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Natural Plant extracts as Corrosion Inhibitors: Thermodynamic's restrictions

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Abstract: The flow of publication of articles on the use of natural plants extracts (NPEs) as corrosion inhibitors is very important in recent years; view the diversity of natural plants in each country. A mapping of the large number of papers on NPEs is added using Scopus from 1993 to 2023 to show both most active authors in this topic. Corrosion inhibition is described by the adsorption of inhibitor's molecules/ions on the metal surface to the metal to create a barrier against the arrival of aggressive ions as H^+ or dissolved oxygen to cause degradation of the metal. The calculation of equilibrium constant, K_{ads}, and free enthalpy, ΔG°_{ads} is possible and correct when one compound is used with known molecular weight, but when two or more compounds are used, the process is regarded as a synergistic intermolecular action.

Keywords: *Natural plants; Corrosion; Inhibition; Adsorption; free enthalpy; Bibliometry*

1. Introduction

The wide-existing literature offers the large variety of natural plant extracts (NPEs) used by humankind since the beginning of life. Fruits, leaves, barks, peels, flowers, roots, seeds, and even whole plant extracts, were necessary to serve food and medicinal treatments. We can speak about the big data gathered and transmitted gradually and from generation to generation to keep safe, healthy and life (Abboud *et al*. (2009); Afia *et al.* (2014); Agidew (2022); Alshameri & Owais, (2022); Habeeb Rahuman *et al.* (2022); Lansky and Newman, (2007)).

The history of NPEs is marked by the well-known Silk-Spices Road connecting China to the Europe and African continents via the Middle East over 4,000 years ago (Loewe (1971); Hammouti et al. (2019); Mishra (2020)). In other words, ensuring the safety, quality and effectiveness of medicinal plants and herbal drugs very recently became a crucial issue in industrialized and developing countries. Associated with historical knowledge, advanced investigations play an essential role in the discovery and exploitation of natural "phytochemical" compounds obtained from NPEs (Ekor, (2014); Rodrigues & Barnes, (2013); Salhi *et al.* (2018)). Survey Literature reported that phytochemical contents of extracts of plant parts, such as flowers, fruits, seeds, roots, peels, and bark, are flavonoids, saponins, alkaloids,

tannins, organic acid, and anthraquinones … (Agidew (2022); Mujeeb *et al.* (2014); Mansoori *et al.* (2020); Hammouti *et al.* (1995)). Most of such phytochemicals have polar functional groups like amide (—$CONH_2$), hydroxyl (—OH), ester (—$COOC_2H_5$), carboxylic acid (—COOH), and amino (—NH_2) that assist in their adsorption (Wei *et al.* (2022); Goyal *et al.* (2018); Chen *et* al. (2022)). The bioactive phytochemical components, medicinal values, therapeutic potential and nutritional properties of NPEs have been extensively studied (Batiha *et al.* (2020); Salhi *et al.* (2018); El Hamdani *et al.* (2018)).

It's well known that natural products are also a good source of green corrosion inhibitors, since their extracts contain the heteroatoms such as O, C, N, and S, as well as cyclic compounds, which are considered the active centers of the adsorption process in corrosion inhibition (Desai *et al.* (2022); Miralrio *et al.* (2020); Bammou *et al.* (2018)).

The scientific production can be also exposed using the bibliometric approach and considered the period (Lrhoul *et al.* (2023); Saputra *et al*. (2022); Hammouti (2010)). Bibliometrics is considered as a tool for mapping the state of the art in a given discipline (Sengupta, (2009)). As pointed out by Waaijer and Palmblad (2015), the first bibliometric maps were manually constructed citation networks by Saputra *et al*. (1964). They studied a book on the history of genetics and compared the dependencies between different studies as described by the author to the citational patterns between the studies, and found that the two methods closely mirror each other. Hence, citation networks are able to show structures in knowledge flows (Waaijer and Palmblad M. (2015)). Scientist published cartography maps to show the importance and the most published authors in each field through the analysis of keywords and the number of citations (Lrhoul *et al.* (2023); El Mohadab *et al.* (2020)). In recent work, an overview of scientific production worldwide and in Africa, based on the SCImago ranking of institutions presents insight about the leaders both in publication and indexed journals. China improves the best country in the World since the year 2020 and Morocco achieves significant improvements in its scientific output, ranking fourth in Africa (Hammouti *et al.* (2023)).

