

## TESTING THE GREEN CORROSION INHIBITORS PRICKLY PEAR AND ALOE VERA ON AN ARCHEOLOGICAL IRON SAMPLE

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### Abstract

*This article presents the results of the application of some natural and green corrosion inhibitors on various industrial metal samples as well as on historical samples. The green inhibitors tested are extracts from the cladodes and fruits of prickly pear (*Opuntia ficus indica*) and from *Aloe vera* leaves. The effect of tannin (an organic substance found in plant tissues and already known for its effectiveness as a natural corrosion inhibitor) was also tested as a reference. The metal samples ( $3 \times 3 \text{ cm}^2$ ) were sawn from pure copper, bronze, and brass sheets, then ground on one side and sterilized with ethanol (concentration 96%). For the historical samples, iron nails of unknown age excavated in the area of Konavle (a municipality southeast of Dubrovnik, Croatia) were used. After preparation, the inhibitors were applied to the samples with a brush or by immersion and then exposed to a microclimate similar to that prevailing in most museums (temperature 18–22°C, relative humidity 45–65%). The samples were inspected at regular intervals to determine the onset of corrosive activity. After a few months, the effect of the different treatments on the metal samples and the archeological sample was evaluated, showing the potential of some of the extracts tested in the area of conservation and restoration.*

**Keywords:** Corrosion inhibitors; Natural extracts; Green conservation-restoration; *Opuntia ficus indica*; *Aloe vera*

### Introduction

The task of the conservator-restorer of cultural heritage is to protect the objects from deterioration and to carry out conservation-restoration procedures on them in order to maintain their stability and to ensure they can be appropriately perceived by the public. One of the main problems faced by conservators of metal objects is active corrosion, which cannot be stopped completely but can be slowed down considerably. Treatments such as cleaning, desalination, stabilization, protection, reintegration, etc. require the use of various chemicals. Many chemicals and materials used in conservation and restoration treatments are not harmless to humans and nature, which is why more and more research is being carried out into new, more environmentally friendly materials.

There are numerous papers on the use of environmentally friendly corrosion inhibitors, which are divided into organic and inorganic substances. Organic substances, which are either derived from natural and/or biological sources, include plant extracts and oils, amino acids, microorganisms, and biopolymers [1]. This paper reports on the results of using plant extracts,

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especially prickly pear and aloe vera. Prickly pear (*Opuntia ficus indica*) and aloe vera are both plants that are cultivated in many Mediterranean countries. Their chemical compositions are well known [2, 3], and their use as anticorrosive agents has even been reported [1, 4, 5].

The aim of this work was to evaluate potential green corrosion inhibitors caused exclusively by external conditions such as temperature, humidity, etc. in an environment similar to that in which cultural heritage metal objects are normally stored. The first evaluation was carried out with industrial metal samples (pure copper, bronze, and brass). Then the inhibitors were tested on historical samples, i.e., excavated iron nails.

The analyses of the tested samples have shown the potential of some of the extracts used, even if the ideal application methodology still needs to be improved, especially with regard to the possible use on cultural heritage objects.

## Experimental part

### Materials

The green inhibitors tested were extracts from the cladodes and fruits of the prickly pear cactus, *Opuntia ficus indica* (OFI), and from Aloe vera leaves (AV) (Table 1). Both plants grow spontaneously in the Mediterranean regions and therefore represent an inexpensive source of raw materials for numerous applications. A 5% tannin solution in distilled water was used for comparison.

**Table 1.** List of tested plants

| Scientific name             | Abbreviation | Order          | Family        | Part of plants used | Collection site     |
|-----------------------------|--------------|----------------|---------------|---------------------|---------------------|
| <i>Opuntia ficus indica</i> | OFI          | Caryophyllales | Cactaceae     | Cladodes and fruits | Dubrovnik (Croatia) |
| <i>Aloe vera</i>            | AV           | Asparagales    | Asphodelaceae | Leaves              | Dubrovnik (Croatia) |

Several metal samples were prepared for testing purposes. The samples (3×3cm<sup>2</sup>) were sawn from pure copper, bronze, and brass (Table 2) sheets with a thickness of 1mm using a pattern saw and then ground on one side using an electric grinder to obtain a clean surface without any kind of impurities. The samples were finally sterilized with ethanol (concentration 96%).

