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A Review on Green Corrosion Inhibitors for Magnesium and its Alloy

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Abstract

The biodegradability and lightweight qualities of magnesium make it an appealing material for usage in aerospace and automotive applications and orthopedics. Magnesium is susceptible to corrosion, which restricts its use. Magnesium should be protected against corrosion in order to be used to its maximum potential. Corrosion inhibitors are one of the most well-liked and affordable techniques to stop corrosion in magnesium and its alloys. Chemicals that are frequently used as corrosion inhibitors include biotoxic ones, which raise serious toxicity issues. There is a great deal of interest in creating a green corrosion inhibitor that is non-toxic and safe for the environment due to the toxicity of the current inhibitors. This paper discusses the common green corrosion inhibitors. The application of ecologically friendly corrosion inhibitors for magnesium and its alloy is still being pursued by a relatively small number of scientists. The research utilizing green corrosion inhibitors for magnesium alloy has been reviewed in detail. In addition, the performances are tabulated and analyzed.

Keywords: *Civil servants, quality of civil servants, local civil servants, Vietnam*

Introduction

The incredible strength-to-weight ratio of Magnesium (Mg) alloys is one of the main reasons they are used in the automotive, aerospace, and electronic industries. The corrosion resistance of magnesium alloys must be increased as a result. Many surface treatments have been suggested for this, including Plasma Electrolytic Oxidation (PEO), Conversion Coating, Electroless plating, Organic Coating, etc. The Korea Food and Drug Administration (KFDA) and Conformite EuropeEmme (CE) have approved part of the research that has been done over the past decade years into the possibility of using magnesium alloys as biological implants. The low standard electrode potential of Mg and its alloys (2.37V) the pure Mg phase (also known as the α " phase") has a lower potential than the second phase (also known as the "β phase") in magnesium substrates.

On the surface of magnesium alloys, MgO, $Mg(OH)_2$, and other magnesium salts create a porous corrosion barrier that anions, particularly Cl, can easily penetrate. The corrosion layer is unable to

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halt the corrosion process in this instance. For their large-scale uses, Mg alloys' rapid corrosion poses a significant concern. Numerous strategies have been put forth by researchers to enhance the corrosion performance of Magnesium based products. Purification is the first step. The Mg substrate has fewer impurities indicating a smaller probability of micro galvanic corrosion. Alloying comes next. In order to change Mg's ability to resist corrosion, alloying elements can interact with it to create intermetallic phases that can either dissolve in the matrix of Mg or spread along the grain boundaries. Improvements in processing technologies come in third.

magnesium substrates are vulnerable to corrosion. It is required to alter the substrates' surface or their chemical makeup to prevent Mg-based substrates from contact with corrosive water. Numerous experiments were done to increase the corrosion resistance of items constructed of magnesium. Due to their distinctive benefits in corrosion prevention, superhydrophobic coatings (SHC) on magnesium alloys have recently attracted a lot of attention. Under several internal and external conditions, such as pH fluctuations, mechanical damage, etc., the corrosion inhibitors may be released from nanocarriers. Since the corrosion process causes local pH changes that are ideal for corrosion-protective coatings, the pH shift is one of many factors that promote the release of corrosion inhibitors. The controlled release of corrosion inhibitors has recently been considered using sol-gel coatings with nanocarriers. The common green corrosion inhibitors are covered in this work. The use of environmentally friendly corrosion inhibitors for magnesium and its alloy is still being pursued by a very small number of scientists. The studies using green corrosion inhibitors for magnesium alloy have been thoroughly evaluated. The performances are also tabulated and examined.

The paper is divided into the following sections: Sections 2 and 3 discuss different sources of green corrosion inhibitors, Section 4 gives an idea about the application of green corrosion inhibitors for Mg and its alloy, and section 5 provides a discussion about various experimental analyses tools and processes also various parameters comparisons and finally, section 6 concludes the paper.