Our contribution in this Handbook is to attract the attention of researchers to the growth exponentially of scientific production of the use of NPEs in corrosion protection as well as the ambiguity committed during the determination of the thermodynamic parameters of adsorption, especially the equilibrium constant as well as the free enthalpy, ΔG°_{ads}. If we can not evaluate ΔG°_{ads} for the study of a synergistic effect of two compounds as organic compounds and halogen ions (I^- is the most studied) (El Katori et al. (2020); Wu *et al.* (2022); Solomon *et al.* (2018)), how can we therefore estimate thermodynamic parameters in the presence of infinite compounds at different contents.

2. Mapping of scientific publications in the domain of corrosion

To have a general landscape of publications in the domain of Adsorption, inhibition and corrosion, we collected a set of Scopus papers from 1993 to 2023. A total number of 1032 paper was retrieved from Scopus database with their meta data like publication title, publication data, authors, index keywords, etc. Our goal is to understand most active authors in the domain and domains that interest majority of authors. We conducted our analysis using Gephi, a mapping tool. As showed in figure 1 and figure 2, we only kept nodes (authors and keywords) with an occurrence count greater than or equal to 20 to gain in clarity and reveal most dominant nodes. According to the resulted cartography (figures 1 & 2) we notice that most active authors (nodes in green) are those with bigger size like: Quraishi (India), Ramezanzadeh (Iran), Hammouti (Morocco), Bahlakeh (Iran), etc. We notice also, with the same analysis (nodes in yellow), that authors are more interested in domains such as: absorption, corrosion, inhibition efficiency, polarization, corrosion inhibitors, etc. Figure 3 exposes a more detailed cartography of most active keywords in the domain.

