Plant extracts as corrosion inhibitors: effect of lyophilisation

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Abstract– Natural plant extracts are being studied as corrosion inhibitors. As a drawback, these products are susceptible to deterioration, especially during storage. In this research, the effect of lyophilization of the aqueous extracts of Oregano and Yerba Mate was analyzed with a comparison between the extract in liquid and lyophilised form. Setting-times, flexural and compression strength of cement mortars were tested, and the extract's inhibitory activity was examined using XRD technique. As a conclusion, it was found that freeze-dried extract form allowed an easier conservation and it showed having a minor effect in setting times.

Keywords—Corrosion, Natural extracts, Plants, Concrete, Lyophilization.

I. Introduction

One of the main problems of reinforced concrete is the corrosion of its steel bars. All materials degrade in contact with the environment and evolve into more stable forms. The rebars embedded in the concrete are protected from corrosion by two effects: the high alkalinity and the physical barrier of concrete. Under these conditions, the steel is covered with a passive layer of oxides which preserves it from corrosion. However, there are several factors capable of destroying this protective film. Globally, a high percentage of reinforced concrete structures require some repair due to corrosion implying a very high economic cost [1].

The use of corrosion inhibitors in concrete is a viable solution to control the corrosion phenomenon because they reduce its speed to tolerable values [2]. Inorganic compounds have been used since the 70s, among which stands out the calcium nitrite that, in the presence of chlorides, delays the initiation of corrosion. However, most synthetic inhibitors have been shown to be toxic to humans and to affect the environment [3]. In order to find more sustainable solutions, organic compounds have been studied to inhibit steel corrosion processes.

Plant extracts are a very interesting alternative to synthetic inhibitors since they are an economic, renewable and safe resource for the environment and human health [4, 5, 6]. The natural gel extracted from the leaves of Aloe vera has been shown to be effective in the inhibition of steel corrosion [7]. Also, products like banana [8], coffee [9] and black pepper [10] extracts, among others, were tested in acid medium as soluble steel corrosion inhibitors.

A particular case of protection is Yerba Mate (*Ilex paraguariensis*). In the aqueous extract, a large number of compounds have been reported [11], which can act as organic inhibitors of corrosion [3]. The aqueous extract of Yerba Mate has been studied as an inhibitor of corrosion of aluminium and copper immersed in sodium chloride solution [12] and SAE 1010 steel [13]. It was demonstrated that extracts can be incorporated as additives in anti-corrosive paints because it generates a protective film on its surface that reduces the corrosion rate of steel.

Moreover, it has been informed that aqueous extracts of Oregano (*Origanum vulgare*) have an important antioxidant activity *in vitro* [14] and they can also be used as inhibitors in the corrosion processes of low carbon steel.

Natural extracts are often prone to deterioration, especially during storage, leading to the loss of active compounds, production of metabolites with no activity and, in extreme cases, production of toxic metabolites. Water promoting oxidation and/or enzymatic reactions, and microbial attack are especially detrimental for plant extracts that are in liquid form [15] [16].

Thinking in a feasible application of natural phenolic extracts, the stability of antioxidant components during storage should be carefully assured. Dry powder extracts are the most suitable forms due to their greater physical and chemical stability in the solid-state. In addition, because of its concentrated form, it gives the possibility of easy storage of large amounts of product.

Vacuum freeze-drying -or lyophilization- of natural products is one of the best methods of water removal, with final products of the highest quality. It is a process where water is frozen, followed by its removal from the sample, by sublimation. The solid-state of water during freeze-drying protects the primary structure and the shape of the products. In addition, the lower temperatures in the process allow maximal bioactive compound retention. It is a drying process applicable to natural products that are thermolabile or otherwise unstable in aqueous solutions for prolonged storage periods, but that are stable in the dry state.

In previous studies of the authors, aqueous extracts of Yerba Mate and Oregano were used to analyze its properties as corrosion inhibitors [17]. There, some problems were recorded in the use of the extracts in liquid form related to the development of fungal colonies over time that may cause variation of the extract composition. This created doubts about the results obtained with the tests, since soon after the extract was used the sample had to be discarded as fungus appeared. Also, the deterioration of the antioxidant compounds generated by the presence of light and oxygen, might lead into a loss of anti-corrosive capacity of extracts. This made it difficult to repeat the tests and it was an inconvenience because it reduced the time-lapse to use this product. This led to vacuum freeze-dry the aqueous extract as a new procedure to storage and repeat the tests with this new product.

In this paper, a comparison was made between aqueous extracts stored in Liquid form (LQ) and in a dry-powder form (vacuum freeze-dried, FD) used as mixing water in cement mixture tests. In these tests, setting times, flexural and compression resistance were compared. In addition, X-ray diffraction (XRD) tests were carried out to determinate the inhibitor qualities of the extracts.

