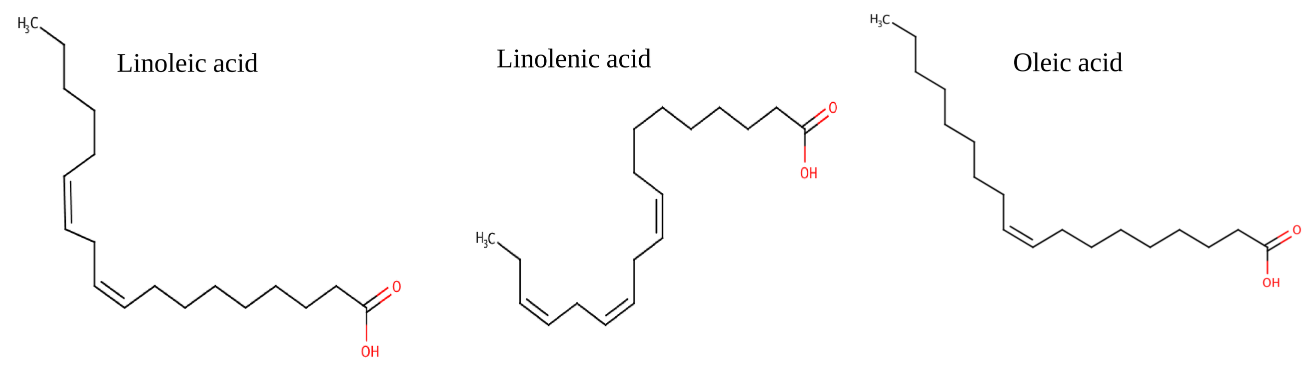
# Development of Cellulose-based Oxygen Scavenging Films for Olive Oil Packaging Applications: Photo-oxidation study

Andrew Freiburger, Mohommadali Azadfar*, Michael Wolcott*

*Composite Materials and Engineering Center, Voiland College of Engineering and Architecture, Washington State University, Pullman, WA, USA

## Background

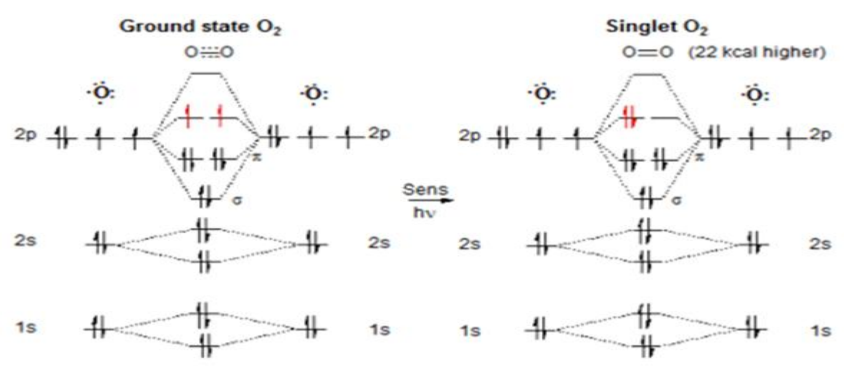
- Fats and oils are composed of fatty acids. The presence of carbon-carbon double bonds in unsaturated fatty acids make them prone to oxidation.
- Oleic acid (monounsaturated/omega 9), Linoleic acid (polyunsaturated/omega 6), and Linolenic acid (polyunsaturated/omega 3) are the most common plant-sourced unsaturated fatty acids.




- Olive oil is particularly sensitive to oxidation because it naturally contains chlorophyll. When photoreactive compounds – called photosensitizes – like chlorophyll pigments become excited under light, they impart that excitement to triplet oxygen and produce singlet oxygen. Singlet oxygen is far more reactive and oxidizes oil faster than triplet oxygen. Reducing singlet oxygen concentration is necessary for preserving oil.
- Conventional methods of preserving foods/oils with antioxidants, such as BHT and BHA (Iverson), or antimicrobial agents, such as sodium metabisulfate (Rencuzogullari), pose health concerns. Offering a non-invasive method of preserving food may provide the same benefit while bypassing health concerns.
- According to BP, there are 1696.6 billion barrels of oil remaining globally(4). At the 2017 consumption rate, this translates into 50.2 years of oil remaining; however, this time is an overestimation because the demand for oil is growing at a rate of ~1% annually (King). The need for renewable plastics increases with each passing year.