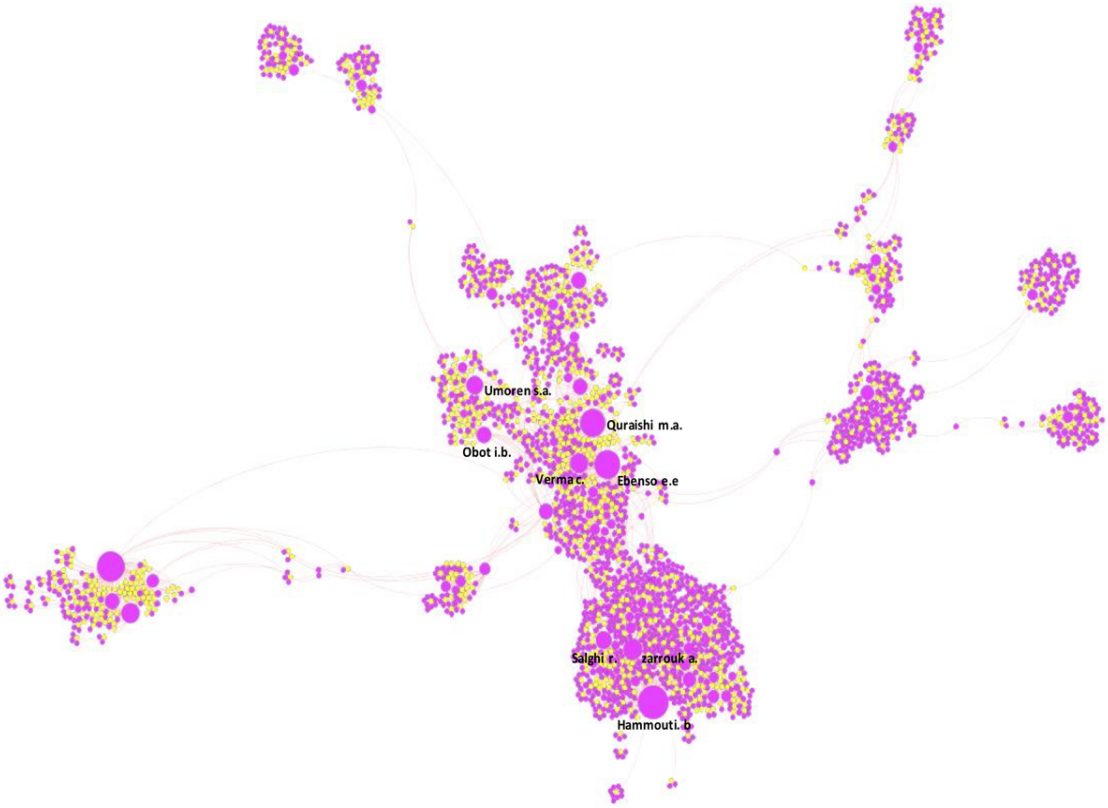


Figure 1 Most productive researchers in the domain of corrosion

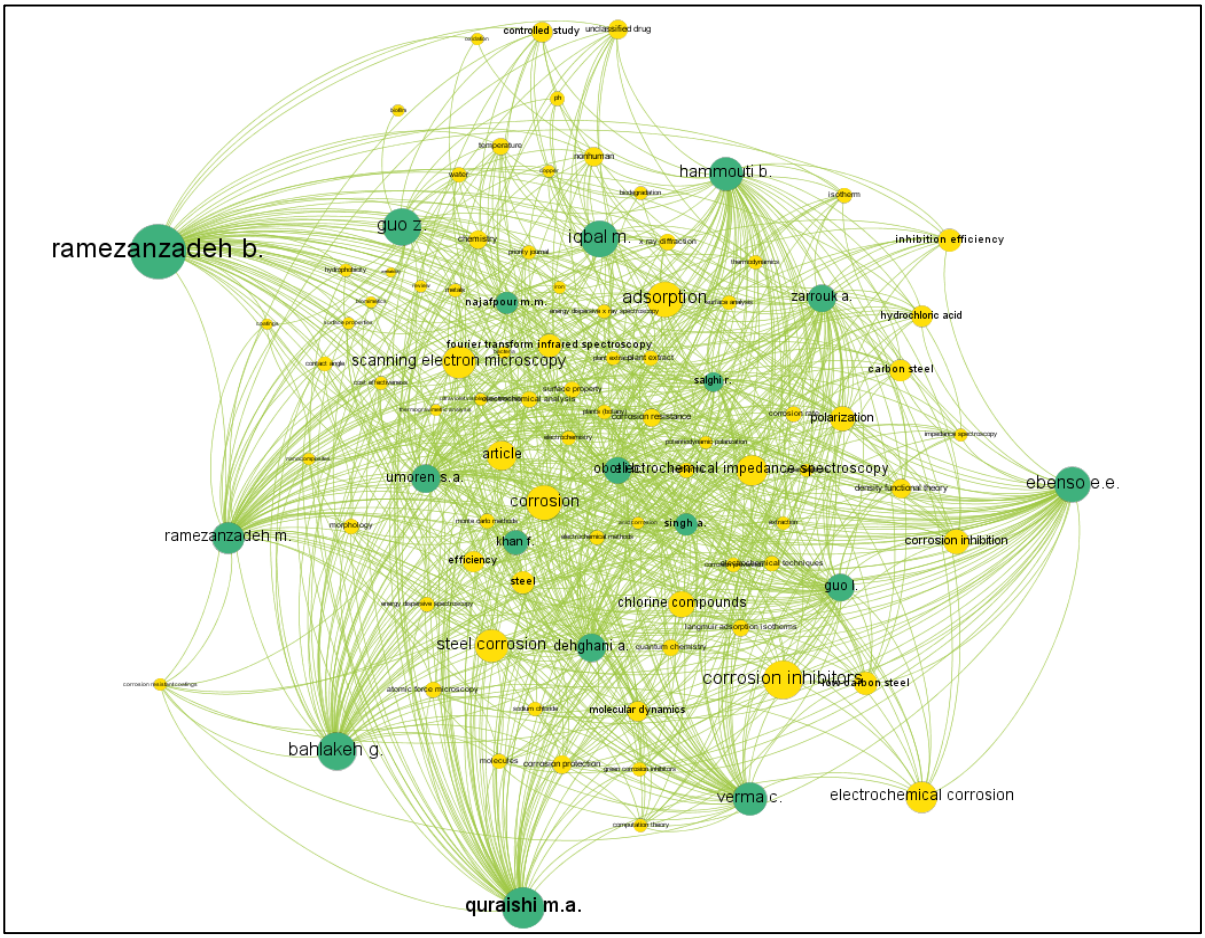


Figure 2a: Cartography of the most active authors in the domain

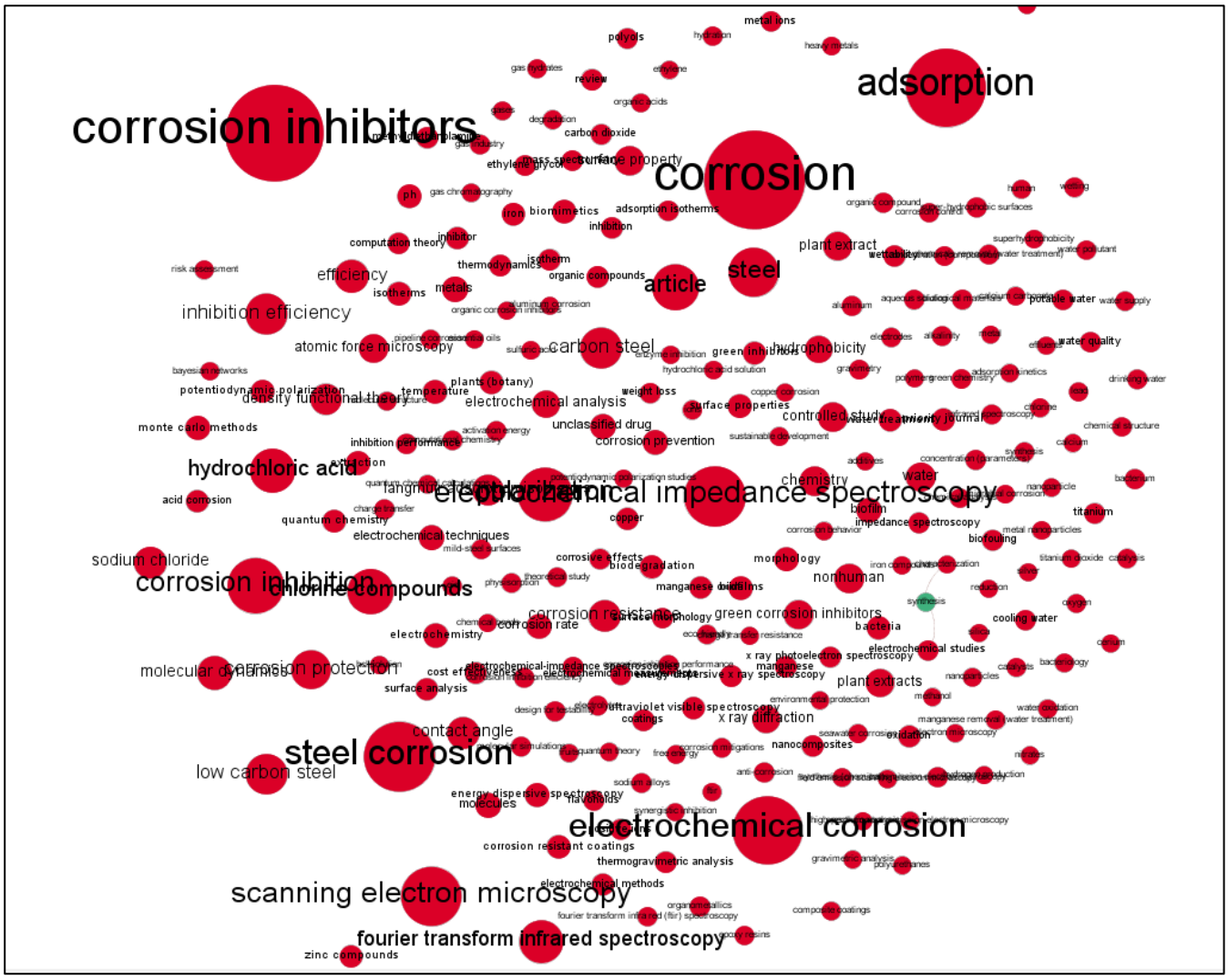


Figure 3: Cartography of most dominant keywords in the domain

3. Adsorption

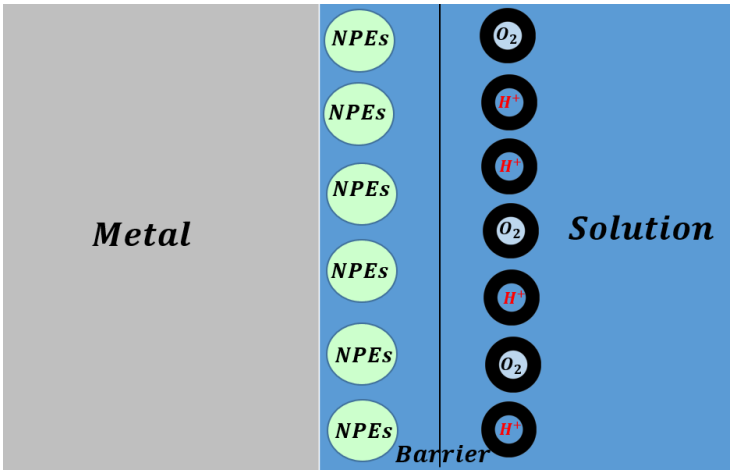
3.1. Adsorption isotherm and parameters

The organic inhibitors function through adsorption on metal surfaces blocking the active sites by displacing water molecules and forming a compact barrier film to decrease or stop the corrosion rate according to the Bockris model (Bockris and Reddy (2000)):

$$inh_{sol} + nH_2O_{ads} \rightarrow inh_{ads} + nH_2O_{sol}$$

The abbreviations in subscript sol and ads indicated the state of compounds in solution or adsorbed.

The adsorption of inhibitor onto the steel could be through physisorption and/or chemisorption mechanism whereby the redox electrochemical process responsible for corrosion and the electrolytic transport of corrosive species are simultaneously suppressed (**Scheme 1**). The adsorption of inhibitors on the metal/solution interface is influenced by: (i) the nature and surface charge of metal; (ii) the type of aggressive electrolyte; and (iii) the chemical structure of inhibitors (Al-Amiery *et al.* (2018); Zaidi *et al.* (2023)). The adsorption isotherm model that best describes the adsorption phenomena are obtained by fitting the concentration, C and the degree of surface coverage of the inhibitor, θ (i.e. the reciprocal of inhibition efficiency) into the various adsorption isotherms models (Langmuir, Temkin, Freundlich, Frumkin, El Awady, and Flory Huggins adsorption isotherm) expressed in linear form as:



Scheme 1 : Schematic presentation of the adsorption process of natural plant extracts

The Langmuir adsorption isotherm model (Langmuir, (1918)):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

