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Synthesis and characterization of an effective green corrosion inhibitive hybrid pigment based on zinc acetate-Cichorium intybus L leaves extract (ZnA-CIL.L): Electrochemical investigations on the synergistic corrosion inhibition of mild steel in aqueous chloride solutions

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ABSTRACT

Mild steel structures are widely used in many applications ranging from oil and gas pipelines to cooling water system and storage tanks. The search for highly effective inhibitors based on sustainable and environmentally friendly compounds for the protection of steel in corrosive environments i.e marine condition, has attracted considerable attention and interest of researchers.

In this study a new generation of corrosion inhibitive pigment based on zinc acetate-Cichorium intybus L leaf extract (ZnA-CIL.L) has been synthesized and characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), UV–visible analysis and thermal gravimetric analysis (TGA). Then, the corrosion inhibition performance of the ZnA-CIL.L hybrid pigment was studied by open circuit potential (OCP) measurements, electrochemical impedance spectroscopy (EIS) and polarization studies in 3.5 wt% NaCl solution on mild steel substrate. The surface morphology and chemistry of the steel panels dipped in the solutions without and with ZnA-CIL.L pigment extract was studied by SEM/EDS and FT-IR analyses. Results obtained from XPS, SEM/EDS, FT-IR, TGA and UV–visible analyses confirmed the successful complex formation of ZnA-CIL.L. The CIL.L extract consists of many corrosion inhibitive molecules i.e Flavone, Caffeic acid and Chicoric acid, that are full of electron-rich groups with high capability of sharing their lone pairs with Zn^{2+} cations, that have empty 3d orbital. Results obtained from OCP, EIS and polarization tests confirmed that the ZnA-CIL.L hybrid pigment, in its extract form in saline solution, could remarkably retard the steel sample from corrosion. Due to the synergistic effect between CIL.L and Zn^{2+} cations both the anodic and cathodic reactions were noticeably suppressed and inhibited in the presence of ZnA-CIL.L extract. The CIL.L molecules adsorption on the anodic sites occurred through chelation with zinc/iron cations, and the zinc cations deposited on the cathodic sites in the form of zinc hydroxide, providing proper inhibition performance for this hybrid green corrosion inhibitive pigment.

1. Introduction

Steel structures are widely used in a large number of applications i.e cooling water system [1], marine application, oil and gas transportation. However, corrosion prevention of carbon steel structures is still a major concern among corrosion scientists [2]. Attempts have been made to find efficient methods for corrosion control of carbon steel in corrosive media. The most important of these methods are cathodic/anodic protection, conversion/organic coatings and corrosion inhibitors. Among these corrosion inhibitors are extensively used as an efficient and practical method for corrosion control of carbon steel [3–7]. Recently, the use of corrosion inhibitors based on heavy metal ions has been strongly

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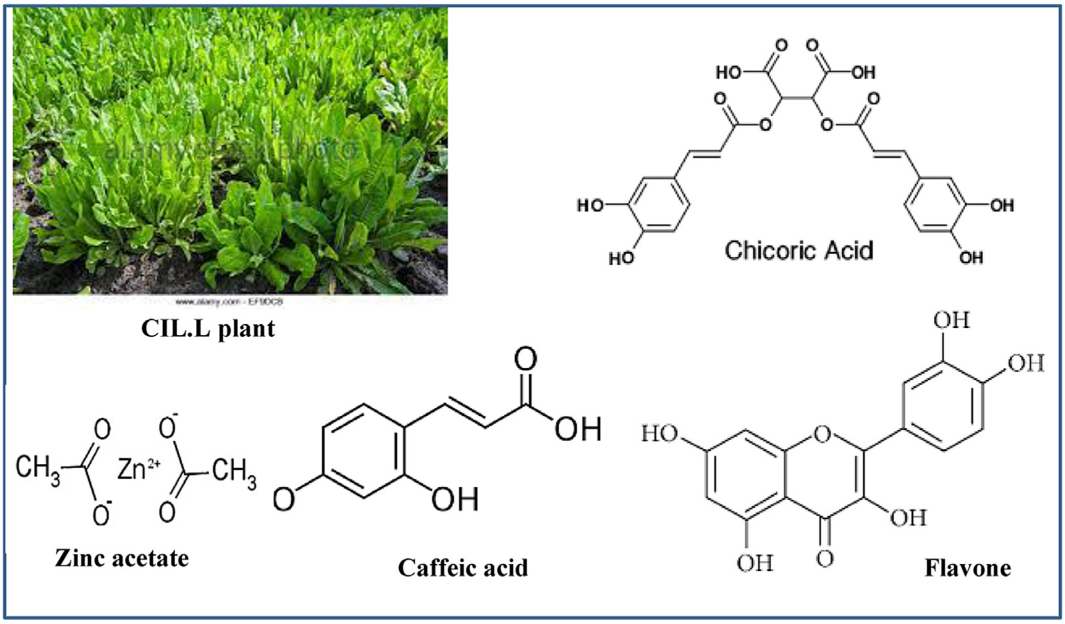

