Fabrication of hydrophobic cellulose aerogel from pineapple waste for oil spill clean-up

Group 01-16

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Abstract

Oil spills pose significant dangers to animals and plants. Cleaning up oil spills is no easy task as well. Current methods of cleaning up oil spills include the use of dispersants and sorbents made from synthetic polymers such as polypropylene. However, these methods have various disadvantages such as not being environmentally friendly, having a high cost and slow degradability rate. This study developed a cost-effective, environmentally-friendly and efficient method for cleaning up oil spills by fabricating cellulose aerogel from the crown of pineapples. Aerogels were synthesised using different volumes of hydrogen peroxide, sodium hydroxide and urea. The oil sorption capacity of the aerogels was then evaluated in pure oil and oil-artificial seawater environments. Results show that the aerogel synthesised using 400 ml of hydrogen peroxide with sodium hydroxide and 100 ml of urea with sodium hydroxide have the highest oil sorption capacity and the most stable structure. The effects of coating the aerogel with titanium dioxide and methyltrimethoxysilane (MTMS) on the hydrophobicity of the best performing aerogel were studied by measuring the water contact angle on the surface of the aerogel. MTMS was found to be able to render the aerogel hydrophobic but titanium dioxide was not. The best performing aerogel was also found to be reusable for up to 5 cycles. Aerogels fabricated from pineapple waste are thus, promising alternatives to the commercial non-renewable oil sorbent, polypropylene, in cleaning up oil spills.

1. Introduction

Oil spills are one of the most devastating occurrences that are seriously endangering the marine ecosystem. Catastrophic oil spills such as those in the Gulf of Mexico have caused significant environmental damage (Nguyen *et al*., 2014). As long as fossil fuels are still needed, oil spills will remain as a big problem (Nguyen *et al*., 2014). Hence, prompt action is needed to develop an environmentally friendly and cost-effective technology for minimizing these environmental consequences.

There are several ways to clean up oil spills at the moment, which can be categorised into chemical, biological, and physical methods (Duong *et al*., 2018). Chemical methods such as dispersion are generally too expensive, biological methods such as use of microorganisms requires a long time and physical methods such as use of booms and skimmers are not able to remove oil from the sea effectively (Duong *et al*., 2018). Oil absorption is a more economical, efficient and environmentally-friendly method of dealing with oil spills (Meng *et al*., 2017). Traditional absorption materials such as polypropylene, zeolite and activated carbon are often used, but they suffer from several disadvantages such as poor reusability, insufficiently selective oil absorption capacity, and a lack of biodegradability (Teas *et al*., 2001). Natural organic materials from plants and animal residues, such as kapok fibre, sugarcane bagasse and rice husk also have disadvantages such as a low selective absorption capacity, weak buoyancy, and poor water resistance (Ali, El-Harbawi, Jabal, & Yin, 2012).

Cellulose aerogels are a promising solution. Aerogels are the lowest-density solid materials in the world - composed of up to 99.98% air by volume while being highly porous and capable of bearing weight many times their own. Aerogels are usually brittle and may fracture if too much force is applied (Nguyen *et al*., 2014). Cellulose aerogels, however, 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).

Plants with a high cellulose content but with a low wax and hemicellulose content are preferred for the fabrication of cellulose aerogel, to maximise the use of the plant matter. Pineapple crown leaves have a cellulose content of 66.2% (Daud, Hatta, Kassim, & Aripin, 2014) while rice husks have a cellulose content of 35% (Johar, Ahmad, & Dufresne, 2012). Sugarcane bagasse has a cellulose content of 43.0% to 45.9% (Sun, Sun, Zhao, & Sun, 2004). Among these 3 cellulosic materials, pineapple leaves have the highest cellulose content and hold great promise to be a source of cellulose for the fabrication of cellulose aerogels.

Pineapple is a common and popular tropical fruit. 16 to 19 million tonnes of pineapple are produced annually around the world (Dai *et al*., 2017). Unfortunately, the pineapple crown is often discarded indiscriminately due to it having little to no economic value, potentially harming the environment and ecosystems. Therefore, making full use of the pineapple crown is of great practical significance.

2. Objectives and Hypotheses

2.1. Objectives

- To optimise the amounts of reagents (hydrogen peroxide and urea) required for the synthesis of aerogel from pineapple crown.
- To study the effect of coating using methyltrimethoxysilane vs titanium dioxide on the hydrophobicity of the aerogel.