II. Materials and Methods

A. *Extracts*

Aqueous extracts of Oregano (OR) and Yerba Mate (YM) were used. The aqueous extract was prepared with 8 g of dry plant material per litre of demineralized water. The mixture was placed for 2 hours at 40°C, in an ultrasonic bath to increase the extraction efficiency of the inhibitor organic components. The supernatant, containing the phenolic compounds, was then separated from the solid residue by centrifugation or filtration. At this point, the aqueous extract is made (Fig. 1).

Fig. 1 Aqueous extracts of Oregano (left) and Yerba Mate (right).

One fraction of these extracts was stored in liquid form at fridge temperature until its use. Meanwhile, the other fraction was freeze-dried. To lyophilizate the aqueous extracts, the samples were first placed in aluminium trays with perforated lids and frozen at -35ºC and atmospheric pressure. Then, it was vacuum freeze-dried at -40 °C and a pressure of 0.040 mmHg for 4 days, a process carried out with equipment Rificor, model L-A-B4. Finally, dry-powder extracts (Fig. 2) were stored in a vacuum desiccant in a dark atmosphere. The yield (Y) of lyophilisation process (g FD/g dry plant material) was 35.68% and 32.39%, for OR and YM, respectively.

Fig. 2 Freeze-dried extracts of Oregano (left) and Yerba Mate (right).

The first studies were conducted using an aqueous extract in LQ; therefore, the input was the dosage of dry plant material per litre. Later on, the FD extract was developed and the same tests were carried out. When using dry inhibitors, it is usual to express the quantity required as a percentage of the cement weight. In order to be able to compare the results of the tests carried out with both extracts, it was required to calculate the equivalence between processes and an equation was formulated to relate the concentration in the LQ with the quantity of FD (Equation 1).

$$F = (w/c) \times C \times Y \times (1/1000) \quad (1)$$

where,

F: FD as percentage of cement in weight (%).
w/c: water-cement ratio.
C: aqueous extract concentration (g dry plant material/liter).
Y: yield from LQ to FD (%).

B. *Cement-paste and mortars tests*

The cementitious pastes were prepared with a cement typified CPC40 and the extracts. The LQ was used directly as mixing water and the FD was first diluted in demineralized water. For mortars, a quartzite sand was used. In the first stage of work on cement mixtures, the amount of water needed to reach a paste of normal consistency according to IRAM 1612 [18] and the setting times according to IRAM 1619 [19] were evaluated. After that, prismatic specimens of 4 x 4 x 16 cm were moulded to evaluate the mechanical performance of cement mortars. Therefore, flexural and compressive strength were determined according to IRAM 1622 [20] at the age of 7 days.

C. *X-ray diffraction*

To verify the inhibitory characteristics of the extracts, SAE 1010 steel bars (used as rebar in concrete) were submerged for 10 days in a saline solution (3.5% NaCl) replicating the sea