Frumkin adsorption isotherm model (Frumkin (1925)):

$$\log\left[C(\frac{1}{1-\theta})\right] = 2\alpha\theta + 2.303\log K_{ads}$$

El-Awady's thermodynamic/kinetic adsorption isotherm model (El-Awady (1992);):

$$\log\ (\frac{1}{1-\theta}) = y\log C + \log K \text{ with } K_{ads} = K^{1/y}$$

Temkin adsorption isotherm model (Temkin & Pyzhev (1940)):

$$\theta = \log C + \log K_{ads}$$

Freundlich adsorption isotherm (Freundlich (1909)):

$$\log\theta = n\log C + \log K_{ads}$$

Flory-Huggins adsorption isotherm (Flory (1941); Huggins (1941)):

$$\log\frac{\theta}{C} = \mathrm{b}\log(1-\theta) + \log K_{ads}$$

The expression for Gibb's free energy change of adsorption, ΔG°_{ads} presented in the following Equation are commonly used to investigate the feasibility and nature of the adsorption:

$$\Delta G^{\circ}_{ads} = -\mathrm{R\ T\ ln}\ (55.5K_{ads})$$

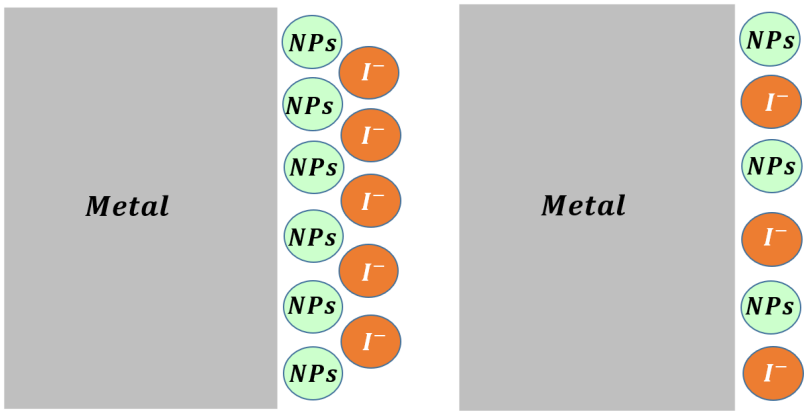
K_{ads} is the adsorption equilibrium constant obtained from the isotherm, and the number 55.5 is the molar concentration of water in the solution.

Contrary to the use of unique component (molecule or ion) with a known molecular weight, the natural extracts (NEs) contain infinite compounds at different percentages from the major compounds to minor ones, without counting the non-identified. The synergistic inhibition effect is evaluated using a

parameter, S_θ, obtained from the surface coverage values (θ) of the anion, organic compound and both. Aramaki and Hackerman (Aramaki et al. (1987)), calculated the synergism parameter S_θ using the following equation:

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} = \frac{1-(\theta_1 + \theta_2) - (\theta_1\,\theta_2)}{1-\theta'_{1+2}}$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\,\theta_2)$; θ_1 = surface coverage by anion; θ_2 = surface coverage by organic compound; θ'1+2 = measured surface coverage by both the anion and organic inhibitor. $S_\theta > 1$ means that the compound system has an obvious synergistic effect. $S_\theta \leq 1$ means that the synergy is not significant or there is an antagonistic effect. The larger the S_θ value, the stronger the synergy between the inhibitors. So, S_θ is defined only for two components acting on the metal surface; then, at our knowledge, there is no relationship to estimate the synergism parameter of more than two inhibitors (Bouklah et al (2006); Kokaji et al. (2023); Mobin et al. (2013)). By the way, the inhibition process is generally regarded as the action of numerous compounds at the metal surface to form a barrier for the arrival of aggressive ions as H^+ or dissolved gases as dissolved oxygen.



