Chemically Modified Pomelo Pith for Oil Sorption

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Abstract:

Oil spills pose as an enormous threat towards the marine ecosystem and cause water pollution. Current oil spill removal methods include burning, using dispersants and boomers and skimmers. Such methods are often limited in effectiveness and expensive. This study proposes to improve the oil sorption capacity of pomelo pith by chemically modifying it. Pomelo pith was treated with methyltrimethoxysilane (MTMS) and oleic acid to increase its hydrophobicity and with sodium hydroxide to increase its surface area. The treated pomelo piths were characterised using a Scanning Electron Microscope (SEM) and their water contact angles were determined. Sorption capacities of the sorbents in various liquids (oil, water and oil-seawater) were also investigated. Results show that chemical treatment with MTMS, oleic acid and sodium hydroxide successfully increase the oil sorption capacity of pomelo pith in pure oil environment. However, in the oil-seawater environment, only oleic acid treated and MTMS treated pomelo pith outperformed the untreated pomelo pith, with the MTMS treated pomelo pith exhibiting the greatest oil sorption capacity, absorbing oil up to almost 8 times its weight.

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1. Background and Purpose of Research

Oil spills have posed a huge threat to the environment for a long time. Prominent cases include the Exxon Valdez oil spill in 1989, where the oil spill contaminated 1000 miles of coastline and hundreds of thousands of animals perished (Taylor, 2014) as well as the Deepwater Horizon oil rig explosion, which spilled 5 million barrels into the open sea and is still currently the biggest oil spill in the US waters (Robertson & Krauss, 2010). Locally, there has been more than 1600 cases of oil spills on roads in 2015 alone (Chia & Teo, 2016). Just recently (on 3 Jan 2017), 300 tonnes of oil gushed into the waters off Singapore after two ships collided off Pasir Gudang Port in Johor, polluting beaches and nearby mangroves and killing fish in costal fish farms near Pulau Ubin. One farm reported loss of 70% of fish meant to be sold during Chinese New Year. The oil spill caused AVA to suspend sale of fish from 12 fish farms, affecting their livelihood (Chia, 2017).

Oil spills are harmful to living organisms, as oil is toxic and can also interfere with animals' ability to retain heat, which would lead to hypothermia (National Oceanic and Atmospheric Administration, 2017). There are several ways of cleaning up oil spills: booms and skimmers, in-situ burning, bioremediation, chemical dispersion and solidification and the use of sorbents (Karakasi & Moutsatsou, 2010). However, booms and skimmers are not very efficient in removing oil (National Oceanic and Atmospheric Administration, 2017), bioremediation is very slow and dependent on multiple factors, such as pressure and temperature (Atlas, 1995) and chemical methods are expensive and not environmentally friendly (Page et al., 2002). Sorbents made with synthetics is commercially used as they are highly hydrophobic and has a high oil sorption capacity (Bayat et al., 2005), however their low degradability is a major environmental concern. In addition, synthetic sorbent such as polypropylene is derived from fossil fuel, a non-renewable resource. Hence there is a need to explore more eco-friendly alternatives to cleaning oil spills.

Natural sorbents can provide a cheap, biodegradable and eco-friendly alternative. There have been studies on the use of natural organic sorbents such as barley straw (Husseien et al., 2009), rice husk ash (Vlaev et al., 2011) and peat-based sorbents (Cojocaru et al., 2011) to clean up oil spill. However, the main drawbacks of these plant-derived sorbents are a relatively low oil sorption capacity due to their low hydrophobicity and poor buoyancy compared to synthetic sorbents such as polypropylene (Chung et al., 2011). Chemical modification of natural organic sorbents has been reported to increase their oil sorption capacities. Teli and Valia (2013) reported that the acetylation of fruits fiber led to a significant increase in acetyl group. The modified fibers were found to absorb less water instead of oil. Researchers from the National University of Singapore has also found that cellulose aerogels treated with methyltrimethoxysilane (MTMS) rendered the aerogel hydrophobic, allowing it to selectively absorb non-polar liquids such as oils (Nguyen et al., 2013).

Pomelo is a tropical fruit, the largest of the citrus family. It is currently being widely cultivated and consumed in countries such as Thailand. However the peel together with the thick pith is often discarded after the fruit is being consumed. Pomelo peels contain about 42% cellulose and the pith is thick and spongy (Chumee & Seeburin, 2014). Hence it has great potential to be used as an oil sorbent. Therefore, this research aims to increase the oil sorption capacity of pomelo pith through different chemical treatments, by treating them with methyltrimethoxysilane (MTMS), oleic acid and sodium hydroxide. MTMS and oleic acid contain hydrophobic alkyl groups which could possibly be grafted onto the cellulose in pomelo pith, rendering it hydrophobic. Treatment with sodium hydroxide, on the other hand could potentially increases the porosity and surface area of pomelo pith, increasing its oil sorption capacity.