Corrosion Inhibitors

They are chemical substances that can be added to gases or liquids to slow down the corrosion of specific materials, typically metals. Metals can avoid rusting and anodic corrosion by using corrosion inhibitors. This is often accomplished by covering the metal surface with a layer of chromate. In order to react with dissolved oxygen in the environment and aid prevent cathodic corrosion, oxygen scavengers can be used as corrosion inhibitors.

Types of corrosion inhibitors

Depending on how they prevent corrosion on the metal, four different types of corrosion inhibitors can be broadly categorised. They are as follows:

Cathodic inhibitor

Anodic inhibitor

Volatile corrosion inhibitor

Mixed inhibitor

Cathodic Inhibitor

In order to prevent eroded elements from diffusing to the metal surface, cathodic inhibitors can either work to slow down the cathodic reaction or to preferentially precipitate on the cathodic regions of the metal.

Anodic Inhibitor

These corrosion inhibitors provide a thin protective oxide layer on the metal's surface. The metallic surface becomes a passivation area as a result of this reaction, which causes a significant anodic shift. This area of passivation aids in minimising metal corrosion.

Volatile Corrosion Inhibitor

The corrosion of condenser tubes in boilers can be stopped by using volatile corrosion inhibitors. They are also known as vapour phase inhibitors. These reduce corrosion by modifying the pH of the outdoor atmosphere to less acidic levels.

Mixed Inhibitor:

A coating also develops on surface of metal as a byproduct of these kinds of corrosion inhibitors. Along with reducing anionic reactions, they also function to diminish cationic reactions. A precipitate is produced on the metal's surface to accomplish this coating.

Green Corrosion Inhibitor

As environmental consciousness grows and laws restricting conventional corrosion inhibitors owing to their toxicity are amended, green corrosion inhibitors are becoming more and more popular. The majority of natural product extracts are excellent sources of environmentally friendly corrosion inhibitors because they contain active elements like O, C, N, and S. These elements facilitate the adhesion of these compounds to metals or alloys and facilitate the formation of a shielding coating that inhibits corrosion.

Plant Extracts as Green Corrosion Inhibitor

The ability of gum arabic (GA) to prevent mild steel corrosion in 0.1 M H2SO4 at different temperatures was examined by Umoren et al. [17] . The IE was conducted on 98.5% pure AA1060 aluminium at 40°C. Investigations [18] into the thermometry and hydrogen evolution of GA (0.5 g/l) showed IEs of 74.2 and 75.9%, respectively. Buchweishaija et al. examined the impact of chlorinated drinking water on the IE of gum exudates from "Acacia seyal var. seyal and Acacia gum from seyal var. seyal on mild steel". Maximum IE for gum exudates was 98.5% at 1000 ppm and 30 °C. When operating at 80°C and a concentration of 600 ppm, acacia gum displayed an IE of 96.8%.

In a 1 M hydrochloric solution, Alo et al. examined the IE and adsorption capabilities of elephant grass extract on mild steel. The inhibitor showed better than 95% efficiency at room temperature, which rose with higher extract concentrations but fell with higher temperatures. Mobin et al. analysed the anticorrosion behaviour of Xanthan Gum (XG) in 1 M HCl as an environmentally safe corrosive inhibitor for mild steel at 30, 40, 50, and 60°C. XG had the highest IE at 1000 ppm and 30°C, with a value of 74.2%.

Drugs as Green Corrosion Inhibitors

Most of these medications can be produced using natural ingredients, which has encouraged their usage as green corrosion inhibitors. Considering that drug molecules contain heteroatoms, the benzene ring, and heterocycles like thiophenes, pyridines, and isoxazoles, they may be potential sources of environmentally safe corrosion inhibitors. Ali et al. used the WL, PP, EIS, and EFM techniques to investigate the inhibitory effect of the candesartan drug on carbon steel in a 1 M hydrochloric acidic medium.

