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ORIGINAL RESEARCH PAPER

EVALUATION OF THE CORROSION INHIBITION POTENTIAL OF *RAPHANUS SATIVUS* AND *SPINACIA OLERACEEA* EXTRACTS PART I: INFLUENCE OF THE COMPOSITION OF THE CORROSIVE MEDIA ON THE CHARACTERISTICS OF PLANT EXTRACTS

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Abstract: This paper presents a simple, ecofriendly, robust and inexpensive method for the preparation of radish (*Raphanus sativus*) and spinach (*Spinacia oleracea*) extracts that are destined to be tested as green corrosion inhibitors.
The obtained extracts proved to be stable in the corrosive media as no significant changes could be observed on the HPLC profile, nor on the UV and FTIR spectra of the extracts solubilized in either the acidic, alkaline or saline media.

Keywords: *extract stability, green corrosion inhibitors, microwave assisted extraction, Raphanus sativus, Spinacia oleracea*

INTRODUCTION

An important problem in the industrial process is represented by the metals corrosion leading to increase of the production costs. Corrosion can be defined as a chemical or electrochemical reaction between a material, (most often a metal) and its environment that leads to the deterioration of the material and its properties [1].
The use of corrosion inhibitors is one of the most popular methods of preventing corrosion. Corrosion inhibitors are substances which added in low concentrations to the corrosive medium reduce or prevent the reaction of the metal with aggressive media. Organic substances as corrosion inhibitors were developed, in the 1950s, in the petroleum industry and were introduced, 40 years later, to the concrete industry. Nevertheless, a major problem was related to their toxicity and their usage was limited by many environmental agencies because of their threat [2]. In the recent years, many experiments were conducted to use the eco-friendly substances as corrosion inhibitors, instead of the harmful synthetic chemicals. It has been recognized that the use of organic inhibitors containing polar functions with nitrogen, sulfur and/or oxygen atoms in the conjugated system, particularly the naturally occurring organic inhibitors of plant origin, are viable and highly beneficial since they are essentially non-toxic, environmentally benign, readily available, renewable and inexpensive [3 – 5]. These include amino acids [6], alkaloids [7], polyphenols [8] and also entire plant extracts [9] largely distributed and of low economic value, including byproducts of agro-industrial processes and agricultural-waste [10, 11].
The literature presents several examples of plant extracts that show corrosion inhibition effects for different metals or alloys in either acidic [12 – 14], alkaline [14 – 16] or saline media [14, 17].
Extracts of Lemon Balm [18], *Saraca ashoka* [19], *Rollinia occidentalis* [20], green tea [21], *Allium sativum* [22], *Chinese gooseberry* [23], Brahmi (Bacopamonnieri) and Henna [24], *Luffa cylindrica* [25] have been reported as effective inhibitors against steel corrosion in various media.
Raphanus sativus (radish) is an edible root vegetable of the family Brassicaceae. The utilization rate of radish leaves is very low; thus they are considered. According to the literature, the most abundant vitamins in radish leaves are ascorbic acid and folic acid [26], both vitamins have shown corrosion inhibition properties [2].
Spinacia oleracea (spinach), edible plant in the family of Amaranthaceae, is an important antioxidant vegetable and a good source of flavonoids, vitamins C and A, iron and potassium [27]. Shivakumar *et al*. tested ethanoic extract of dried spinach leaves as corrosion inhibitors for mild steel in hydrochloric acid media and fond that the metal corrosion rate decreased with the increase of the spinach extract concentration [28]. More recent papers have explored the inhibition potential of radish extracts for the protection of mild steel in 0.5 M sulfuric acid [29] and tap water [30] showing promising results as inhibition efficiency was 93 % and 75 % respectively.
The aim of our study was to investigate the inhibitive performances of *Spinacia oleracea* (spinach) and *Raphanus sativus* (radish) leaves extracts on mild steel corrosion in acid or alkaline media. We present herein the preparation mode of the vegetal extracts and influence of the corrosive media compositions on their characteristics.