**Table 2.** Industrial metals utilized in this research

| Name   | Composition | Color                                                                               |
|--------|-------------|-------------------------------------------------------------------------------------|
| Copper | Cu          |  |
| Bronze | Cu+Sn       |  |
| Brass  | Cu+Zn       |  |

As historical samples, iron nails of unknown age, excavated in the area of Konavle (a municipality southeast of Dubrovnik, Croatia), were used. Nails were covered with traces of soil, lime deposits, and a thick layer of corrosion products, and no conservation or restoration work had been carried out on them (Table 3).

**Table 3.** Historical metal utilized in this research

| Name | Composition   | Excavation site              | Image                                                                                |
|------|---------------|------------------------------|--------------------------------------------------------------------------------------|
| Iron | Fe+impurities | Konavle (Dubrovnik, Croatia) |  |

### Methods

The extraction method known as maceration was used to obtain prickly pear mucilage [6, 7], as well as a modification of this method to reduce the acidity [8].

The surface of the cladodes was cleaned with a 96% ethanol solution, then the outer skin of the prickly pear cladodes was removed, and the inner pulp was cut into small pieces, then immersed in distilled water (1:1) and left in the dark for 48 hours. The pulp was then separated from the liquid by filtration, resulting in a transparent and not relatively thin mucilage with a pH of 5.4.

To obtain a less acidic mucilage, a very similar procedure was repeated in which a 1M calcium hydroxide solution ( $\text{Ca}(\text{OH})_2$ ) was added to the pulp. To 50g of pulp and 250ml of distilled water, 2.5ml of calcium hydroxide solution was added, resulting in a mucilage with a pH of 6.

The extraction from the fruit of the prickly pear was carried out as follows: The skin of the fruit was removed, and the residue was cut into smaller pieces and weighed. Then the same amount of distilled water was added, and the mixture was heated at 50°C for two hours with constant stirring. The resulting mixture was kept in a dry and dark place for 24 hours to produce a dark wine-red slime with a pH of 4.6.

The extraction from Aloe vera leaves (AV) was a very simple process. The aloe leaves were first cleaned with a 96% ethanol solution, then stripped of their spines and cut lengthwise in two. The gel detached from the leaves with a spoon was then crushed and squeezed. The result was a transparent gel with a pH of 4.

The effect of a fourth inhibitor, 5% tannin solution, was tested at pH = 3.77.

The extracts to be tested were either applied to the metal samples with a brush (Figure 1a) or by immersion in the respective mucilage for two hours (Figure 1b).

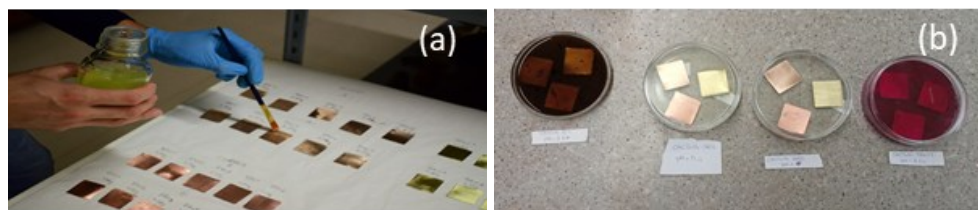


Fig. 1. Application of the inhibitor to the samples: (a) with a brush, (b) by immersion

One part of the treated samples was placed on a table in the workshop and exposed to a microclimate similar to that found in most museums (temperature 18-22°C, relative humidity 45-65%), while the other part was placed in a chamber containing a 9% sodium chloride solution (saline) to simulate a more aggressive environment. All samples were monitored at regular intervals to determine the onset of corrosive activity.

A selection of samples was analyzed under the microscope or with the diffractometer.

#### *Microscopic analysis*

The instrument used was a Zeiss Axioskop 40 microscope in reflection mode.