As a green corrosion inhibitor of mild steel in an acidic solution containing 1 M HCl, Matad et al. [24] looked into the inhibitory characteristics of the anti-inflammatory medication ketosulfone. Both chemical and electrochemical techniques were applied. The maximum IE that ketosulfone could transfer was 96.6% at 30°C and 200 ppm concentration. Both thermodynamic calculations and polarization experiments demonstrate that the inhibitor is mixed-type and follows the Langmuir adsorption isotherm. Quareshi et al. studied the behaviour of corrosion on mild steel in a 1 M hydrochloric acidic media using WL, PP, and EIS methods. It was found that the drug, at a concentration of 150 ppm, had a remarkable IE of 99.1%. The inhibitor mostly exhibits cathodic behaviour, but it also exhibits mixed-type behaviour.Dahiya et al. used "WL, PP, EIS, SEM, and molecular dynamics" to examine the anti-corrosive effects of the ancient medication ethambutol on mild steel in 0.5 M HCl (MD).

Amino Acids as Green Corrosion Inhibitor

An amino acid is a molecule that has both an amino (-NH2) group and at least one carboxyl (-COOH) group attached to the same carbon atom. Given their non-toxicity, biodegradability, availability, solubility in water, ease of synthesis, high purity, and biodegradability, amino acids are seen as environmentally acceptable corrosion inhibitors. The conjugated-electrons system and heteroatoms like N, O, and S found in amino acids make them a significant class of environmentally friendly corrosion inhibitors.

Investigations into the potential anti-corrosive effects of different amino acids on carbon steel employed PP and EIS methodologies. When amino acid molecules' backbones have functional groups like OH, SH, or phenyl, they adsorb more successfully. In a ventilated and oxygen-free environment, Mobin et al.'s research examined the inhibitory impact of the amino acid L-cysteine (CYS), which contains a mercapto group, on mild steel. At 31°C and an inhibitor concentration of 500 ppm, or 85.6%, the maximum IE was attained. By incorporating CPC, SDS, and TX into CYS, the researchers looked at their impacts and discovered that they boosted IE. CYS displayed mixed-type inhibitor behaviour and followed the Langmuir adsorption isotherm both on its own and when combined with surfactants. Zeino et al. examined the effects of polyaspartic acid (PASP) on mild steel in a solution containing 3% NaCl. They employed Monte Carlo simulation and quantum computing to comprehend the complex adsorption mechanism at the molecular level. The IE of formulations based on N-acetyl Cysteine (NAC) on J55, mild steel, and X80 steel was IEs in formulations based on NAC reached 91% at 90°C at varied temperatures (30-90°C) was investigated by Ituen et al.

Green Corrosion Inhibitor for Magnesium

In recent years several researchers are trying to utilize various green corrosion inhibitors for magnesium and its alloy. This provides cheaper corrosion inhibition which is effective and eco-friendly. Some of the inhibitors for the Mg and its alloys are discussed below and the research is reviewed.

Inhibitors

Gossypium hirsutism

In 2 M Sodium Hydroxide solutions, Gossypium hirsutism L leaf extracts (GLE) and seed extracts (GSE) were tested for their ability to suppress corrosion. Gossypium extracts did not corrode magnesium in a NaOH solution. GLE provided 97.05% inhibitory efficiency at the maximum concentration, whereas the GSE supplied 94%.

Chromolaena odorata

Tridaxprocumbens is a typical tropical weed, while Chromolaenaodorata is a flowering shrub that is a member of the Asteraceae family, which includes sunflowers.. As each extract of an inhibitor was added, a reduction in corrosion was observed.