MATERIALS AND MHETODS

Reagents and solvents

Ethanol 96 %, butanol, acetic acid (CH_3COOH), petroleum ether and ethyl acetate were purchased from Chemical Company (Iasi, Romania). Sodium chloride (NaCl), ninhydrin, nitric acid (HNO_3), sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and sodium hydroxide (NaOH) of analytical grade were purchased from Sigma Aldrich (Germany). HPLC-grade acetonitrile and methanol were purchased from J.T. Baker (Noisy le Sec, France). All the HPLC mobile phases were prepared using deionized water, purified using an Elgastat UHQ II system (Elga, Antony, France).
Solutions of 0.1 M HCl, HNO_3, CH_3COOH, NaOH, 0.05 M H_2SO_4 and NaCl 10 %, used as corrosive media, were prepared by dissolving/diluting the appropriately calculated and weighted amount with distilled water.
For the extractions 70 % ethanol solution was prepared according to Gay-Lussac table indications, thus 100 mL of 96 % ethanol were mixed with 40.85 mL of fresh distilled water.

Vegetal material preparation

Spinach and radish leaves were procured form a local market. They were washed with tap water and wiped with paper towels. Both fresh and dry vegetal materials were used for extraction. For the extracts of fresh leaves, the vegetal material was cut in small pieces and it underwent the extraction protocol. For the extracts of dry leaves, the clean leaves were air dried for several days and then the dried vegetal material was ground into a fine powder using a coffee grinder.

Extraction protocol

The 1 to 5 ratio between the plant material and the extraction solvent was adopted. Microwave assisted extraction was carried out using a household microwave oven (LG, model MH6340F, South Korea). The power was set at 510 W. Extraction was realized using flat-bottomed flasks coved with cotton plug in five microwave heating cycles of 30 seconds/cycle. After each heating cycle the extraction mixtures temperature was measured and it varied between 39 and 42 °C. The flasks were cooled to about 25-26 °C under running tap water after each heating cycle. The total extraction time was about 15 minutes.
The obtained extract was filtered through filter paper. The filtrate was concentrated using a rotary evaporating system (Rotavapor, Buchi - Switzerland).

Extracts characterization

Thin layer chromatography on silica plates with butanol / acetic acid / water 4/1/5 v/v was realized for all the prepared extracts. Plates revelation was realized by spraying the plates with 2 % ethanolic solution of ninhydrin, followed by heating.
For the liquid chromatographic analysis (HPLC), a Shimadzu Nexera UPLC (Shimadzu, Japan) system was employed. It was composed of automatic auto sampler (injection

volume set at 20 µL), binary pump (mobile phase flow set at 1 $mL \cdot min^{-1}$), column oven (temperature set at 25 °C) and DAD-UV detector. The chromatographic analyses were realized using an Inertsil column (250 x 4.6 mm, 5 µm) (GL Sciences, Japan). Elution was realized in gradient mode. Solvent A is a water / acetonitrile 98/2 v/v mixture and solvent B is methanol / acetonitrile / water 70/2/28 v/v mixture. The gradient was the following:

- 0 to 25 minutes from 0 % to 40 % B,
- 25 to 40 minutes from 40 % to 50 % B,
- 40 to 45 minutes from 50 % to 85 % B,
- 45 to 50 minutes from 85 % to 0 % B,
- 50 to 60 minutes 0 % B (for column reequilibration).

Before analysis, the vegetal extracts were diluted either with the mobile phase or the corrosive media and were filtered through a 0.45 µm syringe filter (Millipore).
Infrared analyses were determined on a Thermo Scientific ATR Nicolet iS10 and interpreted using OMNIC software (Thermo Fisher Scientific, US). The UV spectra were recorded on a Shimadzu UV-1800 UV-Vis Spectrophotometer (Shimadzu, Japan) using 1 cm diameter cuvettes.

