolation process successfully produced aerogel with comparable properties and slightly higher oil adsorption Although the capacity of rice straw cellulose aerogel was relatively lower than some other reported materials (polyurethane composites – 24 g/g (Martins et al., 2021), carbon foams – 30.3 g/g (Qu et al., 2017), etc.) the facile pilot-scale production and waste utilization make it a promising candidate for industrial application.

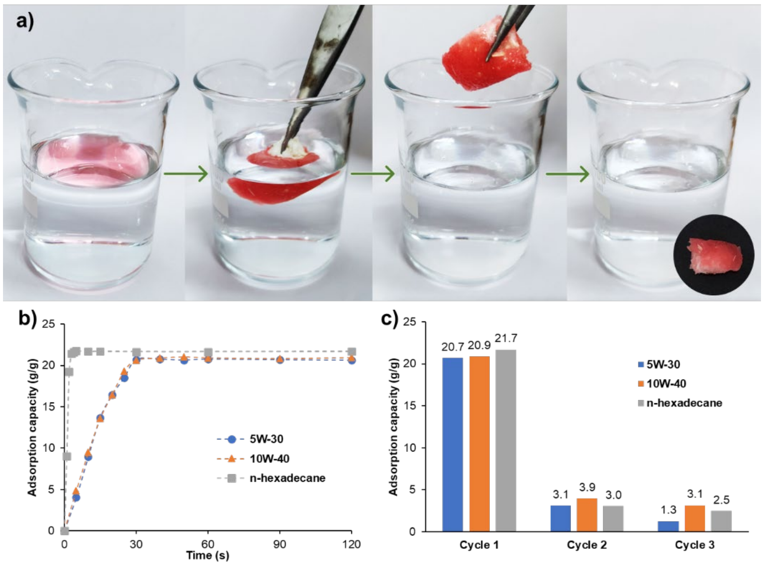

Figure 5: (a) Oil/water separation experiment, (b) adsorption capacity of rice straw cellulose aerogel over time, and (c) recycling experiments

4. Conclusions

In this study, cellulose was successfully recovered from rice straw in a 100-L pilot-scale reactor. The facile process yielded 1.1 kg of cellulose per batch, which was then employed to prepare cellulose aerogel. The fabricated low-density material performed well in adsorbing oil from an oil/water mixture, with maximum capacity of 20.7-21.7 g/g. In general, this study presented a feasible way to scale up the isolation of cellulose from an abundant agricultural waste. Future research involves improving the mechanical strength, reusability, and adsorption capacity of aerogel; investigating the influencing factors of the oil trapping process; and upscaling the experiments. Overall, this would be a promising solution in reducing waste and mass production of environmental-friendly materials.

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