ADSORPTION CAPACITY OF HYDROPHOBICALLY MODIFIED BACTERIAL CELLULOSE AEROGELS UNDER SINGLE-SOLVENT AND EMULSION CONDITIONS

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TÓM TẮT

NGHIÊN CỨU KHẢ NĂNG HẤP PHỤ CỦA AEROGEL ĐƯỢC BIẾN TÍNH KỴ NƯỚC TRÊN CƠ SỞ CELLULOSE VI KHUẨN TRONG ĐIỀU KIỆN ĐƠN DUNG MÔI VÀ NHŨ TƯƠNG

Nghiên cứu này trình bày phương pháp tổng hợp và đánh giá hiệu quả hấp phụ chất lỏng hữu cơ kỵ nước của aerogel cellulose vi khuẩn phủ đồng. Aerogel được tổng hợp theo quy trình biến tính cellulose vi khuẩn bằng đồng trong hệ phân tán thạch dừa trong nước, sau đó sấy đông khô. Ảnh hưởng của hàm lượng chất rắn trong huyền phù đồng đến cấu trúc và hiệu quả hấp phụ của aerogel được khảo sát. Kết quả cho thấy aerogel có cấu trúc mạng lưới 3D từ cellulose vi khuẩn được duy trì, hàm lượng đồng khoảng 14%, diện tích bề mặt giảm khi tăng hàm lượng chất rắn. Aerogel có hiệu quả hấp phụ cao nhất với cyclohexane (44 g/g) và diesel (46 g/g) ở nồng độ huyền phù thấp nhất (1,2%). Khả năng tái sử dụng tốt với hiệu quả hấp thụ cyclohexane giảm 18% sau 10 chu kỳ. Aerogel hấp phụ hiệu quả nhiều chất lỏng hữu cơ khác với khả năng hấp phụ trong khoảng 36-100 g/g. Khả năng chọn lọc hấp phụ được chứng minh qua thí nghiệm với pha nhũ tương diesel trong nước, với lượng dầu diesel hấp phụ đạt 63 mg/g, gấp đôi so với aerogel cellulose vi khuẩn chưa biến tính.

Từ khóa: *biến tính kỵ nước, aerogel trên cơ sở cellulose vi khuẩn, chất lỏng ái dầu, lớp phủ đồng, khả năng tái sử dụng.*

1. INTRODUCTION

Organic compound pollution, particularly petroleum-based products, is a major source of water contamination . The presence of petroleum in aquatic environments is associated with the oil exploitation, transportation, and petrochemical industries [3]. These oleophilic compounds also contain heavy metals, sulfur, and other toxic aromatic hydrocarbons and heterocycles, depending on their origin [5]. Many methods have been proposed and applied for oil spill clean-up, including *in-situ* combustion, biological treatment, physical and chemical methods [6]. Physical adsorption is one of the most popular and widely used technologies for the collection of water-insoluble liquids because of its high efficiency, low cost, wide adaptability, and minimal secondary damage to the surrounding environment [7, 8]. Recent material studies have

focused on developing advanced hydrophobic porous adsorbents that can effectively capture oil substrates in water, offering high adsorption speed, efficiency, reusability, and suitability for large-area applications [9].

Aerogels are porous materials of significant interest because of their remarkable properties, including extremely low weight, high porosity, and large specific surface area. These characteristics render aerogels attractive for various applications. Common aerogel compositions include cellulose, silica, and carbon [9-14]. Among these, cellulose-based aerogels are particularly important in research. They not only exhibit favorable physical and chemical properties but are also biodegradable, environmentally friendly, cost-effective, and amenable to industrial-scale production [15]. The utilization of plant cellulose often requires several intricate and toxic purification steps to eliminate the lignin and hemicellulose. Unfortunately, these purification processes can adversely affect the textural properties of the resulting porous aerogel structure [16-18]. Bacterial cellulose (BC) has several advantages. BC has high purity, a substantial degree of polymerization, robust mechanical strength, and a readily available three-dimensional structure without extensive processing. Additionally, BC exhibits excellent water retention capabilities and its surface properties are easily modifiable [19]. Oil adsorption performance depends on several factors, including density, porosity, surface wetting, and capillary effects [20]. Traditional hydrophobization methods such as chemical vapor deposition and atomic layer deposition are costly and environmentally harmful [21, 22]. Recently, bacterial cellulose aerogels modified with various Cu contents showed promising hydrophobicity, yielding excellent adsorption results for water-insoluble organic solvents [23-25]. As a continuation of this study, the adsorption capacity of Cu-containing bacterial cellulose aerogels prepared at different suspension concentrations was investigated under single-solvent and emulsion conditions to highlight their selectivity for hydrophobic species. Moreover, the hydrophobic aerogel was recycled to trap cyclohexane.