Extract stability evaluation

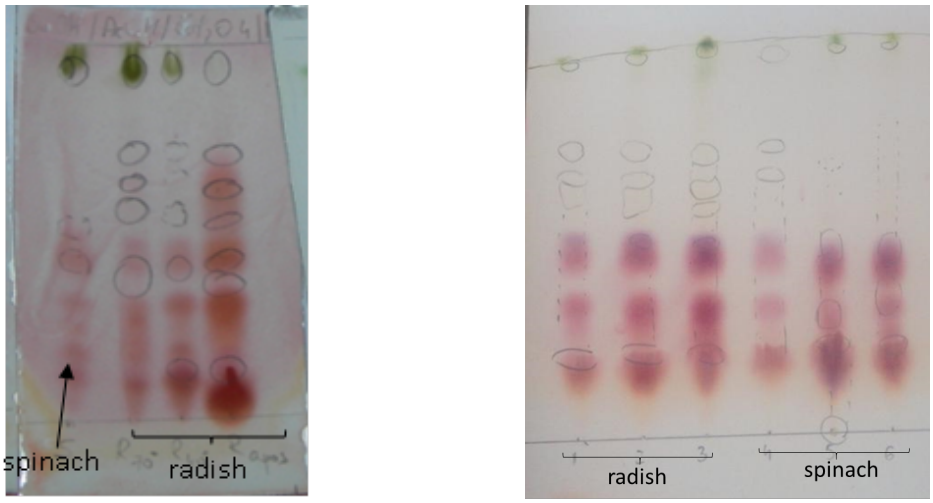
In order to verify the plant extracts stability in the different corrosive media, 50 mL of solution of 0.5 $g \cdot L^{-1}$ radish and spinach extract were prepared using 0.1 M HCl, 0.1 M HNO_3, 0.1 M CH_3COOH, 0.1 M NaOH, 0.05 M H_2SO_4 and NaCl 10 % solutions. The solutions were kept at room temperature for 28 days. Samples were taken for and analyzed using HPLC, UV and FTIR techniques.

RESULTS AND DISCUSSION

Extracts preparation

Modern extraction methods, like: supercritical fluid extraction, microwave assisted extraction, pressurized-liquid extraction or solid phase extraction, are being preferred to the conventional extraction methods as they offer lower solvent consumption and shorter extraction times [31]. Microwave assisted extraction (MAE) was preferred among the modern extraction methods because it is the easiest to realize and the cheapest, as we chose to use a domestic microwave oven which is not a very expensive nor a sophisticated tool. The ethanol water mixture used for the extraction has the advantage of been an ecofriendly solvent. Using these extraction conditions, we obtained extraction yields of 22 % and 25 % for radish leaves and spinach leaves respectively.
Radish and spinach are mainly seasonal crops; thus the fresh vegetal material can cause storage problems in terms of space and temperature and humidity conditions leading to an increase in the inhibitor production costs. That is why we wanted to determine if there were significant differences in the composition of the extracts prepared from fresh and dry leaves. We chose the air-drying method as it doesn't involve any supplementary costs. As it can be seen in Figure 1, the TLC profile of the spinach and radish extracts of

both fresh and dry leaves extracts are similar meaning that drying can be used in order to conserve the vegetal material up to moment the extraction can be realized.



a **b**

Figure 1. *TLC analysis of fresh (a) and dried (b) spinach and radish leaves extract using n-butanol / acid acetic / water (4:1:5, v/v) as mobile phase*
(*the pencil marks represent spots that were visible at 254 nm before the plates were sprayed with ninhydrin)

Figure 1b presents the analysis of three different spinach extracts and three different radish extracts demonstrating the reproducibility of our extraction method, as the chromatographic fingerprint is very similar for an extract to another.

Extract stability in the presence of the corrosive media

The literature often presents differences of the corrosion inhibition potential of plant extract for the same metal in different corrosive media [14, 32]. Thus, we wanted to analyze the influence of the corrosive media on the stability of our extracts.
The FTIR and UV spectra of the radish and spinach leaves realized for the extracts that were diluted to a concentration of 0.5 $mg \cdot L^{-1}$ in the different corrosive media. The samples were also analyzed using HPLC.
For the radish leaves extract no significant difference was noticed on the FTIR spectra whatever the media (Figure 2), the spectra also are similar to the data presented in the literature [29, 30]. On the other hand, the UV spectra of the different samples were very similar with the exception of the NaOH solution (Figure 3).
The HPLC analysis (Figure 4) also show very similar patern in all the corosive media, thus it can be concluded that the radish leaves extracts are rather stabil.