## Triplet vs. Singlet state oxygen

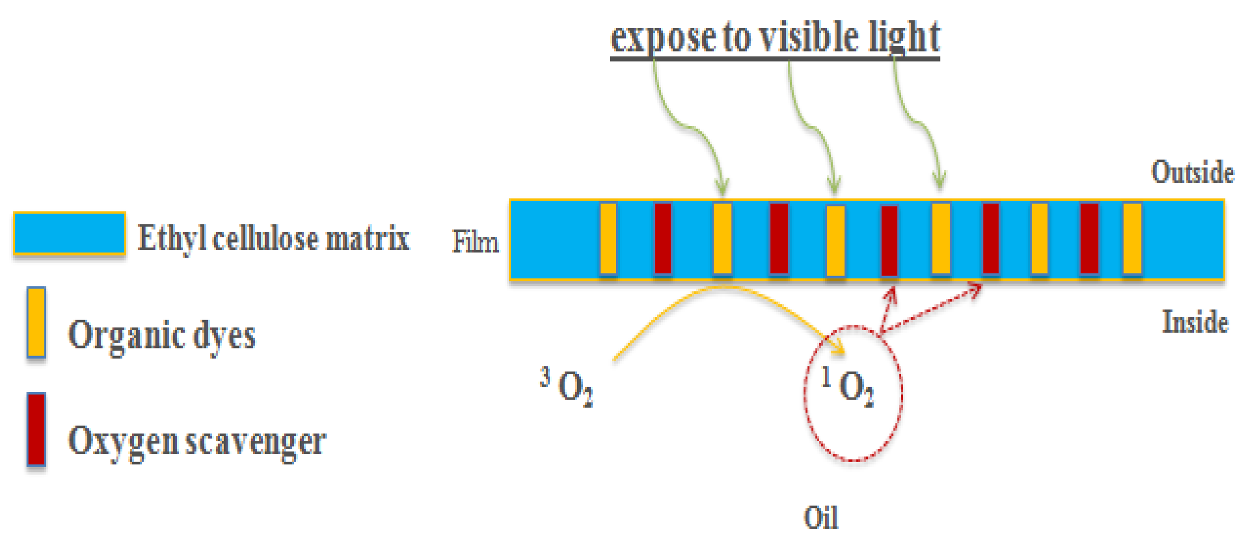
- Triplet oxygen
  - Stable, ground state, diradical configuration of oxygen.
  - Oxidizes *existing* fatty acid radicals, but effectively does not react with virgin fatty acids (Min).
  - Prevention of oxidation from triplet state oxygen:
    - Store oil in low heat/light environments to prevent radical fatty acid formation
- Singlet oxygen
  - Excited state, non-radical, molecular oxygen.
  - Highly reactive and does not require existing fatty acid radicals to oxidize oil.
  - Preventing oxidation from singlet state oxygen:
    - Oxygen scavenging systems that adsorb oxygen, and low light/heat conditions to prevent triplet state oxygen from exciting to singlet state oxygen



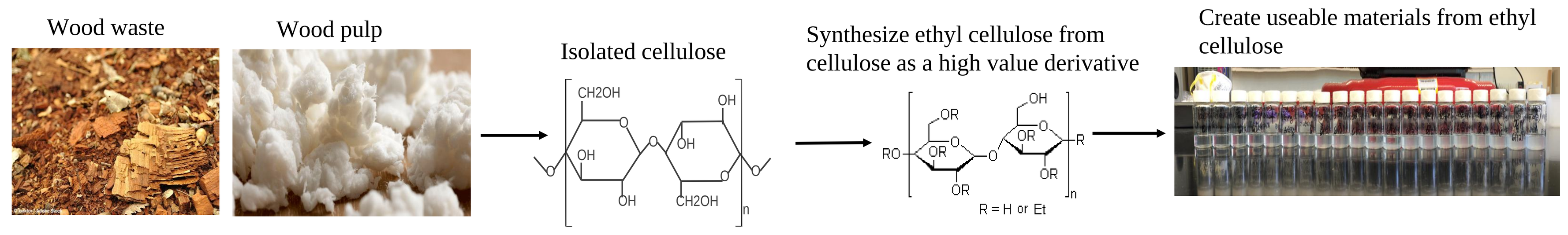

## Research question

- Can an oil packaging film, created from renewable materials such as cellulose, prevent the oxidation of olive oil from singlet oxygen specifically, without directly contacting or contaminating the oil?

