Synthesis of oleophilic and hydrophobic cellulose-based aerogel using newspaper, cardboard and wood pulp through organosolv delignification for the sorption of oil

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Abstract

Oil spills happen frequently and cleaning them up proves to be a difficult task. They have resulted in detrimental impacts both on the environment and humans. Current oil sorbents employed such as Zeolite, Kapok fibers, and Sisal have shown to be low in oil sorption capacity, have poor hydrophobicity, and low reusability with Zeolite also being costly to make. This study aims to synthesize cellulose-based aerogel from corrugated cardboard and newspaper which proves to be eco-friendly, cost-effective, and efficient in the adsorption of oil. The cellulosic material would first undergo a series of organosolv delignification processes before undergoing the sol-gel process and being freeze-dried to obtain the porous cellulose-based aerogel. The aerogel would then be coated with methyltrimethoxysilane to obtain a hydrophobic surface, which has shown to increase its oil adsorption capacity significantly. The synthesized aerogels also proved to have high oil sorption capacities along with high reusability, being able to be reused up to 5 times. Results have also shown that the aerogel's oil adsorption capacity decreases significantly as the number of times it is reused increases. The synthesized aerogels are also successfully rendered to be hydrophobic after being coated with methyltrimethoxysilane. As such, cellulose-based aerogels prove to be an ideal oil sorbent for oil spills with multiple uses, having properties such as high oil sorption capacities, high reusability as well as high hydrophobicity, beating other current oil sorbents employed efficiency-wise.

1. Introduction

In today's world, water pollution caused by oil leakage and organic solvents discharged from the chemical industries are prominent. This damages the aquatic environment, harming marine wildlife as well as mangroves (Michel & Fingas, 2016). Furthermore, oil spills will be a big problem faced by humans as long as there is a demand for fossil fuels (Nguyen et al., 2014).

Frequently used oil-sorbents such as zeolite, suffer from certain disadvantages such as the inability to be reused again, as well as being costly (Khan, 2004). Certain eco-friendly oil sorbents such as Kapok fiber and Sisal are usually low in selective adsorption capacity and also have poor water resistance (Maleki, 2016). Hence, there is an urgent need for the development of an environmentally friendly, cost effective and sustainable technology to curb the detrimental impacts of oil spills.

Cellulose is the most abundant natural polymer on Earth. Cellulose has an array of desirable properties such as thermal stability, chemical stability, sustainability, compostability, and low cost due to abundance in availability, which are not found in petroleum-based polymers. Cellulose-based aerogels are a perfect solution to this problem. Aerogels possess an extremely low density in between 0.001 and 0.2 g/cm^3, high porosity ($\geq$ 90%) with pore size in between 2−50nm, and high specific surface area (200–600 m^2/g) (Zaman et al., 2019). Aerogels also have the renewability, biocompatibility, and biodegradability of cellulose, while also being able to absorb oil well due to their low density, high porosity, and large specific surface area (Long, Weng, & Wang, 2018).

Wood pulp proves to be an ideal cellulosic source for the synthesis of the cellulose-based aerogel as the aerogel synthesized from wood pulp has a considerably low density as compared to other cellulose-based aerogel, of under $0.034gcm^3$ (Long, Weng, & Wang, 2018). A lower density is preferred so that aerogel can absorb more oil per unit volume. It also has a remarkably high porosity percentage as compared to other cellulose-based aerogel of over 98.5% which increases its sorption capacity (Long, Weng, & Wang, 2018). Therefore, making use of newspapers, cardboard and wood chips, all of which is made from wood pulp, yet containing different amounts of lignin (Zhou et al., 2017), are used in the synthesis of cellulose-based aerogel.

2. Objectives and hypothesis

2.1. Objectives

- Synthesise cellulose-based aerogel for the sorption of oil using of delignified cellulosic fibres extracted from newspaper, corrugated cardboard and wood chips

- To investigate the effectiveness of cellulose-based aerogel in sorption of diesel oil
- To evaluate the reusability of the best-performing aerogel (highest oil sorption capacity)

2.2. Hypotheses

- The sorption capacity of the synthesised aerogel will be affected by different lignin content of the cellulosic source used
- The synthesised aerogels have high oil sorption capacities

3. Materials and Methods

3.1. Materials

The cellulosic sources used include wood chips which are obtained from Weber Grills, corrugated cardboard and newspaper which are both obtained from Hwa Chong Institution MakerSpace.

Glacial formic acid and methyltrimethoxysilane were both obtained from Sigma Aldrich. Urea was obtained from Scharlau. Absolute ethanol, glacial acetic acid, hydrogen peroxide and sodium hydroxide were all obtained from GCE Chemicals. Diesel was obtained from a nearby petrol kiosk.