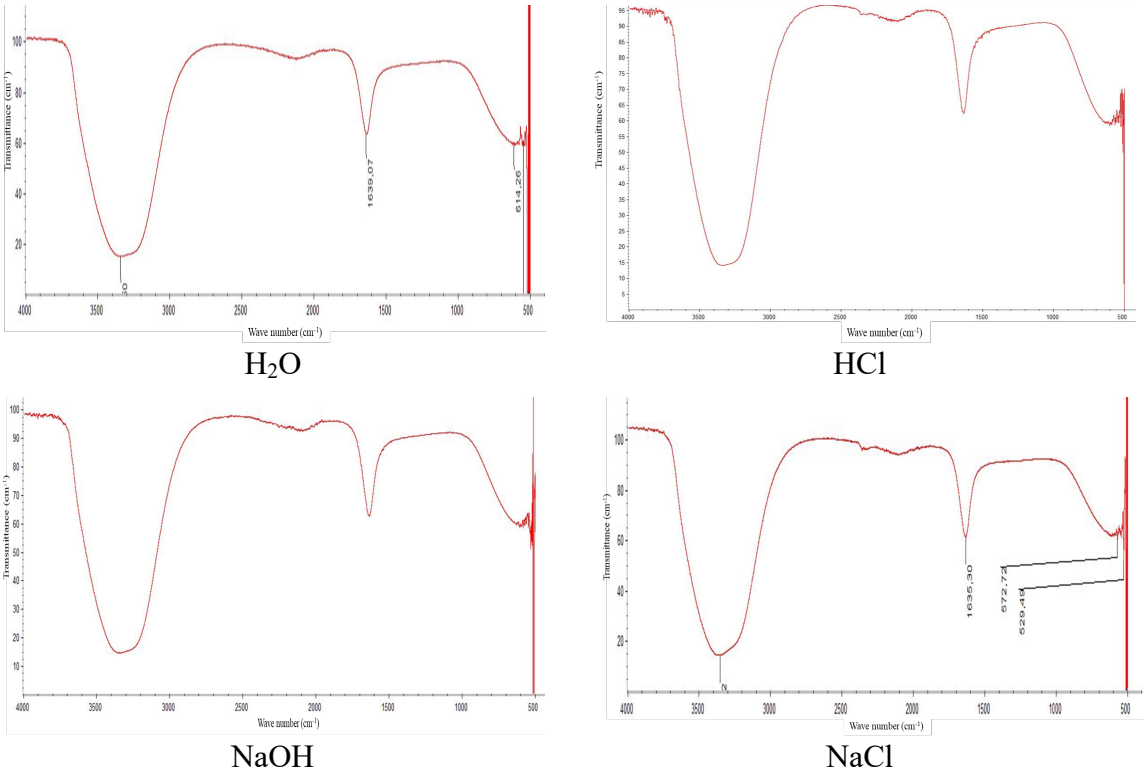


Figure 2. *FTIR spectra of radish leaves extract solubilized in different corrosive media*

