Lignin-Based and Disulfate-Linked Aerogel as a Selective, Controllable, Reusable Superabsorbent

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Background

Oil spills pose a large threat to marine ecosystems. Recently effective oil spill cleanup methods have become a high demand because of the rapid development of petrochemical and marine industries. The current cleanup methods include:

- Chemical dispersion agents
- In-situ burning
- Physical surface oil collection
- Sponges and sorbents

These current methods are harmful to the environment, non-biodegradable, extremely costly, low oil absorption, and time consuming. Therefore, an ecofriendly, highly efficient, low cost, and excellent absorbent is needed.

Recently gelation has been a topic of interest because of the many bio-based applications that are possible. The use of a gel is attractive because of:

- Easy preparation
- Well-recognized performance
- Thermodynamic stability

Motivation

Lignin has huge production, but only a limited market:

- Waste in biomass and ethanol production.
- Cheap and sustainable.
- Highly cross-linked polymer that is the 2nd most abundant biopolymer on earth and represents 15-35% mass weight of the dry biomass.
- Incorporating lignin into an aerogel/organogel could aid in absorbing oil and using alkali lignin could increase hydrophobicity.
- The introduction of epoxy groups into lignin offers more routes for conversion of lignin into value-added products.

Objectives

1. To synthesize a lignin-based high porous sponge for oil absorption.
2. To characterize of the lignin-based sponge.
3. To evaluate the oil absorption lignin-based sponge.
4. To optimize absorption and pore size in the lignin-based sponge by altering the lignin to DMSO ratio.

Here, a potential oil absorbant was prepared by a mild method of modified Alkali Lignin (EAL), trimethylolpropane tris(3-mercaptopropionate) (TMMP) in dimethyl sulfoxide (DMSO) catalyzed by sodium hydroxide (NaOH).

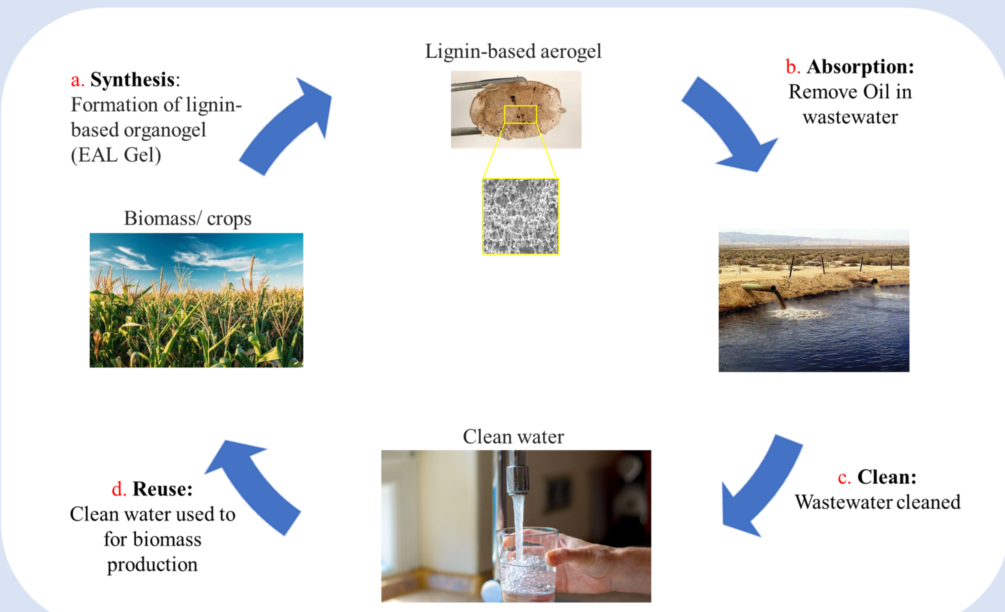


Figure 1. Full cycle using biomass/crops to create the lignin-based aerogel to clean water and reuse for crop irrigation.

Methods

Synthesis of lignin-based organogel

The lignin-based organogel was synthesized using a simple and facile method:

- After the epoxidized alkali lignin (EAL) is achieved, the organogel was prepared by dissolving different amounts (0.00g, 0.05g, 0.09g, 0.15g, 0.18g, 0.27g) of the epoxidized alkaline lignin in dimethyl sulfoxide (DMSO) in a 40 ℃ water bath to achieve different ratios of EAL to DMSO.
- After dissolved, TMMP was added and NaOH pebbles were added and kept in the 40˚C water bath until a brown gel was formed.
- After the brown gel formation, the gel was purified and then freeze dried to achieve the final organogel.