- To evaluate the oil sorption capacities of the synthesised aerogels in pure oil and oil-seawater environment.
- To evaluate the reusability of the best-performing aerogel.

2.2. Hypotheses

- The amounts of reagents used in the synthesis would affect the oil sorption capacity of aerogels synthesised.
- The titanium dioxide (TiO_2) coating was more hydrophobic than the methyltrimethoxysilane (MTMS) coating.
- The synthesised aerogel was reusable.

3. Materials and Methods

3.1 Materials

Sodium hydroxide, hydrogen peroxide and absolute ethanol were procured from GCE chemicals. Urea was obtained from Scharlau. Methyltrimethoxysilane (MTMS) and titanium (IV) isopropoxide were purchased from Sigma Aldrich. Pineapple waste was obtained from local fruit stalls. Diesel was obtained from a petrol kiosk.

3.2. Synthesis of the cellulose aerogel

The pineapple crown leaves were washed with deionised water and dried in an oven until constant mass and blended. Cellulose was extracted from the dried pineapple crown leaves using a mixture of sodium hydroxide (5%w/v) and hydrogen peroxide (6% v/v) solution per 5g of dried pineapple crown leaves at a temperature of 55°C for 2 hours, while stirring vigorously using a magnetic stirrer. It was then washed with deionised water until the pH of the washing was neutral. The cellulose was then dried in an oven at 50°C until constant mass. The dried cellulose was then ground into finer particles with a blender.

To synthesise aerogels, 2g of the dried cellulose was dispersed in a urea/sodium hydroxide (10wt%/1.9wt%) solution by stirring vigorously for 1 hour using a magnetic stirrer, until the mixture was homogeneous. The cellulose mixture was then placed in the freezer for 24 hours to gelate, using the beaker as a mould. After freezing, the mixture was thawed, before absolute ethanol was added for coagulation for 2 days. The gel was then immersed in deionised water until its pH was neutral. The gel was then pre-freezed at -18 °C for 12 hours before being freeze-dried at -98 °C for 48 hours to yield the final aerogel.

For the extraction and dispersion of cellulose, different combinations of volumes of sodium hydroxide and hydrogen peroxide were used to optimise the amounts of reagents required for the synthesis of aerogel, as shown in table 1. Aerogel A0 was synthesized using conditions reported by other researchers (Nguyen *et al.,* 2013). The other conditions were the improvisations made in this study.

Table 1. Volumes of NaOH/H_2O_2 and NaOH/urea solutions used in the extraction of cellulose and synthesis of aerogel.

Total Volume of 5% (w/v) NaOH and 6% (v/v) H_2O_2 solution / ml	Total Volume of NaOH/urea (1.9wt%/10wt%) solution / ml	ID of aerogel synthesised
200	100	A0
400	100	A1
200	200	A2
400	200	A3

3.3. Coating of the cellulose aerogel with MTMS or TiO_2 to render it hydrophobic

To render the aerogels hydrophobic, the aerogels were coated with methyltrimethoxysilane (MTMS). The aerogel was placed in an airtight glass jar containing a vial of MTMS. The jar was heated in an oven for 2 hours at 70°C. MTMS vapour underwent a reaction with the hydroxyl functional groups on the cellulose, changing it to a methyl group instead (Figure 1).

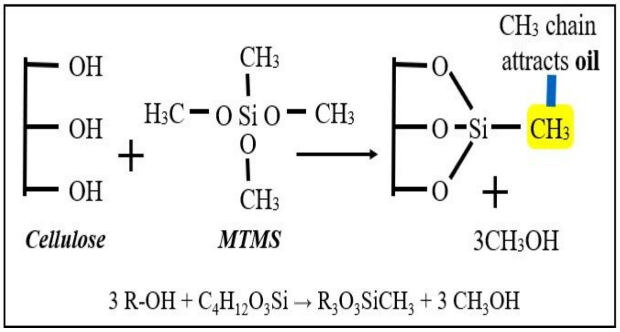

Figure 1. Reaction of cellulose with MTMS.

