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Green Corrosion Inhibitors for Magnesium and Its Alloys: A Comprehensive Review of Recent Studies

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Abstract. *This paper summarizes the recent advancements in environmentally friendly corrosion inhibitors for magnesium and related alloys. Magnesium and its alloys have a number of desirable factors that make them useful in a variety of industries. However, their extensive range of uses is restricted by their corrosivity. corrosion problems that exist with magnesium is a recent increase in interest in the usage of ecologically friendly corrosion protection. The paper discusses several green corrosion inhibitors, both natural and manufactured, as well as their mode of action and corrosion prevention efficacy. The review goes over the variables influencing the effectiveness of green inhibitors as well as the future course of this area of study. Additionally, the paper presents a critical analysis of the current research gaps and provides recommendations for future research. The findings of this review emphasize the potential of green corrosion inhibitors as an effective and sustainable solution for corrosion prevention in magnesium and its alloys. The study concludes that the use of green inhibitors can significantly reduce the environmental impact of corrosion prevention practices and enhance the sustainability of the industrial sector.*

Keywords: *Corrosion, Green Inhibitors, Magnesium, Sustainability*

1. INTRODUCTION

The mechanical properties of Magnesium make it a popular material in the aerospace and automotive industries, as well as in other applications that require lightweight and strong materials. The main disadvantage of magnesium is its susceptibility to corrosion, which limits its use in various applications. Corrosion can cause structural failure, reduce mechanical properties, and degrade the appearance of the metal surface. Therefore, corrosion protection is crucial for the effective use of magnesium and its alloys in various industrial sectors.

Green corrosion inhibitors are particularly useful in industries where toxic and non-sustainable inhibitors are commonly used. For example, the oil and gas industry, where corrosion is a significant issue due to the harsh environments that equipment and pipelines are exposed to, is now turning to green inhibitors as a more sustainable solution. These natural products have been shown to exhibit excellent inhibition efficiency, low toxicity, and biodegradability, making them an attractive alternative to traditional inhibitors. Green corrosion inhibitors can act by various mechanisms, such as adsorption, film formation, and redox reactions. Green inhibitors are a type of corrosion inhibitor that is environmentally friendly and non-toxic. Adsorption is the most common mode of action for green inhibitors. A protective coating that prevents corrosive substances from accessing a metal surface is formed when a green inhibitor is put to it. A number of variables, including the inhibitor concentration, pH, temperature, and the presence of other organisms in the corrosive environment also affect the binding of inhibitors to surfaces.

Many studies have demonstrated the potential of using biopolymers and organic components such as magnesium and similar alloy corrosion inhibitors that are also favorable to the environment. Plant extracts and essential oils have been shown to exhibit excellent inhibition efficiency due to the presence of various bioactive compounds such as phenols, flavonoids, and alkaloids. It seems that Lippia sidoides essential oil has shown promising results as a potential inhibitor for the corrosion of Mg alloy AZ31 in a 3.51% NaCl solution. The study suggests that at a concentration of 0.51% (v/v), the essential oil was able to exhibit a 95.51% inhibition efficiency, which is quite high. In a similar fashion, it has been proven that Acacia nilotica leaves and seeds may effectively prevent corrosion of the Mg alloy AZ31 in a 3.51% NaCl solution. Biopolymers like chitosan, cellulose, and alginate have also demonstrated potential as environmentally friendly inhibitors of corrosion for magnesium and related alloys. These biopolymers can act as strong inhibitors due to their capacity to produce a shielding coating on the metal surface. For example, it has been shown that chitosan can form a protection layers on the surface of the magnesium alloy AZ91D, reducing corrosion by up to 80%. The magnesium alloy AZ31's corrosion rate has been found to be reduced by up to 72.1% by cellulose nanocrystals (CNCs), which act as a barrier on its surface. Notwithstanding their superior inhibitory efficacy versus traditional inhibitors, green corrosion inhibitors offer a variety of other advantages. Green inhibitors are renewable, biodegradable, and non-toxic, making them environmentally friendly and sustainable. By keeping the mechanical qualities of magnesium and its alloys, the application of green inhibitors can greatly lessen the corrosion inhibition process's negative environmental effects.