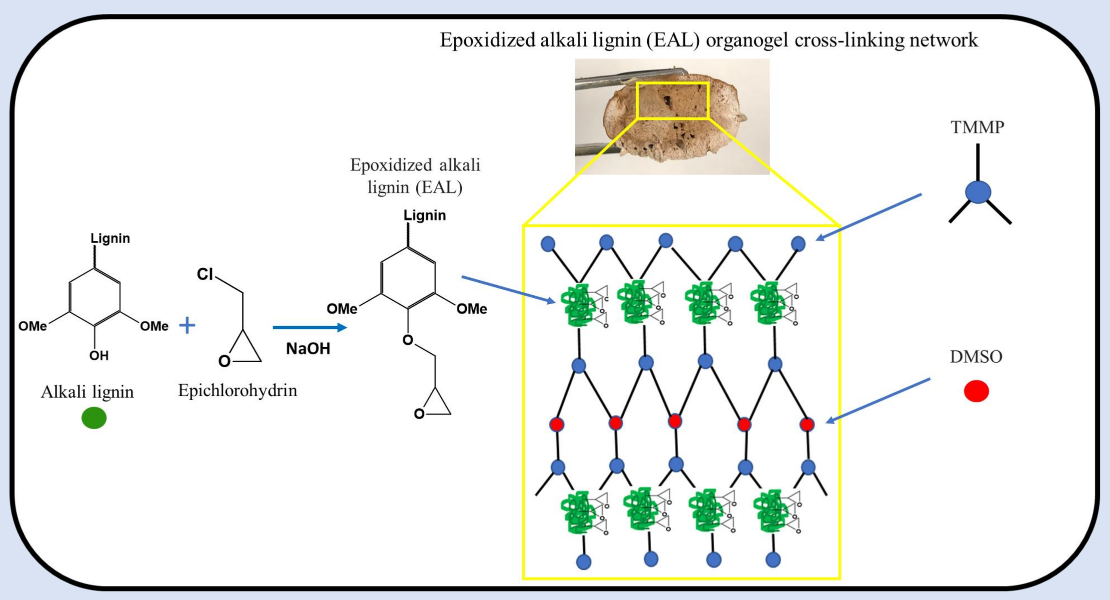


Figure 2. The scheme of formation of alkali lignin aerogel.

Characterization Methods

The formation of oil-absorbent properties were confirmed by Fourier Transform Infrared (FTIR) Spectroscopy, Thermal Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM).

Absorption Method

The oil removal capacity was performed at different contact times in an oil as well as oil/water mixture. The absorbant was made using different percent ratios of lignin to DMSO to create different pore sizes and evaluate the impact on oil absorption.

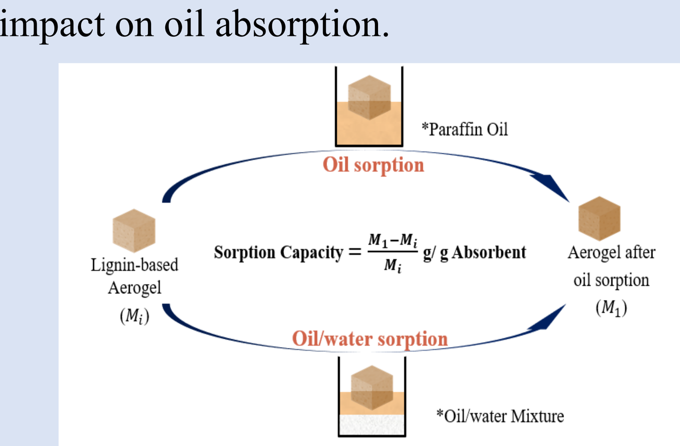


Figure 3. The method used for conducting the oil and oil/water absorption capacity test.

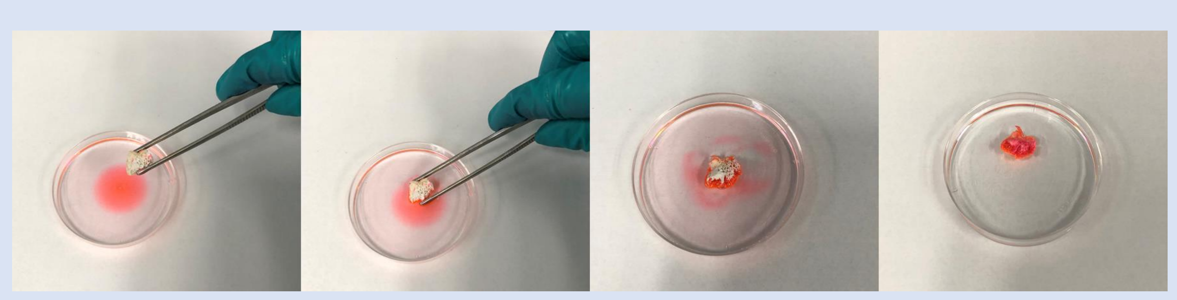


Figure 4. The organogel absorbing red dyed oil in water. It is evident that the organogel absorbs all the oil and turns red from the dye.

