

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Polyphenols and Herbal-Based Extracts at the Basis of New Antioxidant, Material Protecting Products

---

Lucia Camelia Pirvu

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/57183>

---

## 1. Introduction

Considering that many of the classical corrosion and scale inhibitors are toxic compounds that accumulate in the water and soil, finding natural, eco-friendly inhibitors has represented a constant preoccupation in recent years.

Table 1 shows several examples of vegetal compounds and extracts that have been revealed with anti-corrosive properties.

Given this, it is obvious that the utilization of herbal based extracts as new, ecological, material protecting products is a viable approach mainly because vegetal compounds are able not only to remove oxygen and reactive oxygen species in a biological environment (for example polyphenols, known for their capacity to rapidly oxidize thus being very effective scavenger species), but also to counteract scale formation (for example saponins known for their tensioactive properties) and to inhibit microbial corrosion (the typical example being organosulfur compounds from spices, but also polyphenols). Thus, polyphenols class, especially flavonoids and phenyl-carboxylic acids derivatives, likely represent the most feasible alternative of new, natural corrosion inhibitors on basis of their capacity to act as very effective reactive oxygen scavengers, some of them also being antimicrobial species (for example gallic acid, epi(gallo)catechin gallates and tannins). In support, gallic acid has been proved as a double corrosion inhibitor acting as an anodic protector (through capturing oxygen) [36] and also as a microbial development inhibitor by *irreversible changes in membrane properties through hydrophobicity changes, decrease of negative surface charge, and occurrence of local rupture or pore formation in the cell membranes with consequent leakage of essential intracellular constituents* [37].

Moreover, polyphenols compounds have added qualities such as a good thermal stability, high solubility and dispersion into a wide range of solvents, as well as an increasing antioxidant

| Investigated sample                                                                                                                                                                                        | Bibliography               |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| <i>Acacia</i> and <i>Pinus</i> tannins                                                                                                                                                                     | 1, 2, 3                    |
| <i>Quercus</i> (oak) and <i>Castanea</i> (chestnut) tannins                                                                                                                                                | 4, 5                       |
| <i>Mimosa</i> tannins                                                                                                                                                                                      | 6                          |
| <i>Tamarix articulata</i> tannins                                                                                                                                                                          | 7                          |
| <i>Thonningia sanguinea</i> ellagitannins                                                                                                                                                                  | 8                          |
| <i>Rizophora</i> (mangrove) tannins and catechins                                                                                                                                                          | 9, 10, 11                  |
| <i>Strychnos nux-vomica</i> alkaloidic fraction                                                                                                                                                            | 12                         |
| <i>Cannabis indica</i> alkaloidic fraction                                                                                                                                                                 | 13                         |
| <i>Calotropis procera</i> and <i>Calotropis gigantea</i> alkaloidic fraction                                                                                                                               | 14                         |
| <i>Solenostemma arghel</i> , <i>Chamommile</i> , Halfabar, Black curmin, Kidney bean, <i>Lupine</i> and <i>Damssisa</i> extracts                                                                           | 15, 16, 17, 18             |
| <i>Opuntia elatior</i> , <i>Acanthocereus pentagonus</i> , <i>Mimosa tenuiflora</i> , <i>Caesalpinia coriaria</i> , <i>Bumbacopsis quinata</i> and <i>Acacia mangium</i> extracts                          | 19                         |
| <i>Euphorbia falcata</i> , <i>Rosmarinus officinalis</i> , <i>Zenthoxylum alatum</i> , <i>Hibiscus sabdariffa</i> , <i>Aningeria robusta</i> , <i>Euphorbia hirta</i> and <i>Dialum guineense</i> extracts | 20, 21, 22, 23, 24, 25, 26 |
| <i>Psidium guajava</i> <b>seed extract</b>                                                                                                                                                                 | 27                         |
| <i>Spondias mombin</i> <b>fruit extract</b>                                                                                                                                                                | 28                         |
| <i>Phyllanthus amarus</i> leaves extract                                                                                                                                                                   | 29                         |
| <i>Cichorium intybus</i> , <i>Arctium lappa</i> , <i>Centaurea cyanus</i> , <i>Pinus caribea</i> , <i>Eucalyptus citriodora</i> , <i>Piper auritum</i> and <i>Piper guineense</i> extracts                 | 30, 31                     |
| <i>Cuminum Cyminum</i> /cummin, <i>Ferula assafoetida</i> /asea, <i>Capsicum</i> /chilli, <i>Allium sativum</i> /garlic, <i>Ocimum basilicum</i> /basil extracts                                           | 32, 33, 34, 35             |

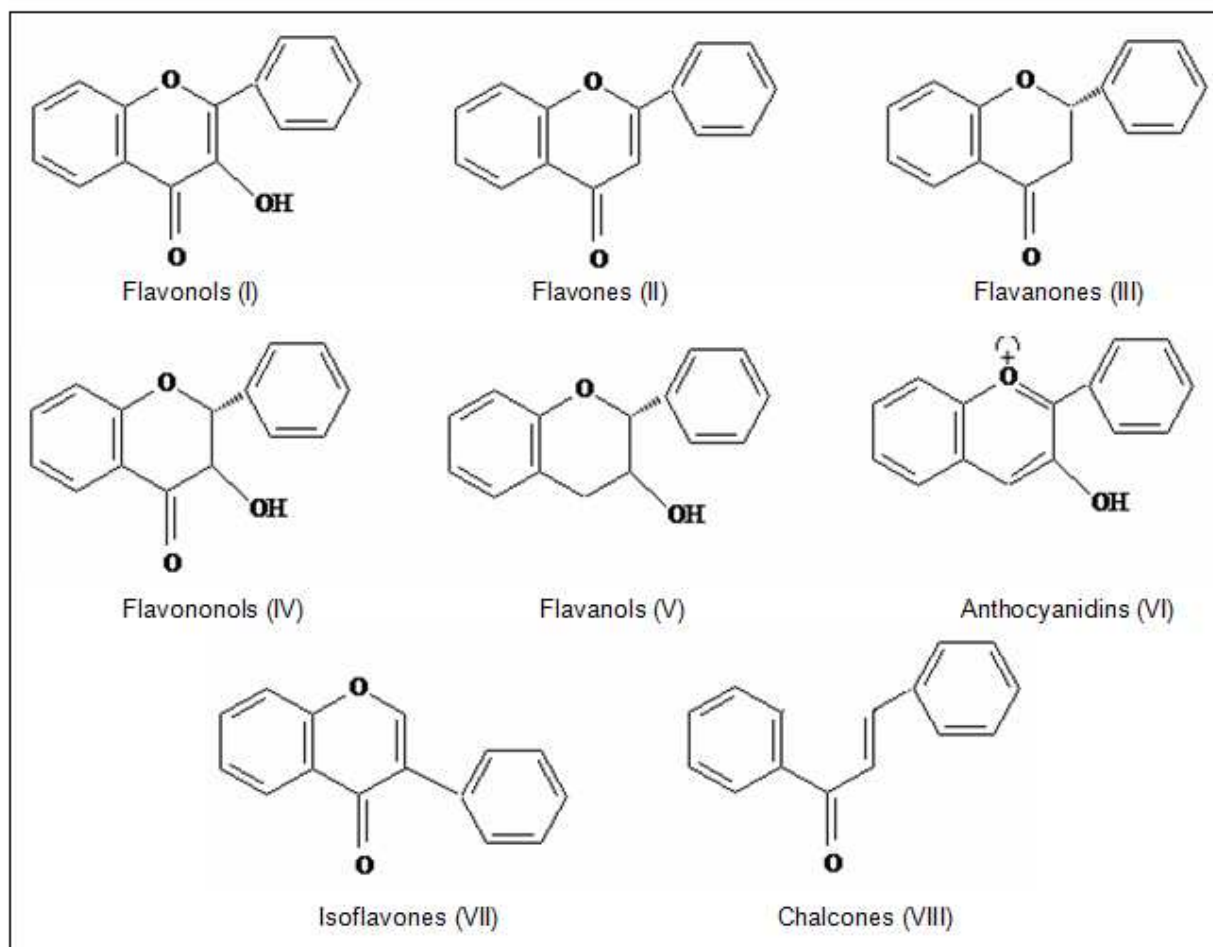
**Table 1.** Examples of previous work in the field of herbal-based anti-corrosion products

activity into acid medium (explained through the fact that the resulted, partly hydrolyzed, compounds are often more active scavengers' species than the origin homologues).

