Investigating the Stability of Organic Materials for Commercial Dyeing

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Abstract - **Sustainability and environmental ethics are major focuses of future developments in many fields of infrastructure and industry. One of these fields is the industry of garment dyeing. With only a handful of garment dyeing facilities in the country, TS Designs, located in Burlington, North Carolina, has developed a niche clientele and craft of the use of natural materials for use in commercial dyeing. Organic materials have been used in textile dyeing since the very beginning of documented history, but limited research has been done in the translation of these practices to industrial contexts. Natural dye can be derived from organic waste products and is a great way to incorporate eco-friendly methods in the industrial production of clothing. Unfortunately, due to the dyes being made from organic materials, the resulting color of the product may change over time as the material degrades, which is not preferable for the sale of a consistent product. It is important to extract dye from materials as they are available before they degrade in order to reduce waste. The goal of our research is to be able to test the dye stability of organic materials and determine proper practices for preserving each dye extract.**

Index Terms – sustainability, organic dyes, preservation, optimization

INTRODUCTION

Organic dye has been a staple throughout human history. One of the earliest known organic dyes is indigo, dating back to 2500 BCE in China and India. The Greeks and Romans obtained indigo through trading between India and introduced red dye from the roots of the madder plant [1]. As time passed the use of organic dyes from a large variety of sources became widespread. In the Middle Ages, people began to cultivate plants for their dye. These plants included woad for its blue dye, weld for its yellow dye, and logwood for its purple dye [1]. This trend of increasingly prevalent organic dye continued until the 19th century, when the first synthetic dye was created [2]. By the 20th century, organic dyes had largely been replaced by synthetic versions due to the lower cost and ease of production. Currently, organic dyes are rarely used in fast fashion; however, they still remain in high end fashion and hand-crafted textiles.

Though natural dyes have been used for thousands of years, there is little research about how to store these sustainable dye extracts to an industrial setting. Naturally sourced materials that are used by companies have the benefits of being cost effective, however, they are unable to be received throughout the year, making it difficult to keep up the dying process. The stability of natural dye materials over time must be investigated to make the use of these materials feasible for the textile industry. Some dye materials have been investigated for long-term storage ability, but those studies suggest that the behavior of each natural material over time depends on its unique chemical composition [4].

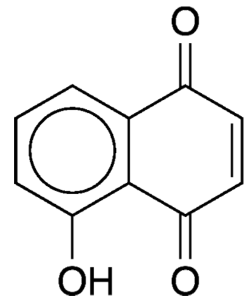

FIGURE 1.
CHEMICAL STRUCTURE OF JUGLONE [3]

Degradation of natural materials in aqueous solution requires molecular motion. Since molecular motion is correlated with the temperature, increasing temperature should accelerate degradation in accordance with the Arrhenius relationship. Similarly, decreasing temperature is associated with decreases in reaction rate and therefore increased stability. This study will examine the effect of storage conditions that accelerate or decelerate molecular motion through different temperature conditions, which would affect the kinetic energy of liquid molecules within the extract. We will also explore the removal of water entirely through the process of lyophilization; since the dye molecules will no longer be able to move, this should completely arrest any degradation reactions. Lyophilization, or freeze-drying, is commonly used for improving stability of pharmaceutical drugs. Freezing should similarly arrest molecular motion but is energy-intensive; therefore lyophilization is preferred as it does not require cold-chain storage.

This experimentation will provide insight into the systems engineering of sustainable dyeing by indicating the effect of these different storage conditions for all natural dye materials of interest. This study will answer the question of how to preserve organic dye extract over time to produce a consistent dyed textile product.

Therefore, the goal for most companies would be to create a surplus of this dye when they can and store it for future use. If dyes can be successfully stored for longer periods of time, it will avoid any excess waste of the products that are created. Limiting any excess waste of these materials also means that there does not have to be a limit on the natural materials being sourced. The possibility of creating effective storage methods would help the sustainability of all natural dying practices, which potentially could cause a significant portion of the garment dyeing industry to implement sustainable practices.