2. MATERIALS AND METHODS

2.1. Materials

Raw *nata de coco* was purchased from Bich Lien Duong company (Ben Tre, Vietnam). The material was then washed with NaOH (1 M) and water, respectively. After such purification, the bacterial cellulose content in *nata de coco* was approximately 0.8 wt%. To create a suspension of *nata de coco* in water, a mixture of 125 g of *nata de coco* pieces (containing approximately 1 g of BC) and 125 g of water was ground using a hand blender (Philips HR2531 hand-blender, 650 W) for 6 min [23, 24].

2.2. Synthesis of Cu-modified aerogels

Cu-modified bacterial cellulose aerogels were fabricated based on a previously reported procedure [23-25]. The resulting suspension mixture (250 g) and $Cu(OAc)_2$ (3.0 mmol) were added to a 1000-mL round-bottom flask. An 80% aqueous solution of hydrazine hydrate ($N_2H_4.H_2O$) (50 equiv.) was slowly introduced into the mixture to reduce Cu(II) to Cu(0) for 15 hours at room temperature. After the completion of the reaction, the Cu-modified BC suspension was collected via gravity filtration and washed with water. The final mixture was distributed to 100-mL polypropylene boxes, which were subsequently frozen at -20 °C for 24 h and freeze-dried for 72 h, yielding

hydrophobic lightweight aerogels. The aerogel samples were denoted as "**X** wt.%" in which X represented the solid content of the final suspension ranging from 1.2 to 2.0 wt.%.

2.3. Characterization of the aerogels

The aerogels were characterized using scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM/EDX) and isothermal nitrogen sorption at 77 K.

2.4. Hydrophobic liquid-trapping studies

In a single-solvent experiment, a defined amount of aerogel (m_o, g) was added to a glass vial containing 10 mL of the corresponding solvent (m_1, g). After 5 min of trapping the solvent, the sample was removed from the liquid phase. Until no further solvent drops were released from the aerogel into the liquid phase, the total vial weight was recorded (m_2, g). The adsorption capacity (Q, g/g) was calculated using Equation (1).

$$Q = (m_1 - m_2)/m_o \qquad (1)$$

Prior to each emulsion experiment, 1 g of diesel was slowly added to 200 ml of an aqueous solution containing 0.05 g of Tween 80 under vigorous stirring. Water was subsequently added to a total weight of 1000 g to yield a 1000 mg/kg diesel-in-water emulsion [26]. Adsorption experiments were performed as described previously. The diesel concentration in the emulsion after the adsorption experiment was determined using a calibration curve of absorbance at a wavelength of 230 nm versus diesel concentration. The adsorption capacity (Q_e, mg/g) was calculated using Equation (2).

$$Q_e = (C_b*m_b - C_a*m_a)/m_o \qquad (2)$$

Where C_b and C_a (mg/g) were the diesel concentration in the emulsion, m_b and m_a (g) were the emulsion weight before and after the adsorption course, respectively, m_o (g) was the aerogel weight [26].

2.5. Recycling study

After the cyclohexane-trapping experiment, the spent aerogel sample was treated at 40 °C under a reduced pressure for the complete removal of cyclohexane. The recovered sample was then applied to the next adsorption cycle without further modification. In detail, the aerogel was allowed to contact cyclohexane in a glass vial for 5 min. The cyclohexane vial weights before and after the contact were recorded for the calculation of the trapping capacity as described in Equation (1).

3. RESULTS AND DISCUSSION

Nitrogen sorption measurements were performed to determine the textural properties of the fabricated Cu/BC aerogels (Figure 1). The N_2 sorption measurements for the aerogel samples prepared by varying the suspension concentration revealed typical type-IV isotherms, featuring a hysteresis loop within the relative pressure range indicative of meso- and macropores in the 3D network of the cellulose fibers generated via bacterial fermentation of carbohydrate solutions [27]. As the solid content in the Cu- and BC-containing suspensions increased, the N_2 adsorption capacity of the aerogels at 77 K decreased significantly, resulting in a significant reduction in the surface area. Indeed, the surface area remained approximately 16 m^2/g for the 1.2 wt.% and 1.3 wt.% samples; the more concentrated suspensions (1.6-2.0 wt.%) produced the aerogel with lower surface areas from 3.6 to 8.0 m^2/g. These results indicated that higher solid/liquid ratios in the suspension led to denser and less porous aerogels, thereby reducing both their surface area and pore volume [23].