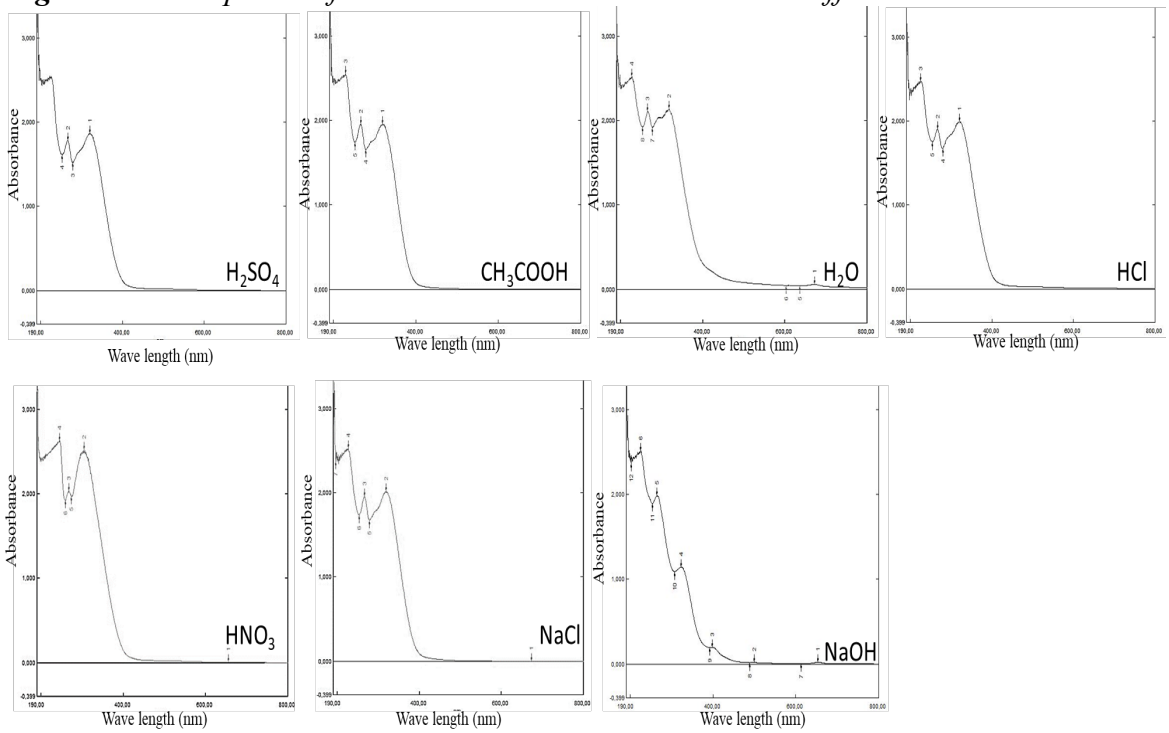


Figure 3. *UV spectra of radish leaves extract solubilized in different corrosive media*

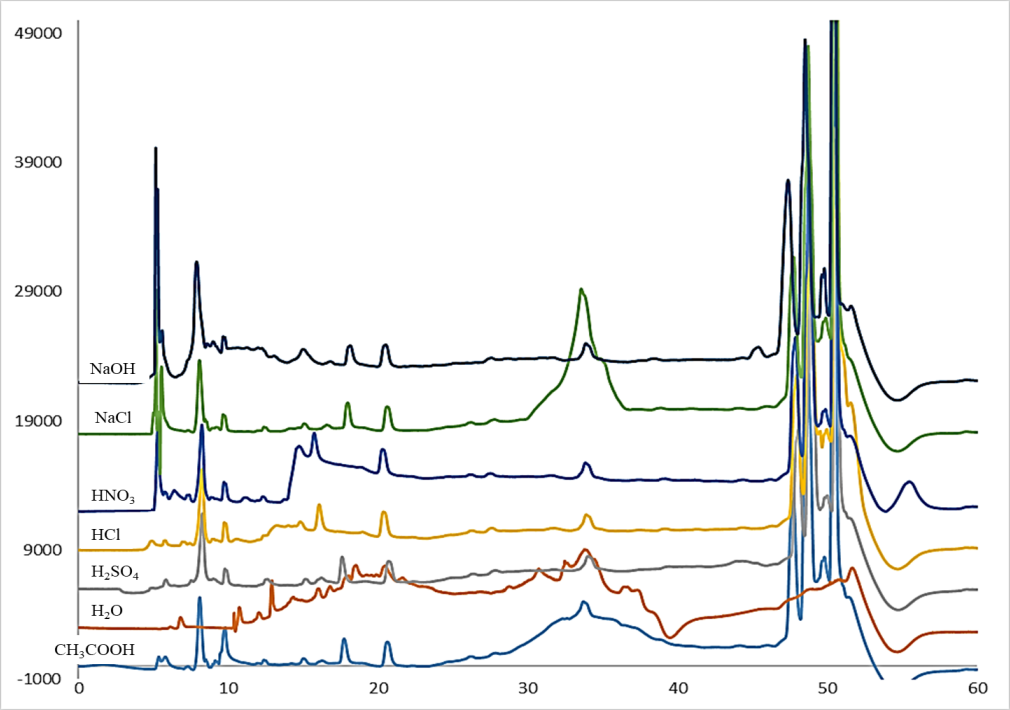
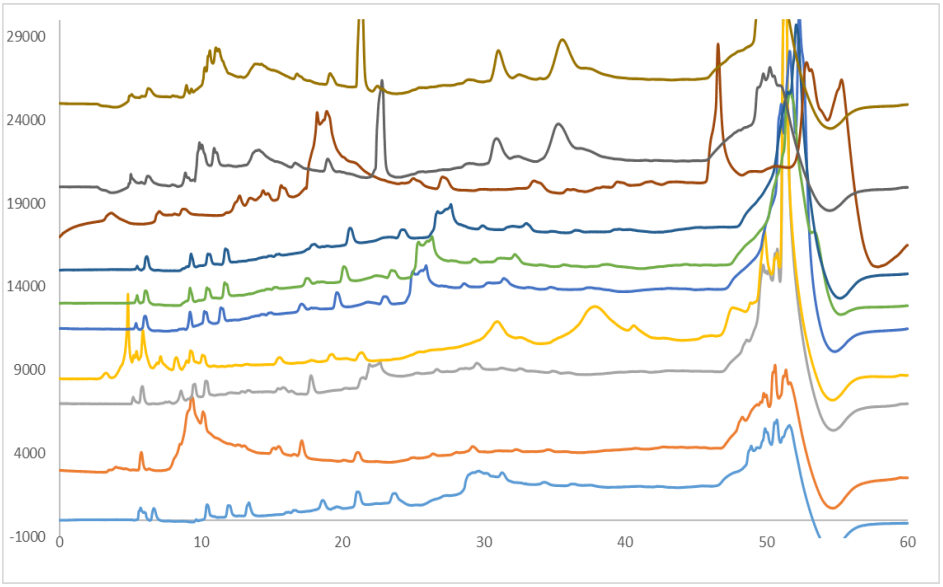