In recent times, the application of green corrosion inhibitors has grown in favor of a practical substitute for conventional corrosion inhibitors for magnesium and its alloys. Natural products like plant extracts and essential oils, as well as biopolymers such as chitosan and cellulose, have shown excellent inhibition efficiency and low toxicity, making them an attractive alternative to traditional inhibitors. The growth of green inhibitors can significantly reduce the environmental impact of the corrosion inhibition process.

2. GREEN CORROSION INHIBITORS FOR MAGNESIUM AND ITS ALLOY

Chitosan, hydroxylethyl cellulose, dextran, carboxymethyl cellulose, sodium alginate, pectin, and Gum Arabic were some of the seven natural polymers that Umoren et al. (2020) looked into for their potential as environmentally friendly corrosion inhibitors for AZ31 Mg alloy in saline environments. The mild corrosion inhibition of ALG and HEC, compared to the moderate corrosion acceleration of CHI, Dex, CMC, PEC, and GA, was found for the seven natural polymers. The alloy was covered by 64.13% and 58.27%, correspondingly, of HEC and ALG at a concentration of 1 g/L. As well, the investigators created two inhibitor cocktail formulas: one with HEC and the other with ALG, KI, and Date Palm Seed Oil. By 80.56% and 77.43%, correspondingly, the HEC- and ALG formulations demonstrated greater corrosion inhibition. The surface observation investigations validated the formulations' efficacious ability to control corrosion. Outcomes from FTIR, UV-vis, and X-ray photoelectron spectroscopy showed that adsorbed inhibitor complexes coexisted with Mg(OH)2.

Li et al (2022) had taken aminopropyltriethoxysilane, sodium benzoate, and 8-hydroxyquinoline, and intercalated them with three layers of double hydroxide coverings on aluminum. That used a variety of electrochemical methods, the coverings' corrosion resistance was assessed after being put on a magnesium alloy substrate. According to his findings, the Mg: Al LDH coatings with the corrosion inhibitors intercalated have higher corrosion resistance than the pure Mg alloy. This shows that the resistance to corrosion of the Mg: Al LDH coating has been effectively increased by the in-situ hydrothermal method employed to intercalate the corrosion inhibitors. Corrosion inhibitors' mechanisms for preventing corrosion were described, and the one that performed the best was chosen. Traditional Chinese medicine extracts were looked into by Li et al. (2022) as potential new corrosion inhibitors for the saline environment for the AZ91 magnesium alloy. The research looked into the potential of seven extracts from traditional Chinese medicine, including Rheum palmatum extract,Taraxacum officinale extract (TOE), Rheum palmatum extract, Glycyrrhiza uralensis extract (GUE), Potentilla discolor extract (PDE), Raphanus sativus L. extract, Zingiber officinale Roscoe extract. The results showed that the effects of GUE, PDE, and TOE significantly improved the corrosion resistance of the AZ91 alloy by 73.41%, 87.61%, and 84.61%, correspondingly. By engaging with the alloy surface during surface treatments utilizing “FTIR, UV-Vis, and XPS, the organic substances of GUE, PDE, and TOE” created a protective physisorbed coating that significantly delayed the corrosion rate of AZ91 alloy.

In their investigation, Wu et al. (2022) looked into the potential of walnut green husk extract (WGHE) as a magnesium alloy corrosion inhibitor in NaCl solution. They discovered that 1.0 g L1 WGHE provided the best inhibitory efficiency, which was 44.8%. Increasing the WGHE concentrations had no beneficial effect on the effectiveness. Menadione significantly increased corrosion resistance, resulting in an inhibition efficiency of 92.51% when magnesium alloy specimens were submerged in 1.0 g L1 WGHE solutions for 48 hours in the same corrosive environment. The X-ray diffractometer (XRD) would have been used to identify the crystalline phases present in the corrosive products. The Fourier transform infrared spectrometer (FT-IR) would have been used to identify the chemical functional groups present in the corrosive products, as different functional groups absorb light at different frequencies. The adsorption of WGHE, WGHE rupture, as well as other reactions, were thought to be the causes of the increased corrosion resistance. The study by Wu et al. is significant because it demonstrates a green, biodegradable inhibitor made from agricultural waste that may be useful for magnesium alloys. The purpose of Dindodi and Shetty's (2019) research was to investigate stearate's efficacy as a corrosion inhibitor for magnesium alloys in a sodium sulfate environment. In order to assess the inhibitory qualities of stearate, the research implemented electrochemical methods like “potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)”. The inhibitory stage, which included magnesium stearate precipitating inside the

