Santolina chamaecyparissus extract as a natural source inhibitor for 304 stainless steel corrosion in 3.5% NaCl

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ABSTRACT

The inhibitive action of Santolina chamaecyparissus extract as a natural inhibitor on corrosion of 304 stainless steel in 3.5% NaCl solution was investigated by potentiodynamic polarization, EIS, and SEM techniques. The results indicate that the extract shows mixed-type inhibition behavior and inhibition efficiency of 86.9% was achieved with the addition of $1.0 \, g \, L^{-1}$ extract. Impedance curves show that increasing Santolina concentration increases charge transfer resistance and decreases double layer capacitance. The corrosion rate decreased with increasing concentration of extract and increased with the increase in temperature of the medium. Adsorption of the extract obeyed the Langmuir isotherm model.

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Introduction

Corrosion is the most devastating problem of modern technology, and pose as a serious threat to many industries. Hence, this is of paramount importance to scientists and engineers. Researchers not only study the corrosion behavior of metals/alloys in various environments, analyze the corrosion mechanism, but also finally aim to find the effective ways to protect the materials. Corrosion plays a very important role in diverse fields of industry and, consequently, in economics.

Many papers and documents are published each year about corrosion and corrosion protection of different metals. Among the metals investigated, most research about corrosion protection concentrates on iron, since iron and its alloys are the basis of modern industry.

Metals, such as iron, aluminum, copper, magnesium, and their alloys are used in a myriad of structural, marine, aircraft applications, and cultural heritage, etc. [1]. While these metals are useful because of their physical characteristics, such as stiffness and high strength to weight ratios, they are highly susceptible to corrosion in aggressive environments [2]. For example although one of the major reasons of using stainless steels is their corrosion resistance, these materials are susceptible to localized corrosion in some environments like chloride containing solutions [3].

The corrosion resistance of these materials arises from the formation of a passive layer on their surface. This is usually a duplex film constituted by an outer iron and chromium oxy–hydroxide layer and water containing compounds formed at the metal/solution interface, and an inner compact layer formed by chromium oxide [4]. The corrosion resistance of passivated stainless steel is often limited by its susceptibility to local breakdown.

Stainless steel is widely used in many fields due to their exceptional corrosion resistance. Most stainless steel equipment failures are caused by chloride ions, especially in cooling water systems.

The most commonly aggressive ion is the chloride anion found in many natural and industrial environments [5]. The passivity of stainless steel can be interrupted by breakdown of the passive films because of the existence of chloride or other aggressive anions.

Chloride ions promote breakdown of the protective passive layer, leading to the formation of corrosion pits [6,7]. Hydrochloric acid, briny water, seawater, and misty fog occurring near the sea are the main sources of chloride ions. The aggressivity of seawater and of marine environments, in general, is due to the abundance of chlorides (Cl^-). It contains about $19 \, g \, L^{-1}$ such as sodium chloride (NaCl) and magnesium chloride ($MgCl_2$).

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There are several methods available for preventing metals from corrosion, the barrier protection, galvanization, and cathodic protection by using antirust solutions and corrosion inhibitors. Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular in corrosive medium. Corrosion inhibitor is defined as the chemical substance, which decreases the corrosion rate when present in corrosion medium at a suitable concentration without significantly changing the concentration of another corrosive agent. Corrosion rate depends upon the availability of moisture, acidic–basic nature, micro-dust particles, and other agents of the environment.

An efficient method to prevent the corrosion of equipment from steel, and consequently extend their life, is the use of corrosion inhibitors. Organic molecules containing sulfur, nitrogen or oxygen atoms produce inhibitory effects toward the corrosion of steel in corrosive media.

N, O, and S atoms present in heterocyclic compounds are the sites, where adsorption is most probably occurring because of the availability of lone pair of electrons on them. These elements possess high electron density and are called as electroactive groups. The inhibition efficiency of a compound is also related to its functional groups, steric effects, and Pi-orbital character of donating electrons. They reduce the rates of either the anodic or the cathodic reactions, resulting in the reduction of the overall corrosion rate of the material.

Unfortunately, these compounds are very expensive. So the development of novel corrosion inhibitors of natural source and non-toxic type, which do not contain heavy metals, has been considered more important and desirable [8–13].

In recent years, the increasing awareness of health and ecological risks arising from the toxic organic inhibitors has drawn more attention toward the invention of non-toxic inhibitors which resists corrosion to a maximum extent, leaving least impact to mankind and nature. The natural inhibitors are green inhibitors due to the environment friendly nature.

