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Fabrication of Cellulose Aerogel from Waste Paper and Banana Peel for Water Treatment

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Industrialization and urbanization have led to water pollution. Pollutants such as metals, oils, and organic dyes can cause serious harm to the environment and human health. Adsorption has been proposed as a suitable method for removing contaminants thank to its efficiency, low cost, and simple operation. In this study, the aerogel from banana-derived biomass, paper waste, and polyvinyl alcohol has been successfully fabricated using a freeze-drying process for water treatment. The physico-chemical properties including morphology and chemical structures of the obtained aerogel were characterized by scanning electron microscope, Fourier-transform infrared spectroscopy, and thermogravimetric analysis. The fabricated aerogels have low density of 0.0235-0.0297 g/cm^3 and extremely high porosity of 97.87-98.37 %. These aerogels exhibit great capability in oil absorption (27.27-32.86 g/g), in methylene blue adsorption (4.23-6.69 mg/g), and in Cu^{2+} adsorption (61.68-85.45 mg/g). Hence, this type of aerogel is a promising candidate that can be applied for water treatment.

1. Introduction

The demand for water treatment has increased rapidly due to rising sources of contaminants from industrial and agricultural activities as well as from the lack of awareness among citizens (Nishil et al., 2018). With the growth of the petroleum industry and the necessity of marine oil transportation, oil spills have become one of the most important threats to the water ecosystem (Nguyen et al., 2014). Organic dyes are also pollutants in wastewater due to the development of textile and garment industry in recent years (Luo et al., 2021). Indeed, oils, organic dyes and heavy metal ions from sewage or effluent are discharged directly into the environment, causing an ecological imbalance, severe pollution, and serious diseases. Numerous methods such as adsorption, filtration, oxidation, electrochemistry, and ion exchange have been studied for improving wastewater treatment. Among these techniques, adsorption has attracted much attention for its high efficiency, facile operation and low cost (Hasanpour et al., 2020). The low-cost adsorbent materials from agricultural and industrial by-products such as waste paper, straw, peanut shells, fly ash, sugar cane, rice husks, 3D porous structure etc. have been developed and tested to effectively remove contaminants from wastewater (Hasanpour et al., 2020). Aerogel, a novel material with outstanding physical properties including super low density, high porosity, ultra low thermal conductivity,.etc has gained tremendous interest for wide applications, especially in wastewater treatment (Maleki, 2021). Cellulose aerogels from various sources of agricultural wastes, industrial wastes have been investigated for application in solving environmental issues. In recent years, cellulose aerogel from waste paper has been investigated as the alternative method for reducing the office paper waste due to its high cellulose content. In fact, office paper waste can only be recycled at 2.4 times on average in pulp production as its durability decreases within each recycling process (Zhang et al., 2015). The expansion in technical applications to convert paper waste into valuable products has attracted much interest. Waste paper aerogel obtained by using freeze-drying method showed the highest oil adsorption capacity of 24.4 g/g and can be utilized in the diaper industry because of its biodegradation (Nguyen et al., 2013). Beside, the amount of pectin and proteins contained in banana peel can create a strong structure. The low cost of banana peel makes it a potential precursor to reduce cost of the process.

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In our study, the aerogel from waste paper, banana peel, and polyvinyl alcohol has been fabricated by freeze-drying method. The obtained aerogel exhibits super high porosity, low density, high capacity of adsorption oils and heavy metal. Hence, our work can add value for waste products as well as can solve current environmental issues.

2. Experiments and methods

2.1 Materials

Office waste paper obtained from Ho Chi Minh University of Technology was prepared. Cavendish banana peels (BP) were bought in Co.opmart supermarket in Ho Chi Minh City, Vietnam. Polyvinyl alcohol was purchased from Shanghai Zhanyun Chemical Com, Ltd.. Sodium hydroxide, hydrogen peroxide and hydrochloric acid were supplied by Xilong Scientific Co., Ltd.. Motor oil 10w30 was purchased from Asian Honda Motor Co., Ltd., and soybean oil was purchased from Co.opmart supermarket. Methylene Blue Hydrate was purchased from Sigma - Aldrich. Cu^{2+} was derived from Copper (II) nitrate trihydrate obtained from Xilong Scientific Co., Ltd.