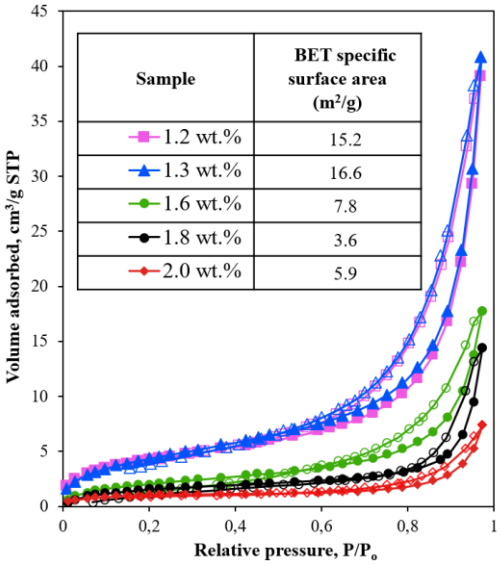

Figure 1. N_2 sorption isotherms of the modified aerogels.

The modified aerogels were reddish brown due to the presence of the coated Cu species (Figure 2a). The SEM images of the unmodified and Cu-containing aerogels showed a 3D interconnected framework composed of non-ordered bacterial cellulose fibers and bundles with diameters ranging from 40 to 80 nm (Figures 2b-c) [23]. Such random arrangements produce high porosity without the need for any further complicated mechanical and chemical treatments. Cu particles with nano- and macro-scale sizes were observed in the reduction-based samples, indicating successful BC modification with Cu. Notably, EDX mapping also showed a uniform distribution of Cu species on the BC surface with a content of approximately 14 wt.% (Figures 2d-e) while the theoretical Cu content was about 16 wt.%. Therefore, a Cu loss was observed probably due to the incomplete reduction and Cu leaching in the washing stage. As mentioned in the literature, the presence of Cu species covering the hydrophilic hydroxyl groups of cellulose leads to a targeted improvement in the hydrophobicity of materials [23, 25]. This feature can be confirmed by the water contact angles of 127-129° detected for all the modified samples (Figures 2f-j), consistent with the previously reported results [23, 25]. Obviously, insignificant changes in the water contact angle on the aerogel were obtained when the suspension concentration was varied. This trend can be predictable since the mass ratio of Cu/BC in the suspension and in the aerogel remained unchanged.

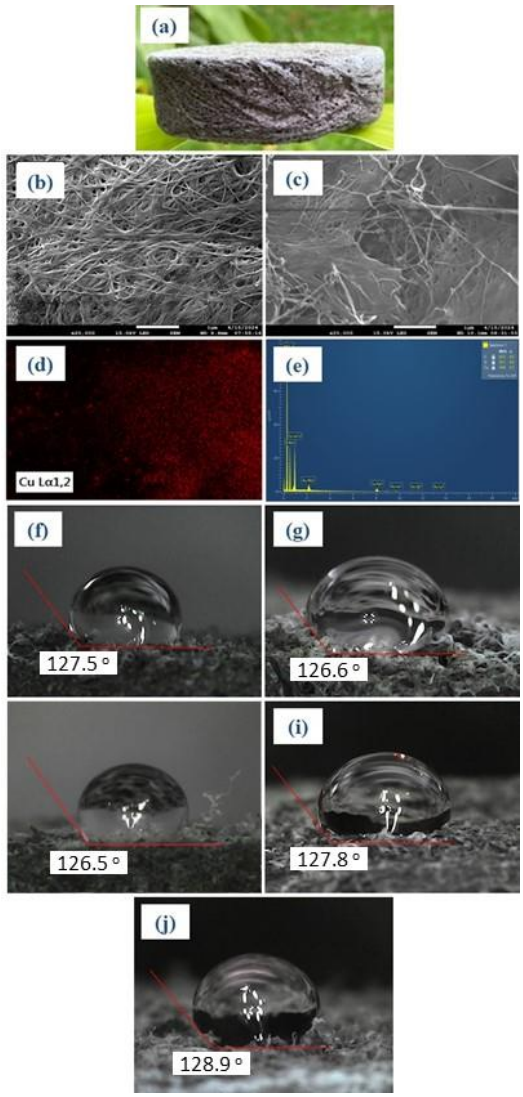

Figure 2. (a) Photograph of the **1.2 wt.%** sample; SEM images of (b) unmodified and (c) modified aerogels; (d) EDX-based Cu mapping and (e) EDX element distribution of the 1.2 wt.% aerogel; Water contact angle of the modified samples including (f) 1.2 wt.%: 127.5 °, (g) 1.3 wt.%: 126.6 ° , (h) 1.6 wt.%: 126.5 °, (i) 1.8 wt.%: 127.8 °, (j) 2.0 wt.%: 128.9 °.

