

Scale- and Corrosion-inhibition Performances as well as Dispersion Capacity for Ferric Oxide of Carrot Extract

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Abstract—Carrot extract was prepared by microwave extraction method. The inhibition performance of as-prepared carrot extract against CaCO_3 scale was evaluated based on static scale inhibition test, where the morphologies of the CaCO_3 scales formed under different inhibition test conditions were observed using a field emission scanning electron microscope. The transmittance of the supernatant of as-prepared carrot extract was measured to evaluate its dispersion ability for ferric oxide. Moreover, the corrosion inhibition performance of as-prepared carrot extract for carbon steel was evaluated by measuring the weight loss of the rotating hung steel slices tested in saline water. It was found that the plant extract was able to efficiently inhibit CaCO_3 scales and had good dispersion ability for Fe_2O_3 as well as good corrosion inhibition ability for carbon steel. The scale- and corrosion-inhibition performances as well as dispersion capacity for Fe_2O_3 of as-prepared carrot extract were highly dependent on time of heating the powdered carrot-water mixture to yield the plant extract and on concentration of the plant extract as a scale- and corrosion-inhibitor. The carrot extract obtained after 3-h heating of the powdered carrot-water mixture showed the best inhibition efficiency of as high as 99.99% against CaCO_3 scale at a concentration of 10 ml/L. The best dispersion capacity for Fe_2O_3 was reached when 50 ml/L of the carrot extract was introduced into the to-be-tested solution, corresponding to a light transmittance of 43.7% of the solution. Moreover, as-prepared carrot extract at a concentration of 30 mg/L had the maximum corrosion inhibition efficiency of as high as 99.99% for carbon steel in saline water; and its corrosion inhibition rate at various tested concentrations was all above 50%, showing promising potential as a green water treatment agent.

Index Terms—carrot extract; scale inhibitor; corrosion inhibitor; scale-and corrosion-inhibition performances; ferric oxide; dispersion capacity

I. INTRODUCTION

Scale and corrosion are usually unavoidable in cooling water facilities and bring about enormous economic loss. Scales formed on the inner walls of pipelines may block

pipes, reduce heat transfer efficiency, and shorten the service life of the cooling water systems [1] which are usually accessible to calcium carbonate scale deposited from natural water. To retard and/or prevent scale formation of various pipelines, researchers have made considerable efforts to seek for feasible and practicable strategies [2]. Of various strategies for that purpose, a variety of chemical and physical methods are of particular significance in engineering, and many kinds of inhibitors have been synthesized and applied to cooling water systems for getting rid of corrosion and scale occurring on the inner walls of pipelines [3]. To name a few, inorganic scale-corrosion inhibitors like chromate and nitrite series inhibitors, polyphosphate salt scale-corrosion inhibitors, and phosphate-based water-treatment agents represent commonly used traditional scale-corrosion inhibitors [4]. Polyphosphate salt scale-corrosion inhibitors have found wide application in industry, due to their good corrosion inhibition and scale inhibition performance as well as high inhibition efficiency[5], but they can cause water eutrophication after they are poured into water. Phosphate-based water-treatment agents possess fair inhibition performance but are liable to form Ca-phosphonate precipitates. More fatally, all these conditional inhibitors and water-treatment agents have high toxicity and poor biodegradability and cause serious damage to environment. In this respect, it is imperative to develop green water-treatment agents, e.g., low or non-phosphorus environmentally-friendly water-treatment agents [6]. To date, polyaspartic acid, polyepoxysuccinic acid, alkyl epoxy carboxylic acid and natural polymers are currently available representative green water treatment agents[7]; and the extracts of some natural plants, such as bamboo leaf extracts[8], garlic extracts [9], rice bran extracts [10] and so on may be potential novel high-performance scale- and corrosion-inhibitors.

Encouraged by that perspective and in response to tougher environmental regulations, we have prepared carrot extract from carrot-roots and investigated its scale-

and corrosion-inhibition performances in the present research. The carrot extract was chosen as a potential scale and corrosion inhibitor, because it contains some chemical compounds such as cellulose, saccharides and ascorbic acid which are effective inhibitors against CaCO_3 scale [11] and it is cheap as a green inhibitor.

This article reports the anti-scaling efficiency of as-obtained carrot extract for calcium carbonate, the transmittance of the supernatant of the plant extract in relation to its dispersion ability for ferric oxide, the corrosion inhibition performance of the plant extract for carbon steel plates in water, and the morphological features of scale precipitates.

II. EXPERIMENTAL PROCEDURE

A. Instruments and agents

Instruments used in the present research include DF-101S thermostatic magnetic stirrer, 722 grating spectrophotometer, high-performance liquid chromatograph (HPLC; Shimadzu Type LC-10AD), ultraviolet-visible light (UV-vis) spectrometer (Shimadzu, UV-1650PC), FA1004A electronic balance, DHT thermostatic electric jacket equipped with a stirrer, AUATAR-360 Fourier transform infrared spectrometer (FTIR) and JSM-7001F field emission scanning electron microscope (FESEM). Analytical grade reagents maleic anhydride, urea, ethanol, acetone, sulfanilic acid, calcium chloride, and sodium tetraborate were used in the present research.