3.2. Methods for synthesis of cellulose-based aerogels

5g of the biomass was blended into fine pieces and placed in a conical flask of $100cm^3$. A mixture of 85% organic acid (ratio of formic acid/acetic acid mixture was 70:30 by volume) was added to the biomass in the flask at a fiber to liquor ratio of 1:20 and allowed to boil in a refluxer for 2 h. After 2 h, flask and its content was allowed to cool to ambient temperature overnight. After the content is filtered in a Buchner funnel, the fibre, which is the residue, was further delignified by treating them with a mixture of Peroxyformic acid(PFA)/Peroxyacetic acid(PAA) solution and letting it boil in a refluxer for 2 h. PFA/PAA solution mixture was prepared by adding 20 ml 6% hydrogen peroxide with 80ml 85% formic acid/acetic acid mixture. The delignified fibers were filtered to separate cooking liquor (lignin, hemicellulose, formic acid and acetic acid) from the cellulose pulp which is the residue and washed with hot water before being oven-dried at 70°C for 3 hours.

150ml of 10% aqueous solution of 1% NaOH/ 9%Urea (9%:1% wt/wt) was added to the cellulose fibre) before it the cellulosic material was dispersed uniformly using a magnetic stirrer for 1h. It is then frozen for a day and thawed at room temperature for another day for coagulation. After that, the coagulated gel is immersed in industrial ethanol (99%) and soaked in DI water for a second day to obtain a neutral pH. The gel was then pre-freezed at -15°C for a day before being freeze dried at 98°C for 2 weeks before the porous cellulose-based aerogel was obtained.

3.3. Coating of MTMS on aerogel to render it hydrophobic

The synthesized cellulose-base aerogel was placed in an airtight glass jar containing a 6ml vial ofm methyltrimethoxysilane, before being heated at 70°C for 2 hours.

3.4. Sorption of aerogel

To measure the aerogel's oil sorption capacity, the cellulose based aerogel was initially weighed before being immersed in diesel for 30 minutes before being weighed again after the sorption of oil. By doing so, the oil sorption capacity of the cellulose-based aerogel was determines using the formula : $Q_t = \frac{m_w - m_d}{m_d}$

Where Q_t (g/g) = the oil sorption capacity of the aerogel in a 30 minutes, m_w (g) = the mass of the aerogel after sorption and m_d (g) = the mass of the aerogel before sorption

3.5. Reusability of the aerogels

The aerogel was immersed in diesel for 30 minutes for the sorption of oil before it was taken out and squeezed to its maximum before being reimmersed in diesel again, where this absorption and squeezing process (Figure 1 and 2) would be carried out for 5 consecutive cycles. The following formula was used to calculate the aerogel's reusability: $Qs = \frac{Mass\ of\ oil\ absorbed}{Mass\ of\ oil\ squeezed} = \frac{m_w - m_d}{m_w - m_s}$

Where Q_s = the squeeze ratio in g/g , m_w (g) = mass of the aerogel after sorption, m_s (g) = the mass of the aerogel after squeezing and m_d (g) = the mass of the aerogel before sorption

Figure 1. Aerogel being squeezed after being immersed in diesel oil for 30 minutes

Figure 2. Aerogel squeezed till maximum compressibility

3.6. Hydrophobicity of the aerogels

The aerogel coated with methyltrimethoxysilane was placed on a glass slide. A drop of water was then added to the surface of the aerogel. The image of the water droplet on the aerogel was captured using a handphone camera at ambient temperature. Figure 3 shows one such water contact angle measurement. Using software *DinoCapture*, the water contact angle of the aerogel was measured.

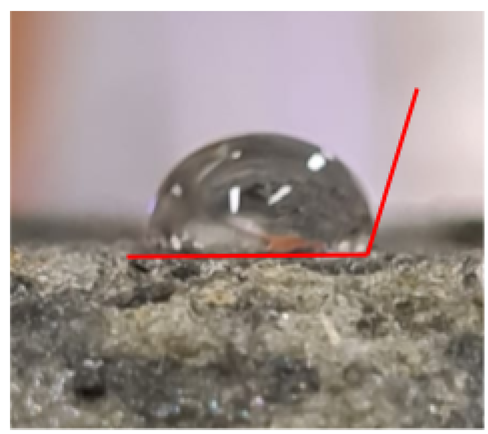

Figure 3. Water contact angle measurement on aerogel

4. Results and Discussion

4.1. Effect of MTMS coating on the hydrophobicity of the aerogel

The MTMS-coated aerogels turned out to be hydrophobic, as measured by its water contact angle. When the contact angle is more than 90°, the material is hydrophobic (Marmur et al, 1970). Results from the water contact angle measurements (Figure 4) showed that the water contact angles were greater than 90 degrees, indicating that the MTMS coated aerogels were hydrophobic.

