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Natural Polymers as Green Corrosion Inhibitors in Carbon Steels for Applications in Acid Environment

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Corrosion represents one of the major problems in using materials. As a result, finding ways to control it has become a permanent and complex task for industries, using toxic and dangerous techniques, producing great and serious problems for humanity. Natural polymers have emerged as one of the most promising alternatives for accurately and adequately mitigating corrosion through the use of biodegradable, non-toxic, inexpensive and effective materials. A series of studies on the inhibition efficiency of gums and lignins as natural corrosion inhibitors was compiled and analyzed in this study, focusing on avoiding the environmental impact of traditional corrosion inhibitors in carbon steels for acidic applications. Within the results, inhibition efficiencies were identified in gums from 74% to 97% and lignins from 79.9% to 92%, showing that, in general, the efficiency increases with a higher concentration of the inhibitor, however, when the temperature increases, tends to decrease the efficiency of physical adsorption, unlike chemical adsorption that tends to increase.

1. Introduction

One of the major problems that currently exist and that has been experienced for many years in the use of materials is corrosion (Song et al., 2022). Approximately 80% of pipeline accidents are caused by corrosion, largely due to ferrous metals that are not adequately protected. Equipment deterioration should be minimized to avoid prolonged downtime and unnecessary expenditures (Orozco-Agamez et al., 2022). The corrosion of mild steel in acidic media has been extensively studied in recent years due to its industrial relevance. Acid solutions have been widely used in cleaning, descaling, pickling, and oil well acidizing, requiring the use of corrosion inhibitors to reduce their corrosion attack on metallic structures or materials (Hussin et al., 2016). This problem has generated great concern on the part of research entities and companies around the world, who have developed measures that manage to limit, mitigate, and control this process. Many of the methods used have not been the most appropriate, since their processes do not protect the environment, and even become toxic to humans; this has generated research to focus on finding measures that attack corrosion, and that, in turn, benefit ecology and the economy. In this context, natural polymers currently represent an attractive alternative that adjusts to what is required from sustainable development in the fight against corrosion, due to its easy biodegradation, non-toxicity, reduced cost, availability, molecular structure, and the effect of coverage on the metal surface (Wei et al., 2020).
Corrosion inhibitors are the type of coating that seeks to prevent the corrosion of materials, with the main objective of interrupting the electrochemical process by forming a layer. The inhibitors can be classified according to the chemical composition in organic and inorganic, in the same way, according to the mechanisms of action they can be anodic, cathodic, and mixed, the latter being capable of inhibiting or hindering the anodic and cathodic reactions simultaneously.

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As a result of physisorption or chemisorption, organic-type inhibitors can form a layer on the material surface, which can act as a physical barrier and provide protection (Merchan-Arenas et al., 2018). Generally, natural polymers are macromolecular substances composed of relatively simple structural units with low molecular weight and are found in plants and animals, especially in natural gums and in the lignin extracted from wood (Devi et al., 2020).Gums have as main specifications that they are high molecular weight molecules made up of polymers of monosaccharide units and derivatives, linked by glycosidic bonds, achieving the formation of long chains, specifically locating in the cell walls of plants and microorganisms; while lignin stands out for being a type of natural polymer formed by a diversity of organization of monomers that are deposited in the cell walls of plants, in wood or bark, due to its excellent rigidity (Umoren et al., 2008). The most abundant aromatic natural biopolymer on earth, lignin, is produced primarily as a byproduct of papermaking and biorefineries. In addition, it can be extracted from agricultural wastes (such as bagasse and straws) with low production costs. Lignin is considered a natural polyol since it contains many OH groups. In practice, lignin has been used to fabricate bio-based PU coatings. As a result of the high number of aromatic groups, the coating is highly hydrophobic as well as UV-blocking (Gao et al., 2021). Lignin has significant advantages over phosphates or silicates: i) lignin can adsorb on the steel surface through the interaction of the acid moieties with metal hydroxide film which provides a protective layer against water or oxygen; ii) lignin is an inexpensive, abundant and renewable organic resource; and iii) has no zinc load; it is also compatible with the environment, economical for application, and produces the desired effect when present in small concentrations. Lignins don't contain any components that are considered toxic by any Government agency. Thus, its health rating is zero, which means that exposure offers little or no risk to either plants or humans (Abu-Dalo et al., 2013). There are several studies reporting the inhibition efficiencies of different natural polymers used in specific ways. Nevertheless, there are many doubts surrounding the potential use of natural polymers such as gum and lignin as corrosion inhibitors. This research work mainly aims to respond to the relationship that exists between the variables temperature, concentration, and immersion time with respect to the inhibition efficiency and corrosion rate of different natural polymers used in acid media. These variables mentioned represent critical variables of the processes, and it is imperative to identify the correlation between them. As a result, the main challenges for future research in the area are identified.