The process was repeated with titanium (IV) isopropoxide to coat the aerogel with titanium dioxide. The reaction could be represented by the following equation:

$$Ti\,[OCH(CH_3)_2]_4 + 2H_2O \rightarrow TiO_2 + 4(CH_3)_2CHOH$$

3.4. Oil sorption test in pure oil environment

The aerogel was cut into small pieces and weighed, before being immersed in 50ml of diesel oil for 1 hour. The aerogel was then removed from the oil and rested on a sieve to remove excess oil present on the surface before being weighed again. The following formula was used to determine the oil sorption capacity: $Q_t = \frac{m_w - m_d}{m_d}$

Where Q_t (g/g) = the oil sorption capacity of the aerogel in 60 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 test

The aerogel was weighed and immersed in 50ml of diesel oil for 1 hour. Thereafter, it was weighed again and pressed between pieces of tissue paper under 5kg of brass weights for 30s, to remove the oil absorbed, before being weighed once more. This process was repeated for 5 cycles. The mass of oil that could be recovered through squeezing was calculated using the squeeze ratio: $Q_s = \frac{Mass\ \ of\ oil\ absorbed}{Mass\ \ of\ oil\ squeezed} = \frac{m_w - m_s}{m_w - m_d}$

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.

3.6. Water contact angle measurement on the MTMS or TiO_2 coated aerogel

A small piece of cellulose aerogel that was coated with MTMS or titanium dioxide was placed on a glass slide. A drop of water was dripped onto the aerogel before the image was captured with a USB digital microscope. The software *DinoCapture* was used to measure the water contact angle. Figure 2 shows one such measurement. This measurement was not conducted on uncoated aerogel due to the drop of water being absorbed into the aerogel before any picture could be taken.

Figure 2. Water contact angle measurement on aerogel.

3.7. Test for the sorption capacity of the aerogel in oil-artificial seawater conditions

To simulate an oil spill in the sea, 10ml of diesel oil and 100ml of artificial seawater were added to a small piece of aerogel in a conical flask. Artificial seawater was prepared by dissolving

56g NaCl, 17g $MgCl_2$, 8.19g $MgSO_4$, 2.5g $CaSO_4$ and 2g KCl in 2 litres of deionised water. The flask was then shaken in an orbital shaker at 150rpm for 1 hour, before hexane was added to extract the diesel oil. The seawater was drained away in a separating funnel. Any remaining water in the hexane and diesel oil mixture was removed using anhydrous sodium sulfate. The hexane was then separated from the diesel oil in a rotary evaporator. The diesel oil collected was then weighed and the oil sorption capacity of the aerogel was calculated with the formula in section 3.4.

4. Results and Discussion

4.1. Characterisation of the pineapple cellulose by FTIR

Fourier-transform infrared spectroscopy (FTIR) was used to analyse the structure of the pineapple cellulose. The FTIR spectrum (Figure 3) reveal peaks corresponding to functional groups characteristic of cellulose, including the O-H stretch (3423 cm^{-1}), C-H stretch (2920 cm^{-1}), C-O stretch (1163 cm^{-1}) as well as the C-O-C stretch (1111 cm^{-1}). These peaks were in agreement with cellulose extracted by Fan, Dai and Huang (2012).

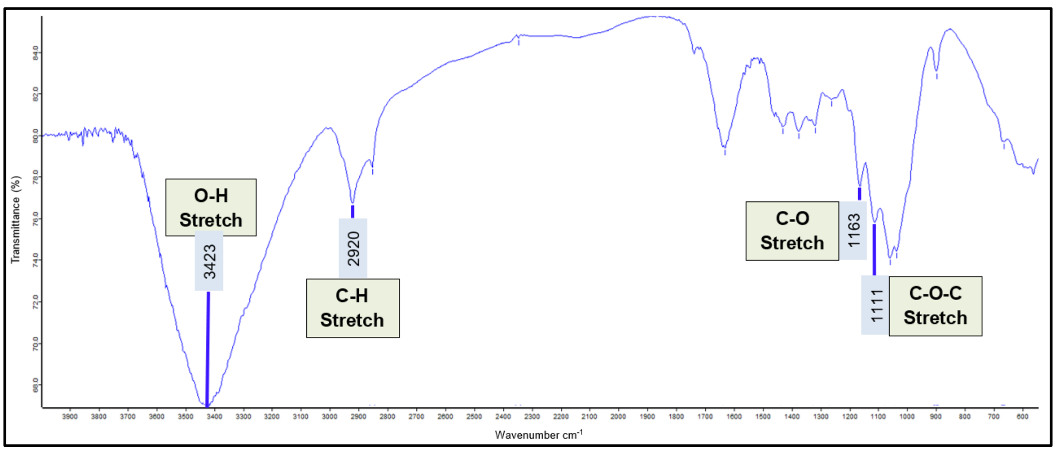

Figure 3. FTIR spectrum of cellulose extracted from pineapple waste.