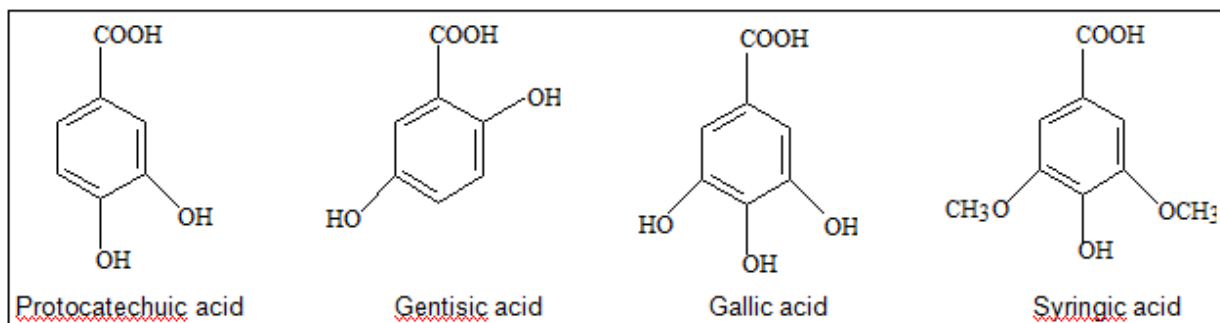
Summing, polyphenols class seems to convene most of the demands of a composite anti-corrosion/anti-biodeterioration product, also having the advantage of being less toxic than other natural compounds (for example alkaloids).

As for their role, polyphenols are secondary metabolites of the plants involved in defense against ultraviolet radiation and pathogens aggressions. The richest sources of polyphenols are onion, apple, tea, grapes, red wine and grape juice as well as strawberries, raspberries, blueberries and cranberries fruits. They are usually classified into four different groups by their number of phenol rings and by their different structural elements that bind these rings to one another. The four classes are phenolic acids, flavonoids, stilbenes and lignans, also classified as non-flavonoids and flavonoids. In the following are presented general chemical structures of the

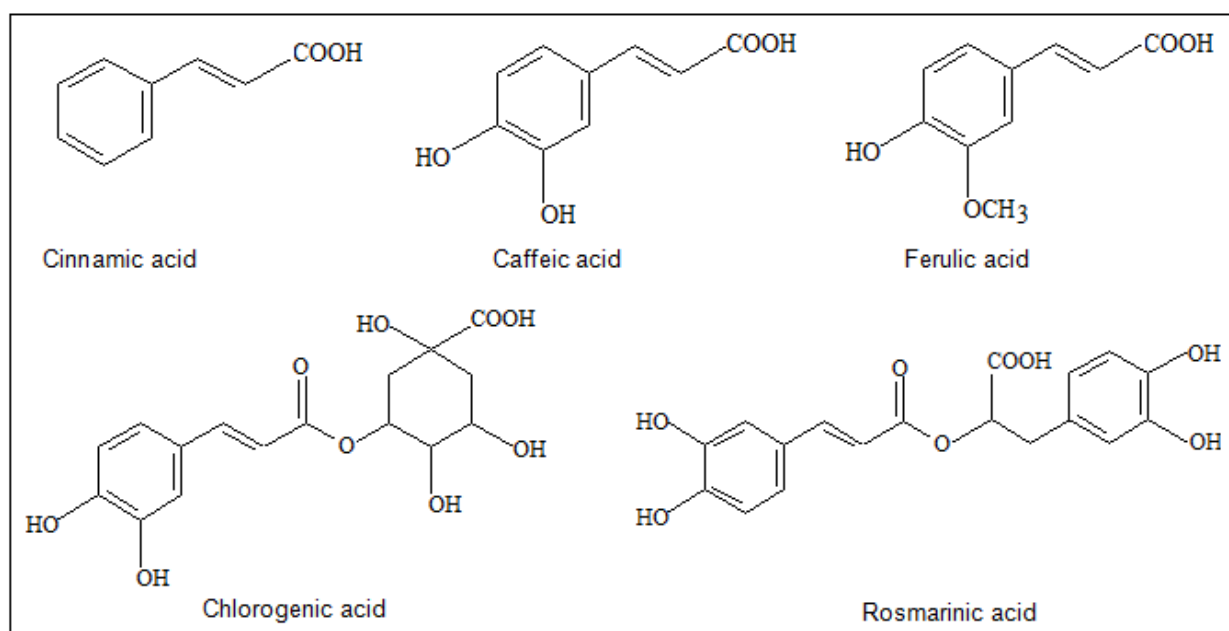
most commonly vegetal polyphenols, respectively flavonoids (flavonols, flavones, flavanones, flavononols, flavanols, anthocyanidin, isoflavones and chalcones derivatives) and phenyl-carboxylic acid (protocatechuic and cinnamic acids derivatives) (sub)classes.