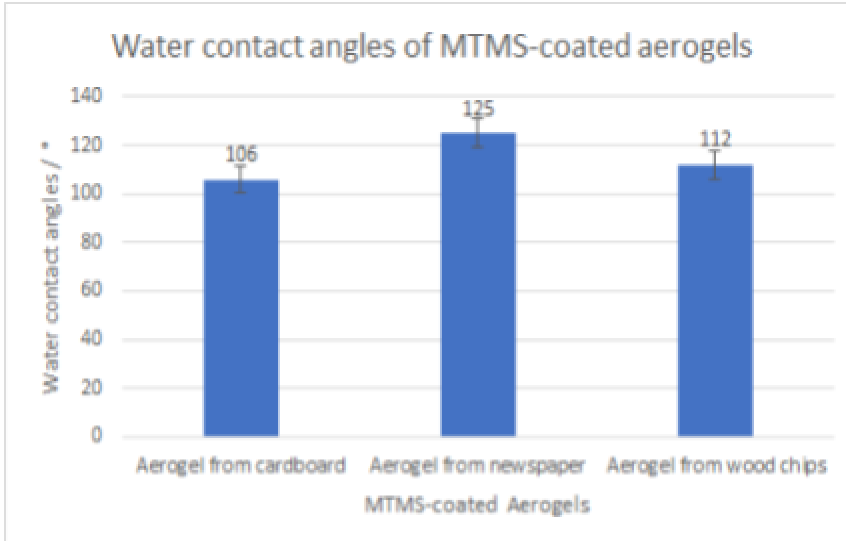

Figure 4. Water contact angles of MTMS-coated aerogels

4.2. Oil sorption capacity in pure oil

All 3 aerogels were immersed in oil for 30 minutes to measure their oil sorption capacity. As shown above (Figure 5), the aerogel synthesized from newspaper, had the highest sorption capacity of 6.92. This could be attributed to how newspaper has the lowest lignin content as compared to the other cellulosic materials used (Zhou et al., 2017) which increases in porosity and thus its oil sorption capacity (Vitas, Segmehl, Burgert, & Cabane, 2019).

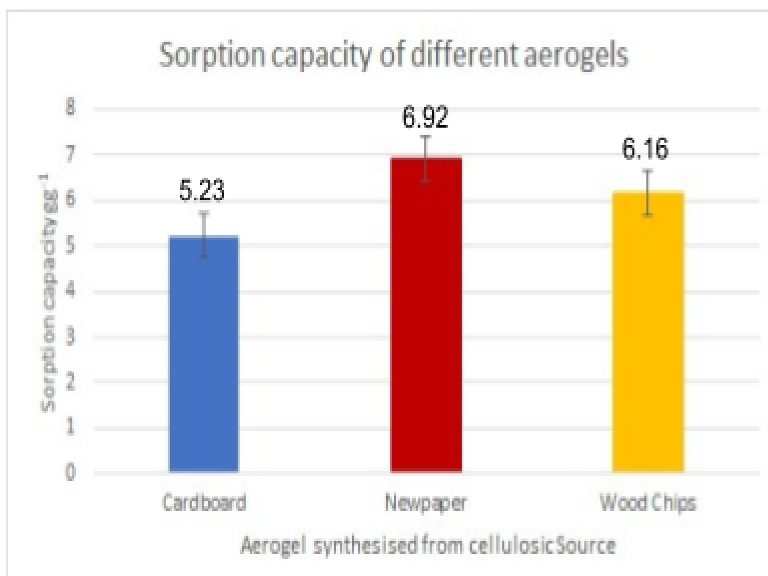

Figure 5. Sorption capacities of uncoated aerogels in pure oil environment

The aerogel synthesized from newspaper which had the best sorption capacity was coated with MTMS before being tested again. The results shown above (Figure 6) showed that the hydrophobic MTMS coating of the aerogel increased its sorption capacity but the difference was not that significant, of only 0.21 in oil sorption capacity