4.2. Characterisation of the cellulose aerogel by Scanning Electron Microscopy (SEM)

SEM was used to analyse the structure of the cellulose fibres before and after freeze-drying. After freeze-drying (Figure 5), air spaces could be seen in between the fibres, suggesting that the aerogel was porous, in contrast to the denser cellulose fibres before freeze-drying was carried out (Figure 4).

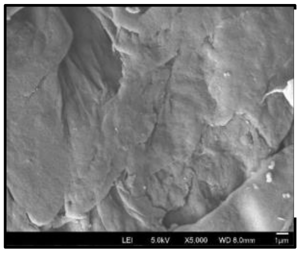

Figure 4. SEM of the pineapple cellulose

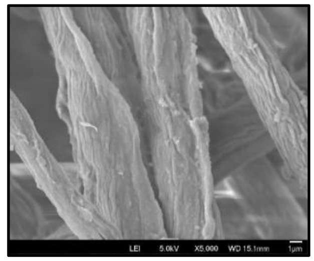

Figure 5. SEM of the cellulose aerogel after freeze-drying

4.3. Effects of the TiO_2 and MTMS coatings on the hydrophobicity of the aerogel

Unfortunately, the titanium dioxide-coated aerogels were not hydrophobic because the titanium dioxide was only physically deposited onto the surface of the aerogel, and not chemically deposited as with MTMS. The titanium dioxide formed as powder (Figure 6) on the aerogel surface, which could be easily removed.

Figure 6. Titanium dioxide-coated cellulose aerogel.

In contrast, the MTMS-coated aerogels were hydrophobic. The water contact angle measures the hydrophobicity of the aerogel. When the contact angle is more than 90 degrees, the material is hydrophobic (Förch, Schönherr & Jenkins, 2009). Results from the water contact angle measurements (Figure 7) showed that the contact angles were more than 90 degrees, which indicated that the MTMS coated aerogels were hydrophobic.

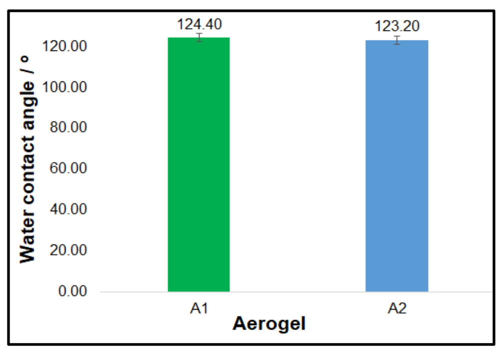

Figure 7. Water contact angles of MTMS-coated aerogel

Energy-dispersive X-ray spectrum (EDS) of the MTMS-coated aerogel (Figure 8) indicated the presence of silicon, confirming that the MTMS had been successfully coated onto the aerogel.

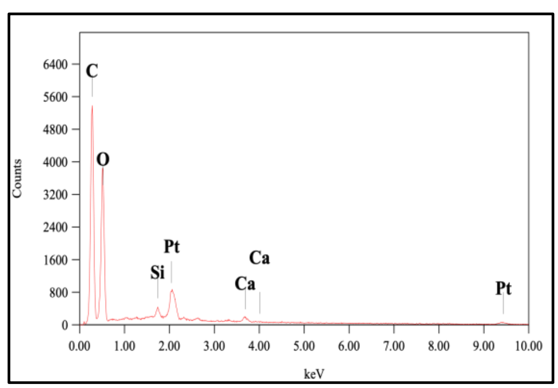

Figure 8. EDS of the MTMS-coated A1 aerogel

4.4. Oil sorption capacities of aerogels in pure oil environment

Results from the oil sorption test (Figure 9) showed that among the 4 aerogels, aerogels A1 and A2 had the best oil sorption capacities. However, their oil sorption capacities were not significantly different from the rest as the P-value for the Kruskal-Wallis test was 0.40, which was more than 0.05.