**Figure 1.** Flavonoids subclasses



**Figure 2.** Protocatechuic (phenyl-carboxylic) acid derivatives



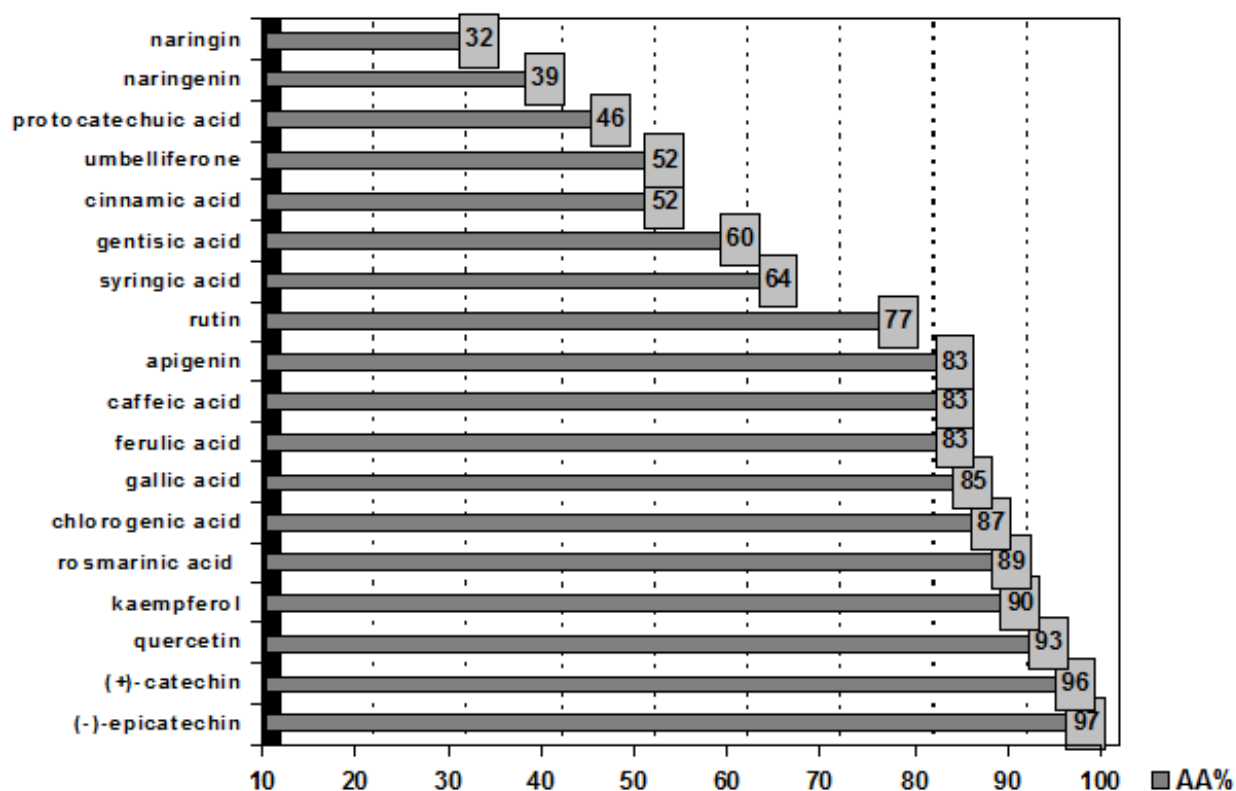
**Figure 3.** Cinnamic (phenyl-carboxylic) acid derivatives

## 2. Problem statement and application area

Given the complexity of this domain, in fact an inter-, multi- and even trans-disciplinary approach, there is some short-comings need be solved, respectively it should be done much more analytical and microbiological characterization assessments on vegetal extracts tested as new eco-friendly material protecting products for both purposes, practical and scientific, respectively to achieve the quality control of the vegetal extracts and the effectiveness of certain phytocompounds in the ultimate goal of the obtaining of characterized and effective anti-corrosion products.

Data referring to the antioxidant activity of the polyphenols compounds may also be very useful.

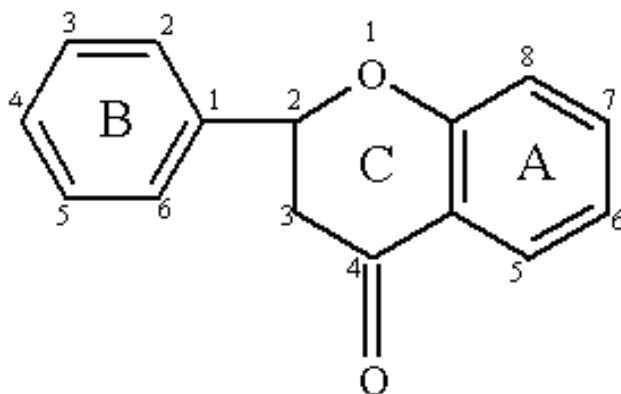
For example, some studies [38] carried out on eighteen commonly vegetal polyphenols indicated that the antioxidant activity (AA%) of the flavonoids and phenyl-carboxylic acid compounds depends on both, the number and the position of free hydroxyl ( $-\text{OH}$ ) groups; it should be noticed that studies were made by using chemiluminescence method, luminol/ $\text{H}_2\text{O}_2$  system,  $\text{pH}=8.6$  [39]. Precisely, studies (see Figure 1) has revealed that if (-)-epicatechin, (+)-catechin (belonging to flavan-3-ol subclass), quercetin and kaempferol (belonging to the flavonols subclass) are the most effective antioxidant species (AA% between 90 and 97%), naringin and naringenin (belonging to the flavanones subclass) are the less active (AA% between 32 and 9%). Gallic acid, chlorogenic acid and rosmarinic acid, belonging to the phenyl-carboxylic acid class, are also good scavenger species their antioxidant activities (AA%) varying between 85 and 89% [39].



**Figure 4.** Antioxidant activity (CL method) of eighteen (18) commonly vegetal polyphenols

As for the capacity of the vegetal polyphenols to stop bacterial corrosion, on basis of a comprehensive review [40], structure–activity relationship for antibacterial activity of flavonoids compounds has been summarized as follows:

- 2,4\_- or 2,6\_-dihydroxylation of the B ring and 5,7-dihydroxylation of the A ring in the flavanone structure is important for their antimicrobial/anti-methicillin resistant *Staphylococcus aureus* (MRSA) activity;



**Figure 5.** Flavonoid general structure

- substitution at the 6 or 8 position with a long chain aliphatic group such as lavandulyl (5-methyl-2-isopropenyl-hex-4-enyl) or geranyl (trans-3,7-dimethyl-2,6-octadienyl) enhance antimicrobial activity, and substitution with C8 and C10 chains enhanced the activity of flavonoids belonging to the flavan-3-ol class;
- 5-hydroxyflavanones and 5-hydroxyisoflavanones with hydroxyl group at position 2\_ are also very active;
- chalcones are more effective against MRSA than flavanones or flavones, hydroxyl groups at the 2\_ position being very important for their anti-staphylococcal activity;
- methoxy groups drastically decrease the antibacterial activity of flavonoids.

For example, using *Staphylococcus aureus* to guide the isolation process, some studies [41] on a methanolic extract isolated from dried leaves of *Physena madagascariensis* indicated two monomeric flavanones containing lavandulyl units in the limonene form as being very active against this bacterium. Similarly, studies [42] on some butanol and dichloromethane extracts of root of *Flemingia strobilifera* (a flowering plant in the legume family, *Fabaceae*) indicated flemingiaflavanone (8, 3-diprenyl-5, 7, 4'-trihydroxy flavanone) with significant antimicrobial activity against Gram-positive (*Staphylococcus aureus*, *Staphylococcus epidermidis*, methicillin resistant *Staphylococcus aureus*/MRSA), Gram-negative bacteria (*Pseudomonas aeruginosa*, *Escherichia coli*) and fungi (*Candida albicans*); genistin (5, 4 dihydroxy isoflavone 7-O-glucoside) showed moderate activity against Gram-positive, Gram-negative bacteria and fungi.