## Research Idea




## Goals



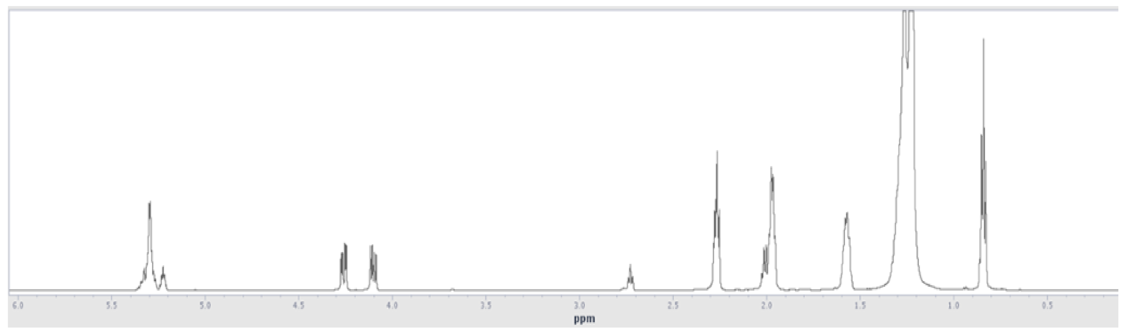

► Investigate the potential of ethyl cellulose to produce polymeric solutions for casting

► Prepare homogeneous solutions with organic dyes and singlet oxygen scavengers in the ethyl cellulose matrix in binary solvents ethanol and ethyl acetate.

► Develop a film that is capable of preventing the oxidation of olive oil in the presence of visible light at room temperature

► Assess sample and control oils via liquid-state $^1$H NMR spectroscopy

## Results



| Peak | δ (ppm) | Proton | Compound |
|---|---|---|---|
| 1 | 5.29 | CH=CH | All unsaturated fatty acids |
| 2 | 5.15 | CHOCOR | Glycerol |
| 3 | 4.19 | $CH_2OCOR$ | Glycerol |
| 4 | 2.76 | $CH=CHCH_2CH=CH$ | Linoleyl and linolenyl |
| 5 | 2.2 | $CH_2COOH$ | All acyl chains |
| 6 | 2.02 | CH2CH=CH | All unsaturated fatty acids |
| 7 | 1.6 | $CH_2CH_2COOH$ | All acyl chains |
| 8 | 1.2 | $(CH_2)_n$ | All acyl chains |
| 9 | 0.95 | $CH_2CH_2CH_2CH_3$ | Linolenyl |
| 10 | 0.85 | $CH=CHCH_2CH_3$ | All acids except linolenyl |

**Figure 1:** The spectrum is a proton NMR spectra of pure extra virgin olive oil. This was the basis of comparison for all other samples.