1.1 Lignin

This amorphous aromatic biopolymer comes primarily from the dry part of the plant, varying from 15 to 40% by weight (Shahini et al., 2021). It works as a binder to hold the fibers together, making them rigid (Hussin et al., 2015). Its main means of obtaining it is through the production of paper and other processes, leaving this material as a by-product or waste in large quantities. Certain uses have been found for this material such as batteries, ceramics, pharmaceuticals, among others. These macromolecules are among the most abundant renewable resources in nature and their applications have not been exploited to the full due to the complexity and heterogeneity in their structures and their high molecular weight distributions (Gao et al., 2021). It is also the second most abundant biopolymer after cellulose (Shahini et al., 2021). Furthermore, a sufficiently high efficiency as a corrosion inhibitor, preventing the risk of pitting in the tested materials, has been reported (Shahini et al., 2021). This is due to the high and diverse content of functional groups and phenylpropanoid structure, making lignin act as a neutralizer of oxidation processes thanks to reactions by oxygen radicals and their respective species (Hussin et al., 2016).

1.2 Gums

Vegetable gums are ecological, economical, readily available, non-hazardous and renewable (Mobin et al., 2020), have very varied uses such as pharmaceutical materials, food industries and many more, being of special interest when looking for good inhibitors of corrosion, and they are so thanks to their long polymeric structures, with their functional groups (OH, COOH, NH_2, etc) that form complexes with metal ions, covering the surface, and in turn preventing metal corrosion. Natural gums are insoluble in most of the organic solvents including alcohol, ethanol, and hydrocarbons. Oils are also insoluble in them (Kumar et al., 2022). Due to its composition, it contains high levels of oligosaccharides, polysaccharides, glycoproteins, arabinogalactans, and sucrose, as well as nitrogen and oxygen atoms that serve as adsorption centers (Wei et al., 2020). These reasons prove the excellent corrosion inhibitor properties of natural gums:

1. They form complexes (due to their functional groups) with metal ions on the surface of the metal.
2. These complexes comprise a vast surface dimension as large as possible and act as a blanket for the surface and protect the metal to come in contact with corrosive agents.
3. Due to the presence of sucrose, glycoproteins, polysaccharides, arabinogalactan, oligosaccharides all of these consist of compounds of nitrogen as well as oxygen atoms that act as the center of surface assimilation.

4. Numerous gums encompass COOH groups, that further augment the participation of charge transmission and promote inhibitory activity via surface assimilation.

2. Temperature

The temperature is a very important variable because directly affects the efficiency that natural polymers achieve on metal surfaces. When the temperature rises and exceeds the activation energy threshold, the corrosion inhibitor undergoes a desorption process. The type of organic inhibitor is codependent with its adsorption mechanism, varying whether it is physical or chemical.

Lignin occurs as green inhibitors, which generally attribute a greater weight loss to an increase in temperature, which may indicate a lower efficiency of the inhibitor, caused by the desorption of the corrosion inhibitor (Shahini et al., 2021). The type of adsorption matters and is evidenced in the activation energy required for each case, since for a type of chemical adsorption there will generally be a much higher activation or barrier energy, while in a physical adsorption, reaction will be relatively low.

In the research work carried out by (Azzaoui et al., 2017), where the effect of gum Arabic as a corrosion inhibitor in carbon steel in an acid medium was studied, it was possible to demonstrate that at higher temperatures, a highly complex effect on inhibition may occur on the metal surface because etching, rupture, and desorption of inhibitor molecules. In this study, the weight loss measurements were used to investigate the effect of temperature on the corrosion inhibition properties of mild steel in the range of 303–333 K. As the temperature increased, a direct relationship with corrosion rate was found on the contrary, the inhibition efficiency presented a significant decrease from 95 % at 303 K to 83 % at 333 K. The above is at a concentration of 1 g/L of inhibitor and a 1.0 M of HCl solution.