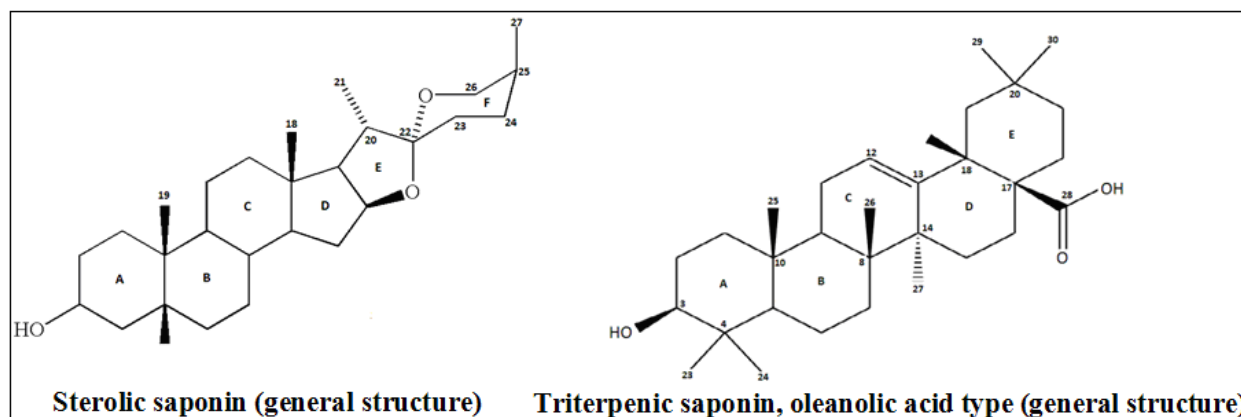
Other studies [43] on some crude methanolic extracts isolated from *Grewia asiatica*, *Eugenia jambolana* and *Carissa carandas* separated, each one, into four major fractions respectively, 1)phenolic acids, 2)flavanols, 3)flavonols and 4)anthocyanins fractions indicated that, besides being the most active on microbial strains, phenolic acid fractions also inhibited all tested fungal species. Similarly, studies on Tunisian Quince (*Cydonia oblonga* Miller) pulp and peel polyphenolic extracts [44], shown as very rich in caffeoyl derivatives demonstrated that chlorogenic acids acts in synergism with other components of the extracts to exhibit their total antimicrobial activities. Other comparative studies [45] on some common phytochemicals respectively, 5 simple phenolics - tyrosol, gallic acid, caffeic acid, ferulic acid, and chlorogenic acid; chalcone - phloridzin; flavan-3-ol - (-)epicatechin; seco-iridoid - oleuropein glucoside; 3 glucosinolate hydrolysis products - allyl isothiocyanate, benzyl isothiocyanate and 2-phenylethyl isothiocyanate, but also on some dual combinations of streptomycin with these phytochemicals against *Escherichia coli*, *Pseudomonas aeruginosa*, *Listeria monocytogenes* and *Staphylococcus aureus* indicated that the isothiocyanates had significant antimicrobial activities, while the phenolics were much less efficient; no antimicrobial activity was observed in the case of phloridzin (chalcone derivative).

Differently, studies [46] reported that the marine paint mixed with 2-methoxy-2',4'-dichloro chalcone considerably reduced the formation of biofilm by *Vibrio natriegens*, a marine bacterium, on polycarbonate (PC), polymethylmethacrylate (PMMA) and glass fiber reinforced plastic (GFRP). Precisely, it has been revealed that the surfaces coated with dichloro chalcone containing marine paint had the lowest number of colony forming units (CFU)( $1.5 \times 10^6$ ), proteins (20-30  $\mu\text{g}/\text{cm}^2$ ) and carbohydrates (5-10  $\mu\text{g}/\text{cm}^2$ ) attached to them after 28 days of

exposure to the organism when compared to surfaces coated with CuSO<sub>4</sub> mixed paint (20-40×10(6) CFU/ml, proteins of 50-60 µg/cm<sup>2</sup> and carbohydrates of 40-50 µg/cm<sup>2</sup>) or plain marine paint (30-40×10(6) CFU/ml, proteins of 120-150 µg/cm<sup>2</sup> and carbohydrates of 40-60 µg/cm<sup>2</sup>). Also, results indicated that the biofilm on PMMA was 7, 10 and 12 µm thick on chalcone, copper and plain paint coated surfaces, respectively. Furthermore, the first two paints increased the surface roughness but decreased the surface hydrophobicity when compared to the plain paint. The obtained results suggested that the low amount of biofilm formed in the presence of dichlorochalcone can be associated to its antibacterial and slimicidal activity and also its ability to reduce the hydrophobicity of the surface.

As for the solvent effectiveness, some studies [30] on different aqueous, acetonetic, and ethanol extracts of *Cichorium intybus* L., *Arctium lappa* L., *Centaurea cyanus* L. (Asteraceae), *Allium sativum* L. (Liliaceae), *Pinus caribea* Mor. (Pinaceae), *Eucalyptus citriodora* Hook. (Mirtaceae) and *Piper auritum* Kunth (Piperaceae) against different microorganisms (*Pseudomonas fluorescens*, *Bacillus cereus*, *Bacillus polimixa*, *Enterobacter agglomerans* and *Streptomyces* sp.,) associated with biodeterioration indicated that the aqueous extracts did not show any antibacterial activity, the antimicrobial activity from bacteria isolated from biofilms being present only in the ethanol extracts.

Referring to the scale issue, with their well known tensioactive properties, triterpenic (acidic) saponins appears as the most viable approach, the neutral ones, respectively sterolic saponins, being very toxic (see below the general chemical structure of sterolic and triterpenic saponins, respectively spirostane and oleanolic acid types).



**Figure 6.**

For example, studies on 39 plant materials indicated that the birch bark (containing betulinic acid), plane bark (also containing betulinic acid), olive leaves, olive pomace, mistletoe sprouts and clove flowers (all containing oleanolic acid), apple pomace (containing ursolic acid) and rosemary leaves (containing an equal mixture of these three triterpene acids) are the richest sources of triterpenic saponins [47]. Other vegetal materials demonstrated as being abundant in triterpenic acids are *Satureja parvifolia* and *Eucalyptus* species. Thus, in the first case, studies on methanolic extracts lead to the isolation of eriodictyol, luteolin and ursolic and oleanolic

acids [48]. In the second case, studies on the outer bark of *E. globulus*, *E. grandis*, *E. urograndis*, *E. maidenii* and *E. nitens* indicated triterpenic acids contents varying between 4.5 g/kg in *E. urograndis* and 21.6 g/kg in *E. Nitens*, but out of these species, temperate and Mediterranean *E. nitens* and *E. globulus* were also revealed as very rich in triterpenic acids; precisely, *E. globulus* outer bark was found as the richest source of ursane acids, while *E. nitens* outer bark was revealed as the richest source of oleanane and lupane acids [49].

Summing, olive oil appears as one of the most complete source of corrosion inhibitors on basis of its content in phenolics (4-hydroxybenzoic acid, protocatechuic acid, syringic acid, 4-hydroxy-phenylacetic acid, homovanillic acid, ferulic acid, sinapic acid), flavonoids (apigenin and luteolin derivatives), lignanes, isochromans, tyrosol and hydroxytyrosol derivatives [50] as well as in triterpenic acid derivatives (oleanolic, ursolic and maslinic acids) [51] theoretically able to manage all, oxidative stress, microbial development, and scale formation.

### 3. A case study

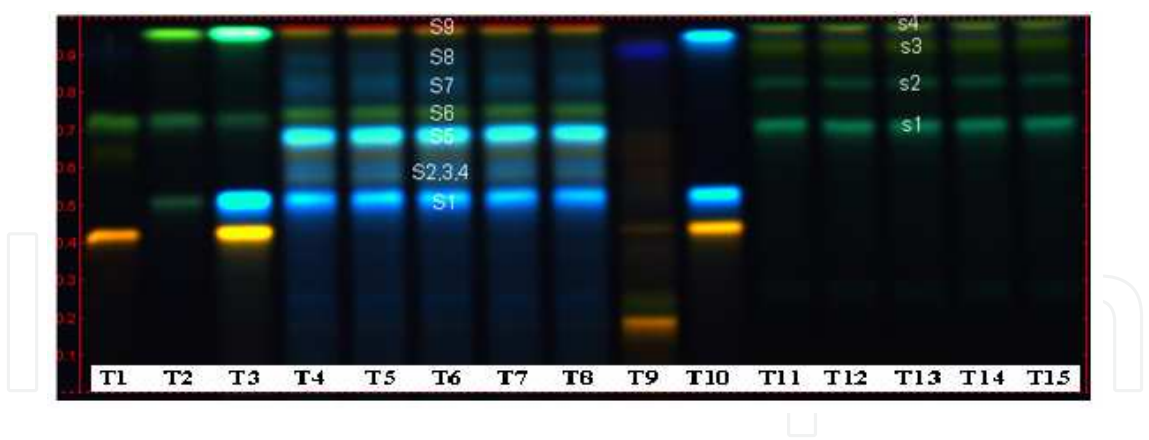
Below it is presented a case study on four vegetal extracts for the purpose of assessing scavenger/antioxidant activity and corrosion inhibition effectiveness of certain flavonoids and phenyl-carboxylic acid derivatives combinations.