2.2 Synthesis of pretreatment materials

The office watse paper was cut into small pieces, 4 g of these cut papers were then put into 250 mL HCl solution 1 wt% at room temperature within 24 h. Then, the mixture was stirred for 2 h to disperse the paper. The solid was filtered and washed with distilled water until the pH = 7, then was dried at 60 °C within 24 h to obtain pre-treated waste paper.
Banana peel was cut at both ends, then dried to reduce the amount of water and ground into powder. 2 g of banana peel powder was bleached by 200 mLH_2O_2 solution 1 wt%, adjusted to pH = 11 by NaOH and stirred at 50 °C for 2 h. Later, the solid was filtered and washed until pH = 7 with distilled water. Then it was dried at 60 °C within 24 h to obtain the pre-treated banana peel.

2.3 Preparation of waste paper - banana peel aerogel (WPBP aerogel)

1 g of pre-treated waste paper and 0.5 g of pre-treated banana peel were mixed with water, then added polyvinyl alcohol into the mixture of pre-treated waste paper and pre-treated banana peel with the mass ratio as 1:3, 1:6, and 1:12 corresponding to WPBP1, WPBP2, and WPBP3 aerogel. The mixture was stirred for 1 h at 40 °C, then was kept at room temperature for 30 min. The gel was stored in the refrigerator for 24 h and then freeze-dried for 48 h at -40 °C to obtain WPBP aerogel.

2.4 Characterizations

The porosity, φ (%) of aerogels was calculated by Eq(1) and Eq(2) (Feng et al., 2015):

$$\varphi = \left(1 - \frac{\rho_{\text{aerogel}}}{\rho_{\text{bulk}}}\right) \times 100 \tag{1}$$

$$\rho_{\text{bulk}} = \frac{x_{cellulose} + x_{banana\ peel} + x_{PVA}}{\frac{x_{cellulose}}{\rho_{\text{cellulose}}} + \frac{x_{banana\ peel}}{\rho_{banana\ peel}} + \frac{x_{PVA}}{\rho_{PVA}}} \tag{2}$$

where ρ_{aerogel} (g/cm^3) is the density of aerogel and ρ_{bulk} (g/cm^3) is the average density of ingredients in Eq(2). $\rho_{\text{cellulose}}$, $\rho_{banana\ peel}$, and ρ_{PVA} are the density of cellulose, banana peel and PVA. $x_{cellulose}$, $x_{banana\ peel}$, and x_{PVA} are the ratio mass of cellulose, banana peel and PVA.
The morphology of the aerogels was scanned by using a scanning electron microscope (FE-SEM S-4800, Hitachi, Tokyo, Japan). The functional group of aerogel was observed by Fourier transform infrared spectroscopy spectra (InfraRed Bruker Tensor 37, USA). The changes in the weight of aerogel due to increasing temperature was analyzed in thermogravimetric analysis in air in the temperature range of 30 – 800 °C (TGA/DSC3 + LF, Mettler, Toledo, Switzerland).
The mechanical strength of the material was determined by measuring on an M350-10CT Testometric (UK). Aerogel sample of a rectangular shape with defined dimensions is placed between two square metal plates of 5 cm side. The aerogel was compressed at a rate of 1 mm/min by the force of 500 N. Stress and strain curves are plotted using the obtained data.

2.5 Adsorption methods

2.5.1 Adsorption of motor oil and soybean oil

The obtained aerogel was coated with a hydrophobic layer to create hydrophobicity for the aerogel. Methyltrimethoxysilane (MTMS) is the hydrophobic compound used in this study because of its simple process

and it has been used extensively in previous studies. The samples are placed in a large glass container, the MTMS contained in a small beaker is also placed in the box. Then cover the container and place in the oven at 70 °C for 24 h. The coated sample was placed in a vacuum cabinet to remove residual MTMS and used in an oil adsorption experiment.
The oil adsorption capacity of the aerogel was determined based on the method ASTM F726 - 06 (Nguyen et al., 2013). The two oils used for adsorption are 10W30 motor oil (244.9 cP at 25 °C) and soybean oil (5.6 cP at 25 °C) . The aerogel was weighed and placed in a 250 mL becher containing 100 mL of oil for a certain period of time. Then, the wet sample was removed from the liquid and allowed to drain the surrounding excess oil for one minute. The survey experiment was performed several times. The amount of oil adsorbed by the aerogel was calculated, as shown in Eq(3):

$$Q_t = \frac{m_w - m_d}{m_d} \tag{3}$$

where Q_t (g/g) is the oil adsorption after the time t (second), m_d (g) is the first mass of the aerogel before adsorption, m_w (g) is the mass of aerogel after adsorption. Through the surveying time points, the maximum amount of oil adsorbed was calculated when the weight of the aerogel after adsorption is unchanged.