Hypothesis:

Chemical modification of pomelo pith will increase its oil sorption capacity in both pure oil and oil-seawater environment.

2. Materials and Methods

2.1 Materials

Diesel was purchased from petrol kiosks. Oleic acid and MTMS were obtained from Sigma Aldrich. Sodium hydroxide was procured from GCE Chemicals.

2.2 Preparation of sorbent

Pomelos were procured from local supermarket and the peels separated from the fruit. The pomelo pith was separated from the peel and cut into 1 cm x 1 cm x 1cm cubes. The cubes were washed with deionised water and dried in an oven for 24 hours until constant mass.

2.3 Chemical modification of pomelo pith

2.3.1 By oleic acid

Oleic acid (2 g) was added to the pomelo pith cubes (10 g) suspended in 500 ml of n-hexane containing 0.25ml of concentrated sulfuric acid as catalyst. The mixture was refluxed at 65°C for 6 hours using a Dean-Stark apparatus set-up. The long alkyl chain from the oleic acid was grafted onto the cellulose present in pomelo pith by esterification reaction between the hydroxyl group of cellulose and the carboxyl group on the oleic acid. After the reflux, the grafted sorbents were washed with n-hexane and dried in an oven until constant mass.

The equation for the reaction is shown below:

$R\text{-}OH + C_{17}H_{33}COOH \leftrightharpoons R\text{-}OCOC_{17}H_{33} + H_2O$

2.3.2 By MTMS

The pomelo pith cubes were placed in a glass vial. A vial containing 5ml of MTMS was placed into the bottle which was then capped. The bottle containing both the pomelo pith and MTMS was heated in an oven at 70°C for 2 hours.

The cellulose present in pomelo pith was coated with MTMS via chemical vapor deposition. MTMS vapor undergoes a reaction with the hydroxyl (-OH) functional groups on the cellulose, forming hydrophobic methyl (CH_3) groups on the surface instead.

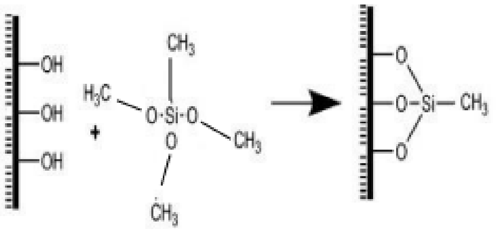

Figure 1: Reaction of cellulose with MTMS

The reaction is shown below:

$3\ R\text{-}OH + C_4H_{12}O_3Si \rightarrow R_3O_3SiCH_3 + 3\ CH_3OH$

2.3.3 By sodium hydroxide

10 g of pomelo pith cubes were soaked in1M sodium hydroxide for 24 hours. The cubes were then separated, washed until neutral and dried until constant mass.

2.4 Characterization of modified pomelo pith

Both the unmodified and modified pomelo piths were analysed using a Scanning Electron Microscope (SEM) to compare their morphology before and after chemical modification.

2.5 Effect of chemical modification on hydrophobicity of sorbents

2.5.1 Water absorption test

Modified pomelo pith cubes (1 g) were immersed in 70 ml of deionised water for 1 hour. After 1 hour, the sorbents were separated using a sieve and excess water was drained. The final mass of sorbents was measured.

By taking the difference between the final and initial mass, the amount of water absorbed can be determined. If the chemical modification is successful, the amount of water absorbed should decrease due to the sorbent being more hydrophobic after the chemical modification.

2.5.2 Water contact angle

A piece of modified pomelo pith cube was placed on a glass slide and a drop of water was placed onto its surface. The image was captured using a USB digital microscope. The contact angle was determined using a computer software known as Dinocapture. Water contact angle of more than 90°C would suggest that a surface is hydrophobic.

2.6. Determination of oil sorption capacity of unmodified and chemically modified pomelo

2.6.1 In pure oil environment

The initial masses of pomelo pith cubes were measured before the cubes were immersed in 70ml of diesel. After 1 hour, the pomelo pith was removed and the excess oil present on the surface of the cubes was allowed to drain off before weighing.

Oil sorption capacity was determined using the following formula:

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

Where
Q_t is the oil sorption capacity in g/g
m_w is mass (in g) of pomelo pith after sorption
m_d is mass (in g) of pomelo pith before sorption

2.6.2 In oil-seawater environment

The purpose of conducting such an experiment is to simulate an oil spill in seas. By comparing the amount of oil absorbed by the modified and unmodified pomelo pith cubes, the effect of the chemical modification on the oil sorption capacity of the pomelo pith cubes can be determined.