Thus, there were compared four series of whole and selective ethanolic extracts, respectively:

- extracts containing <sup>2</sup>chlorogenic acid derivatives aside small quantities of kaempferol, apigenin, quercetin and catechin derivatives isolated from leaves of *Fagus sylvatica* L. (see Figure 2, T4-T8 tracks, respectively Table 2);
- extracts containing <sup>1</sup>quercetin and derivatives isolated from scales of *Allium cepae bulbis* (see Figure 2, T11-T15 tracks, respectively Table 2);
- extracts containing a mixture of <sup>3</sup>quercetin and chlorogenic acid derivatives isolated from leaves of *Juglans regia* L. (see Figure 3, T4-T9 tracks, respectively Table 3) and
- extracts containing a mixture of <sup>4</sup>quercetin, luteolin and apigenin derivatives aside small quantities of chlorogenic acid isolated from *Agrimonia eupatoria* L.-herba (see Figure 3, T10-T15 tracks, respectively Table 3).

Chemiluminescence studies (luminol/H<sub>2</sub>O<sub>2</sub> system, pH=8.6) carried out on these four series of whole and selective vegetal extracts isolated from scales of *Allium cepae bulbis*, leaves of *Fagus sylvatica* [52], leaves of *Juglans regia* and the aerial part (*herba*) of the *Agrimonia eupatoria* [53] indicated maximum antioxidant activities (AA%) of 91% to 97% for *total phenols content* ranging between 3 and 57mg per 100mL ethanolic extract (see Table 4).

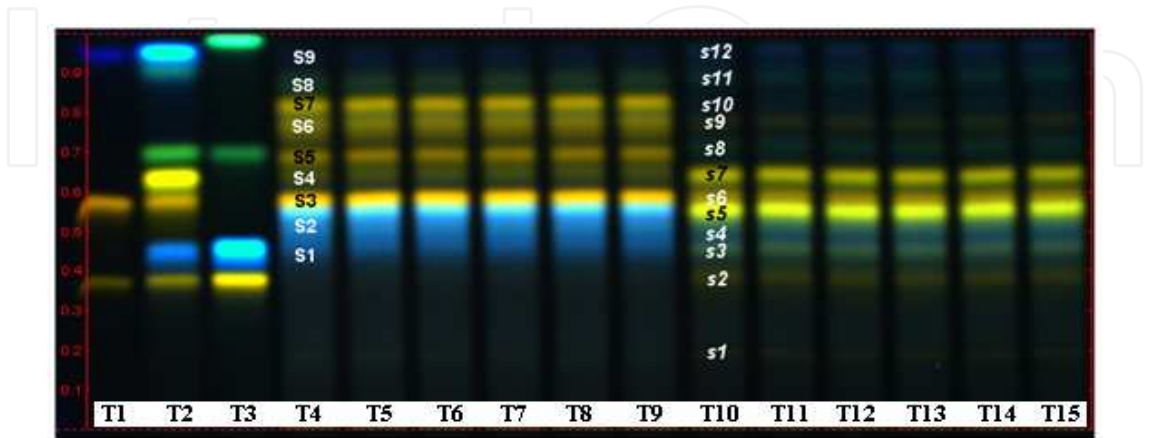
Subsequently comparative studies [55] on carbon steel corrosion in acidic (0.5M H<sub>2</sub>SO<sub>4</sub>) solution model indicated that all studied extracts presented anti-corrosion properties, *Fagus sylvatica* L. leaves whole ethanol extract being the most potent anti-corrosion product, also presenting anti-scale properties. Results were patented [56].



**Figure 7.** (HP)TLC aspects of *Fagus sylvatica* L. leaves (T4-T8 tracks) and *Allii cepae bulbis* L. scales (T11-T15 tracks) whole ethanol extracts [52]

| Tested sample                                | Spot | Rf~  | Colour spot                   | Attributed compound                                  |
|----------------------------------------------|------|------|-------------------------------|------------------------------------------------------|
| <i>Fagus sylvatica</i> L. leaves extracts    | S1   | 0.52 | Light blue, fluorescent (fl.) | Chlorogenic acid                                     |
|                                              | S2   | 0.56 | Brown, non-fl.                | Catechin derivate                                    |
|                                              | S3   | 0.58 | Blue, fl.                     | Neochlorogenic acid                                  |
|                                              | S4   | 0.64 | Brown, non-fl.                | Catechin derivate                                    |
|                                              | S5   | 0.69 | Blue-green, fl.               | Kaempferol derivate (likely Lespedin)                |
|                                              | S6   | 0.75 | Green, fl.                    | Apigenin derivate (likely Vitexin)                   |
|                                              | S7   | 0.83 | Blue, fl.                     | Isochlorogenic acids (two isomers)                   |
|                                              | S8   | 0.90 |                               |                                                      |
|                                              | S9   | 0.97 | Yellow, fl.                   | Quercetin                                            |
| <i>Allii cepae bulbis</i> L. scales extracts | s1   | 0.72 | Green-blue, fl.               | Quercetin-4'-O-glycosides (also called spiraeosides) |
|                                              | s2   | 0.84 | Green-blue, fl.               |                                                      |
|                                              | s3   | 0.94 | Green and                     | Isorhamnetin and Quercetin                           |
|                                              | s4   | 0.98 | Yellow fl.                    |                                                      |

**Table 2.** Chemical qualitative composition of *Fagus sylvatica* leaves and *Allii cepae bulbis* scales extracts [52]



**Figure 8.** (HP)TLC aspects of *Juglans regia* L. leaves (T4-T9 tracks) and *Agrimonia eupatoria* L. aerial part (T10-T15 tracks) whole ethanol extracts [53]