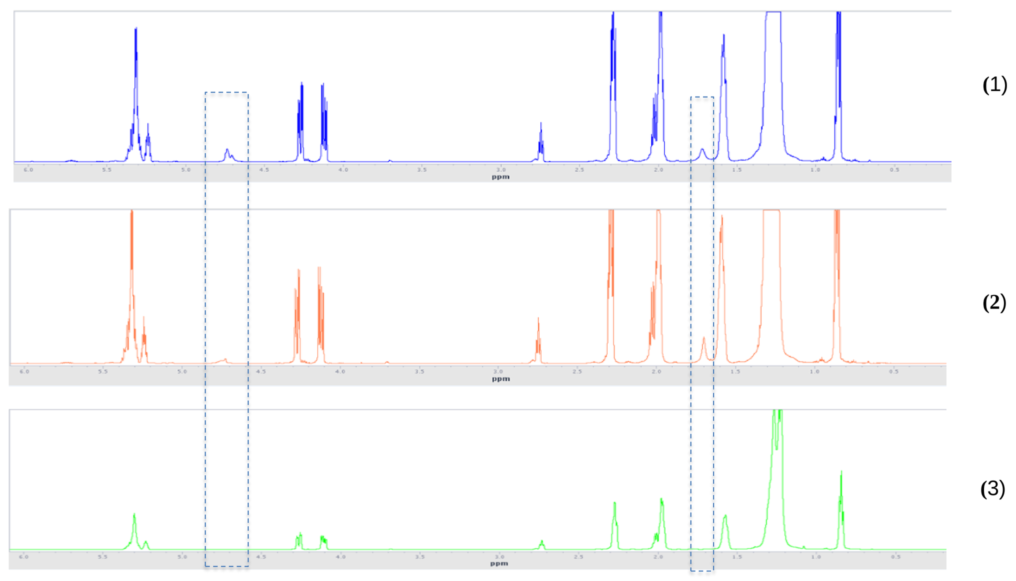



**Figure 2:** Proton NMR spectra of extra virgin olive oil samples. From top to bottom:
1. Oil exposed to light without any protective film
2. Oil exposed to light under an organic dye+ethyl cellulose film
3. Oil exposed to light under an organic dye+oxygen scavenger+ethyl cellulose film.

The lack of peaks in the highlighted region of the bottom spectra suggests that the film with dyes+oxygen scavengers prevented the oxidation of oil.