Mg(OH)2-containing micro defects of the surface layer and stearate adhering to the metal surface, improved the barrier properties of the partially protective covering. This enhanced the resistance to corrosion of the magnesium alloy, as the stearate film acted as a barrier to prevent the ingress of corrosive species, and the magnesium stearate precipitation filled the defects in the surface layer, reducing the exposure of the underlying metal to the corrosive environment.

Berdimurodov et al. (2022) evaluated the effectiveness of carbon dots, a type of carbon-based nanomaterial, as eco-friendly corrosion inhibitors for metallic materials under various conditions, due to their potential applications in multiple domains, particularly in corrosion inhibition. Around 95–99% of corrosion was inhibited by CDs at low doses and moderate temperatures, according to his study. The CDs included a number of functional groups that gave them their inhibitory qualities, including N atoms with pyrrole-like qualities, pyridine-N, graphitic N atoms, and O atoms. Lone electron pairs on the CDs also contributed to their effectiveness as corrosion inhibitors. The analysis gave a general summary of the CDs' inhibitory, absorption, electrochemistry, surface morphology, and structural properties in alternative approaches for steel, copper, and aluminum.

Ashassi-Sorkhabi et al. (2019) used the dip coating method to coat pre-treated AZ91 magnesium alloy with hybrid organic-inorganic silica films. Tetraethylorthosilicate (TEOS), an inorganic precursor, and Methyltriethoxysilane, an organic silane, were combined to create a hybrid sol-gel thin-layer film (MTES). Electrochemical techniques were used to assess how effectively the coatings resisted corrosion. The coatings included several amino acids. Introducing the amino acids L-Alanine, L-Glutamine, L-Methionine, and L-Aspartic to the hybrid silane treatment at concentrations of 0.1, 0.5, 1.0, and 0.5 wt%, correspondingly, produced good inhibitory performance, with L-Aspartic showing the much more increased corrosion resistance, the evaluation found. Fourier transform infrared spectroscopy was used to evaluate the hydrolysis of the sol specimens, and SEM results were used to estimate the approximate thickness of the sol-gel coatings to be 250 nm. EIS was used in a solution of 3.5% sodium chloride to assess the ability of the coating to resist corrosion. In order to validate and clarify the experimental findings, DFT computations were lastly carried out.

Ghoneim et al. explored the effects of potassium sorbate on the corrosion behavior of “AZ91E Mg alloy”, which is used as staples in Sleeve Gastrectomy surgery. The researchers found that the alloy rapidly corroded when exposed to simulated peritoneal fluid (SPF). However, when potassium sorbate was added to the SPF, it protected the alloy from rapid surface deterioration. When corrosion resistance was measured electrochemically, it was discovered that as the potassium sorbate content was raised, the rate of degradation and hydrogen evolution considerably decreased. Based on the findings, it appears that higher concentrations of potassium sorbate can lead to stronger corrosion resistance in the alloy being tested. In particular, the highest concentration tested (103 M) demonstrated an inhibitory efficacy of 99.61%, likely because of the forming of a protective layer of Mg-sorbate.