| Tested sample                                            | Spot | Rf~  | Colour spot     | Attributed compound                       |
|----------------------------------------------------------|------|------|-----------------|-------------------------------------------|
| <i>Juglans regia</i> L.<br>leaves extracts               | S1   | 0.45 | Light-blue, fl. | Chlorogenic acid                          |
|                                                          | S2   | 0.50 | Light-blue, fl. | Neochlorogenic acid                       |
|                                                          | S3   | 0.56 | Orange, fl.     | Quercetin derivate (likely Hyperoside)    |
|                                                          | S4   | 0.63 | Green, fl.      | Apigenin derivate (likely Isovitexin)     |
|                                                          | S5   | 0.69 | Orange, fl.     | Quercetin derivate (likely Isoquercitrin) |
|                                                          | S6   | 0.76 | Orange, fl.     | Quercetin derivate (likely Avicularin)    |
|                                                          | S7   | 0.81 | Orange, fl.     | Quercetin derivate (likely Quercitrin)    |
|                                                          | S8   | 0.87 | Green-blue, fl. | Quercetin derivate (likely Juglanin)      |
|                                                          | S9   | 0.96 | Dark-blue, fl.  | Protocatechuic acid                       |
| <i>Agrimonia eupatoria</i> L.<br>aerial part<br>extracts | s1   | 0.20 | Orange, fl.     | Quercetin derivate                        |
|                                                          | s2   | 0.38 | Orange, fl.     | Quercetin derivate (likely Rutin)         |
|                                                          | s3   | 0.44 | Orange, fl.     | Quercetin derivate                        |
|                                                          | s4   | 0.50 | Light-blue, fl. | Neochlorogenic acid                       |
|                                                          | s5   | 0.55 | Yellow, fl.     | Luteolin derivate (likely Isoorientin)    |
|                                                          | s6   | 0.58 | Orange, fl.     | Quercetin derivate (likely Hyperoside)    |
|                                                          | s7   | 0.63 | Yellow, fl.     | Luteolin derivate (likely Orientin)       |
|                                                          | s8   | 0.73 | Green, fl.      | Apigenin derivate (likely Cosmosiin)      |
|                                                          | s9   | 0.78 | Orange, fl.     | Quercetin derivate                        |
|                                                          | s10  | 0.80 | Blue, fl.       | Isochlorogenic acid isomer                |
|                                                          | s11  | 0.87 | Green, fl.      | Apigenin derivate                         |
|                                                          | s12  | 0.98 | Deep-blue, fl.  | Rosmarinic acid                           |

**Table 3.** Chemical qualitative composition of *Juglans regia* leaves and *Agrimonia eupatoria* aerial part extracts [53]

| Parameters                                                                            | Raw material description               |      |                                     |      |                                   |      |                                              |      |
|---------------------------------------------------------------------------------------|----------------------------------------|------|-------------------------------------|------|-----------------------------------|------|----------------------------------------------|------|
|                                                                                       | <i>Allium cepae bulbos</i> L.<br>scale |      | <i>Fagus sylvatica</i> L.<br>leaves |      | <i>Juglans regia</i> L.<br>leaves |      | <i>Agrimonia eupatoria</i> L.<br>aerial part |      |
| Type of extract:<br>Whole (W) or Selective (S)                                        | W                                      | S    | W                                   | S    | W                                 | S    | W                                            | S    |
| Antioxidant activity:<br>(AA%)                                                        | 92                                     | 95   | 91                                  | 94   | 95                                | 97   | 94                                           | 97   |
| Total phenols content:<br>mg/100mL (expressed as<br>gallic acid equivalents)          | 3.1                                    | 6.7  | 20.2                                | 39.2 | 35.6                              | 64.4 | 48.4                                         | 56.8 |
| Total flavones content:<br>mg/100mL (expressed as<br>quercetin* or rutin equivalents) | 2.3*                                   | 4.6* | 7.2                                 | 10   | 23.2                              | 58.6 | 21.6                                         | 17.6 |

Note: Analytical measurements were done by using classic methods [54], respectively total phenols content was measured by using *Folin* reagent and the results were expressed as gallic acid equivalents and total flavones content was measured by using  $\text{AlCl}_3$  in base (sodium acetate) medium and the results were expressed as quercetin\*, respectively, rutin equivalents

**Table 4.** Antioxidant activities of the four series of whole and selective vegetal extracts

## 4. Results and comments

This case study has revealed the following aspects:

- *whole* vegetal extracts presented similar antioxidant activities (AA%) with selective vegetal extracts but at the lesser amounts of total phenols, thus suggesting the benefit of the vegetal compounds, respectively polysaccharides and proteins, lacking in the selective extracts;

- *Allium* polyphenols (quercetin and derivatives) indicated the highest antioxidant effectiveness, meaning that *Allium cepae bulbis* extracts presented the maximum antioxidant activity (respectively, 92%) at the lowest total phenols content (respectively, 3.1 mg/100mL whole ethanol extract).
- *Fagus sylvatica* leaves extracts (containing mainly chlorogenic acid derivatives added to only small quantities of flavonoid derivatives) also were very effective antioxidant products emphasizing an augmented antioxidant activity (91%) at moderate total phenols content (respectively, 20.2 mg/100mL whole ethanol extract);
- *Juglandis* leaves extracts (containing dominantly quercetin derivatives aside moderate levels of chlorogenic acid derivatives), similar to *Agrimonia herba* extracts (containing a mixture of quercetin, luteolin and apigenin flavonoids aside small quantities of chlorogenic acid derivatives) both required high total phenols contents (35.6 mg/100mL and, respectively, 48.4 mg/100mL extract) in order to present the same magnitude of the antioxidant activity (95% and, respectively, 94%);
- *Fagus sylvatica* leaves whole ethanol extract was the most potent anti-corrosion product presenting anti-scale properties, as well.

## 5. Conclusion

Literature data driven indicated that phytochemicals and herbal-based extracts are of increasing interest in this field of new, eco-friendly material protecting products. Accordingly, it has been revealed that on basis of their capacity to consume oxygen and reactive oxygen species added to the capacity to inhibit microbial development, polyphenols based extracts seems to convene most of the demands of a composite anti-corrosion/anti-biodeterioration product, also having the advantage of being less toxic than other vegetal extracts (for example alkaloids extracts). With effective tensioactive properties, triterpenic saponins also appear as very useful anti-corrosion ingredients by decreasing scale formation and increasing phytochemicals solubility.

In support, a case study aiming the comparison of the antioxidant activity and corrosion inhibition effectiveness of four whole and, respectively, selective vegetal extracts isolated from four vegetal species selected in a manner to contain different combinations of flavonoids and phenyl-carboxylic acid derivatives revealed that quercetin compounds had the highest antioxidant/scavenger activity at the lowest concentration in respective environment, thus suggesting high anti-corrosion potential of quercetin based extracts. Subsequently, comparative anti-scale/anti-corrosion studies indicated that, besides containing polyphenols species with high antioxidant/scavenger activity, the co-presence of other protecting, synergetic or boosting compounds seems to be more important for the final anti-corrosion effect. As proof, *Fagus sylvatica* leaves whole ethanol extract abundant in chlorogenic acid derivatives aside only small quantities of flavonoid (quercetin, apigenin, kaempferol and catechin) derivatives, but containing some saponins derivatives [57] offered the most proper protecting conditions on carbon steel corrosion in acidic ( $\text{H}_2\text{SO}_4$ ) solution model.

Given these, it has been concluded that it should be done much more analytical and microbiological characterization assessments on vegetal extracts tested as new eco-friendly material protecting products for both purposes, practical and scientific, respectively to achieve the quality control of the vegetal extracts and the effectiveness of certain phytocompounds in the ultimate goal of the obtaining of characterized and effective anti-scale/anti-corrosion products.

Therefore, further studies in this area may be done on those vegetal extracts or combinations of vegetal extracts offering the whole range of material protecting compounds, respectively polyphenols with augmented antioxidant activity and/or polyphenols with strong antimicrobial activity, saponins with tensioactive properties and other vegetal macromolecules, such as polysaccharides and proteins, with protective, synergistic or boosting effects all contributing to the achieving of a highly effective corrosion, biodeterioration and scale inhibitor product.

## Acknowledgements

The author is very grateful to Dr Mahmood Aliofkhazraei for analyzing preliminary drafts of the manuscript and subsequently advices.

