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Performance of *Centaurea cyanus* aqueous extract towards corrosion mitigation of carbon steel in saline formation water

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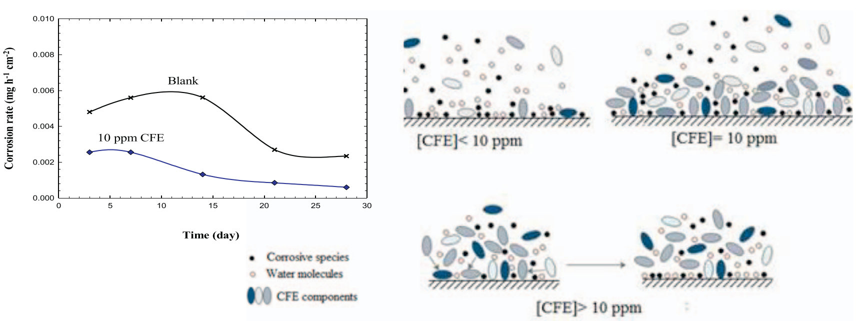
GRAPHICAL ABSTRACT



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ABSTRACT

The paper aimed to investigate and evaluate the performance of natural aqueous cornflower (*Centaurea cyanus*) extract (CFE) to mitigate carbon steel corrosion in harsh saline formation water. Weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques were all used for this assessment. The polarization results showed that CFE could act as a mixed-type inhibitor with a reasonable protection efficiency of ~69% at very low extract addition of 10 ppm. CFE retained its inhibitive effect even at elevated temperatures where it showed an inhibition efficiency of 63.95% at 313 K. The adsorption behavior of the main CFE constituents on carbon steel surface was well described following Langmuir adsorption isotherm. Thermodynamic activation parameters that govern carbon steel corrosion in blank and extract-containing saline formation water were calculated from the temperature dependence and then discussed. The effect of immersion time on the weight loss rate indicated that CFE not only keeps its inhibitive activity for carbon steel in saline water, but also improves its effectiveness over the long term immersion due to synergistic influence of the corrosion products which offer an additional protection. Structural characterization by using SEM-EDX images and FT-IR analysis further supported the obtained chemical and electrochemical results.

1. Introduction

Due to the benefits of their low cost, high strength and fabricability, carbon steel alloys have been extensively applied in transmission pipelines and storage tanks for water, liquid chemicals and petroleum products [1,2]. Corrosion of metallic materials, especially carbon steel, is an annoying problem in most industries [3,4] caused by different corrosive media mainly acids (e.g. HCl, H_2SO_4, H_3PO_4, etc.) [5], sea water [6] and saline formation water. Formation water is one of the most aggressive environments in oil fields due to the presence of huge

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amounts of dissolved salts such as chloride and sulfate salts besides some dissolved corrosive gases (e.g. CO_2 and H_2S) [7,8]. In petroleum oilfields, the disposal of formation water separated from crude oil represents a nuisance for the workers in petroleum industry because it is highly saline and polluted by oil. Hence, this water is re-injected into the oil wells so as to stimulate the crude oil stuck to rocks in the oil reservoir to be recovered making the advantage of increasing the oil productivity on one hand and the disposal of formation water on the other hand in a process called hydraulic fracturing. Before injection, some chemicals are added to this fluid such as scale and corrosion inhibitors to prevent scale deposition inside oil pipelines and also to prevent their corrosion [9,10].

Corrosion is inevitable but can be controlled [11] via several ways such as metal coatings [12], cathodic protection [13] and corrosion inhibitors [14]. The latter has been considered as the most suitable method owing to its high efficiency, economic advantages, and wide applicability in various technical sectors [15,16]. Compounds containing oxygen, nitrogen and sulfur as well as aromatic rings or multiple bonds are highly effective for inhibiting metal corrosion [17,18]. Unfortunately most of these organic compounds are toxic materials thereby imposing heavy burden on potential health hazards as well as environmental pollution.

To this level, there is a growing need to produce green corrosion inhibitors that are compatible for human health and environment [19]. In this regard, plant extracts are considered as rich sources for naturally synthesized chemical compounds that are eco-friendly, biodegradable, renewable, cost effective and can be extracted by simple methods [20,21]. Substances extracted from flowers, leaves or seeds as corrosion inhibitors encompass mixtures of organic compounds containing sulfur, oxygen, nitrogen, multiple bonds and aromatic rings [22]. Cornflower plant (also called blue bottle) has the botanical name *Centaurea cyanus*. The natural products present in such flowers are flavonoids (e.g. anthocyaninis), phenyl carboxylic acids, derivatives of some compounds including quercetin (e.g. quercetin-7-O-glucoside), caffeic acid (e.g. chlorogenic and isochlorogenic acids), apigenine (e.g. apigenine aglicone and apigenin-7-glucoside), coumarin and para-coumaric acid [23,24]. Some of these compounds are displayed in Fig. 1.