2.5.2 Adsorption of Dye and Cu^{2+}

The dye adsorption capacity of the aerogel was determined by measuring the concentration of methylene blue (MB) in MB solution after each defined time interval since the aerogel sample started to adsorb. The study was started by putting the sample into 100 mL MB solution 4 ppm and shaking the solution 150 rpm. The concentration of MB solution was determined by using the Spectro UV-VIS RS UV-2502 Spectrophotometer (USA) at 664 nm.
The Cu^{2+} adsorption capacity of the aerogel was determined by measuring the concentration of Cu^{2+} solution after each defined time interval since the aerogel sample started to adsorb. The study was started by putting the sample into 500 mL MB solution 100 mg/L and shaking the solution 150 rpm. The concentration of Cu^{2+} solution was determined by using the AAS Perkin Elmer AAnalyst 300 (USA).
The equilibrium adsorption (Q_e) was calculated using Eq(4) :

$$Q_e = \frac{(C_0 - C_e).V}{m_0} \tag{4}$$

where V (L) is the volume of solution used for adsorption, C_0 (mg/L) is the initial concentration, C_e (mg/L) is the equilibrium concentration of solution, m_0 (g) is the mass of aerogel.

3. Result and discussion

3.1 Morphology and properties of the WPBP aerogels

The density and porosity of the aerogels with different PVA concentrations are showed in Table 1.

Table 1: Material components (mass ratio), density, porosity and the Young's modulus of WPBP aerogel

Sample	Waste paper	Banana peel	PVA	Density (g/cm^3)	Porosity (%)	Young's modulus (kPa)
WPBP1	8	4	1	0.0235±0.0008	98.37±0.06	731±3
WPBP2	8	4	2	0.0256±0.0011	98.19±0.08	813±4
WPBP3	8	4	4	0.0297±0.0012	97.87±0.09	906±4

In Table 1, the WPBP aerogels have low density (0.0235-0.0297 g/cm^3) and high porosity (97.87-98.37 %), which are lighter and more porous than aerogel from waste paper (0.04 g/cm^3 and 97.3 %) (Nguyen et al., 2013). In the obtained aerogel, cellulose from waste paper is the main ingredient in banana peels strengthen the 3D skeleton structure of the aerogel. PVA, a semi-crystalline polymer that carries many hydroxyl groups, is added as a binder to form hydrogen bonds with cellulose. Cellulose with a large number of hydroxyl groups (-OH) in the molecule combined with the hydroxyl groups in PVA to form hydrogen bonding. The higher the amount of PVA, the greater the ability to create cross-links, and the stronger the gel system is. Polymers and polysaccharides such as hemicellulose and banana peel proteins are added to enhance the structural strength of the sample. We observe the increasing in compressive Young's modulus in accordance with the increasing of PVA. The trend of density and porosity of these aerogels is represented in Figure 1a.
In Figure 1a, it can be seen clearly that when PVA decreases, the density of aerogel increases and the porosity increases. We obtained the lowest value of density (0.0235±0.0008 g/cm^3) and the highest porosity (98.37±0.06

%) for WPBP1 aerogel. In Figure 1b, the compression strength analysis of aerogel has been performed on samples with different PVA ratios. The compressive Young's modulus of WPBP aerogels is higher than hybrid coffee-cotton aerogels (5.41-15.62 kPa) (Zhang et al., 2019), and cellulose-based aerogels from sugarcane bagasse (88 kPa) (Thai et al., 2020).

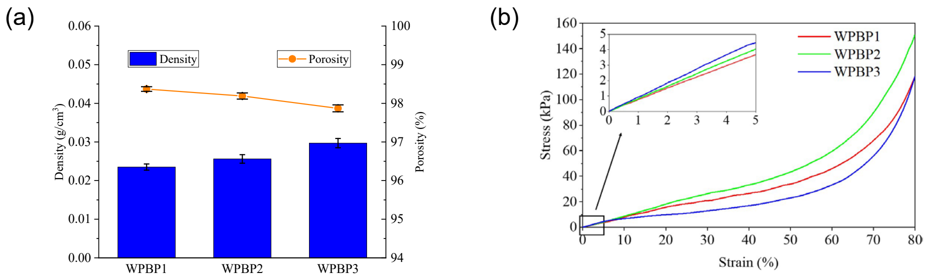

Figure 1: (a) Density and porosity of obtained aerogels with (b) stress – strain curves