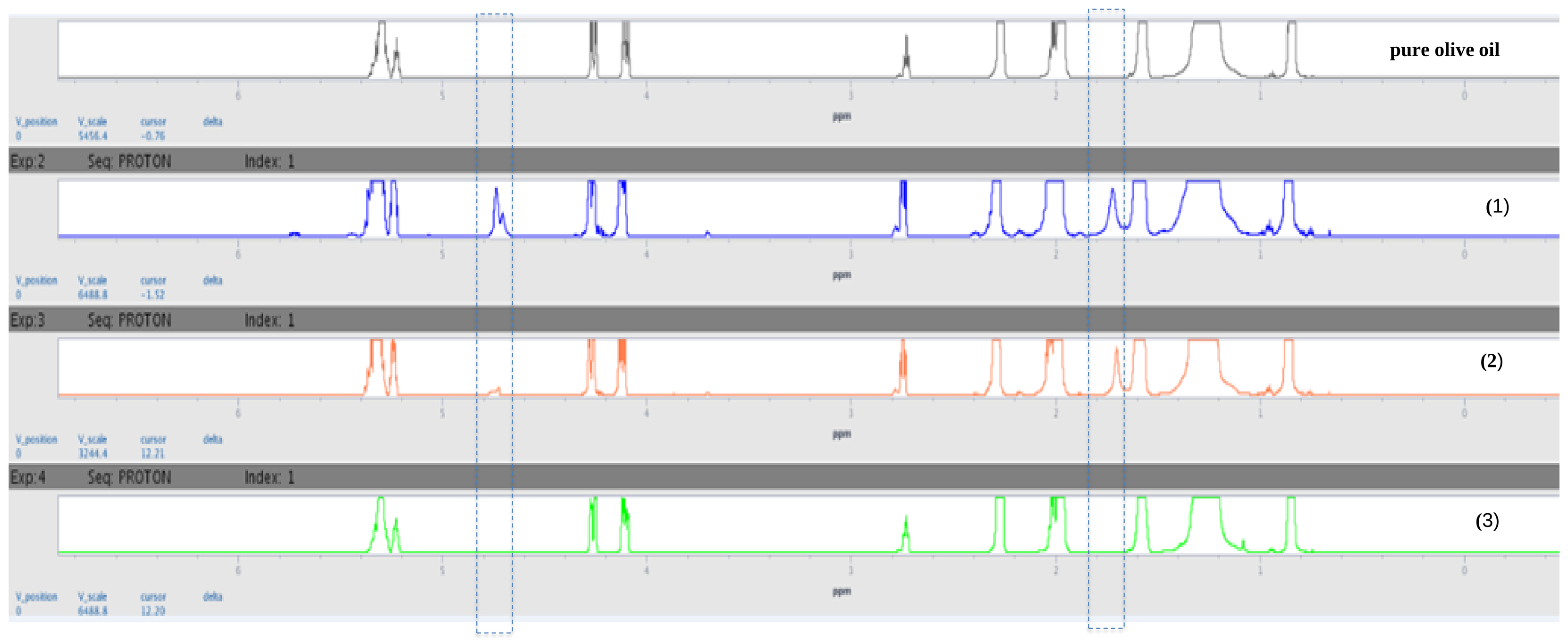



**Figure 3:** The proton NMR spectra compares pure oil – top spectra – with the same 3 sample spectra from figure 2 in the same order. The similarity of the top and bottom spectra supports that the dye+oxygen scavenger combination in the ethyl cellulose film preserved oil against light exposure.

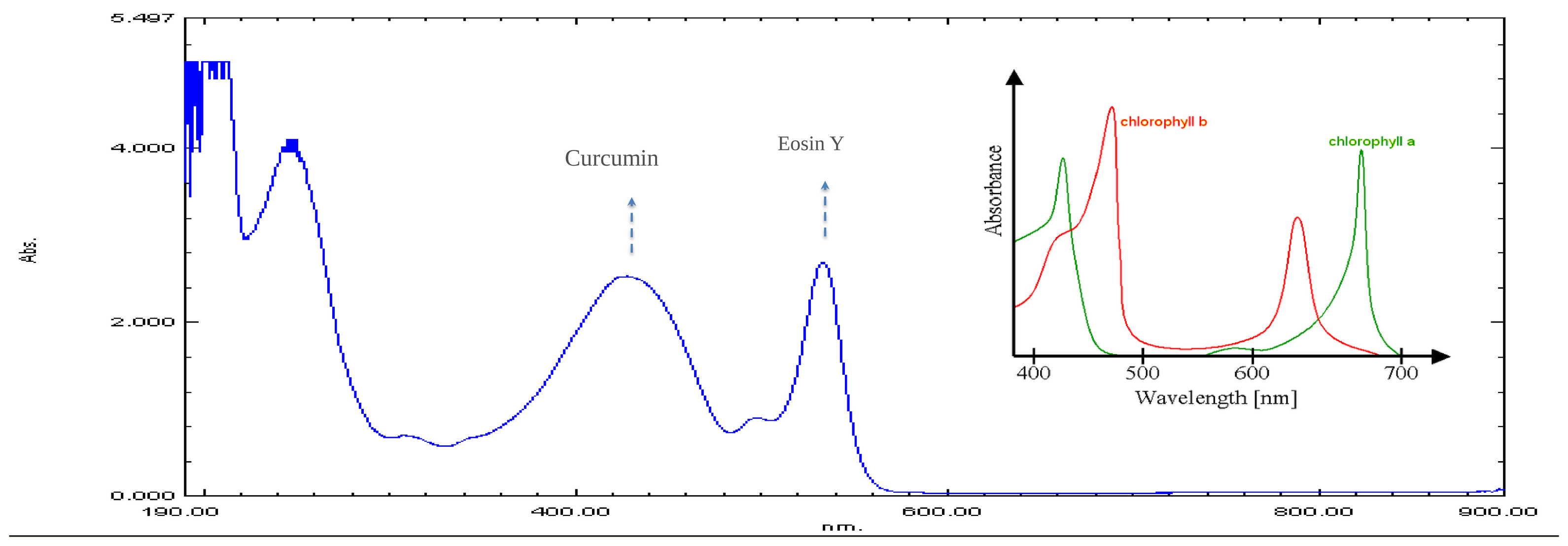



**Figure 4:** The above figures are UV-Vis spectra for our dye-ethyl cellulose solution and chlorophyll a and b. The spectra demonstrates that curcumin and chlorophyll absorb a similar range of light between 400-500 nm. This is significant because preventing chlorophyll excitation helps reduce the rate of oil oxidation.