Green corrosion inhibitors have a promising future for the quality of environment because they do not contain heavy metals or other toxic compounds. In addition, they are biodegradable and renewable source of materials [14]. Plant products are organic in nature and some of the constituents, including tannins, organic and amino acids, alkaloids, and pigments, are known to exhibit inhibiting action [15–19]. Moreover, they can be extracted from plants by simple procedures at low cost. In modern life with the scientific and technological advancement much attention is paid to safety and sanitation of the environment.

Recently, natural products, for example, lupine extract [8], *Murra yakoenigii* leaves extract [20], *Punica granatum* extract [21], *Oxandra asbeckii* extract [22], *Phyllanthus amarus* extract [23], *Ephedra sarcocarpa* extract [24], and *Calligonum comosum* extract [25] all have been reported to be effective in reducing the corrosion rate of metals in corrosive media. The inhibiting action of such extracts is often attributed to some organic constituents of the extracts (phytochemicals), whose electronic structures resemble those of conventional organic corrosion inhibitors.

The inhibition performance of plant extracts is ascribed to the presence of their composition of complex organic compounds containing nitrogen, oxygen, and sulfur atoms as well as triple bond, conjugated double bonds or aromatic rings in their molecular structures, being the major adsorption centers. However, the literature reveals that no study on the use of the *Santolina chamaecyparissus* as natural inhibitor for 304 stainless steel corrosion in NaCl solution has been done.

Knowledge of the surface chemistry of adsorbed organics is important for elucidating the mechanism of inhibitor action and, to achieve this, surface analytical techniques are required.

Inhibitors are being found to inhibit corrosion of metals by means of adsorption of ions and molecules on the metal surface. In this way a protective covering is formed around the metal surface, which denies the access of corrosive environment. They reduce the corrosion rate by polarizing the anodic and cathodic potential, reducing the diffusion rate of reactants to the metal surface, decreasing the electrical resistance of metal surface, and decreasing the double layer capacitance.

The aim of this study is to investigate the inhibition effect of the extract of *S chamaecyparissus* on 304 stainless steel corrosion in 3.5% NaCl solution by potentiodynamic polarization and electrochemical impedance spectroscopy methods. At the same time, the 304 stainless steel surfaces were examined by scanning electron microscopy (SEM).

Experimental

Preparation of plant extract

The aerial parts of *S chamaecyparissus* were collected in summer 2014 from Kashan area (Isfahan Province, Iran), dried in the shade and ground (80 mesh). An authenticated specimen of the plant was also deposited in the herbarium of the Kashan Research Botanical Garden, Research Institute of Forests and Rangelands, Kashan, Iran.

Ten grams of the powdered plant were Soxhlet-extracted with 500 mL of methanol for 8 h. Solvent removal by rotary evaporation (Buchi, Flawil, Switzerland) and drying the residue in vacuum oven at 323 K.

Electrodes and solutions

The experiments were carried out using 304 stainless steel samples of composition 0.08% C, 2.00% Mn, 0.045% P, 0.030% S, 18.00% Cr, 8.00% Ni, 0.100% N, 0.75% Si, and remaining Fe. The metal sheet was cut into rectangular samples of 1 cm^2 area soldered with Cu-wire for an electrical connection. The metal sheet then mounted onto the epoxy resin to offer only one active flat surface exposed to the corrosive environment. These samples were polished mechanically by using different grades of emery paper (220, 600, 1000, 2000, and 2500) and then further sonicated with acetone and alcohol for 15 min to remove all polishing debris. The test solution was prepared from sodium chloride (was purchased from Merck) analytical grade chemical and bi-distilled water. The extract concentrations were taken in grams per liter for all investigations.

Electrochemical measurements

Electrochemical measurements were performed in a conventional three electrode glass cell using a μ-AUTOLAB potentiostat/galvanostat model μΙΙΙ AUTO 71174 connected to a Pentium IV personal computer through a USB electrochemical interface and were carried out at 300 K. A steel specimen, a platinum wire, and a saturated (3 M) Ag/AgCl electrode were used as working, auxiliary, and reference electrodes, respectively. The open circuit potential (OCP) was obtained by immersing the working electrode in the test solution 3.5% NaCl for 60 min. Electrochemical impedance spectroscopy (EIS) measurements were carried out at corrosion potentials (OCP) across the frequency range 100 kHz−10 mHz, with a 10 mV amplitude of waveform. For potentiodynamic polarization measurements, potential was scanned in the range −200 to +200 mV at a scan rate 0.5 mV s^{-1}. All data for electrochemical measurements were analyzed using the NOVA 1.6 software.

The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic (β_a) and cathodic (β_c) Tafel slopes were generated from the software