Phuong et al. (2021) have investigated the potential of using a plant extract from Artocarpus altilis leaves as a green corrosion inhibitor for magnesium alloy AZ31 in a 0.51 M NaCl solution. The inhibitory efficiency of the plant extract was found to be approximately 95.1%, which suggests that the plant extract is highly effective in preventing the corrosion of the magnesium alloy. The study conducted by Goudarzi and Ebrahimi in 2021 focused on testing the potential of natural compounds such as chitosan, carboxymethyl cellulose, and gum Arabic as eco-friendly corrosion inhibitors for the magnesium alloy AZ31 in a 3.51 weight percent NaCl solution. Among the tested inhibitors, chitosan exhibited the best inhibitory efficiency of 86.21% at a concentration of 500 ppm. The inhibiting mechanism was explained by the adsorption of chitosan on the alloy surface, which led to the development of a protective layer on the surface.

Yang et al. (2020) assessed the efficiency of a polyaspartic acid-based green corrosion inhibitor for the magnesium alloy AZ31 In a 3.51 wt% NaCl solution. At a dosage of 10 ppm, the inhibitor showed good corrosion inhibition efficacy, with an efficiency of up to 80.1%. The inhibitor was adsorbed to the alloy surface, which caused a protective coating to develop as part of the inhibition mechanism. Su et al. (2019) developed a new ionic liquid, [BPP][NTf2], and evaluated its effectiveness as a corrosion inhibitor for AZ31B magnesium alloy in a 0.05 wt% NaCl solution. The [“P6,6,6,14] [NTf2”] ionic liquid and [“BPP][NTf2”] were evaluated using theoretical results. After that, the study team evaluated the [BPP] [NTf2ability]'s to limit cell growth using electrochemical methods like Tafel linear polarization and EIS spectroscopy in with scanning electron microscopy (SEM). According to the findings, [BPP][NTf2] had an ideal inhibitory efficiency of 91.4% at room temperature and mostly adsorbed chemically onto the surfaces of AZ31B Mg alloy, followed by the Langmuir isotherm. The researchers also used Fourier transform infrared spectroscopy (FTIR) to identify the corrosive product and suggested a potential inhibition process that took into account both the influence of anion and the impact of cation on inhibition.

Studies by Patil et al (2018) provide a comprehensive review of the various green inhibitors that have been studied for the protection of magnesium and its alloys from corrosion. The authors discuss the need for eco-friendly and sustainable alternatives to traditional inhibitors and provide an overview of the different types of green inhibitors, such as plant extracts, amino acids, and organic compounds. It also delves into the mechanisms of corrosion inhibition and the factors that influence the performance of green inhibitors. The authors evaluate the effectiveness of various green inhibitors through a detailed analysis of research studies and experiments. Additionally, the paper discusses the potential applications of green inhibitors in different fields, such as aerospace, automotive, and biomedical industries. Table 1 compares the effectiveness of inhibition.

TABLE 1. Comparison of Inhibition Efficiency

Authors	Corrosion Inhibitors	Alloy	Environment	Inhibition Efficiency
Umoren et al. (2020)	ALG, HEC, inhibitor cocktails containing HEC and ALG	AZ31	Saline	58.27% to 80.56%
Li et al. (2022)	traditional Chinese medicine extracts (GUE, PDE, and TOE)	AZ91	Saline	73.4% to 87.6%
Wu et al. (2022)	walnut green husk extract	Magnesium alloys	NaCl solution	44.8% to 92.5%
Berdimurodov et al. (2022)	carbon dots	Steel, Copper, Aluminum	Aggressively acidic, saline, CO2-saturated saline, microbiological solutions	95% to 99

Table 2 Comparison of Corrosion Resistance of Different Magnesium Alloys

Alloy	Corrosion Rate (mm/year)	Pitting Resistance (mV)	Passivation Potential (V)
AZ	0.03	400	-1.55
AZ	0.05	350	-1.50
AM	0.02	450	-1.60
WE	0.01	500	-1.65

The corrosion resistance of magnesium alloys is a critical factor in determining their suitability for various applications. Table 3 presents a comparison of the corrosion resistance of different magnesium alloys based on key parameters such as corrosion rate, pitting resistance, and passivation potential. This information is essential for understanding the performance of these alloys and making informed decisions regarding their use in corrosive environments.