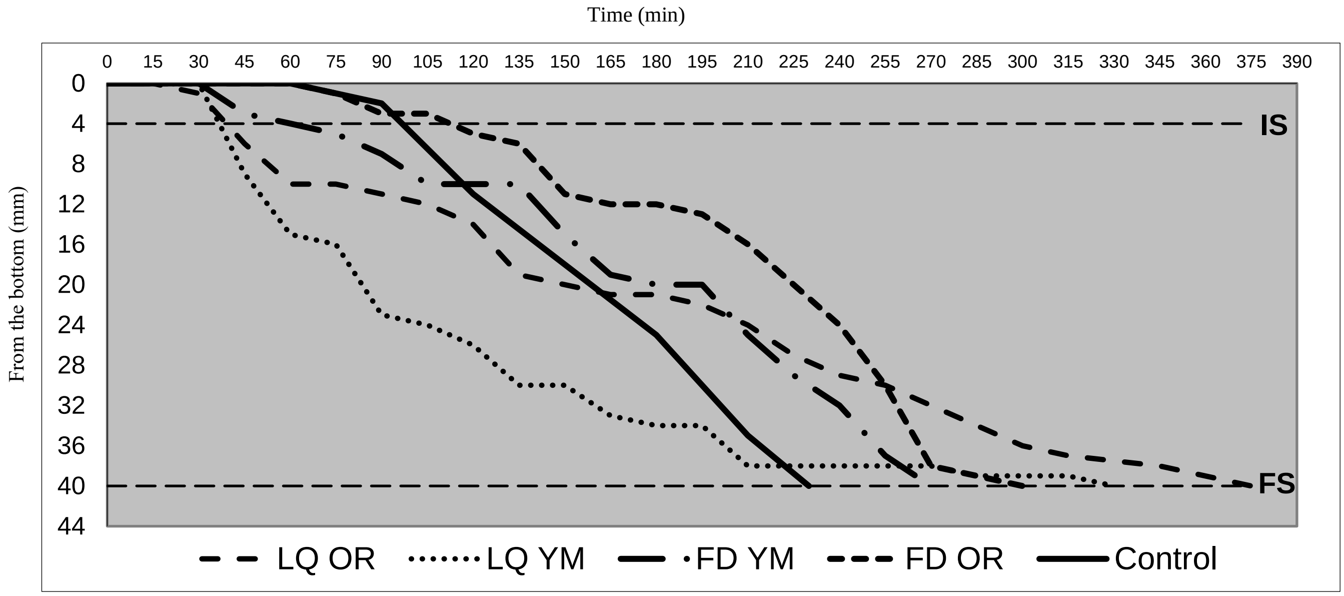

Fig. 3 Setting times of pastes.
IS: initial setting time and FS: final setting time.

water concentration. Samples with and without the incorporation of extract were made. Then, these solutions were centrifuged and the precipitate that contains the formed compounds was dried in the oven at 60 °C. The obtained product was grinded to perform the X-ray diffraction (XRD) test. The analysis was performed using a Rigaku X-ray diffractometer, DMax IIIC with graphite monochrome, which operated at a voltage of 35 kV and a current of 15 mA. Diffractograms were obtained from 2θ = 3º to 2θ = 60º.

III. Results and discussion

A. *Cement-paste and mortars tests*

Figure 3 shows the setting-time curves for a control cement-paste and how this is modified with the addition of Oregano and Yerba Mate extracts both in LQ and FD.

In order to analyze this graphic, it is important to take into account the standard which specifies that the minimum initial setting time for CPN 40 is 60 minutes [21]. Cement-pastes with LQ extracts did not comply with the standard because their initial time were 39 and 37 minutes for LQ OR and LQ YM, respectively; while the ones with FD extracts did comply. Their initial times were 113 and 60 minutes for FD OR and FD YM, respectively.

It is also valuable to make a comparison between the control cement- paste and the ones with additions. Bearing in mind that the initial setting time for control is 97 minutes, it can be observed that the incorporation of FD extracts altered only 16% (with FD OR) and 38% (with FD YM) the initial setting times while LQ extracts altered 60% both additions. This last modification with the addition made the cement-paste did not comply with the minimum stated in the standard. Therefore, the use of extracts in the FD form ensures conformity with the standard values concerning the initial setting time.

Moving to the final setting time, there is no limit according to the standard but it can be observed a larger modification with the addition of LQ extracts than the one caused by FD extracts.

The use of the extracts in LQ form brought forward the start of the setting and delayed the corresponding time values at the end of the setting compared to the control sample and to the FD form sample, for both Oregano and Yerba Mate extracts.

The reason for the changes in the setting times with the addition of these extracts could be linked to issues related to differences in the presence of organic material in the cement-pastes. This material has a negative effect in setting times because it shortens the beginning of setting and extends the ending.

When using the aqueous extract as LQ, there is a time-lapse between its production and the tests, where deterioration of the components took place, although at a low rate. On the contrary, the freeze-dried extract is diluted immediately before its use, which avoided its deterioration. As a result of it, there could be a difference in the chemical composition of the organic material between these two products. This may give an explanation to the fact that the initial setting time of the cementitious pastes with FD are within the limits while LQ are not.

Regarding the mechanical behavior, the lyophilization of the extracts does not affect it substantially. Table 1 shows the results of flexural and compressive strength. The difference in the values between LQ OR and FD OR were not much significant. The same applies to the difference between LQ YM and FD YM.

TABLE 1
FLEXURAL AND COMPRESSIVE STRENGTH RESULTS

Extract type	Flexural (MPa)	Compression (MPa)
P	6.3	34.7
LQ OR	6.2	30.0
LQ YM	4.1	12.5
FD OR	6.1	32.3
FD YM	4.2	17.3

It is interesting to note that, while preparing the mortars for the tests, it was perceived foam in the mixtures with LQ. Later, this presence of spume was less significant when working with FD. It could be also linked to changes in the organic materials.

B. XRD analysis

First, the Yerba Mate extract as a FD form was analyzed with the X-ray diffraction technique and the pattern shown in Figure 4 was obtained. In this case, as plant extracts do not have crystalline structure, it can be observed undefined peaks with abundant noise. This is a typical characteristic of amorphous structures.

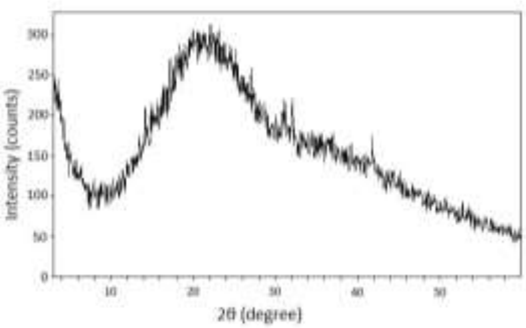

Fig. 4 XRD pattern for FD YM.