This project intends to identify the effect of storage conditions on natural dye extracts and the resulting color of the dyed materials over time. Extracts of Osage orange, madder root, pomegranate peels, and black walnuts were selected as subjects of interest in this project. The methods used for the dye process follow the procedure used by a garment dyeing company as this project is to directly impact their business model and inform how they will go about storing the natural materials they obtain as seasonal crops or donations.

Of the different dyestuffs used in this experiment, two fall into the same classification. Black walnut and madder root both fall under the classification of quinonoids [5], Pomegranate peels would be classified as tannin and finally, Osage orange does not fall neatly under any dye classification although it does have a high concentration of tannins, so it is expected to react similarly to the pomegranate [6]. For madder root, it is known to react to temperature, pH, and mordanting by changing shade thus leading to a stark difference in shade after the storage of the dye is complete [7]. It is unknown if the Osage orange will react similarly to changes in temperature. These classifications are based on both chemical structure and shade of dye meaning that we hope to see similarities between classifications of dyes to include as an aspect of the results section.

Methods and Materials

A. Prepping Fabric: First, a non-reactive cooking pot was filled with enough water for the fabric to move freely. Then the fabric was added, followed by Mercoscour TS at a mass of 1.00% Weight of Fiber (WOF) and 1.00% WOF of Soda Ash Liquid. Next, the bath was heated to 180°F and held at this temperature for 15 minutes, stirring the bath occasionally. Finally, the fabric was removed and rinsed thoroughly.

B. Mordant: Mordanting is the preparatory step that ensures proper and even dyeing of the fabric material. First, a non-reactive cooking pot was filled with enough water for the fabric to move freely. Then, in a separate container, aluminum acetate was dissolved at a volume of 5.00% WOF in water that had been heated to about 175°F and stirred well before adding the mixture to the bath. Next, the scoured fabric was added, followed by Mercoscour TS at a mass of 1.00% WOF. The bath was then heated to 100°F and held at that temperature for 45 minutes. The water was then removed from the bath and discarded. The fabric was rinsed, and a fresh pot of water was prepared. In a separate container, calcium carbonate was dissolved at a mass of 5.00% WOF in water that had been heated to 175°F and stirred well before adding the mixture to the bath. Next, the fabric was added back into the bath and heated to 100°F and held at that temperature for 45 minutes. Following this step, the bath was discarded, and the fabric was removed from the bath, rinsed thoroughly, and contained in a sealed container until it is dyed.

C. Extraction: Osage orange, madder root, and pomegranate peels were obtained from Botanical Colors (WA, USA). Osage orange and pomegranate peel dyestuff was extracted from the natural state of the materials, and madder root dyestuff was extracted from a ground-up powder form. Black walnuts were foraged locally (NC, USA). Each material was measured to 40% WOF and extracted in 1 quart of water in a non-reactive cooking pot at 175°F for 1 hour. The extract was then strained of all dyestuff.

D. Storage: The extract of each natural material was divided and stored in various methods for a period of 4 months. Two samples from each extract were stored in a conical tube at room temperature, shielded from bright light. One of these samples was used for dyeing as a control trial within two weeks of the extraction. The other room temperature sample remained in storage for 4 months, as well as the samples of differing methods of storage. A third sample of each extract was frozen in 20 mL glass vials, which will then be lyophilized and kept in a freeze-dried state at room temperature. A fourth sample was kept at 100°F in an incubator, a fifth sample was kept at 0°F in a standard freezer, and a sixth ample was kept at 40°F in a refrigerator.

E. Dye: Once the denoted amount of time has passed, the extracts were used to dye the prepped and mordanted fabric, with the following steps being repeated for each extract sample. First, a non-reactive cooking pot was filled with enough water for the fabric to move freely. Next, the extract sample was added to the bath and stirred well, followed by the wet, mordanted fabric. The bath was then slowly heated to 90°F and held at that temperature for 30 minutes, stirring occasionally. Then the bath was slowly heated to 180°F and held again for 30 minutes, continuing to stir the bath occasionally. Finally, the fabric was removed from the bath and rinsed well until no dye came off the fabric.