According to (Barrodi et al., 2023), where the effect of Tragacanth Gum in an acidic medium was studied, an increase in temperature weakens the interaction between the inhibitor molecules and the metal surface, justifying the reduction of inhibition efficiency at elevated temperatures. The influence of temperature on the inhibition effect of β-cyclodextrin modified xanthan gum was investigated. When the inhibitor concentration was 200 mg/L at 293 K, the corrosion current density increased and inhibition efficiency reduced to 92.62 %, 90.38 %, and 89.73% at 303 K, 313 K, 323 K, respectively. In general, the effect of temperature rise was manifested in two ways: (1) The corrosion current density was increasing, resulting in a rise in charge transfer resistance, thus accelerating corrosion. (2) Elevated temperature might cause the inhibitor to be removed from the surface of X80 steel, reducing its corrosion inhibitory effect (Cao et al., 2021)

Likewise, in a study where almond gum was evaluated, which presented a mixed type of adsorption, in which the temperature increased the inhibition percentage, reaching 85.5 % at 30 °C up to 96.37 % at 60 ºC (Mobin et al., 2020). For some cases of chemical or mixed adsorption, there is a slight increase in the adsorption capacity and therefore in the inhibition efficiency as the temperature increases, until the activation energy limit is reached.

3. Concentration

At the concentration of 150 mg/L, the corrosion inhibition efficiency of Lignin-Acyclic Acid was 82.16 % and the corrosion inhibition efficiency of Lignin-acrylamide was 51.2 %. The electrochemical results showed that as the concentration of corrosion inhibitor increased, the charge control resistance increased, and the corrosion process was controlled by the charge-transfer mechanism. From the SEM and AFM images, less significant corrosion of the steel surface was observed when lignin derivatives (specially lignin-Acyclic Acid) were used (Gao et al., 2021).

For the other hand, in a study carried out on the natural polymer polyethylene glycol in an acid medium, it was determined that as the concentration of said polymer increased, the inhibition percentage tended to increase, evidencing a directly proportional relationship. Likewise, for RaphiaHookeri gum, the inhibition efficacy increased when the concentration of said polymer increased (Arthur et al., 2013).

Based on the study by (Barrodi et al., 2023) on the synergy between Tragacanth Gum and Ceftriaxone as an environmentally friendly corrosion inhibitor for mild steel in HCl 1M solution, the increase in the inhibitor concentration resulted in an increase in the charge transfer resistance due to the adsorption of inhibitor molecules and the formation of protective layers on steel surfaces, blocking the active sites of the surface. The smoothness or homogeneity of the surface, also increases with increasing the inhibitors concentrations, implying that the inhibitors form a more homogeneous protective layer on the steel surface at higher concentrations. Likewise, by increasing inhibitor concentrations in corrosive solutions, corrosion current density is reduced and inhibition efficiency increases. Accordingly, it is speculated that the inhibitor molecules form a protective layer on the steel surface, presenting a barrier between the corrosion-prone surface and the corrosive environment (Barrodi et al., 2023).

The study "Floxacins: as Mediators in Enhancing the Corrosion Inhibition Efficiency of Natural Polymer Dextrin" shows the relationship between the concentration and the variables inhibition efficiency and corrosion rate, taking the natural polymer Dextrin as a case study. The different electrochemical measurements show how the concentration and the type of the polymer structure help to improve or deficient the percentage of inhibition. Figure 1 shows the behaviour of the concentration vs the percentage of inhibition efficiency (%IE), as well as the concentration vs corrosion rate (CR). It is observed that as the concentration of said polymer increases, the inhibition efficiency grows proportionally, as well as a decrease in the corrosion rate (Devi et al., 2020).

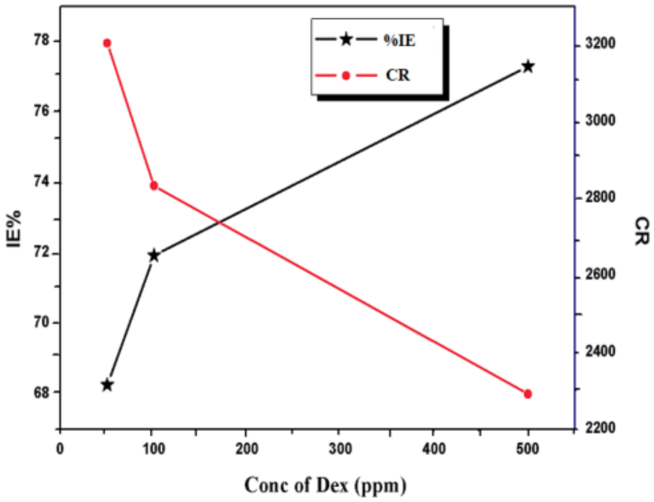

Figure 1. Dextrin behavior with respect to concentration, inhibition efficiency percentage and corrosion rate (Devi et al., 2020).