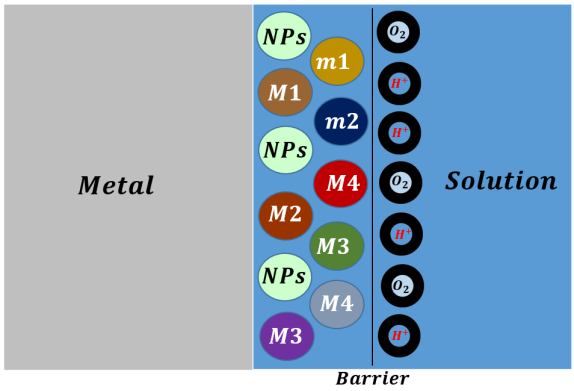
cooperative or competitive corrosion inhibition

Scheme 2 : Schematic presentation of in the absence and presence of synergistic anion (I^-)

In such case, co-adsorption is interpreted by cooperative or competitive at the metal surface to ensure the formation of one or more layers as shown in **Scheme 2**, (Alhaffar et al. (2023); Kartsonakis et al. (2018).

2.2. Adsorption isotherm and limitations

The inhibition process is interpreted by the intermolecular synergistic effect of all components having the ability to interact chemically and/or physically with the metal surface as summarized in **Scheme 3**, (Sharma et al. (2023); Khadom et al. (2022); Benali et al. (2013); Aouniti et al. (2022)). Furthermore, the concentration of NPEs extract is expressed by mg/L, g/L, mL/L …The determined values of ΔG°_{ads} found in the literature are wrong and have no physical meaning in one hand; on the other hand, values are too lower and expressed by mol/L. These errors are accompanied by an explanation as the "extract" acted as physical adsorption based on literature: the electrostatic interaction between the charged metal and the charged inhibitor molecules (physical adsorption) was obtained when ΔG°_{ads} was up to −20 kJ.mol−1, whereas chemical adsorption was obtained when ΔG°_{ads} was around −40 kJ.mol−1 due to the transfer or sharing of electrons from the molecules to the metal surface to form a bond coordinate type (Labriti et al. (2012); Lgaz et al. (2016); Ibeji et al. (2023)).



Scheme 3 : Schematic presentation of the intermolecular synergistic effect of various components of NPEs (*Major and minor compunds*)

In various published papers, the anodic branches present a slight decrease of anodic current densities generally explained by a competitive cathodic reaction resulting by the interaction of metal ions with the molecule of inhibitor leading to the formation metal-inhibitor complex (Figure 4). In natural extracts, the possibility of complex formation is more probable due to the presence of one or several bioactive components (Al-Amiery et al. (2022); Benabdellah et al. (2016); Rodríguez et al. (2020)).

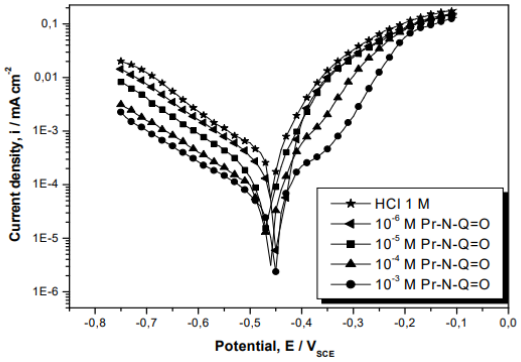


Figure 4 : i-E curves (ability to form complexes with metal surface in anodic domain) ((El-Hajjaji et al (2014))

Conclusion

Through this contribution, we wanted to draw the attention of researchers to be quite vigilant about the determination of adsorption parameters (equilibrium constant, K_{ads}, and free enthalpy, ΔG°_{ads}). To convince the researchers, we took the study of the synergistic effect of two compounds for which the thermodynamic parameters of adsorption could not be determined. When the synergy of several compounds that contribute to the adsorption process, the determination of K_{ads} and ΔG°_{ads} when the adsorption process is ensured by several compounds, the evaluation of these values will no longer have any physical meaning.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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