Review on Use of Green Corrosion Inhibitor for Magnesium

Umoren, et al. investigated "chitosan (CHI), dextran (Dex), carboxymethyl cellulose (CMC), sodium alginate (ALG), pectin (PEC), Hydroxyethyl Cellulose (HEC), and gum arab (GA)" to see if they could prevent corrosion of the AZ31 Mg alloy in a 3.5 wt.% sodium chloride solution. While CHI, Dex, CMC, PEC, and GA significantly aided alloy corrosion, ALG and HEC only slightly reduced it. HEC protected the alloy 64.13%, while ALG protected it 58.27% (1 g/L). With the aid of KI, Date palm seed oil, and either HEC or ALG, two inhibitor mixtures were made. The HEC formulations reduced alloy corrosion by 80.56% and ALG by 77.43%. when compared to the EIS method. In surface tests employing SECM, AFM, SEM, and EDX result from FTIR, UV-vis, and X-ray photoelectron spectroscopy demonstrated that adsorbed inhibitor complexes co-existed with $Mg(OH)_2$.

Wu, et al. evaluated orange peel extracts' (OPE) ability to prevent corrosion of magnesium alloys using surface analysis using SECM, potentiodynamic polarisation curves, and electrochemical impedance spectra. With an effectiveness of 85.7% at a very low dosage of 0.030 g L1, OPE would be a potent inhibitor. When sodium fluoride and DL-malic acid were mixed, Mg-Al-Mn magnesium alloy demonstrated synergistic corrosion inhibition effects in the pH-neutral sodium chloride solution, according to Qiu et al.

High-throughput screening and visual identification were the foundation of their strategy. The high inhibitory efficiency (94.1%) and synergistic factor (3.8) were found when the components were mixed in equal amounts (0.05 M). The hybrid inhibitor can inhibit synergistically because a perovskite layer with a complex structure forms during its synthesis.

Experimental Discussion

In this section, various performance measures, experimental analysis techniques, and surface measurement observations are discussed.

Electrochemical experiments

For the electrochemical experiments, electrochemical impedance spectroscopy and potentiodynamic polarization measurement are used.

Electrochemical impedance spectroscopy

A non-destructive, intrusive, leading, probe technique for detecting general corrosion is electrochemical impedance spectroscopy. The technique is challenging to apply in systems with significant temperature and operational changes because of the longer time needed to collect accurate data

Potentiodynamic Polarization Measurement

One of the most popular DC electrochemical methods in corrosion measurements is the Potentiodynamic Polarisation measurement. In PDPs, various ranges of potential are given to the test electrode as a result of which, depending on the polarisation direction, a dominating oxidation or reduction reaction occurs on the metal surface and an appropriate current is produced. The corrosion potential and rate of the metal under the specified conditions can be calculated using the polarisation curve (Tafel slope).

Surface Observation Investigations

Scanning Electrochemical Microscopy (SECM)

Compared to traditional electrochemical methods, SECM features many operational modes, superior spatial resolution, and a lower iR drop.The SECM mapping images of bare AZ31 Mg

substrates, however, do not indicate a distinct localized behavior due to the strong diffusion of more H2 gas during a longer immersion time toward the UME tip.

Scanning Electron Microscope (SEM)

An electron beam is produced by a high voltage in a vacuum in a SEM. The beam produces secondary electrons that escape from the substrate's surface after being focussed by electrical lenses and scanned over it. The number of escaping electrons is largely determined by the surface's atomic mass and to a lesser extent by the crystal orientation. Similar to a typical black-and-white photograph, these secondary electrons are identified and produce a black-and-white image with changing intensity.

Atomic Force Microscopy (AFM)

AFM is useful for analyzing the corrosion behaviour of metals as well as advancing research on the corrosion resistance of a metal. It has many important advantages, including the ability to describe the development of early corrosion product films and analyse the formation process and microstructure of corrosion product films on a metal surface. An offspring of the scanning tunneling microscope, AFM is a part of scanning probe microscopy.

X-ray Photoelectron Spectroscopy(xps)

To investigate a material’s surface chemistry, an approach known as XPS is used. The constituent elements of a compound can be identified by their elemental composition, empirical formula, chemical state, and electronic state using XPS.