F. Finish: This step involved several washing steps meant to remove any excess dye and seal in the color to the fabric. First, a non-reactive cooking pot was filled with enough water for the fabric to move freely. Next, the fabric was added, followed by Mercoscour TS at a volume of 1.00% WOF. The bath was then be heated to 160°F and held at that temperature for 10 minutes. Then the water was removed from the bath and the fabric was rinsed and added to a fresh pot of water. Mercoscour MAD was incorporated at a volume of 5.00% WOF. The bath was then heated to 100°F and held at that temperature for 5 minutes. Following this step, the fabric was removed from the bath, and as much liquid was squeezed out as possible before the fabric was dried in a clothes dryer.

TABLE I
SUMMARY OF KNOWN ABSORPTION PEAKS OF DYE EXTRACTS

Extract	Wavelength (nm)
Osage Orange	339 [8]
Pomegranate Peel	400 [9]
Black Walnut	416 [10]
Madder Root	250 [11]

RESULTS AND DISCUSSION

Qualitative analysis was done on the resulting dyed fabric to determine the effect of the various storage methods on each individual organic extract. Visual differences in color were documented and compiled as well as informed suggestions of optimal storage methods for each material for the intended purpose of maintaining color over time. UV-Visual Spectroscopy was performed and compared to the known absorption peaks of each extract material, summarized in TABLE I.

FIGURE 2
SUMMARY OF ALL DYED MATERIALS VS STORAGE CONDITION

Osage orange at the selected concentration yielded a light-yellow color. After four months of storage at the tested conditions, the frozen extract yielded the most similar color. The room temperature extract and the refrigerated extract storage yielded similar colors to each other, both slightly darker and brighter than the control trials. As hypothesized, the storage at 0°F arrested molecular motion, and resulted in little to no degradation of the Osage orange extract. Also as expected, the incubated trial degraded the extract, with brown undertones and dull color compared to other trials. The lyophilized trial yielded unexpected results, with a dull, orange color with brown undertones. This result was very dull compared to the control trial and other trials. Based on these results, Osage orange extract is recommended to be frozen to arrest color change that occurs from degradation.

Pomegranate peel at the tested concentration yielded a yellow-orange color. None of the storage conditions tested in this experiment were successful at maintaining color of the control trial. Refrigerated, frozen, and lyophilized extract all resulted in a brighter, deeper orange color. Room temperature storage yielded a slightly more dull color, with brown undertones. The incubated trial was slightly brighter and had more dull, green undertones.

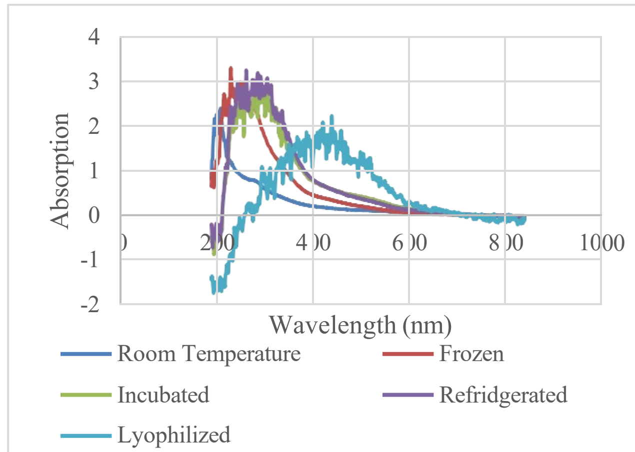

FIGURE 3
UV-VIS ABSORBANCE OF MADDER ROOT EXTRACTS

Madder root at the tested concentration yielded a light, bright pink color. Due to the concentration of Madder Root material used in this experiment to create the extract, being relatively low for this material, the color for all of the madder root trials were much lighter than the typical vibrant red color of textiles dyed with madder root, making visual differences difficult to detect. Slight visual differences between the control trial, which was relatively bright, compared to the trials dyed with stored extracts were observed. The fabric dyed with lyophilized extract was the most dull in color, and had slightly brown undertones. Despite only slight visual differences, the absorption spectra of the various extracts used to dye demonstrated variability in absorption peaks, as seen in FIGURE 3. The absorption peak of the lyophilized extract corroborated the visual differences, with a highly skewed absorption spectra and peak around 450 nm, compared to all other trials with peaks below 350 nm. Purified madder extract has been found to have an absorbance peak around 250 nm [11], which was observed in the frozen extract. The refrigerated and incubated trial both exhibited peaks around 280 nm, slightly higher than the known peak for this dye material. These results indicate that freezing madder root extract may yield the least variance in color, and lyophilization causes high variance in resulting color.