Results and Discussion

Characterization

FTIR

- The band at 931cm-1 is associated with the epoxy group.

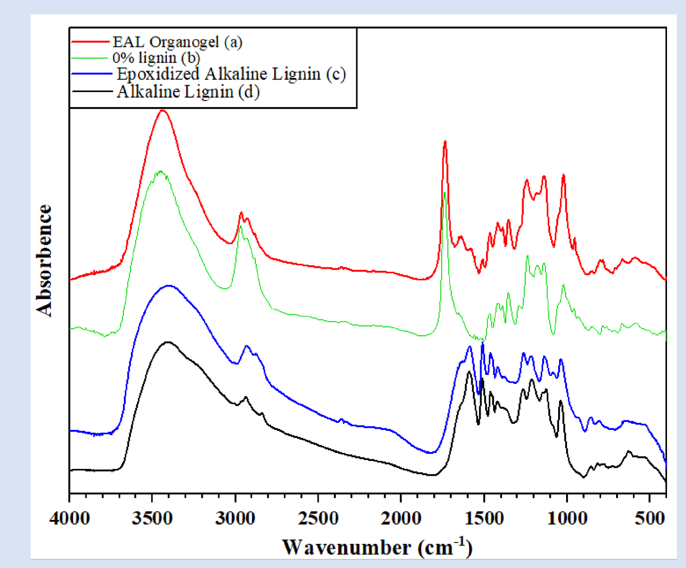
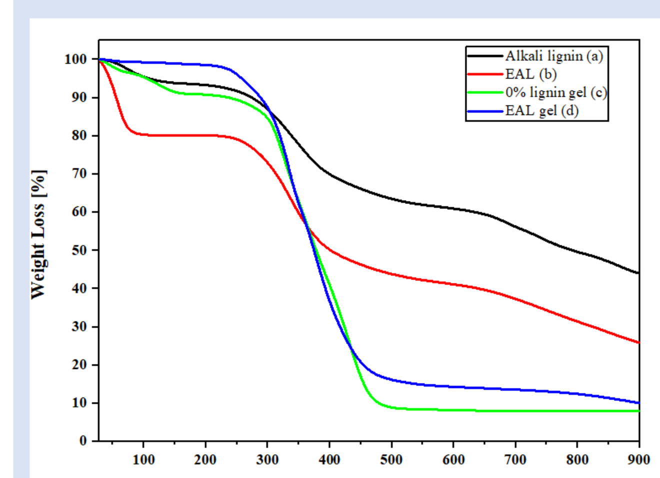


Figure 5. FTIR results of (a) organogel, (b) 0% lignin gel, (c) EAL, (d) Alkali lignin.

TGA



- The residual mass left after heating up to 900℃ is 8.7% for the organogel.

Figure 6. TGA results of (a) alkali lignin, (b) EAL, (c) 0% lignin gel, (d) organogel.

SEM

- The smallest pore sizes are observed in (c) the 1.5% gel, this corresponds with the high absorption capacity observed with the oil absorption test.

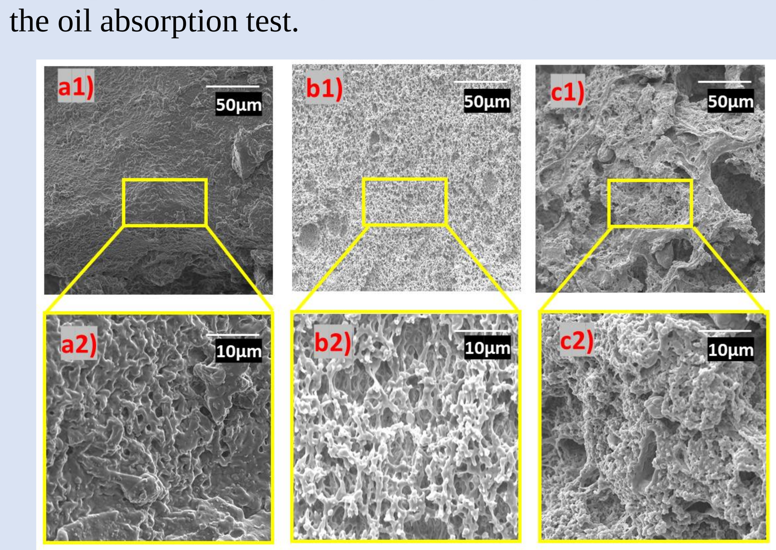


Figure 7. SEM images of surface morphology of various organogels (a) 0%, (b) 1.5%, (c) 4.5%.