Artificial sea water 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. 10g of diesel was added to 100ml of artificial seawater in a conical flask to simulate an oil spill. The initial mass of pomelo pith cube was measured. It was then added to the oil-seawater mixture. The flask was shaken at 150rpm for 1 hour. Using a separating funnel, hexane was used to extract the remaining diesel that has not been absorbed. Unabsorbed diesel was recovered using a rotary evaporator. Remaining water in the diesel sample was removed using anhydrous sodium sulfate. Mass of diesel recovered was then measured.

Mass of diesel absorbed = Initial mass of diesel – mass of diesel recovered

Oil sorption capacity was then determined by the formula as described in 2.6.1

3. Results and Discussion

3.1 Effect of MTMS and oleic acid treatment on hydrophobicity of pomelo pith

3.1.1 Water sorption capacity

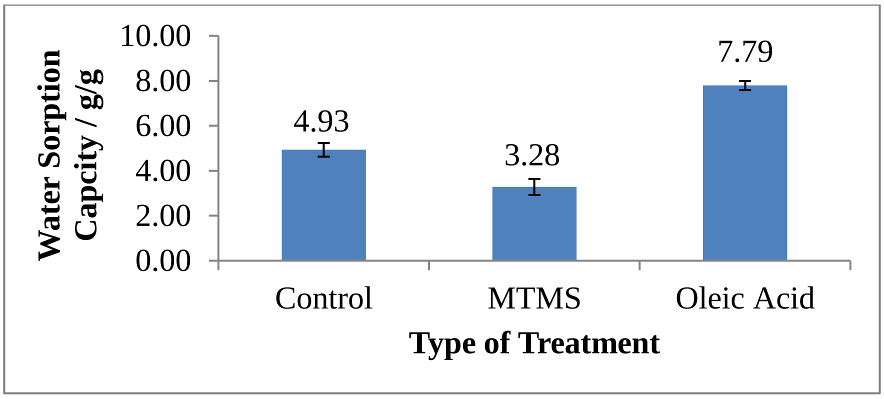

Figure 2. Water sorption capacities of pomelo pith after treatment

The purpose of the water sorption capacity is to ascertain whether the treatment has rendered the pomelo pith hydrophobic, meaning water-repelling.

Out of the 3 sorbents, MTMS treated pomelo pith absorbed less water than control, suggesting that MTMS treatment has successfully enhanced the pomelo pith's hydrophobicity. On the other hand, the oleic acid treatment does not give the expected result of decreased water sorption capacity. This could be due to the fact that the morphology of pomelo pith changed after oleic acid treatment. It was observed that the pomelo pith had broken up into smaller fragments (figure 4) and this could be attributed to the concentrated sulfuric acid (catalyst used in the grafting of oleic acid) dehydrating the cellulose in the pomelo pith. This would increase its porosity and explains the unexpectedly high water sorption capacity.

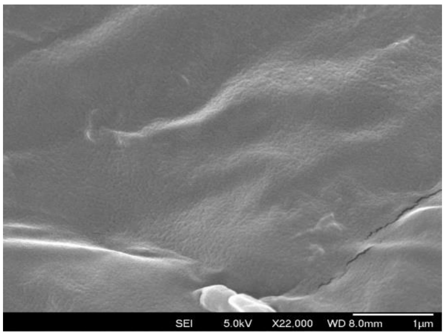

Figure 3. SEM image of untreated pomelo pith

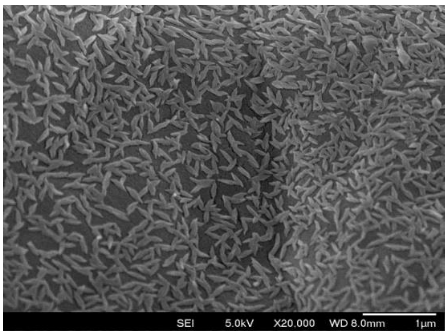

Figure 4. SEM image of oleic acid treated pomelo pith

3.1.2 Water contact angle

The water contact angle of the pomelo pith was tested using a Dino-Lite digital microscope. The larger the water contact angle, the more hydrophobic the surface is. MTMS treated pomelo pith has a greater water angle than the control (figure 5, 6 and 7) which signifies that it is more hydrophobic and agrees with the decreased water sorption capacity. Mann Whitney U test reveals that the difference in the contact angle between the control and MTMS treated pomelo pith is significant as the p value is 0.011 at a significance level of 5%. No data can be obtained for oleic acid treated pomelo pith as it was porous and water seeps in immediately.