#### *X-ray diffraction (XRD) analysis*

X-ray diffraction patterns were recorded using a Bruker D8 Advance X-ray diffractometer in the range of 10° to 70° 2theta with a step size of 0.02° per step and a dwell time of 0.6 s per increment. The analyzed samples were obtained by scraping a powder from the three nail sections.

### Results and discussion

After 30 days of exposure in the workshop, the surface discoloration was observed in the brush-treated samples, and partially active corrosion was observed in some samples (Figure 2), which was due to uneven application of the inhibitor. The reason for the uneven application is that the inhibitor droplets collected in the wet zones due to the surface tension and later left spots in the form of gel droplets. The result was much more uniform for the samples immersed in the extracts. As it is desirable in the field of conservation and restoration to preserve the appearance of the original surface of the object as far as possible, it was concluded that applying the inhibitor with a brush was not suitable for the treatment of the object.



**Fig. 2.** One example of discoloration on brush-treated sample

**Fig. 3.** Microscope images for untreated and AV treated samples from the chamber

A selection each of immersion-treated samples and brushed samples, some of which were on the table and some in the chamber, were analyzed after six months under a Zeiss Axioskop 40 microscope in reflection mode. The results obtained are shown in Figures 3 and 4.



**Fig. 4.** Microscope images for untreated samples and samples treated for immersion with different extracts

In the images in Figure 3 of the aloe vera-treated samples that have spent six months in the chamber, the deterioration of the surface to which the inhibitor was applied with a brush is evident, i.e., the formation of new corrosion products on the treated area and the discoloration of the surface. This confirms once again that the application of the inhibitor with a brush is not optimal. However, it can be seen from the images that the areas of the samples that remained covered by the inhibitor in a thin layer (i.e., where the inhibitor droplets that caused this type of stain were not present) do not have active corrosion products visible on the entire surface of the untreated samples.

As can be seen from the images in Figure 4, the local formation of active corrosion products is evident in all untreated samples, but also in the samples treated with OFI cladode inhibitor at pH 5.4. However, some differences were observed in the other treated samples:

- For copper, fair results were obtained for the sample treated with OFI-Fruit, while the best outcome is observed for the sample treated with OFI-Cladodes +  $\text{Ca}(\text{OH})_2$ .

- For brass, the surfaces of the samples treated with OFI-Fruit and OFI-Cladodes +  $\text{Ca}(\text{OH})_2$  are uniform and without visible changes in the form of active corrosion products. In this case, the tannin gave comparable results to the OFI-Fruit and OFI-Cladodes +  $\text{Ca}(\text{OH})_2$ -based inhibitors.

- In the case of bronze, the surface of the sample treated with the tannin-based inhibitor is almost completely uniform, but the OFI-cladode-based inhibitor with  $\text{Ca}(\text{OH})_2$  also gave very good results, while the surface of the OFI-fruit-treated sample is also visually acceptable, although a slight discoloration is visible.

Following these results, only the extract of OFI-cladodes +  $\text{Ca}(\text{OH})_2$  was tested on iron nails, together with the extract of Aloe vera leaves, which was not tested on industrial metal samples. Specifically, one end of a corroded iron nail was immersed in the AV extract and the other end in the extract of OFI-cladodes +  $\text{Ca}(\text{OH})_2$  extract, while the middle part was left untreated (Figure 4).



**Fig. 4.** Iron nail treated with OFI cladodes and AV extracts

Like the other samples, the nail treated in this way was left on a table in the workshop for about 4 months.

Due to the appearance of the nail, it was not possible to perform any kind of visual analysis, either with the naked eye or under a microscope. Therefore, we decided to perform an X-ray diffraction (XRD) analysis. The analyzed samples were obtained by scraping a powder from the three nail sections.

The obtained diffraction patterns (Figures 5-7) showed no significant differences in the appearance of crystal phases except for the absence of one phase in the sample treated with AV

in comparison with the other two. The analysis revealed the presence of some of the typical corrosion products normally identified in archeological iron [9]. The corrosion products revealed were magnetite ( $\text{Fe}_3\text{O}_4$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), and goethite ( $\alpha\text{-FeOOH}$ ) for all samples, and akaganeite ( $\beta\text{-FeOOH}$ ) only for the untreated sample and for the sample treated with OFI gel. In addition to these corrosion products, the presence of quartz  $\text{SiO}_2$  was also detected, probably originating from the surrounding rock and soil.