The black walnut control fabric is a very light yellow-brown color. After the storage period, each of the resulting trials were significantly deeper brown than the control trial.

preserving the color of the control trial after the 4 month period, similarly to the pomegranate peel trials. The incubated extract yielded the deepest brown color, suggesting that black walnut extract deepens in its brown color over time as incubation accelerates organic degradation. The trial that yielded the most similar color to the control was lyophilization. Though the color resulting from the lyophilized extract was slightly more dull, the difference was minimal compared to the degradation of lyophilized extract from other trials. Based on these results, it is recommended that Black walnut extract is lyophilized in order to preserve the color of a large batch over extended time. Though there were significant visual differences in the resulting color of the dyed material, UV-Vis did not demonstrate differences in absorption peaks as seen in FIGURE 4.

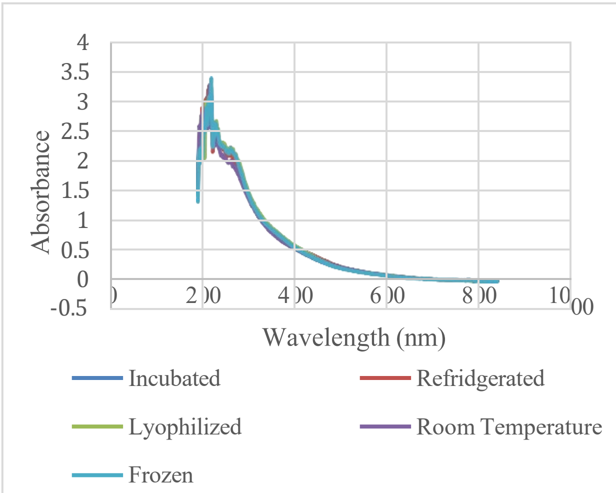

FIGURE 4
UV-VIS ABSORBANCE SPECTRA OF BLACK WALNUT EXTRACTS

CONCLUSION

The effects of extract storage conditions for natural dyes on the degradation and color of extracts and the dye processes was investigated. The storage conditions accelerated, decelerated, arrested, or completely removed water molecules from extracted dye materials. The effect of the tested storage conditions was unique to each dye material of interest in this study. This result establishes the importance of individualized consideration of the chemical composition of a dye material when making decisions on the best system to process and store natural materials for use of industrial textile dyeing. Though lyophilization removes water from the dye extracts and was hypothesized to stabilize the natural pigments, the process of lyophilization degraded dye extracts and caused a change in brown undertones and dullness across most materials. Future experimentation on the prospect of using lyophilization in the system of organic textile dyeing could examine lyophilizing the materials themselves rather than the extracts, or keeping the lyophilized extracts at various temperatures to examine the degradation process at many stages.

Furthermore, since individualized consideration is required for each natural dye material of interest, similar experiments must be conducted to inform systems engineering for materials not tested in this experiment. Future experiments should include mordanting materials and processes, as well as dyestuff concentration for extraction, that are optimal for the dye material of interest. Additionally, the makeup of the fabric or material being dyed may also affect the dye-uptake. Longer periods of time can also be investigated to discover even longer-term effects of storage conditions on the identified extracts as the duration of this experiment was about 4 months. Finally, the UV-Vis analysis suggests that there are many organic compounds within dye extracts that may have complex effects on the degradation of the pigment and the visible changes of dyed fabric. Future experimentation should look into methods of purification for the dye extracts to isolate the pigment compounds of interest for the material. Experiments that use UV-Vis or other spectroscopy methods to analyze organic dye extracts may consider using HPLC to isolate the dye pigment for analysis.

This experimentation was valuable in investigating the unique stability properties of Osage orange, pomegranate peel, black walnut, and madder root extracts. However, as demonstrated through this experiment, and corroborated through similar published investigations each organic material behaves differently over time based on its unique chemical composition [4].

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