According to (Barrodi et al., 2023), where the effect of Tragacanth Gum in an acidic medium was studied, with the increase of inhibitor concentration, the corrosion inhibition efficiency improved. At the metal/solution interface, corrosion inhibitor molecules might have replaced H_2O molecules, forming a dense barrier film. The formation of the barrier film obstructed the charge transfer process, resulting in effectively preventing the corrosion of the carbon steel. This could be attributed to two aspects: (1) Since the dielectric constant of inhibitor molecules were smaller than that of H_2O molecules, the local dielectric constant was reduced in the presence of the corrosion inhibitor, (2) Due to that the volume of inhibitor molecules was much larger than that of H2O molecules, the thickness of the electric double layer capacitance was increased (Cao et al., 2021).

4. Immersion time

The immersion time is a fundamental variable for an adequate selection of the inhibitor to achieve high inhibition efficiencies, which, like the concentration of the polymer, or the temperature become critical variables. In a study carried out on the inhibition efficiency of moringa gum in an acid medium, it was possible to establish that as the immersion time increases, the inhibition efficiency increases, although this happens until 6 hours reaching an inhibition efficiency of 95.46% at 10 mg/L, however, decreases an immersion time of 8 hours, where at this same concentration value the inhibition efficiency decreases to 65.60%. This occurs because the natural polymer biodegrades, thus affecting the inhibition efficiency (Jalajaa et al., 2019). In table 1, CR is the corrosion rate and %IE represents the percentage of inhibition efficiency.

The immersion time is an important variable that is directly related to the inhibition efficiency and the morphology of the materials. When immersion time is increased, gums and lignins exhibit a higher inhibitory efficiency, but a limit can be reached. Since natural polymers can undergo biodegradation over long periods of time, which would affect inhibition properties, controlling the times in which they are used becomes essential.

Table 1: concentration vs time immersion. Adapted from (Jalajaa et al., 2019).

Concentration	1 hour		2 hours		4 hours		6 hours		8 hours	
Goma Moringa (g/L)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
2	0.01668	63.33	0.02199	63.46	0.01621	66.27	0.02066	75.61	0.03878	29.48
4	0.01596	64.89	0.02000	66.77	0.01362	71.65	0.00670	92.10	0.03100	43.62
6	0.01251	72.50	0.01200	80.06	0.00931	80.63	0.00518	93.89	0.02280	58.53
8	0.01195	73.75	0.00749	87.56	0.00554	88.46	0.00489	94.24	0.01858	66.21
10	0.00906	80.08	0.00711	88.35	0.00536	88.86	0.00386	95.46	0.01891	65.60

5. Conclusions

Considering the variables of temperature, concentration, and immersion time in relation to corrosion rate and inhibition efficiency in carbon steels for applications in acid environments, natural polymers such as gums and lignins were evaluated. Temperature is a critical variable when using natural inhibitors such as lignin and gums, from the review study carried out it is possible to conclude that temperature has an adverse effect on the inhibition efficiency, mainly since it generates desorption of inhibitor on the surface. Among the main challenges to achieving greater applicability of natural inhibitors such as gums and lignins in industrial processes, it is necessary that these can be used at high temperatures, therefore, this topic currently represents a study challenge very important.

In general terms, the increase in the concentration of the inhibitors has a direct effect on the inhibition efficiency, thus reducing the corrosion rate of carbon steels in acidic media. In this context, lignin copolymers have currently been developed, as well as the application of natural gums with drugs, achieving in both cases better inhibition efficiencies than when the current natural polymers independently.

Finally, the immersion time variable also represents a critical variable to achieve greater interest in the large-scale use of natural polymers such as lignin and gums in industrial processes. The challenge is focused on achieving inhibition efficiencies greater than 90% for long immersion times.

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