Fig. 1. Chemical structures of Zinc Acetate and some important compounds existed in CIL.L.

restricted due to environmental regulations. So researchers' attentions have shifted toward finding environmentally friendly corrosion inhibitors. Apart from environmental regulations, effectiveness at low concentrations and cost are other important criteria for employing various inhibitors for corrosion control of mild steel [8]. Generally, the corrosion inhibitors can be divided into two categories of organic/inorganic inhibitors depending on their chemical structures.

Most of the organic inhibitors have functional groups containing hetero-atoms i.e O, N, P and S. These are electron rich groups that can donate the lone pair of electrons with metal ions i.e Fe^{2+}, which have empty 3d orbitals. The modern corrosion inhibiting approaches are based on the synergistic effect between the organic/inorganic corrosion inhibitors. Recent findings show that the corrosion of mild steel samples immersed in near neutral environments can be significantly inhibited as a result of the synergistic effect between the organic/inorganic corrosion inhibitors [9–13]. The effective synergistic behavior between sodium, zinc and calcium salts, and gluconic acid for corrosion inhibition of mild steel in neutral saline solutions has been reported previously. It has been reported that the phosphonic acids, which are well-known corrosion inhibitors for carbon steel in neutral media, show effective synergistic behavior with Fe^{2+}, Fe^{3+} and Zn^{2+} ions. The phosphonic acids include many electron rich groups that can share their electrons with Fe^{2+}, Fe^{3+} and Zn^{2+} ions, which have empty 3d orbitals, leading to organic/inorganic complex formation on the steel surface [14,15]. The synergistic effect between dicarboxylic acids and Zn^{2+} on the corrosion inhibition of carbon steel has also been reported [16,17]. Rao et al. [18] reported the synergistic effect among phosphonated Glycine, Zn^{2+} and Citrate for corrosion inhibition of mild steel in nearly neutral aqueous solution with low concentration of Cl^- ions. Mahdavian et al. [19] revealed remarkable corrosion inhibition effect between Zn^{2+} cations and benzimidazole in wt.% NaCl solution for mild steel. Popoola et al. [20] has reported the significant synergistic effect between gluconates and Zn^{2+} cations on the corrosion inhibition of mild steel in different corrosive environments. The synergistic effect between zinc phosphate and benzotriazole [21], and zinc acetate and benzotriazole [22] on the corrosion control of steel have been studied in our recent studies. The results obtained revealed significant improvement of the corrosion inhibition performance of the combination of organic/inorganic compounds for corrosion control of steel in saline solution.

Recently the plant extracts have been introduced as a new class of effective, cheap and green corrosion inhibitors from renewable sources. There are a large number of reports depicting the good inhibition efficiency of the inhibitors present in plant extracts [23–32]. However, most of these inhibitors are only efficient in acidic media and do not show efficient inhibition performance in neutral solutions. One effective strategy for enhancing the inhibition role of these green compounds in neutral solutions is using them in combination with inorganic compounds. There are many electron rich groups in the compounds that exist in plant extracts, which are candidates for sharing their lone pairs with metal cations i.e Zn^{2+} and Fe^{2+}, leading to complex formation on the metal surface. So the synergistic effect between the plant extracts and metal cations would be one strategy for obtaining effective inhibition performance in neutral media. There are many reports on the synergistic effects of anions i.e halide ions, on the corrosion inhibition of metals in acidic media [33–35]. However, to the best of our knowledge there are no systematic studies on the synergistic effects between metal cations i.e Zn^{2+} and plants extracts in neutral saline solutions. In this study the synergistic effect between the Cichorium intybus L leaves extract and Zn^{2+} cations is investigated. The main components that are detected in Cichorium intybus L leaves are luteolin-7-O –glucuronide, caffeic acid, flavonoids, chichoric acid, quinic acid, isorhamnetine, apigenin, apigenin-7-O-L-arabinoside, uercetin -3-O-glucuronide, campheroil -3-O-

Table 1
Steel samples chemical composition.

Chemical composition	Weight percent%
Fe	99.18
Mg	0.3–0.6
S	≤0.05
P	≤0.04
C	0.08–0.13