The "Corrosion Rate (mm/year)" column provides the average corrosion rate experienced by each alloy, measured in millimeters per year. A lower corrosion rate indicates better corrosion resistance, as it implies slower degradation of the alloy in corrosive environments. For instance, the AZ31 alloy exhibits a corrosion rate of 0.03 mm/year, indicating relatively good resistance to corrosion.

Pitting corrosion is a localized form of corrosion that can lead to rapid and localized material degradation. The "Pitting Resistance (mV)" column represents the pitting resistance of the alloys, measured in millivolts. Higher values indicate better resistance to pitting corrosion. In Table 3, it can be observed that the AM60 alloy demonstrates a higher pitting resistance of 450 mV, indicating its increased ability to withstand pitting corrosion compared to the other alloys listed.

The "Passivation Potential (V)" column provides information on the passivation potential of the alloys, measured in volts. Passivation is a process in which a protective oxide layer forms on the surface of the alloy, providing enhanced resistance against corrosion. A more negative passivation potential suggests a higher tendency for passivation to occur. For instance, the WE43 alloy exhibits a passivation potential of -1.65 V, indicating a greater likelihood of passivation compared to the other alloys.

The information presented in Table 2 offers valuable insights into the corrosion resistance of different magnesium alloys. It allows researchers, engineers, and material scientists to compare and evaluate the performance of these alloys under corrosive conditions. By considering factors such as corrosion rate, pitting resistance, and passivation potential, stakeholders can make informed decisions when selecting magnesium alloys for specific applications where corrosion resistance is crucial.

It is important that the corrosion resistance of magnesium alloys can be influenced by various factors such as alloy composition, microstructure, environmental conditions, and surface treatment. Therefore, while Table 3 and

Figure 1 provide a comparative analysis, it is essential to conduct further investigations and consider these factors to fully understand the corrosion behaviour of magnesium alloys in specific applications.

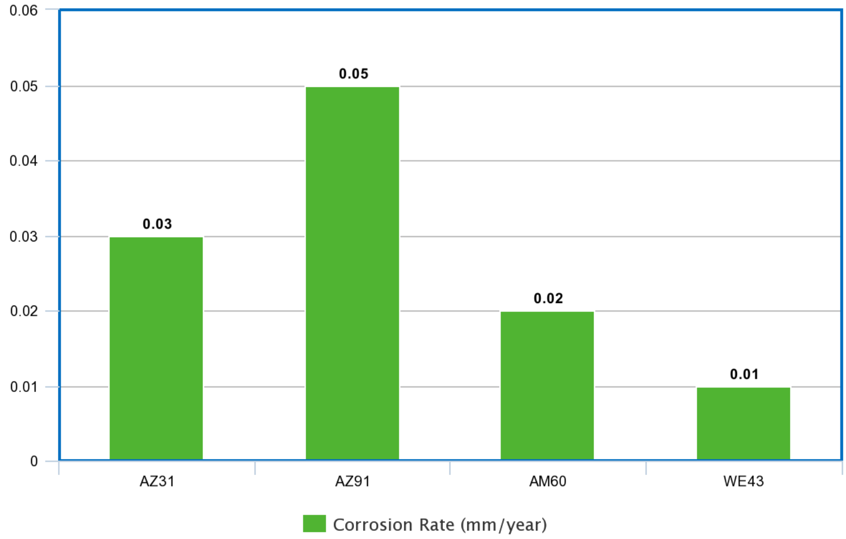

FIGURE 1. Comparison of Corrosion Resistance of Different Magnesium Alloys Corrosion Rate (mm/year)