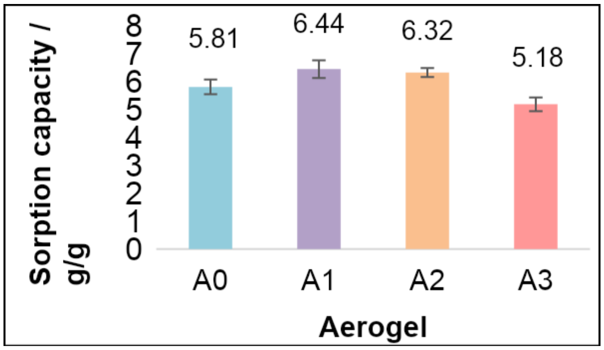

Figure 9. Sorption capacities of uncoated aerogels in pure oil environment

Aerogels A1 and A2, which had the best oil sorption capacities, were coated with MTMS and tested again. The results (Figure 10) showed that the hydrophobic coating improved their sorption capacities slightly, but the difference was not significant. The P-value of Mann-Whitney test between A1 coated and uncoated was 0.86, while that for A2 coated and uncoated was 0.93.

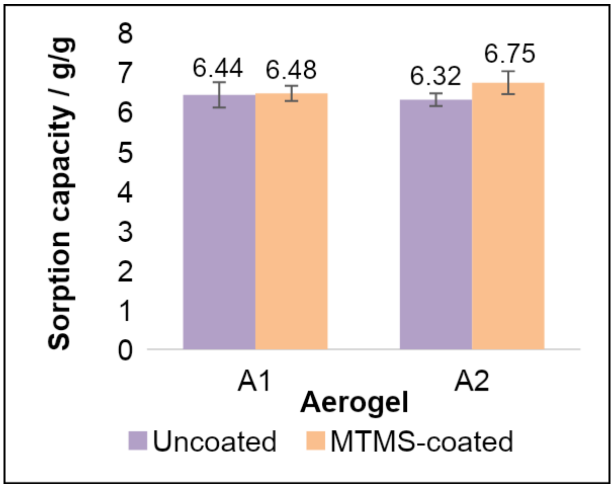

Figure 10. Sorption capacities of aerogels A1 and A2 in pure oil environment

Another interesting observation made was that A2 aerogel had an irregular structure (Figure 11) due to it collapsing during the coagulation process, impairing its ability to absorb oil. This could have been due to the excessive volume of sodium hydroxide/urea solution used during the synthesis of A2 aerogel, which may have caused it to damage the cellulose chains, making it more prone to collapse.

Figure 11. Irregular structure of A2 aerogel

Figure 12. Regular structure of A1 aerogel

4.5. Oil sorption capacity in oil-artificial seawater conditions

The MTMS-coated aerogels absorbed substantially more oil than the uncoated aerogels (Figure 13). There was a significant difference between the sorption capacities of uncoated and MTMS-coated aerogels, the P-values being 0.03 and 0.04 for aerogel A1 and A2 respectively. MTMS coated A1 aerogel outperformed other oil sorbents such as kapok and milkweed, with oil sorption capacities of 10.6 g/g and 7.3 g/g respectively (Karan, Rengasamy, & Das, 2010).

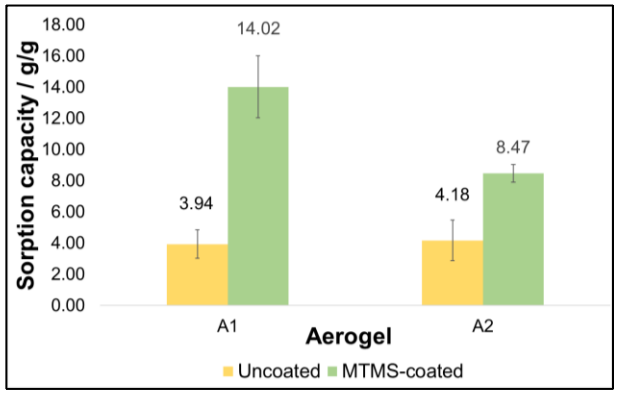

Figure 13. Sorption capacities of coated and uncoated aerogels A1and A2 in oil-seawater environment.

The MTMS present on aerogel improved the hydrophobicity of the aerogel due to its hydrophobic methyl group, which repels water but attracts oil via dispersion forces (Figure 14).

