UNDERSTANDING THE DEGRADATION OF VERDIGRIS & DEVELOPING STRATEGIES FOR ITS CONSERVATION IN ARTWORK

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Abstract

Conservation science focuses on the preservation and protection of artwork. One of the most difficult challenges faced by conservation scientists is understanding how the components of an artwork interact with the environment. For paintings in particular, pigment degradation poses a considerable threat due to altering the color profile of the artworks. The focus of this project was verdigris, an organometallic pigment used in ancient and modern artwork[1]. Its history dates back to ancient times when it was the brightest green pigment available, making it widely used in artwork. Furthermore, verdigris is known to irreversibly degrade over time[2]. In this project, we studied the degradation profile of verdigris through various thermal and photodegradation experiments. Analysis of the degradation was conducted using UV/Vis spectroscopy. Our results demonstrated that verdigris is both thermally and photosensitive. Additionally, we employed the use of a member of a new class of transition metal carbide nanomaterials, MXenes ($Ti_3C_2T_x$), to determine its effects on the degradation profiles of verdigris. MXene has demonstrated the capacity to absorb UV light which may prevent direct exposure of verdigris to harmful radiation[3] and help protect the pigment against degradation.

Methods

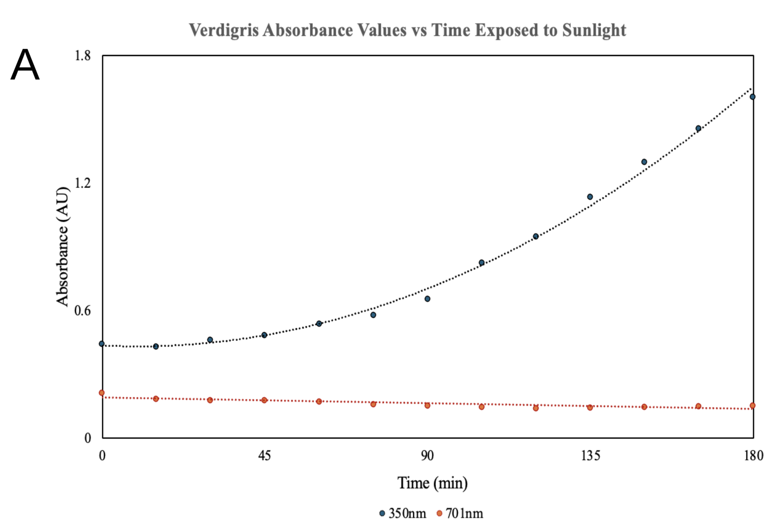
Verdigris (copper (II) acetate) pigment was dissolved in 20 mL of 95% ethanol to make 2.583 mM solutions. Three 20 mL vials of 2.583 mM solution were placed outside in direct sunlight where they were exposed for a total of three hours and the absorption was monitored through UV/Vis spectrometry every fifteen minutes (**Fig. A**).

Three 2.583 nM solutions of verdigris in ethanol were made and heated to 50ºC in round bottom flasks for one hour. Absorption was monitored through UV/Vis spectrometry every ten minutes (**Fig. C**).

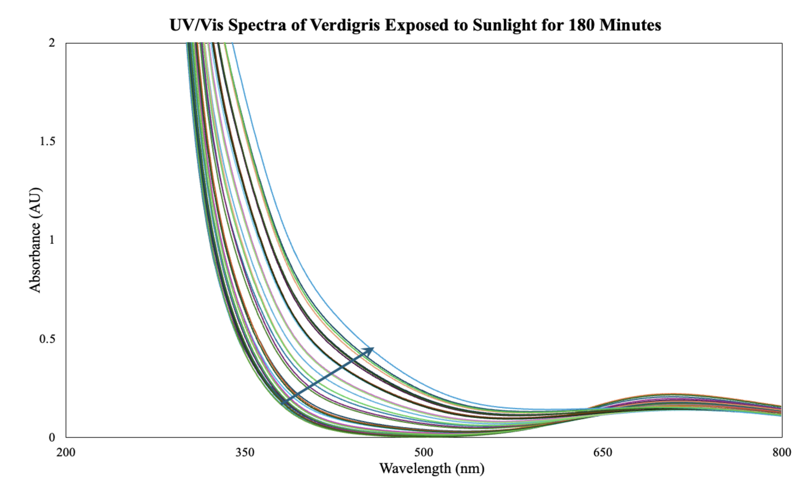
2.583 mM verdigris solutions in ethanol were divided into six samples: three containing only verdigris, and three containing verdigris with 0.034 mg/mL MXene. The samples were placed in a Rayonet photoreactor at 350 nm and exposed for two hours. Absorption was monitored through UV/Vis spectrometry every fifteen minutes (**Fig. F**). The same procedure was repeated with a Rayonet photoreactor at 420 nm (**Fig. G**).

Sunlight Trials

A



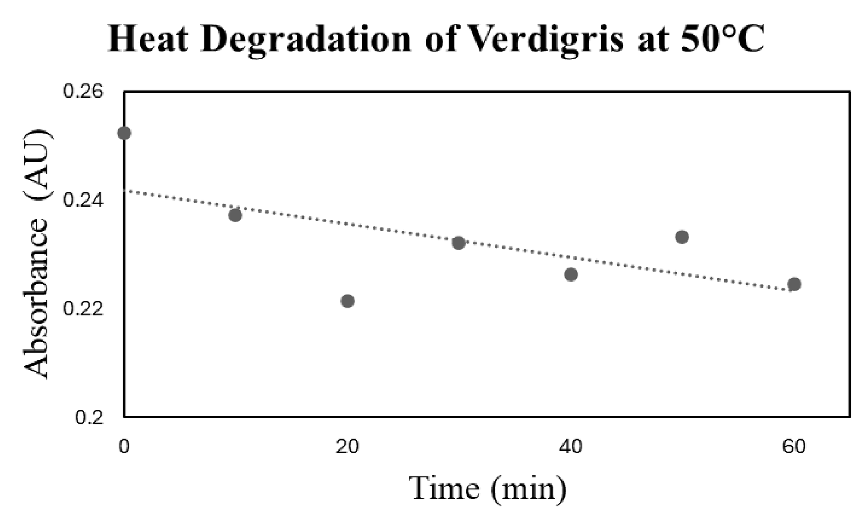
B



Results of the sunlight trials indicate that verdigris degrades when exposed to sunlight. Both a bathochromic (red-shift) and absorption peak depletion were observed through UV/Vis spectrometry (**Fig. A,B**). The bathochromic shift was accompanied by a visible change in solution color (**D,E**).