## Author details

Lucia Camelia Pirvu

National Institute of Chemical-Pharmaceutical R&D, Department of Pharmaceutical Biotechnologies, Plant Extraction Laboratories, Bucharest, Romania

## References

- [1] Gust J. Application of infrared spectroscopy for investigation of rust phase component conversion by agents containing oak tannin and phosphoric acid. *Corros NACE* 1991;47(6) 453-457.
- [2] Matamala G, Smeltzer W, Droguett G. Comparison of steel anticorrosive protection formulated with natural tannins extracted from acacia and from pine bark. *Corros Sci* 2000;42 1351-1362.
- [3] Palma G, Freer J, Baeza J. Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions. *Water Res* 2003;37 4974-4980.
- [4] Martinez S, Stalgar I. Correlation between the molecular structure and the corrosion efficiency of chestnut tannin in acidic solutions. *J Mol Struct (THEOCHEM)* 2003;640 167-174.

- [5] Pardini OR, Amalvy JL, Di Sarli AR, Romagnoli R, Vetere VF. Formulation and testing of a waterborne primer containing chestnut tannin. *J Coat Technol* 2001;3(913) 99-111.
- [6] Martinez S, Stern I. Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel/mimosa tannin/sulfuric acid system. *Appl Surf Sci* 2002;9149 1 -7.
- [7] Mabrou J, Akssira M, Azzi M, Zertoubi M, Saib N, Messaoudi A, Albizane A, Tahiri S. Effect of vegetal tannin on anodic copper dissolution in chloride solutions. *Corrosion Science* 2004;46(8) 1833-1847.
- [8] Ohtani II, Gotoh N, Tanaka J, Higa T, Gyamfi MA, Aniya Y. Thonningianins A and B, New Antioxidants from the African Medicinal Herb *Thonningia sanguinea*. *J Nat Prod* 2000;63 676-679.
- [9] Afidah AR, Rocca E, Steinmetz J, Kassim MJ, Adnan R, Ibrahim MS. Study of mangrove tannin and flavanoid monomers as alternative steel corrosion inhibitors in acidic medium. *Corros Sci* 2007;49 402-417.
- [10] Afidah AR, Rocca E, Steinmetz J, Kassim MJ. Inhibitive action of mangrove tannins and phosphoric acid on pre-rusted steel via electrochemical methods. *Corros Sci* 2008;50 1546-1550.
- [11] Kang Wei Tan, Mohd. Jain Kassim, Chuan Wei Oo. Possible improvement of catechin as corrosion inhibitor in acidic medium. *Corrosion Science* 2012;65 152-162.
- [12] Bothi Raja P, Sethuraman MG. *Strychnos nux-vomica* an eco-friendly corrosion inhibitor for mild steel in 1 M sulfuric acid medium. *Materials and Corrosion* 2008;60(1) 22 – 28.
- [13] Abd-El-Nabey BA, Abdel-Gaber AM, Said Ali MEL, Khamis E, El-Housseiny S. Inhibitive action of cannabis plant extract on the corrosion of copper in 0.5 M H<sub>2</sub>SO<sub>4</sub>. *International Journal of Electrochemical Science* 2013;8(4) 5851-5865.
- [14] Sudesh Kumar, Surendra Arora, Manish Sharma, Paresh Arora, Suraj Prakash Mathus. Synergistic effect of *Caloptris* plant in controlling corrosion and mild steel basis solution. *J. Chil. Chem. Soc* 2009;54(1) 83-88.
- [15] Abd-El-Gaber AM, Khamis E, Hefnawy A. Utilizing Arghel Extract as Corrosion Inhibitor for Reinforced Steel in Concrete. *Materials and Corrosion* 2011;62 1159.
- [16] Abd-El-Gaber AM, Abd-El-Naby AM, Sidahmed IM, El-Zayady IM, Saadawy M. Effect of Some Natural Extracts on the Corrosion of Zinc in 0.5 M NaCl. *Corrosion science* 2006;48(9) 2765-2779.
- [17] Abd-El-Naby AM, Abdullatef OA, Abd-El-Gaber AM, Shaker MA, Ismail G. Effect of some natural extracts on corrosion of Zinc in 0.5M NaCl. *Int. J. Electrochem. Sci.* 2012;7 5864-5879.

- [18] Lampart-Szczapa E, Korczak J, Nogala-Kalucka M, Zawirska-Wojtasiak R. Antioxidant properties of lupin seed products. *Food Chem* 2003;83 279-285.
- [19] Jaen JA, Garcia de Saldana E, Hernandez C. Characterisation of reaction products of iron and aqueous plant extracts. *Hyperfine Interact* 1999;122 139-145.
- [20] El Bribri A, Tabyaoui M, Tabyaoui B, El Attari H, Bentiss F. The use of *Euphorbia falcata* extract as eco-friendly corrosion inhibitor of carbon steel in hydrochloric acid solution. *Materials Chemistry and Physics*, in press (2013).
- [21] Kliskic M, Radosevic J, Gudic S. Aqueous extract of *Rosmarinus officinalis* L. as inhibitor of Al-Mg alloy corrosion in chloride solution. *Journal of applied electrochemistry* 2000;30(7) 823-830.
- [22] Gunasekaran G, Chauhan LR. Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium. *Electrochimica acta* 2004;49(25) 4387-4395;
- [23] El Bribri A, Tabyaoui M, Tabyaoui B, El Attari H, Bentiss F. The use of *Euphorbia falcata* extract as eco-friendly corrosion inhibitor of carbon steel in hydrochloric acid solution. *Materials Chemistry and Physics*, in press (2013).
- [24] Emeka E. Oguzie. Corrosion Inhibitive Effect and Adsorption Behaviour of *Hibiscus Sabdariffa* Extract on Mild Steel in Acidic Media, *Portugaliae Electrochimica Acta* 2008;26 303-314.
- [25] Obot IB, Umoren SA, Obi-Egbedi NO. Corrosion inhibition and adsorption behaviour for aluminium by extract of *Aningeria robusta* in HCl solution: Synergistic effect of iodide ions. *J. Mater. Environ. Sci.* 2011;2(1) 60-71.
- [26] Nnanna LA, Onwuagba BN, Mejeha IM, Okeoma KB. Inhibition effects of some plant extracts on the acid corrosion of aluminium alloy. *African Journal of Pure and Applied Chemistry* 2010;4(1) 011-016;
- [27] Vinod Kumar KP, Sankara Narayana Pillai M, Rexin Thusnavis G. Seed Extract of *Psidium guajava* as Ecofriendly Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Medium. *Journal of Materials Science & Technology* 2011;27(12) 1143-1149.
- [28] Obi-Egbedi NO, Obot IB, Umoren SA. *Spondias mombin* L. as a green corrosion inhibitor for aluminium in sulphuric acid: Correlation between inhibitive effect and electronic properties of extracts major constituents using density functional theory. *Arabian Journal of Chemistry* 2012;5(3) 361-373.
- [29] Olusegun K. Abiola, Otaigbe JOE. The effects of *Phyllanthus amarus* extract on corrosion and kinetics of corrosion process of aluminum in alkaline solution. *Corrosion Science* 2009;51(11) 2790-2793;
- [30] Guimet PS, Gomez de Saravia SG. Natural Products Isolated From Plants Used In Biodeterioration Control. *Pharmacologyonline* 2006;3 537-544.