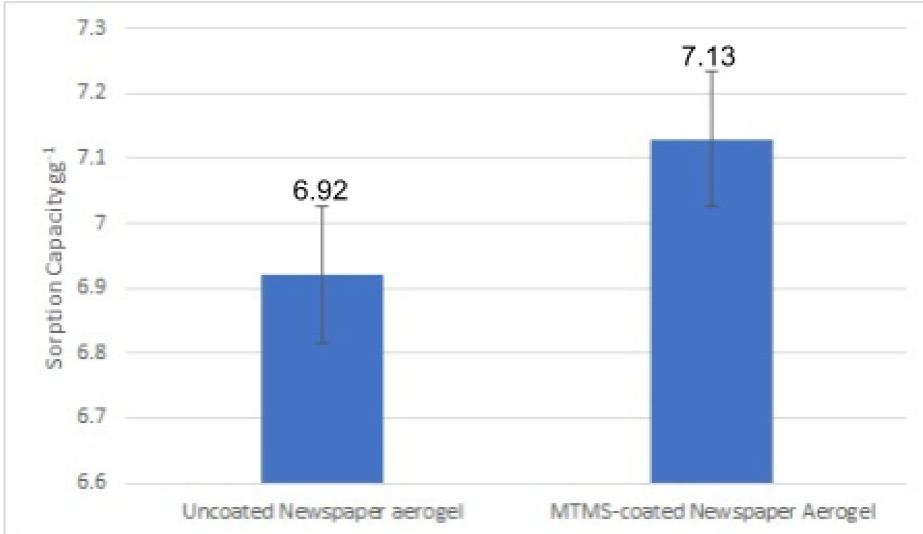

Figure 6. Sorption capacities of aerogel synthesized from newspaper in pure oil environment

4.3. Reusability of aerogels

As shown above (Figure-7), there was a general decrease in the sorption capacity of MTMS-coated aerogel A2 , and this could be attributed to the porous structure of the aerogel collapsing as it was squeezed (Nguyen et al., 2013), hence decreasing the aerogel's sorption capacity but only by insignificant margins per cycle.

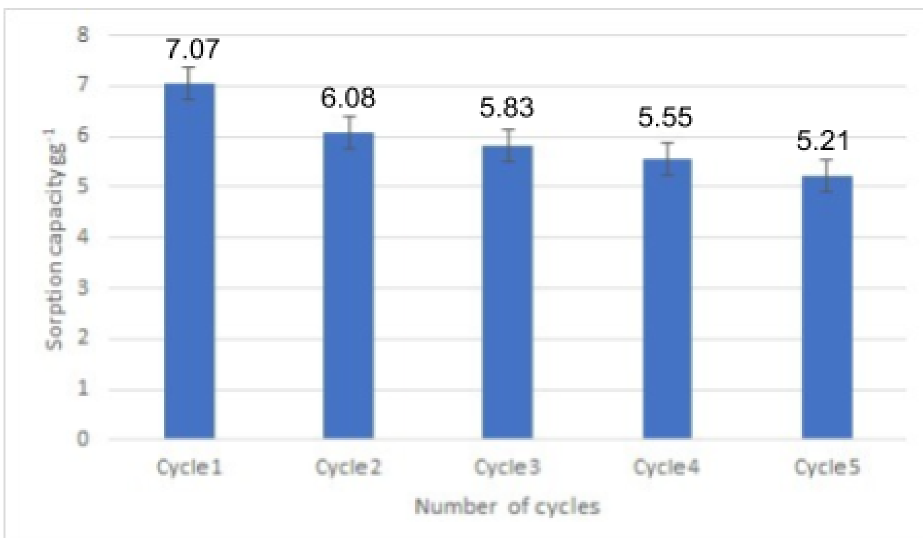

Figure 7. Reusability of MTMS-coated aerogel synthesized from newspaper in the sorption of diesel oil for 5 cycles

Figure 8 shows that the squeeze ratio of the MTMS-coated aerogel for the 5 cycles were generally close to 1, meaning that close to all the oil could be recovered after each cycle of sorption and squeeze, and this indicates that the aerogel is reusable as it is capable of the sorption of oil after each cycle of squeezing and eco-friendly as the oil recovered could be reused

Figure 8. Reusability of MTMS-coated aerogel synthesized from newspaper in the sorption of diesel oil for 5 cycles in terms of squeeze ratio

5. Conclusions and Recommendations for future work

5.1. Conclusions

Hydrophobic and oleophilic cellulose-based aerogels were successfully synthesized from cellulosic sources newspaper, cardboard and wood chips. The best performing aerogel was synthesized from newspaper which has the highest oil sorption capacity. The cellulose-based aerogel was also reusable, being able to absorb significant amounts of diesel oil even after 5 consecutive cycles of sorption and squeezing. These characteristics of the cellulose-based aerogel enable it to function as an eco-friendly, cost effective, efficient and sustainable tool to clean up oil spills, beating other current oil sorbents employed to clean up oil spills.

5.2. Future Works

In future, synthesis of cellulose-based aerogels from other cellulose sources can be explored and investigated. Further studies could also be done to investigate the effect of varying lignin concentration of cellulosic sources used to synthesize the aerogel could affect the aerogel’s oil sorption capacity. It would also be interesting to explore the use of other delignification methods such as the Kraft Process in the synthesis of cellulose-based aerogel. Finally, more studies could also be done to explore other applications of aerogels as the unique structure of the aerogels gives them incredible properties that may serve several purposes.

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