The adsorption experiment for single solvents, namely cyclohexane and diesel, demonstrated that the trapping performance of the modified samples was affected by the suspension concentration during aerogel preparation (Figure 3a). As shown above, diluting the Cu/BC suspension can increase the material porosity, thereby affording more free cavities for capturing hydrophobic liquids [28]. Consequently, the adsorption capacity of the resulting aerogel was significantly improved. In detail, the 1.2 wt.% aerogel exhibited the adsorption capacities of 45-47 g/g for cyclohexane and diesel, respectively, which were approximately 150% more than those of the sample derived from the 2.1 wt.% suspension. It should be noted that in this study, the sample with a suspension concentration lower than 1.2% could not be completely dried under identical freeze-drying conditions, probably because of its high-water content, which might require a longer drying time.

The ability to recover and reuse an oil adsorbent is crucial for its long-term application in cleaning oil spills. Given its superior performance, the 1.2 wt.% sample was selected for the recycling experiment. The cyclohexane trapping capacity of the spent sample decreased slightly. However, after the first five cycles, more than 90% of its initial capacity remained, and the adsorption capacity for cyclohexane was recorded at approximately 40 g/g for the 10th cycle (Figure 3b). These results demonstrate that shrinking of the framework during the elimination of cyclohexane, if any, was insignificant because the fiber surface coated with the Cu species was strengthened, thereby preventing it from collapsing [29]. High structural stability is also a desirable feature of commercially viable adsorbents.

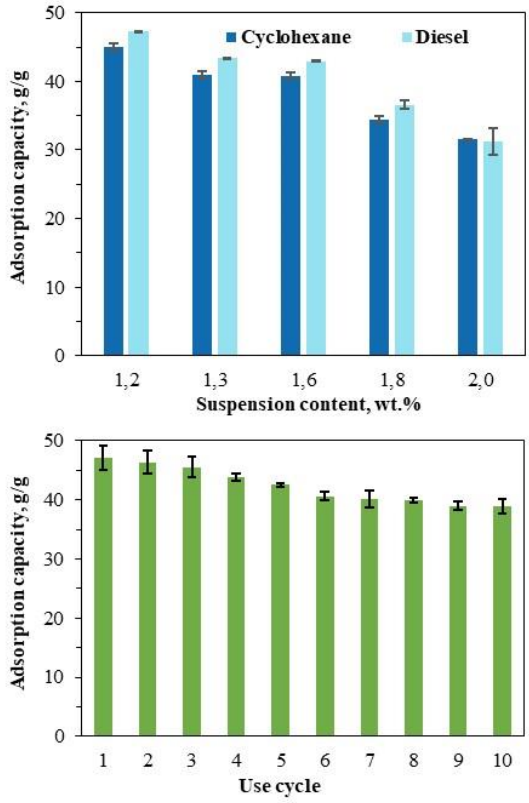

Figure 3. (a) Effect of the suspension content in the aerogel preparation on the cyclohexane and diesel oil adsorption capacity; (b) Recycling studies for the adsorption of cyclohexane over the 1.2 wt.% aerogel.

To further investigate the promising performance of the Cu-modified aerogel adsorbent derived from *nata de coco*, the research was extended to the use of various hydrophobic organic liquids, including *n*-hexane, toluene, tetrahydrofuran, ethyl acetate, chlorobenzene, 1,2-dichlorobenzene, chloroform, dichloromethane and soybean oil. In general, the uptake of the aerogel for the single liquids increased with their density, which is consistent with previous literature [23, 25]. Each gram of the 1.2 wt.% sample was able to capture from 36 to 100 grams of these hydrophobic solvents, which was slightly lower than the earlier results (Figure 4) [23]. However, it should be noted that the conditions for the aerogel preparation were modified to achieve hydrophobicity

for all the composite materials, which was not the focus of the previous work [23].