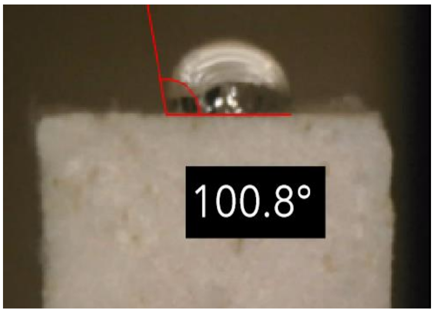

Figure 5. Water contact angle of untreated pomelo pith

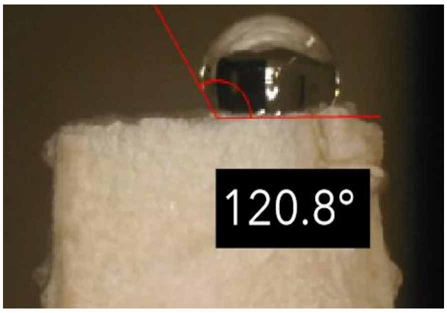

Figure 6. Water contact angle of oleic acid treated pomelo pith

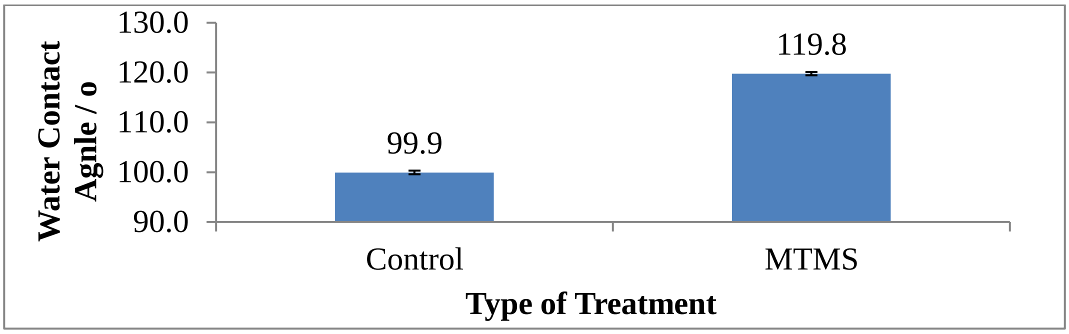

Figure 7. Water contact angle of pomelo pith before and after MTMS treatment. N=5

3.2 Oil sorption capacity

3.2.1 Oil sorption capacity in pure oil environment

Figure 7 shows the oil sorption capacities of pomelo pith modified using different methods as compared to the control in the pure oil environment. All the modified pomelo pith has higher oil sorption capacity than that of control, with MTMS coated pomelo pith displaying the highest oil sorption capacity. This could be attributed to the hydrophobic MTMS coating which attracts oil and hence increases the amount of oil sorbed. Treatment by oleic acid increases the porosity of the pomelo pith, allowing more oil to be sorbed. On the other hand, treatment with sodium hydroxide removes lignin and hemicellulose from pomelo pith, thus altering its morphology and resulting in more folds on its surface (figure 10), thus increasing its surface area for oil sorption.