***Figure 4**. Chromatographic fingerprint of radish leaves extract solubilized in different corrosive media*

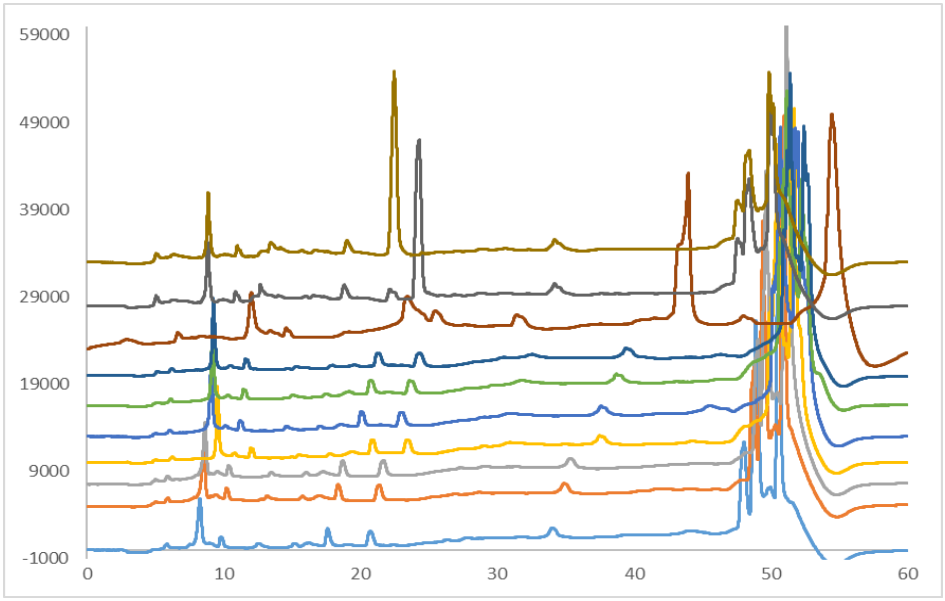
The same results were obtained for the spanish leaves extracts (data not shown). These results lead us to belive that our extracts are stable under the tested conditions, and any differences regarding the corrosion inhibitive potential of one of these extracts can not be linked to extract stability isues.

In order to verify the extracts stability in time, the samples of the radish and spinach extracts diluted with each of the corrosive media were left to stand at room for 28 days. Samples were taken for HPLC analysis every 24 h from day one to seven and then in days 14, 21 and 28.

Figure 5 presents the evolution in time of the chromatographic profiles of the spinach and radish leaves extracts diluted with H_2SO_4 0.1 M. No significant changes can't be observed on the profiles of both radish and spinach leaves during the first seven days. Significant changes started to appear from the 14th day, but they seem to slow down after the 21st day.



a



b

Figure 5. *Time evolution of chromatographic profile of the spinach (a) and radish (b) extracts diluted in H_2SO_4 0.1 M*

CONCLUSIONS

We can conclude that the adopted extraction protocol allowed us to obtain spinach and radish extracts with reproducible characteristics. Also, the obtained extracts proved to be stable in the corrosive media as no significant changes could be observed on the HPLC profile, nor on the UV and FTIR spectra of the extracts solubilized in either the acidic, alkaline or saline media.

The following step in our research is to test the inhibition potential of our extracts in the selected media for different type of metals.

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