Heat Trials

C



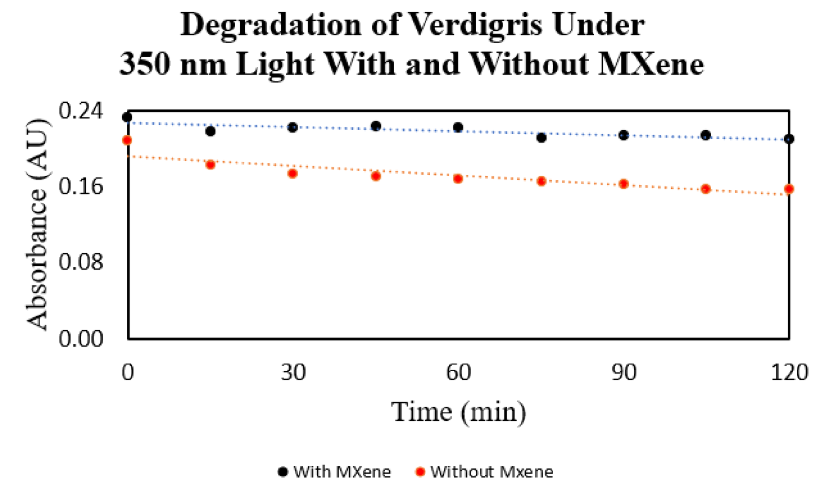
D

E

When heated at 50°C for one hour (**Fig. C**), verdigris undergoes thermal degradation. A noticeable color change and bathochromic shift in the UV/Vis spectrum around 350 nm was observed (**D, E**).

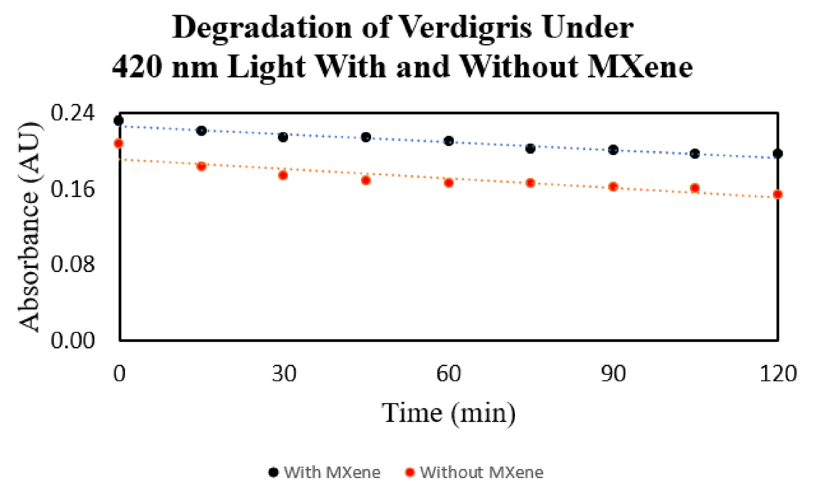
Rayonet Trials

F



From the 350 nm Rayonet photoreactor trials, the addition of 0.034 mg/mL MXene reduced the photodegradation of verdigris. The absorption data indicates that the solution with MXene degraded less over time than the solution without MXene. The absorbance with MXene decreased by 0.0228 AU between its initial and final absorbance readings, in comparison to the solution without MXene which decreased by 0.0505 AU.

G



Similar results can be seen in the 420 nm Rayonet photoreactor trials. A decrease of 0.0356 AU between its initial and final absorbance readings was less than the decrease in absorption seen in the solution without MXene, which was 0.0534 AU. In comparison with the 350 nm Rayonet light, there was a greater decrease in absorbance in the MXene solution under 420 nm. More research is needed to fully understand the cause of this occurrence.

Conclusion

In the experiments using sunlight as the degradation factor, it was found that verdigris degraded over time and experienced a bathochromic shift. This shift corresponds to an electronic transition from n to π in a carbonyl group which may help explain its discoloration[4].

Verdigris was also shown to thermodegrade at 50°C when heated in round bottom flasks for a period of over 60 minutes. When heat was added to the system, verdigris experienced a similar bathochromic shift to the samples exposed to sunlight.

With the addition of MXene, the photodegradation of verdigris under 350 nm and 420 nm light decreased significantly. MXene is known to absorb strongly at 200-300 nm (UV) and at 700-800 nm (near IR)[3]. The addition of MXene helped protect the pigment from degradation by preventing direct exposure to the near UV and visible light.

The results of these studies confirm previous results that indicate verdigris is thermo- and photosensitive. The initial results with the addition of MXene to the pigment solutions indicate that when used as an additive, MXene may confer a certain degree of protection against pigment degradation.

Further research will be conducted to investigate the effects of MXene on preventing thermo- and photodegradation of pigments and the mechanisms by which these effects arise. Ultimately, we hope to develop MXene as an additive for the prevention of pigment degradation and a tool for conservation science.

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