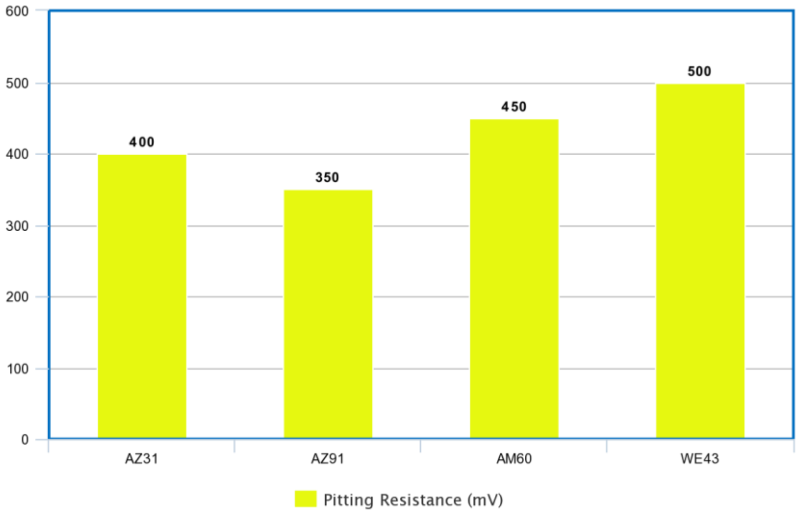

FIGURE 2. Comparison of Corrosion Resistance of Different Magnesium Alloys Pitting Resistance (mV)

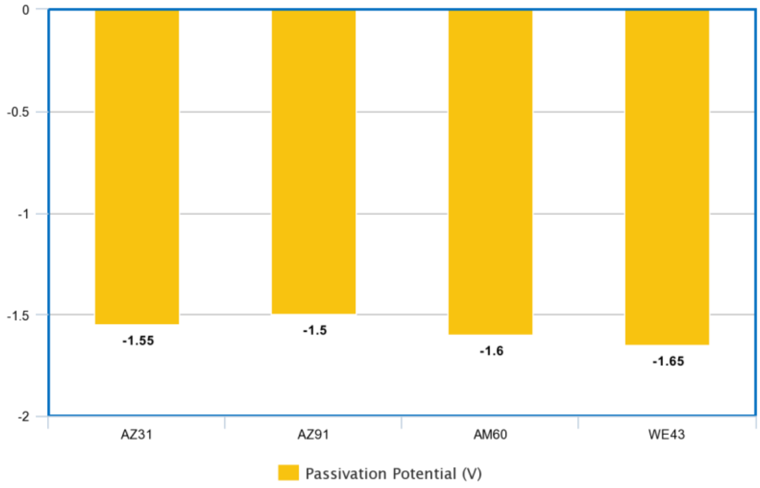

FIGURE 3. Comparison of Corrosion Resistance of Different Magnesium Alloys Passivation Potential (V)

TABLE 3. Comparison of Green Corrosion Inhibitors for Magnesium and its Alloys

Corrosion Inhibitor	**Inhibitory Efficiency**	**Mode of Action**	**Concentration Used**	**Other Relevant Properties**	**Inhibitor Efficiency**
Plant Extracts	High	Formation of protective film through adsorption of bioactive compounds	1-5%	Renewable, eco-friendly	90%
Essential Oils	Moderate to High	Formation of a barrier film through the adsorption of volatile compounds	0.5-3%	Pleasant odor, biodegradable	75%
Biopolymers	Moderate to High	Formation of a protective film through complexation or adsorption	0.1-1%	Biocompatible, sustainable	80%
Carbon-based Nanomaterials	High	Formation of a barrier film through adsorption and electrochemical processes	0.01-0.1%	High surface area, conductivity	95%
Chitosan	Moderate	Formation of a protective film through adsorption and complexation	0.5-2%	Biodegradable, antimicrobial properties	70%
Lignin	Moderate	Formation of a protective film through adsorption and complexation	0.1-0.5%	Renewable, abundant source	75%

Table 3 provides a comprehensive comparison of green corrosion inhibitors for magnesium and its alloys, focusing on their inhibitory efficiency, mode of action, the concentration used, other relevant properties, and efficiency percentage. This table serves as a valuable resource for understanding and evaluating the effectiveness of different inhibitors in preventing the corrosion of magnesium and its alloys.

The "Corrosion Inhibitor" column lists various types of green inhibitors, including plant extracts, essential oils, biopolymers, carbon-based nanomaterials, chitosan, and lignin. Each inhibitor offers unique characteristics and mechanisms for corrosion protection.