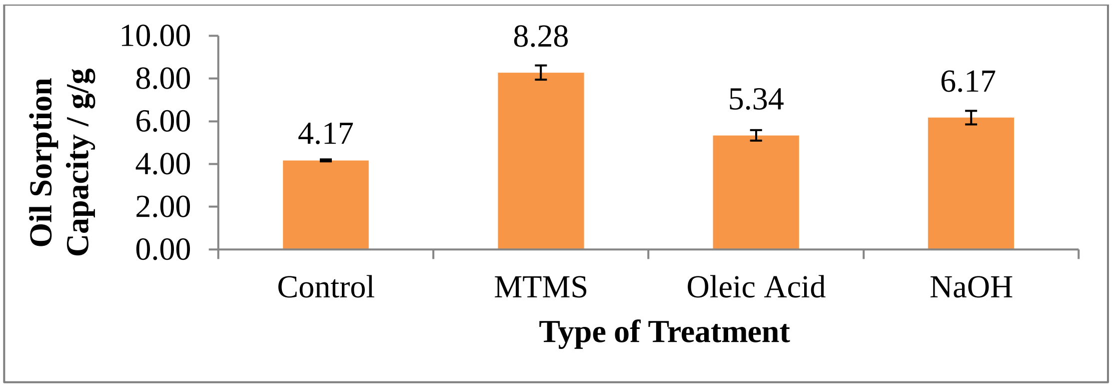

Figure 8. Oil sorption capacity of chemically modified pomelo pith. N =5

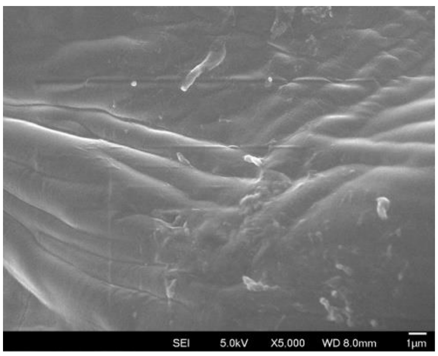

Figure 9. SEM image of untreated pomelo pith

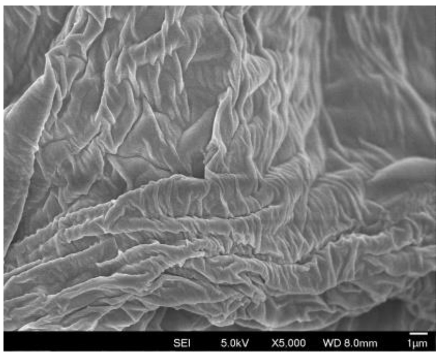

Figure 10. SEM image of NaOH treated pomelo pith

3.2.2 Oil sorption capacity in oil-seawater environment

Figure 11 shows that MTMS treated pomelo pith exhibited the highest oil sorption capacity in the oil-seawater environment among the 4 types of pomelo pith. This is again attributed to the hydrophobic MTMS coating on the pomelo pith, which attracts oil but repels water, hence allowing selective sorption of oil and increasing its oil sorption capacity.

Oleic acid modified pomelo pith also shows an increase in oil sorption capacity in oil-seawater environment as compared to the control. This is due to the fact that in addition to the increased porosity, it also has the long chain alky chain from oleic acid on it which attracts oil.

In contrast, sodium hydroxide treated pomelo pith does not show any significant improvement in the oil sorption capacity in oil-seawater environment as compared to control. Although treatment with sodium hydroxide increases the porosity of pomelo pith, the modified pomelo pith would attract both oil and water as there is no hydrophobic coating on it. Hence its oil sorption capacity in oil-seawater environment is lowest among the 4 types of pomelo pith.

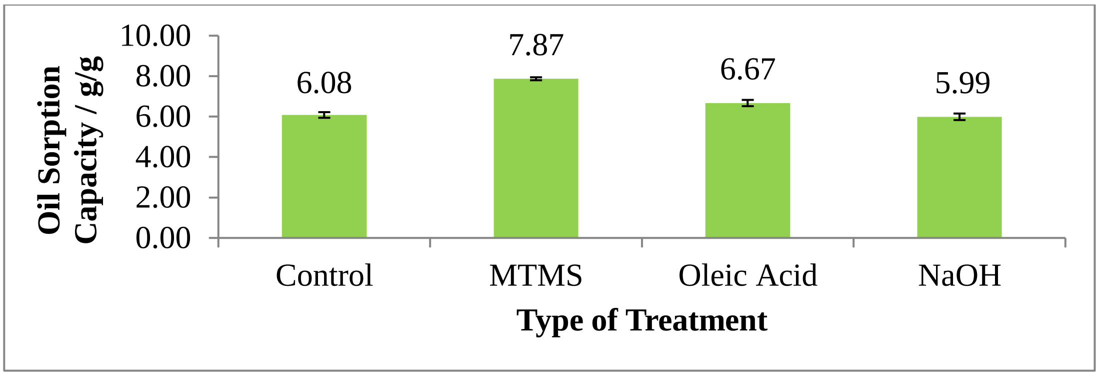

Figure 11. Oil sorption capacity of chemically modified pomelo pith in oil-seawater environment. N=5

4. Conclusion

Pomelo pith is a natural waste that is fibrous, spongey and thick, making it a potential oil sorbent. The recycling of pomelo pith into oil sorbents help to reduce environmental problems by reducing waste, at the same time mitigating the problem of oil spill. Chemically modifying the pomelo pith could further increase its oil sorption capacity. Pomelo pith modified with MTMS exhibited greatest oil sorption capacity in both pure oil and oil-seawater environments, showing great promise to be an environmentally friendly alternative to current methods of resolving oil spills

In future, synergy of sodium hydroxide and MTMS treatments could be explored. The pomelo pith could be first treated with sodium hydroxide to increase its porosity, followed by coating with MTMS to render its surface hydrophobic. Such treatments could potentially increase the oil sorption capacity of pomelo pith in oil-seawater environment.

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