The morphology and features of the WPBP sample is shown in Figure 2. In Figure 2a, by SEM technique, the morgolophy of WBPB aerogel can be observed. Through the raw material pretreatment processes, lignin and hemicellulose were largely removed, and cellulose aerogel can be seen as a highly porous structure with holes formed. As the amount of PVA increased, more adhesion sites between the cellulose fibers appeared. In addition, increasing PVA content leads to the occupation of more space inside the aerogel, reducing its porosity.

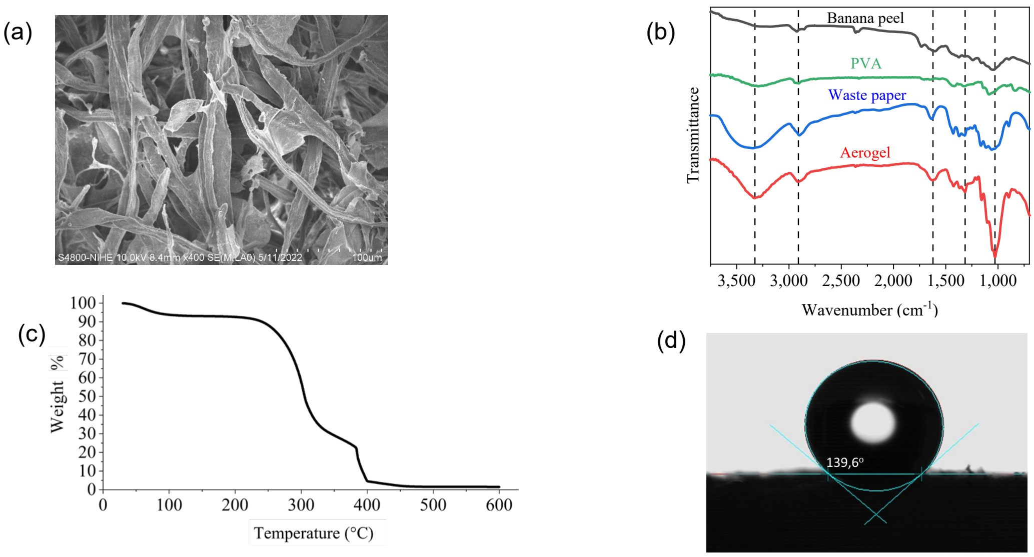

Figure 2: Morphology and properties of WPBP2 aerogel: (a) SEM image: the network of components in aerogel, (b) FT-IR of aerogel and its pre-treated starting materials, (c) TGA analysis of WPBP2 sample and (d) water contact angle of MTMS-coated aerogel

The FT-IR analysis of the obtained aerogel is illustrated in Figure 2b. The sample has characteristic peaks of cellulose aerogel (Liu et al., 2015), including 3,325 cm^{-1} peak representing hydroxyl groups, 2,910 cm^{-1} and 1,315 cm^{-1} peaks representing -C-H bonds, 1,622 cm^{-1} peak showing C=O bonds, 1,158 cm^{-1} peak showing C-O-C bonds, 1,029 cm^{-1} peaks exhibiting -C-O-(H) bonds that are specific to the ether and alcohol groups present in the cellulose structure (Pandey et al., 2003).
The TGA analysis of aerogel, with thermal degradation in three steps, is presented in Figure 2c. In the temperature range of 30-150 °C, the sample weight decreased by approximately 7 % due to the removal of adsorbed water vapor and any residue solvent inside the sample (Thai et al., 2020). In the range of 230-430 °C, a massive weight loss is seen due to the decomposition of cellulose aerogel structures (Zhang et al., 2019). Above 500 °C, the sample was almost completely decomposed.
In Figure 2d, the water contact angle of MTMS-coated aerogel can be seen. The material exhibits hydrophobicity after MTMS coating with the water contact angle of 139.6 ° and can be used for oil adsorption experiments.