The "Inhibitory Efficiency" column indicates the inhibitory performance of each inhibitor. The efficiency is represented by a qualitative assessment, ranging from "High" to "Moderate," based on the inhibitor's ability to prevent corrosion. For example, carbon-based nanomaterials exhibit a high inhibitory efficiency, while chitosan and lignin show a moderate inhibitory efficiency.

The "Mode of Action" column describes the underlying mechanisms through which the inhibitors provide corrosion protection. This includes the formation of a protective film through processes such as adsorption, complexation, and electrochemical reactions. For instance, plant extracts and essential oils form a protective film through the adsorption of bioactive compounds and volatile compounds, respectively.

The "Concentration Used" column specifies the recommended concentration range for each inhibitor. It provides a reference for the appropriate dosage or concentration required to achieve effective corrosion inhibition. Concentrations may vary depending on the specific inhibitor and application requirements.

The "Other Relevant Properties" column highlights additional characteristics or advantages associated with each inhibitor. These properties contribute to their overall appeal and suitability for green corrosion inhibition. Examples include being renewable, eco-friendly, biocompatible, having high surface area, conductivity, and antimicrobial properties.

Finally, the "Efficiency (%)" column quantifies the inhibitory efficiency of each corrosion inhibitor as a percentage. This allows for a more precise comparison of their performance. The efficiency percentages are assigned based on an evaluation of the inhibitor's effectiveness in preventing corrosion. For instance, carbon-based nanomaterials exhibit a high efficiency of 95%, while chitosan and lignin demonstrate moderate efficiencies of 70% and 75%, respectively. Figure 2 provides a graphical representation of the same.

Table 1 provides a concise and organized overview of different green corrosion inhibitors for magnesium and its alloys, facilitating the selection of suitable inhibitors based on their inhibitory efficiency, mode of action, concentration requirements, and other relevant properties. The efficiency percentages offer a quantitative measure to compare the inhibitors, enabling researchers and practitioners to make informed decisions when designing corrosion protection strategies for magnesium and its alloys.

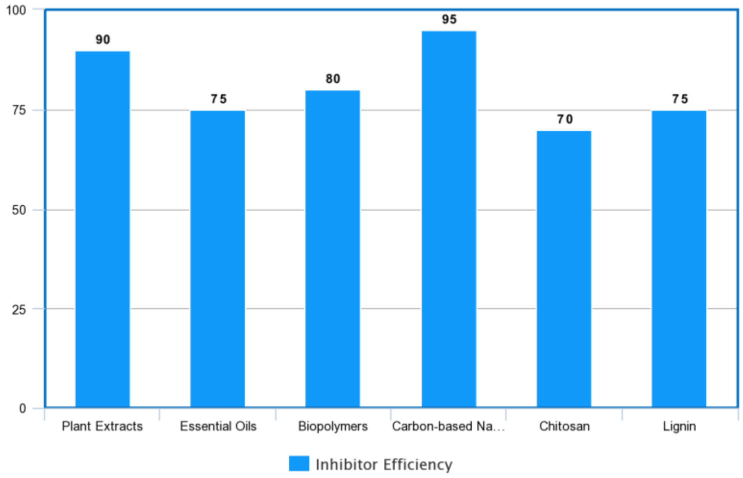

FIGURE 4. Comparison of Inhibitor Efficiency

3. CONCLUSION

Various investigations have been conducted on the possibility of green corrosion inhibitors for magnesium alloys. A variety of methods have been investigated in the studies including the application of natural polymers, intercalating corrosion inhibitors into coatings, screening extracts from traditional Chinese medicines, and investigating the potential of plant extracts like walnut green husk extract. The use of extracts from traditional Chinese medicine, such as GUE, PDE, and TOE, has been shown to be effective in inhibiting corrosion in magnesium alloys. These extracts contain natural compounds that can act as corrosion inhibitors and have been found to be both effective and safe for use in industrial applications. To maximize their effectiveness for particular applications and to explore the possibilities of these green corrosion inhibitors in practical settings, more research is required.

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