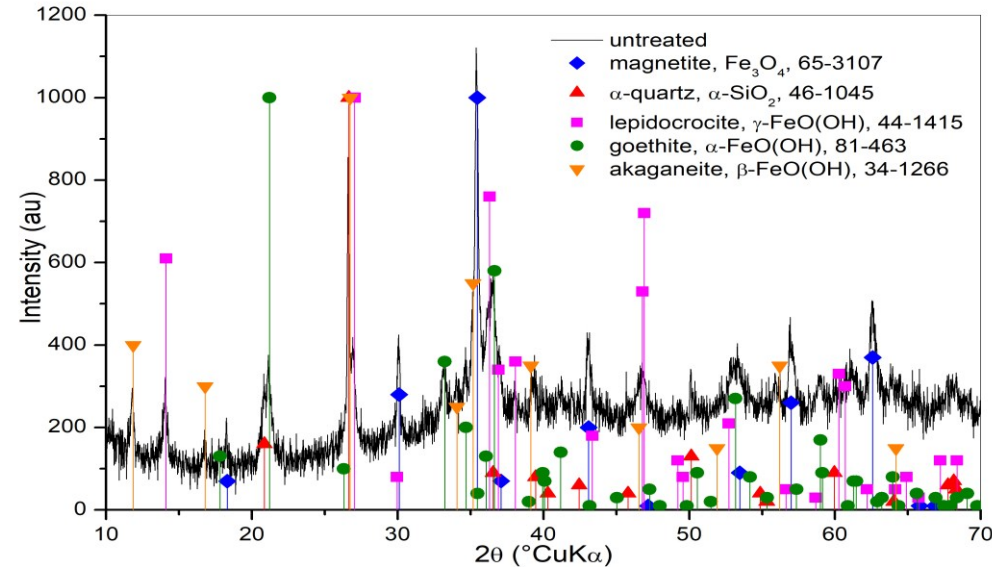


Fig. 5. XRD diffractogram of untreated iron sample

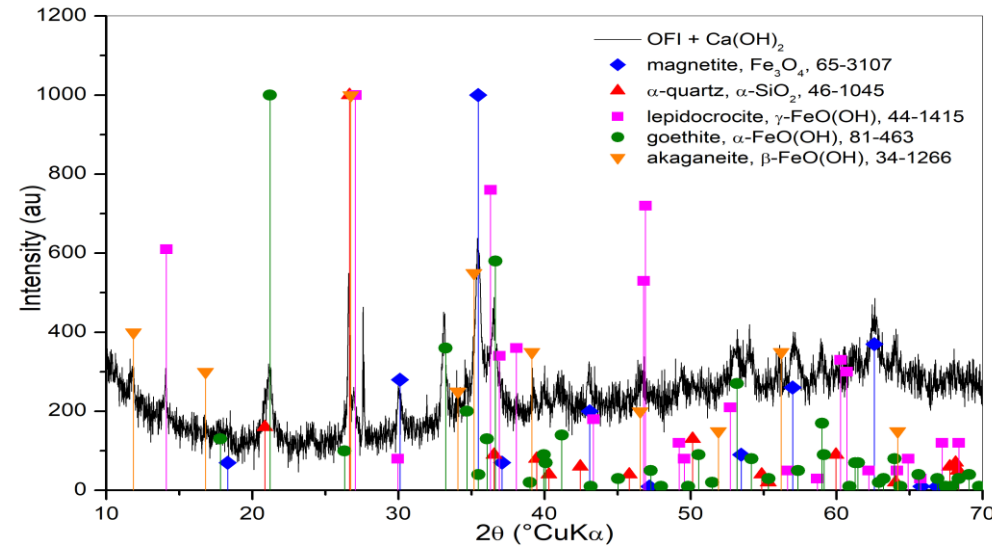


Fig. 6. XRD diffractogram of iron sample treated with OFI +  $\text{Ca(OH)}_2$  extract