The rebar was exposed for 10 days to saline solutions without extract and with OR and YM extracts.

The steel bar without extracts showed a red layer in the surface of the rebar and this formed also a red precipitate, which is the characteristic color of corrosion phenomenon. This precipitate formed after the exposure was analyzed with XRD (Fig 5).

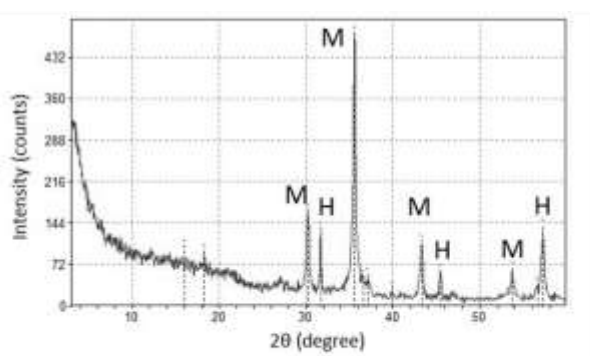

Fig. 5 XRD pattern from precipitate of solution without extract.

In this spectrum, it can be observed the peaks *H* corresponding to the crystalline structure of Halite (NaCl) and the peaks *M* indicative of the presence of the structure of Magnetite (Fe_3O_4). This last compound is characteristic of the corrosion of steel which indicated the deterioration of the material.

When adding the organic extracts to the saline solution, these red products did not appear. Instead, a thin dark blue protective layer was produced, which composition will be analyzed at a later stage. It was also noticed a dark blue precipitate generated by the aforementioned layer, which was analyzed with XRD (Fig. 6 and Fig.7).

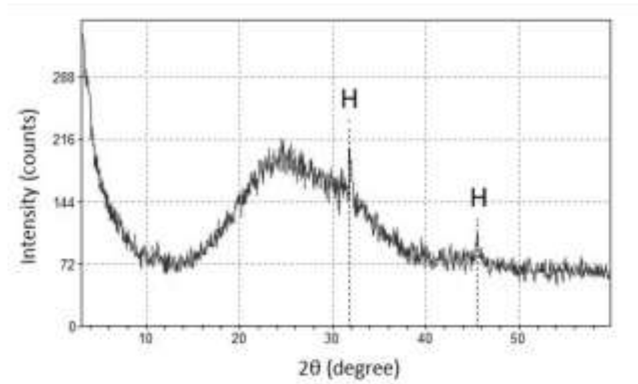

Fig. 6 XRD from precipitate of solution with FD OR.

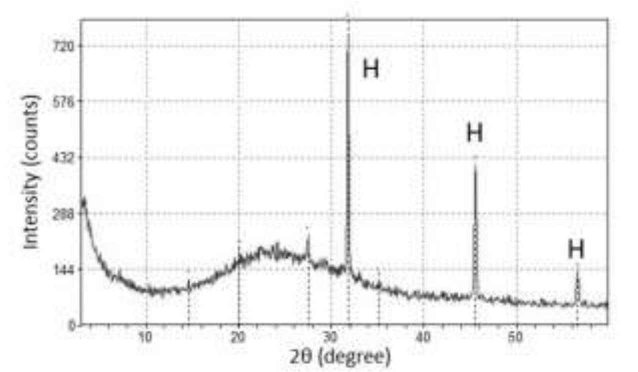

Fig. 7 XRD from precipitate of solution with the addition of FD YM.

In contrast with Figure 5, in the samples where the extracts were incorporated, only peaks of Halite and an amorphous structure similar to Fig. 4 are observed. The absence of oxides' characteristics peaks confirmed the benefits of using these organic extracts as corrosion inhibitors of the steel rebars.

According to these XRD results, the extracts would have successfully inhibited the formation of oxides on the surface of the steel in contact with the saline solution.

IV. CONCLUSIONS

The storage of natural extracts in a vacuum freeze-dried form proved to be superior than the liquid alternative. It allowed an easier conservation because of its concentrated form which gave the possibility to storage it in a smaller place. In addition, its composition remained more stable over time than liquid form extracts.

The effect of employing the freeze-dried extract instead of the liquid form was notorious in the setting times because it made it possible to be within the standard values. This procedure of lyophilization of the extracts did not affect substantially the mechanical properties of mortars.

Finally, according to the results obtained in XRD, the Oregano and Yerba Mate extracts behaved as corrosion inhibitors as they successfully prevented the formation of oxides on the surface of the steel in contact with the salt solution.

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