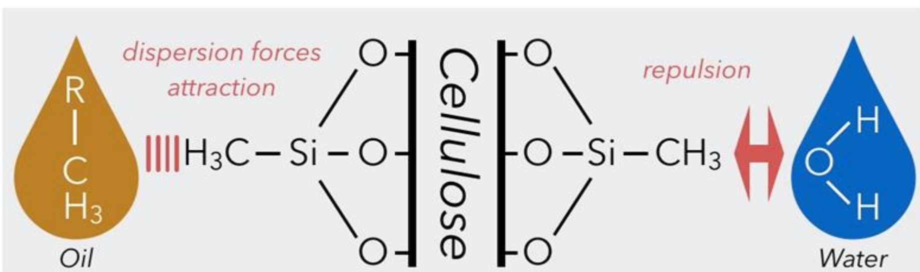

Figure 14. Interaction between the MTMS-coated aerogel and oil and water

4.6. Reusability of the MTMS-coated aerogel and squeeze ratio

Figure 15 shows that after the first cycle, sorption capacity decreased. This could have been due to the aerogel structures collapsing, decreasing the mass of oil that it could absorb. However, the insignificant differences (P-value = 0.12) between the sorption capacities from cycle 2 onwards suggested that the aerogel had the potential to be reused.

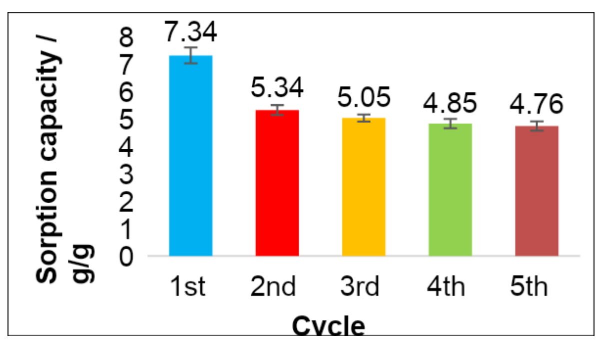

Figure 15. Reusability of MTMS-coated aerogel A1 in absorbing diesel for up to 5 cycles in terms of sorption capacity

The squeeze ratio measured the amount of oil that could be recovered through squeezing. Figure 16 shows that around 60% of the oil could be recovered from the aerogel after the first cycle. However, the squeeze ratio was close to 1 for subsequent cycles, which showed that almost all of the diesel could be recovered from the aerogel. This showed that the aerogels were eco-friendly, as the oil they absorbed could be recovered and possibly reused.

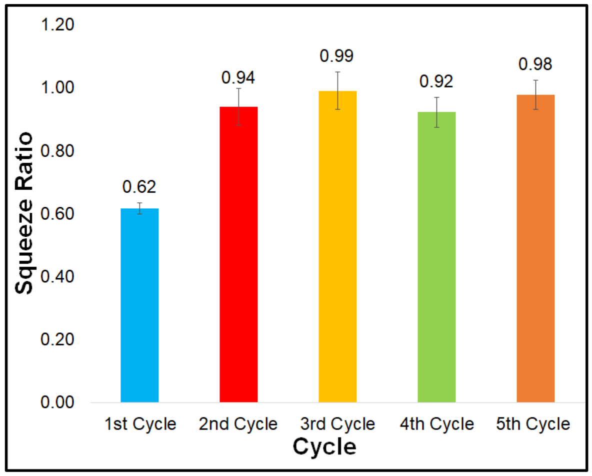

Figure 16. Reusability of MTMS-coated aerogel A1 in absorbing diesel for up to 5 cycles in terms of squeeze ratio

5. Conclusions and Recommendations for future work

5.1. Conclusions

Hydrophobic cellulose aerogels were successfully synthesised from pineapple waste. The optimum volumes of reagents for the synthesis of aerogel was 200ml of $NaOH/H_2O_2$ solution, for the extraction of cellulose, and 100ml of NaOH/urea solution for the dispersion of cellulose (Aerogel A1). This method of synthesising aerogel allowed food waste to be utilised in a meaningful way, reducing waste. Using pineapple waste was also an eco-friendlier way of tackling the problem of oil spills, rather than using commonly used, petroleum-derived polypropylene as a sorbent. The MTMS coating enhanced the hydrophobicity of the aerogel in oil-seawater and pure oil conditions, increasing its oil sorption capacity. The oil sorption capacity of MTMS coated A1 aerogel outperformed other oil sorbents such as kapok and milkweed fires. The cellulose aerogel was also reusable, with the oil absorbed being able to be recovered through squeezing. These characteristics enable the aerogel to function as an eco-friendly, affordable and effective clean-up tool for oil spills.

5.2. Future studies

In future, synthesis of cellulose aerogels from other waste products can be explored. Oil sorption can be conducted on other types of oil such as motor oil. The effect of the MTMS coating on the biodegradability of aerogels can also be investigated. Finally, it would be interesting to explore other applications of aerogels, such as evaluating their insulating properties and using them as thermal insulators.

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