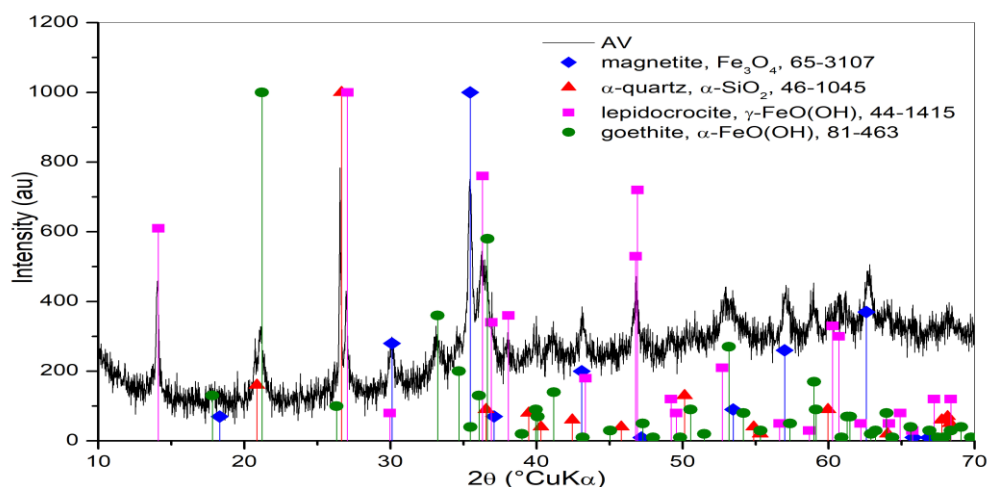


Fig. 7. XRD diffractogram of iron sample treated with AV extract

The presence of goethite,  $\alpha$ -FeOOH, and magnetite,  $\text{Fe}_3\text{O}_4$ , indicates a very long preservation of the base metal and its stability after excavation, while the presence of akageneite ( $\beta$ -FeOOH) indirectly indicates the presence of chloride ions [10]. For this reason, the absence of akageneite in the sample treated with AV is a surprise.

## Conclusions

The plant extracts were first tested on pure metal samples. Their effect was assessed both with the naked eye and under the microscope. The results show that the prickly pear extract modified with calcium hydroxide ( $\text{OFI} + \text{Ca}(\text{OH})_2$ ) applied by immersion has the best anti-corrosion effect among all extracts tested.

For this reason, this extract and the extract from Aloe vera leaves (AV) were tested on an archeological iron nail. The XRD analysis showed that only the part of the nail treated with AV did not contain akageneite. This indicates that the akageneite that was present on the iron nail (it was detected on both the untreated area and the area treated with  $\text{OFI} + \text{Ca}(\text{OH})_2$  extract) was removed by the treatment with the AV gel, probably as a result of a reaction of the inhibitor and the corrosion products on the sample surface. Additionally, the formation of protective AV film on the surface can inhibit or prevent the contact of chloride with iron.

It is also worth noting that the results obtained with both  $\text{OFI} + \text{Ca}(\text{OH})_2$  and AV extracts are even better than those achieved with tannin, already known for its effectiveness as a natural corrosion inhibitor and widely used in practice.

Considering that akageneite is an unstable corrosive compound that can release chloride ions in the presence of moisture and then trigger further corrosion [11, 12], it is usually very important to treat the archeological iron objects quickly after excavation to remove or convert akageneite into a more stable iron compound. In this work, we have shown that the extract of Aloe vera could be used for this purpose.

The potential of some of these natural extracts as corrosion inhibitors is the subject of extensive research, focusing primarily on their application to "modern" metals. However, a particularly important finding of this study is their effectiveness on archeological nails. This suggests that these natural, non-toxic, inexpensive, and readily available inhibitors have great potential for the field of conservation. Further research into their application is crucial, as it could pave the way for transforming traditional conservation methods into more environmentally friendly and sustainable practices. In this way, we could reduce the environmental impact of corrosion protection, especially in the preservation of cultural heritage.

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