In fact, very little research has been executed on testing plants extracts for inhibiting carbon steel corrosion in saline formation water. Deyab [25] evaluated seaweed extract as a corrosion inhibitor for carbon steel in this saline aggressive medium, where the inhibition efficiency increased with the increase in extract concentration up to 93.6% at 1.2% (v/v) following Temkin adsorption isotherm but decreases with rising temperature. In one of our recent work [26], the anticorrosion performance of *Camellia sinensis* (green tea) leaves extract was scrutinized for carbon steel in produced water. It was found that the inhibition efficiency increases with increasing the extract concentration up to 77.7% at 400 ppm due to adsorbing the extract constituents on the steel surface. In the current work, we attempted to investigate and evaluate the mitigation effect of the eco-friendly CFE against corrosion of carbon steel in harsh saline formation water. The study was conducted using the chemical weight loss method and electrochemical AC/DC measurements together with surface examination of steel samples by SEM and EDX techniques in addition to FT-IR analysis.

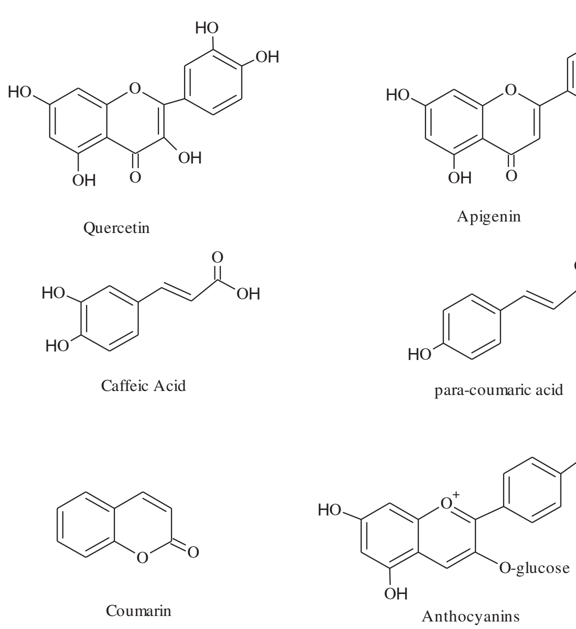

Fig. 1. Some components in *Centaurea cyanus* plant.

2. Experimental

2.1. Materials

Carbon steel samples used in the various tests have the nominal chemical composition (in wt%) of: 0.200 C, 0.350 Mn, 0.024 P, 0.003 Si and the balance Fe. The test electrodes as well as coupons for weight loss experiments were all abraded with various grades of emery papers ranging from 400 to 2500 grits, degreased with acetone, washed with distilled water and dried in air before use. The corrosive solution under study was saline formation water free from oil and grease being collected from Egyptian oilfields. The physical properties and chemical composition of the saline formation water were as previously reported in our recent work [26]. The *Centaurea cyanus* aqueous extract was purchased from Symrise Company as a trade name Extrapone® cornflower extract (CFE) and used without further purification.

2.2. Practical methods

2.2.1. Gravimetric methods

The weight loss experiments were performed according to the standard method (ASTM, G 31–72) to study the effect of CFE addition and immersion time. Carbon steel samples of dimensions 1 cm × 0.9 cm × 0.3 cm were first prepared as described above and weighed accurately using the analytical balance Precisa 205A (precision ± 0.1 mg). Then, the samples were immersed in 250 mL formation water free or containing different concentrations of CFE for two weeks. The loss in weight of each carbon steel sample was determined after cleaning from any corrosion products, washing, drying and reweighing. Values of the weight loss rate (ν in mg cm^{-2} h^{-1}) and percentage protection efficiency (η_w%) were calculated from the following two expressions [27,28]:

$$\nu = \frac{\Delta w}{t \times A} \tag{1}$$

$$\eta_w\% = \frac{\nu_0 - \nu}{\nu_0} \times 100 \tag{2}$$

where Δw is the specimen weight loss in mg, A is the specimen total surface area in cm^2 and t is the immersion time in hour, ν_o and ν are the weight loss rates of carbon steel in formation water in the absence and presence of the extract, respectively.

2.2.2. Electrochemical methods

A conventional three-electrode glass cell assembly with a capacity of 100 mL was used for all electrochemical experiments. A large platinum sheet and a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. The carbon steel working electrode was designed with a fixed exposed surface area of 0.285 cm^2. Electrochemical experiments were always carried out without stirring or deaeration of the test medium using the electrochemical workstation