- [31] Oguzie EE, Ogukwe CE, Ogbulie JN, Nwanebu FC, Adindu CB, Udeze IO, Oguzie KL, Eze FC. Broad spectrum corrosion inhibition: Corrosion and microbial (SRB) growth inhibiting effects. *Electrochem. Sci.* 2012;7 8543–8559.
- [32] Lakshmi Priya, S.; Chitra, A.; Rajendran, S.; Anuradha, K. Corrosion behaviour of aluminium in rain water containing garlic extract. *Surface Engineering* 2005;21(3) 229-231.
- [33] Sangeetha M, Rajendran S, Sathiyabama J, Prabhakar P. Asafoetida Extract (ASF) as green Corrosion Inhibitor for Mild Steel in Sea Water. *International Research Journal of Environment Sciences* 2012;1(5) 14-21.
- [34] Gopal Ji, Sudhish Kumar Shukla, Priyanka Dwivedi, Shanthi Sundaram, Eno E. Ebenso, Rajiv Prakash. Green Capsicum annum Fruit Extract for Inhibition of Mild Steel Corrosion in Hydrochloric acid solution *Int. J. Electrochem. Sci.* 2012; 7: 12146 – 12158.
- [35] Ambrish Singh, Eno. E. Ebenso, M. A. Quraishi. Theoretical and Electrochemical Studies of Cuminum Cyminum (Jeera) extract as Green Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution. *Int. J. Electrochem. Sci.* 2012;7 8543–8559.
- [36] Ostovari A, Hoseinnieh SM, Piekari M, Shadizadeh SR, Hashemi SJ. Corrosion inhibition of mild steel in 1M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawson, Gallic acid,  $\alpha$ -D-Glucose and Tannic acid). *Corrosion Science* 2009;51(9) 1935–1949.
- [37] Borges A, Ferreira C, Saavedra MJ, Simoes M. Antimicrobial activity of ferulic and gallic acids against pathogenic bacteria. *Microb Drug Resist* 2013;19(4):256-65. doi: 10.1089/mdr.2012.0244. Epub 2013 Mar 12.
- [38] Pirvu L, Nichita C, Giurginca M, Meghea A. Structure - antioxidant activity relationship between some of the most commonly vegetal polyphenols compounds. *Chemistry Magazine* 2007;58(9) 914-917.
- [39] Meghea A, Iftimie N, Giurginca M, Papadopoulos K. Oxidative stress quantifying in biosystems. I. Chemiluminescence testing of the antioxidant activity of some molecules of biological interest. *Chemistry magazine* 2003;54(11) 885-887.
- [40] Tim Cushnie TP, Andrew J. Lamb. Antimicrobial activity of flavonoids (Review). *International Journal of Antimicrobial Agents* 2005;26 343–356.
- [41] Rahmanullah Siddiqi, Shahina Naz, Samia Ahmad, Syed Asad Sayeed. Antimicrobial activity of the polyphenolic fraction derived from *Grewia asiatica*, *Eugenia jambolana* and *Carissa carandas*. *International Journal of Food Science & Technology* 2011;46(2) 250-256.
- [42] Fattouch S, Caboni P, Coroneo V, Tuberoso CI, Angioni A, Dessi S, Marzouki N, Cabras P. Antimicrobial activity of Tunisian quince (*Cydonia oblonga* Miller) pulp and peel polyphenolic extracts. *J Agric Food Chem.* 2007;55(3): 963-9.

- [43] Rahmanullah Siddiqi, Shahina Naz, Samia Ahmad, Syed Asad Sayeed. Antimicrobial activity of the polyphenolic fractions derived from *Grewia asiatica*, *Eugenia jambolana* and *Carissa carandas*. *International Journal of Food Science & Technology* 2011;46(2) 250-256.
- [44] Fattouch S, Caboni P, Coroneo V, Tuberoso CI, Angioni A, Dessi S, Marzouki N, Cabras P. Antimicrobial activity of Tunisian quince (*Cydonia oblonga* Miller) pulp and peel polyphenolic extracts. *J Agric Food Chem*. 2007;55(3): 963-9.
- [45] Saavedra MJ, Borges A, Dias C, Aires A, Bennet RT, Rosa ES, Simoes M. Antimicrobial activity of phenolics and glucosinolate hydrolysis products and their synergy with streptomycin against pathogenic bacteria. *Med Chem*. 2010;6(3): 174-83.
- [46] Sivakumar PM, Prabhawathi V, Mukesh Doble. 2-Methoxy-2',4'-dichloro chalcone as an antimicrofoulant against marine bacterial biofilm. *Colloids Surf B Biointerfaces* 2010;81(2): 439-46.
- [47] Sebastian Jäger, Holger Trojan, Thomas Kopp, Melanie N. Laszczyk, Armin Scheffler. Pentacyclic Triterpene Distribution in Various Plants – Rich Sources for a New Group of Multi-Potent Plant Extracts. *Molecules* 2009;14, 2016-2031.
- [48] van Baren C, Anao I, Leo Di Lira P, Debenedetti S, Houghton P, Croft S, Martino V. Triterpenic acids and flavonoids from *Satureja parvifolia*. Evaluation of their antiprotozoal activity. *Z. Naturforsch C*. 2006;61(3-4): 189-92.
- [49] Domingues R. M. A., Patinha D. J. S., Sousa G. D. A., Villaverde J. J., Silva C. M., Freire C. S. R., Silvestre A. J. D., Pascoal Neto C. Eucalyptus biomass residue from agro-forest and pulping industries as sources of high-value triterpenic compounds. *Cellulose chemistry and Technology* 2011;45(7-8) 475-48.
- [50] Dimitrios Boskou. Health Properties of olive oil minor constituents. <http://www.soci.org/News/~media/Files/Conference%20Downloads/OFI%20Abu%20Dhabi%20Apr%2008/Boskou.ashx> (accessed 21 June 2013).
- [51] Allouche Y, Jimenez A, Uceda M, Aguilera MP, Gaforio JJ, Beltran G. Triterpenic content and chemometric analysis of virgin olive oils from forty olive cultivars. *J Agric Food Chem* 2009;57(9): 3604-10.
- [52] Pirvu L, Armatu A, Bubueanu C, Pintilie G, Nita S. Obtaining and chemical characterization of some vegetal extracts with corrosion-scaling inhibition properties. Part I. *Fagus sylvatica* and *Alii cepae bulbus* extracts. *Romanian Biotechnological Letters* 2010;15(6) 5683-5689.
- [53] Pirvu L, Barbulescu D, Nichita C, Nita S, Colceru-Mihul S. Obtaining and chemical characterization of some vegetal extracts with corrosion-scaling inhibition properties. Part II. *Juglandis folium* and *Agrimoniae herba* extracts. *Romanian Biotechnological Letters* 2011;6(1) 5937-5943.
- [54] Romanian Pharmacopoeia, Xth edn., Bucharest: Medicala; 1993.

- [55] Cojocaru A, Maior I, Vaireanu DI, Lingvay C, Lingvay I, Caprarescu S, Badea GE. Ethanol extract of *Fagus sylvatica* leaves as an eco-friendly inhibitor for carbon steel corrosion in acidic solution. *Journal of Sustainable Energy* 2010;1(3) 64.
- [56] Lingvay I, Pirvu L, Vaireanu DI, Lingvay C, Nita S, Cojocaru A, Colceru-Mihul S, Maior I. Simultaneously corrosion and scale formation controlling ecological inhibitor and the obtaining technology. Patent application no A/00900/13.09(2011).
- [57] Romussi G, Bignardi G. *Fagus sylvatica* L. Terpenoids. *Arch. Pharm* 1987;320(20) 153-8.