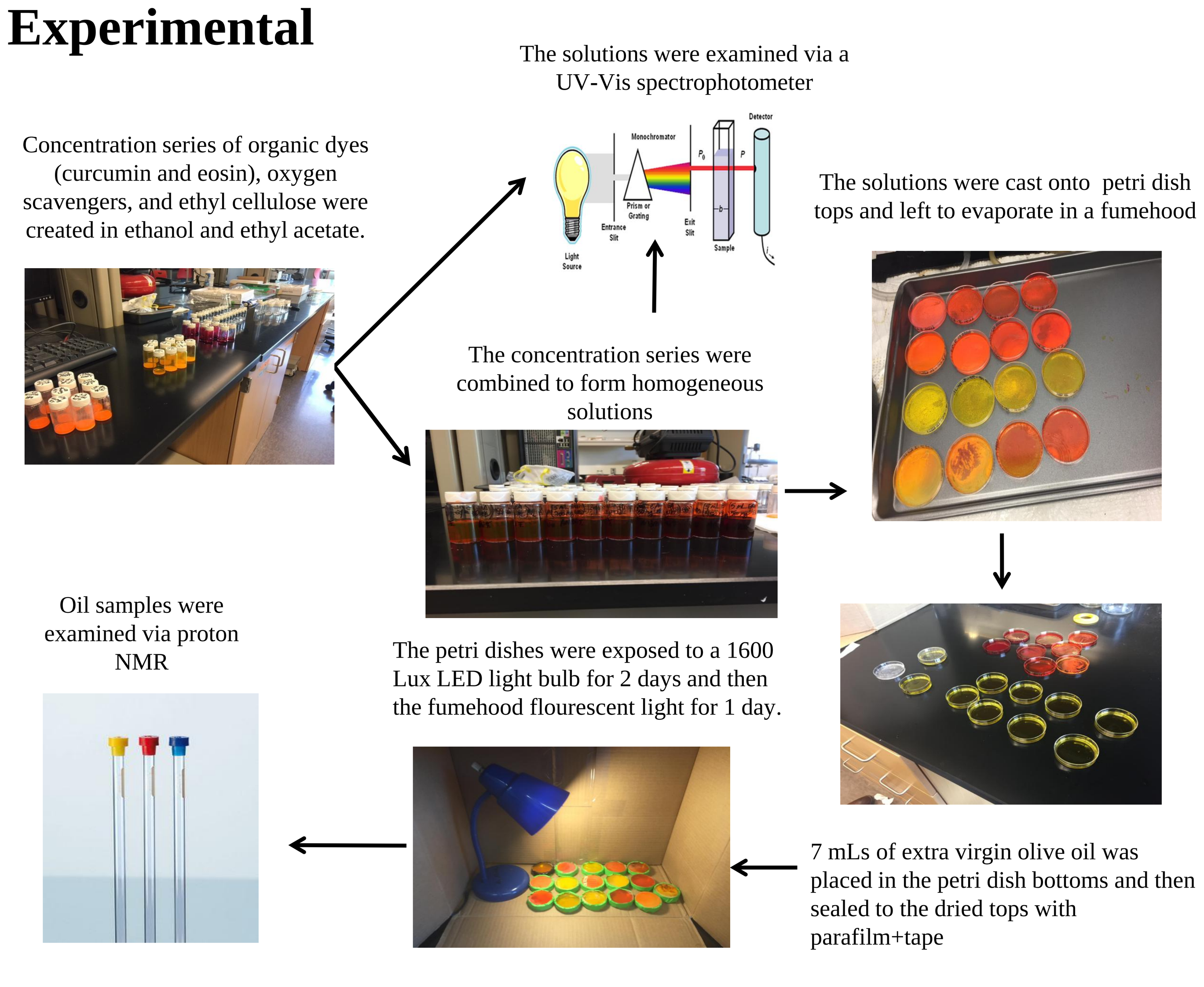
## Conclusions

The work presented here described the modification of ethyl cellulose-based polymeric solution with organic dyes eosin, curcumin and ascorbic acid in ethyl acetate-ethanol binary solvent with particular reference to the stability of extra virgin olive oil against visible light.

The organic dyes, eosin and curcumin, with similar visible light absorption regions compared to the chlorophyll in ethyl cellulose matrix have the potential to be considered as an organic barrier between oil and light.

The presence of ascorbic acid in the matrix showed capable of protecting olive oil against visible light, significantly.

## Experimental




## Acknowledgments

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