Pore size and porosity

- The pore size is the smallest at 0.16μm for the 1.5% gel. The 1.5% gel also has high oil absorption.

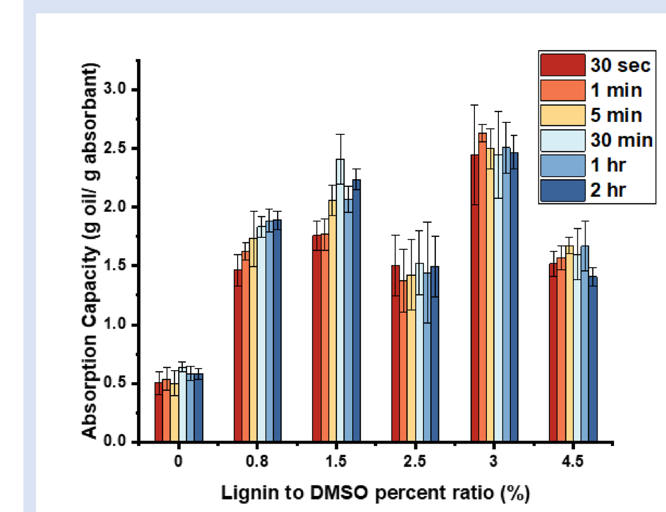
Sample (%)	Porosity (%)[α]	Pore size (μm)[α]
0.0	35.0	-
0.8	83.0	42.75
1.5	90.7	0.16
4.5	88.0	0.30

α Calculated from SEM images with the aid of ImageJ 1.46 s/w by randomly selecting 125 pores.

Table 1. Pore size and porosity results using SEM images with Imagej tech`nology.

Absorption

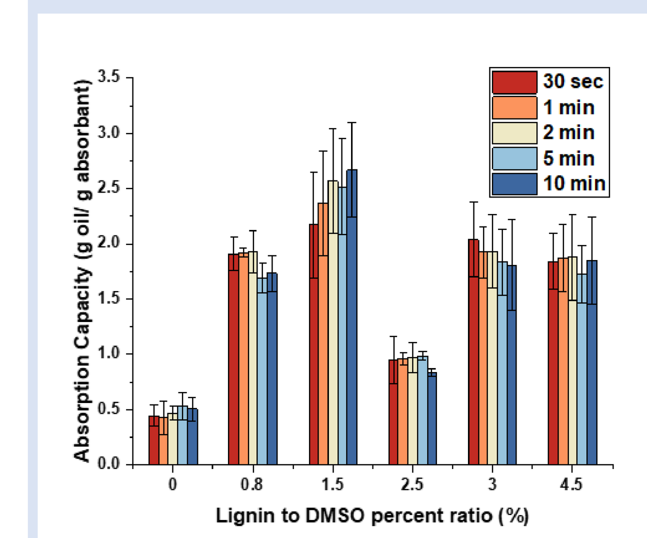
Oil absorption



- The 3% lignin to DMSO gel has the highest absorption capacity. It is also evident that adding lignin aids in absorption capabilities.

Figure 8. Oil absorption capacity results.

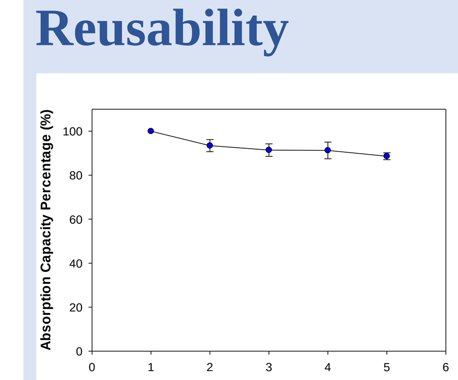
Oil-water separation



- The 1.5% lignin to DMSO gel has the highest absorption capacity.

Figure 9. Oil-water separation absorption capacity results.

Reusability



- The organogel was successfully washed with chloroform, dried, and reused 5 times.

Figure 10. Absorption capacity after washing and reusing. After 5 trials, the organogel had an absorption capacity percentage of 88.6%.

Conclusion

- A selective and reusable lignin-based superabsorbent was successfully synthesized by thiol-epoxy/ene click polymerization.
- The organogel had an absorption capacity up to 2.7 g oil/ g absorbant.
- The 1.5% and 3% ratio of lignin to DMSO yielded the highest absorption capacity.

References

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