Fourier Transform Infrared (FTIR)

Used FTIR to distinguish between organic and, in some situations, inorganic materials. This method plots the sample material's infrared radiation absorption against wavelength. The infrared absorption bands help to determine the parts and structures of molecules. When absorbed by a substance, infrared radiation often excites molecules into a higher vibrational state. The maximum wavelength of light that a specific molecule may absorb depends on the energy difference between its vibrational modes when it is at rest and when it is stimulated. The wavelengths that the sample absorbs provide information about its molecular makeup.

UV-Visible Spectroscopy

Absorption spectroscopy in the ultraviolet-visible portion of the light spectrum is referred to as UV-Visible Spectroscopy (UV-Vis). Absorption and reflectance spectroscopy are two types of spectroscopies that are included in ultraviolet-visible (UV-vis) spectroscopy. In order to be excited to higher anti-bonding molecular orbitals, molecules with n- or -electrons can absorb ultraviolet or visible light energy. In the ultraviolet or visible range, molecules go through electronic transitions, but in the infrared region, they go through vibrational transitions.

Comparative Analysis

The performance and effectiveness of the reviewed papers are compared and analysed. In the given analysis Hydroxyethyl cellulose (HEC), sodium alginate (ALG), orange peel extracts (OPE), DL-malic acid (DMA), walnut green husk extract (WGHE), Glycyrrhiza uralensis extract (GUE), Potentilla Discolour Extract (PDE), Taraxacumofcinale Extract (TOE), stearate, and VT13C, VT13CT amino acids sol-gel coating were utilized as green corrosion inhibitors. The inhibition efficiency η (%) is tabulated in table 1. The inhibition efficiency on different concentrations of inhibitors such as 0.50, 1.00 and 2.00 in g/L is shown represented in table 2.

Table 1 Inhibition efficiency of green corrosion inhibitors

Sl.No	**Inhibitor**	**η (%)**
1	ALG	77.43
2	HEC	80.56
3	OPE	82.7
4	DMA	**94.1**
5	WGHE	92.5
6	GUE	73.4
7	PDE	87.6
8	TOE	84.6

Table 2 Inhibition efficiency on different concentrations of inhibitors

Sl.No	**Inhibitor**	**η (%)**		
		0.5 (g L^{-1})	**1 (g L^{-1})**	**2 (g L^{-1})**
1	ALG	38.69	55.97	44.47
2	HEC	43.76	63.3	53.63
3	OPE	80.9	64.5	50.2
4	WGHE	38.3	51.9	49.4
5	GUE	40.24	47.14	73.4
6	PDE	60.81	66.9	87.57
7	TOE	51.58	58.21	84.59
8	Stearate	72.06	78.97	91.09

The electrochemical parameters using "Potentiodynamic Polarization (PDP) Corrosion current density (i_{corr}), corrosion potential (E_{corr}), and Tafel slopes (β_a, and β_c)" of the green corrosion inhibitor coatings are presented in table 3. The electrochemical parameters of green corrosion inhibitors using Electrochemical impedance spectroscopy are represented in table 4.

Table 3 Comparison of electrochemical parameters of green corrosion inhibitors using PDP

Sl.No	Inhibitor	C (gL^{-1})	$-E_{corr}$(mV)	i_{corr} ($\mu A\ cm^{-2}$)	β_a (mV dec^{-1})	β_c (mV dec^{-1})
1	ALG	0.5	1427	32.28	5.7	175.5
		1	1441	30.14	7.5	166.6
		2	1456	38.43	7.6	160.1
2	HEC	0.5	1555	30.72	5.9	194.9
		1	1524	75.87	25.3	151.6
		2	1450	27.6	6.5	156.3
3	Mg: Al LDH	0.5	1550	11.3	55.5	117.7
4	OPE	0.5	1440	2.33	68	71
		1	1456	4.33	69	80
		2	1450	6.07	72	75