3.2 Adsorption capacity

3.2.1 Adsorption capacity of motor oil and soybean oil

The oil adsorption capability (motor oil and soybean oil) of the aerogel with various PVA ratios is illustrated in Figure 3a. The obtained aerogels have the oil adsorption capacity of 27.27-32.86 g/g, approximate 1.5 and 1.8 higher than the motor oil and soybean oil capacity of aerogel from waste paper (18 g/g and 17.6 g/g) (Nguyen et al., 2014). As the PVA content increases, the amount of oil adsorbed by the aerogel decreases. This is consistent with the oil adsorption mechanism where porosity is the leading cause that affected the oil adsorption capacity of the aerogel. The time of equilibrium adsorption is shown in Figure 3b.

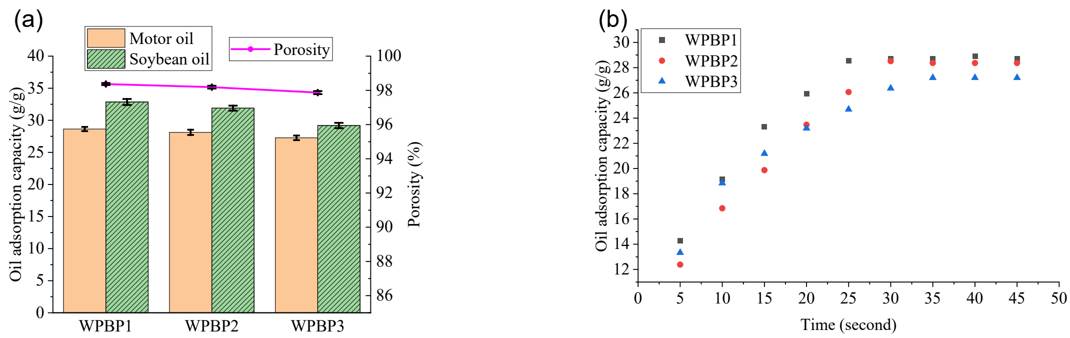

Figure 3: (a) Oil adsorption capacity of the sample with (b) their time adsorption

The WPBP aerogels can adsorb oil rapidly and the equilibria are reached within 35 s. This proves that the obtained aerogels easily adsorb oil due to their high porosity.

3.2.2 Methylene blue and Cu^{2+} adsorption capacity of WPBP aerogels

The capability of MB adsorption of aerogels is presented in Table 2.

Table 2: Methylene blue (4 ppm) adsorption of WPBP aerogels

Sample	Waste paper	Banana peel	PVA	Methylene blue adsorption capacity (mg/g)
WPBP1	8	4	1	6.69
WPBP2	8	4	2	6.56
WPBP3	8	4	4	4.23

The highest MB adsorption could be 6.69 mg/g after 2 h for the case of WPBP1 aerogel. These samples show the MB adsorption lower than cellulose aerogels from coir fibers, with a maximum adsorption capacity is 17.68 mg/g (Nguyen et al., 2021), but more efficient than cellulose aerogels from TOCN, polyvinyl alcohol, and M-K10, which adsorption capacity is 2.28 mg/g (Luo et al., 2021). The adsorption capacity of the aerogels increased with the decreasing PVA concentration. When reducing the amount of PVA in the aerogel sample, the number of functional groups remaining on the aerogel surface increases, leading to the possibility of forming more electrical attraction between MB and these groups. When the amount of PVA is reduced significantly, the aerogel sample can no longer keep the structure stable. The capability of Cu^{2+} adsorption of aerogels is presented in Table 3.

Table 3: Cu^{2+} adsorption capacity of WPBP aerogels in Cu^{2+} solution of 100 mg/L

Sample	Waste paper	Banana peel	PVA	Cu^{2+} adsorption capacity (mg/g)
WPBP1	8	4	1	84.78
WPBP2	8	4	2	85.45
WPBP3	8	4	4	61.68

It can be noticed that the highest Cu^{2+} adsorption capacity is 85.45 mg/g after 1.5 h in case of WPBP2 aerogel. This value is higher than other modified cellulose IV (69.4 mg/g) (Gurgel and Gil, 2009). When increasing the concentration of PVA in the sample, the adhesive ability increases so that the sample does not dissolve in water but reduces the adsorption capacity.

4. Conclusion

In this paper, the low-cost materials and environmental method were used to fabricate WPBP aerogel from waste paper, agricultural by-products of banana and PVA for application in water treatment. The obtained aerogel is potential to be friendly-environment materials thanks to the facile fabrication. With its super high porosity, low density, very high oil adsorption capacity, and capability of adsorption of dye and heavy metal ion, this green aerogel is an ideal material to be used in oil spill cleanup and wastewater treatments.

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