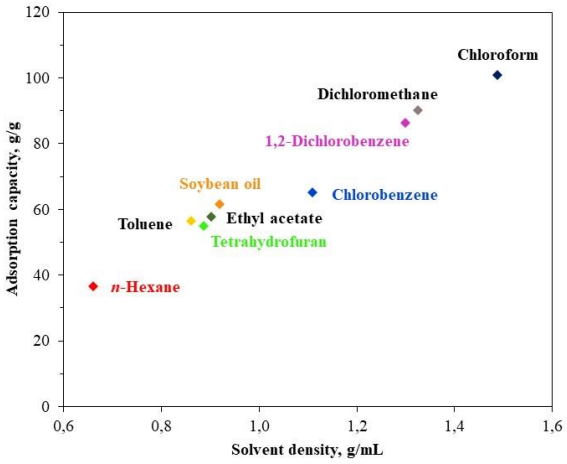

Figure 4. Effect of liquid density on the adsorption capacity of the modified aerogel for hydrophobic organic liquids.

The treatment of oil-contaminated water remains a significant challenge. Oil particles tend to disperse in water to form an emulsion. Selective adsorption is required to remove these contaminants effectively. To highlight the hydrophobic behavior of the aerogel, a diesel-in-water emulsion was prepared to simulate a real polluted water phase. Subsequently, the diesel adsorption capacity of the 1.2 wt.% sample in the emulsion phase was recorded at different intervals. The remaining oil concentration in the emulsion was determined by UV-vis measurements at a wavelength of 230 nm using an established calibration curve [26]. In the case of the pure BC aerogel, which was highly hydrophilic, as shown in Figure 5, adsorption occurred unselectively for all components in the emulsion. A diesel-trapping efficiency of approximately 30 mg/g was recorded at 15 min of the adsorption process, and the value remained almost unchanged afterwards. In contrast, diesel removal by the Cu-containing sample rapidly proceeded for 60 min and reached a plateau at approximately 60 mg/g. The oil adsorption capacity of the emulsion system was significantly lower than that a of single oil phase. The hydrophilic ends of the surfactant molecules cover the outer surface of the oil particles, dispersing the oil well and hindering their interaction with the material surface. This leads to competitive adsorption with water [25]. The Cu-modified aerogel clearly showed higher selectivity and efficiency for diesel in the emulsion phase than the pure BC aerogel (Figures 5a, b).

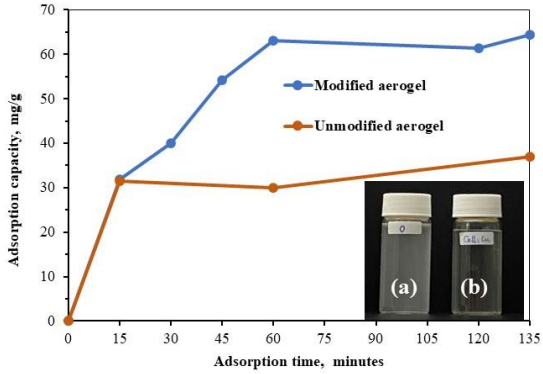

Figure 5. Diesel adsorption from the emulsion; diesel-in-water (a) before and (b) after adsorption using the 1.2 wt.% aerogel.

4. CONCLUSION

In this study, a series of Cu-coated BC aerogels was prepared by varying the suspension concentration. SEM/EDX analysis confirmed the successful dispersion of copper species on the bacterial cellulose surface, resulting in a hydrophobic material. The as-synthesized aerogels exhibited a high-water contact angle of 127-129 °. By increasing the solid content (from 1.2 to 2.1 wt.%) in the final suspension led to the formation of denser aerogels. Consequently, the trapping efficiency of both cyclohexane and diesel decreased significantly (by 40%). Interestingly, the 1.2 wt.% sample displayed remarkable stability, with only an 18% loss in cyclohexane trapping efficiency even after 10 cycles. This highlights the broad applicability of

aerogels for adsorbing various water-insoluble organic solvents. Furthermore, the 1.2 wt.% sample demonstrated superior performance in the diesel-in-water emulsion phase, absorbing twice as much diesel as the unmodified one. These findings strongly support the stable and efficient adsorption of hydrophobic liquids by Cu-coated BC aerogels under both single-component and emulsion conditions. Research on recycling materials for high-boiling-point liquids and upscaling aerogel preparation is currently on going.

Conflict of Interest: The authors declare that they have no conflict of interest.

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