Table Continues

5	WGHE	0.5	1480	16.7	81.57	18.12
		1	1482	13.07	51.63	28.16
		2	1532	13.76	70	20.56
6	GUE	0.5	1544	62.56	183.3	132.3
		1	1553	55.34	143.8	167
		2	1542	27.85	124.4	89.3
7	PDE	0.5	1573	41.03	147.9	120.9
		1	1540	34.65	136.7	151.9
		2	1520	13.01	76.3	95
8	TOE	0.5	1554	50.69	139.3	161.4
		1	1562	43.75	175	169.8
		2	1529	16.13	97.9	71.7
9	Stearate	0.5	1644	145.48	-	186
		1	1639	109.53	-	178
		2	1626	46.4	-	149
10	VT13C	0.5	1610	266.6	-	-
11	VT13CT	0.5	1388	25	-	-

Table 4 Comparison of electrochemical parameters of green corrosion inhibitors using EIS

Sl. No	**Inhibitor**	**C ($g\ L^{-1}$)**	**R_s ($\Omega\ cm^2$)**	**R_f ($\Omega\ cm^2$)**	**R_p ($\Omega\ cm^2$)**	**CPE_{dl} ($\mu\ \Omega^{-1}S^ncm^{-2}$)**	**L ($H\ cm^2$)**	**R_L ($\Omega\ cm^2$)**	**$\chi^2 \times 10^{-3}$**	**η_E (%)**
1	ALG	0.5	6.8	18.16	86.51	-	40.76	156.3	86.5	38.73
		1	7.98	49.18	127.04	-	133.5	257.9	127.04	58.27
		2	7.87	19.51	101.46	-	134.2	178.6	101.46	47.75
2	HEC	0.5	183.2	12.03	88.89	-	52.75	163.2	88.89	40.37
		1	262.3	25.26	147.8	-	163.8	304.1	147.8	64.13
		2	222.2	10.63	99.68	-	75.56	174.3	99.68	46.82
3	OPE	0.5	556	-	3693	19.4	-	-	297	81.5
		1	516.3	-	2382	19.2	-	-	523	71.4
		2	469.1	-	1455	20.3	-	-	137	53.1
4	WGHE	0.5	141	183.9	2606.7	14.018	-	-	-	35.4
		1	143.2	162.1	3049.1	15.61	-	-	-	44.8
		2	128.6	230.4	2971.4	11.306	-	-	-	43.3
5	GUE	0.5	31.36	929.85	553.35	8.04	542.7	1147.21	-	49.61
		1	27.86	862.35	533.18	7.73	934.3	1188.62	-	50.66
		2	27.37	1328.12	945.71	9.56	1009	2127.54	-	71.36
6	PDE	0.5	26.95	1208.54	703.81	7.73	840.2	1438.03	-	61.14
		1	33.12	1362.64	829	9.28	1164	1810.68	-	68.27
		2	38.59	1654.21	1476.65	8.37	1623.2	4904.53	-	81.71
7	TOE	0.5	44.41	1033.21	660.72	8.76	1653.1	1324.83	-	57.33
		1	41.63	1310.46	824.43	8.37	1371.7	1912.35	-	68.09
		2	38.94	1502.47	1304.57	6.95	2553.8	4013.73	-	79.22
8	Stearate	0.5	182.8	128.9	-	-	-	-	-	74.82
		1	204.3	169.5	-	-	-	-	-	77.47
		2	530.6	296	-	-	-	-	-	91.32

Conclusion

It has taken a lot of work to prevent corrosion in magnesium and magnesium alloys with corrosion inhibitors, increase biocompatibility, and produce a variety of functional properties. Common corrosion inhibitors include biotoxic chemical substances, which pose major toxicity concerns. As a result, scientists are more interested in environmentally suitable corrosion inhibitors for various metals and their alloys. In this paper, the researchers employed the green corrosion inhibitors for Mg, and its alloys have been reviewed. In addition, the parameter comparison also takes place to analyze the inhibition efficiency of various green corrosion inhibitors. It results that the DL-malic acid provides the highest inhibition efficiency followed by the walnut green husk extracts. The current study will help scientists who want to work on eco-friendly corrosion inhibitors for magnesium and its alloy.

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