B. Preparation of carrot extract

Carrot extract is an extract prepared from the root of Chinese carrot. Microwave treatment could improve the extraction of carrot when the carrot (10g) were extracted with ethyl ethanoate and anhydrous ethanol at 2:1 in volume at 50 °C water bath for 1 h after 10 second microwave processing. Then the mixture were centrifuged. The filtrate was concentrated by circum-evaporator for 30 minutes at 3900r/min, and the carrot extract was obtained with cyclohexane and ethanol as extractant [12].

The procedures for preparing carrot extract have not been reported elsewhere. Briefly, 100 g of carrot extract was added in deionized water until a total volume of 1 L was reached. Resultant carrot extract-water mixture was heated at 80 °C for 3 h before it was cooled to room temperature in air. As-cooled mixed solution was stored at ambient conditions for 12 h and then filtered. The filtrate was analyzed by means of HPLC and UV-vis to determine the content of cellulose, saccharides and ascorbic acid in the carrot extract. It has been confirmed in our previous research that as-prepared carrot extract contains approximately 14.74% (mass fraction; hereinafter inclusive) of cellulose, 23.05% of saccharides, and 33.77% of ascorbic acid. The as-prepared carrot extract is directly used as an inhibitor in this research [13].

C. Evaluation of scale- and corrosion-inhibition performances of carrot extract

1. Inhibition performance of carrot extract against CaCO_3 scale

Static scale inhibition tests were conducted according to China National Standard method (GB/T 16632-1996) to evaluate the scale inhibition efficiency of carrot extract against CaCO_3 scale [13]. Briefly, in a volumetric flask (capacity 1 L) was prepared an aqueous solution of 250 mg/L Ca^{2+} and 250 mg/L HCO_3^- . Resultant solution was uniformly mixed with a known amount of carrot extract as the scale inhibitor and allowed to react in a water bath at 80 °C for 6 h. At the end of the reaction, resultant mixed solution was collected and cooled to room temperature. The concentration of Ca^{2+} in the solution was measured using titration of ethylene diamine tetracetic acid (EDTA). The scale inhibition efficiency of the carrot extract against CaCO_3 scale is calculated as:

$$\eta_{\text{CaCO}_3} = \frac{V_1 - V_0}{V_2 - V_0} \times 100\% \quad (1)$$

Where V_0 (ml) is the volume of EDTA consumed by a certain amount of calcium cation in the absence of scale inhibitor in to-be-tested solution (control test); V_1 is the volume of EDTA consumed by a certain amount of calcium cation in the presence of scale inhibitor in to-be-tested solution; and V_2 is the volume of EDTA consumed by all calcium cations in to-be-tested solution.

2. Ability of carrot extract to disperse ferric oxide

A solution containing 150 mg/L Ca^{2+} and 10 mg/L Fe^{2+} was prepared. The pH value of the solution was adjusted to 9.0 with borax. Then the solution was evenly mixed with a known amount of carrot extract. Resultant mixed solution was stirred for 15 min and then heated at 50 °C for 5 h before being cooled to room temperature and centrifugally separated. The transmittance of the supernatant was measured with a 722-spectrophotometer (710 nm, 1 cm cuvette; in relation to distilled)[14]; and it was supposed that a smaller light transmittance referred to a better dispersion ability of the carrot extract.

3. Corrosion inhibition efficiency of carrot extract

Corrosion tests of rotating hung steel slices in saline water were carried out at a temperature of 45 °C, rotating speed of 80 rev/min, and a pre-coating time of 72 h to evaluate the corrosion inhibition efficiency of the carrot extract. Briefly, 1L of pre-coating solution containing 0.555 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.493 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was mixed with a known amount of carrot extract as the inhibitor. Into resultant mixed solution was added 0.168 g of NaCl, followed by dilution to 1 L. The corrosion rate and corrosion inhibition rate of carbon steel slices (surface area: 28.00 cm²; mass fraction: C, 0.17% ~ 0.23% Si, 0.17% ~ 0.37% Mn, 0.35% ~ 0.65% Cr, ≤0.25% Ni, ≤0.3% Cu, ≤0.25% and balance Fe) in as-prepared dilute mixed solution were determined

according to China National Standard GB/T 18175-2000 for “Performance measurement of corrosion inhibitor in water-treatment with arotating apparatus” [15]. The corrosion efficiency is calculated as:

$$\eta = \frac{87600 \times [(m_1 - m_0) - \Delta m]}{S \times D \times T} \quad (2)$$

Where m_1 is the mass of carbon steel hung slices before test; m_0 is the mass of carbon steel hung slices after test; Δm is the mass loss of carbon steel hung slices caused by washing in acid; S is the surface area of carbon steel hung slices (28 cm²); T is time of test (72 h); and D is the density of carbon steel hung slices (7.85 g/cm³).

III. RESULTS AND DISCUSSION

A. Influence of carrot extract concentration on inhibition efficiency against CaCO₃ scale

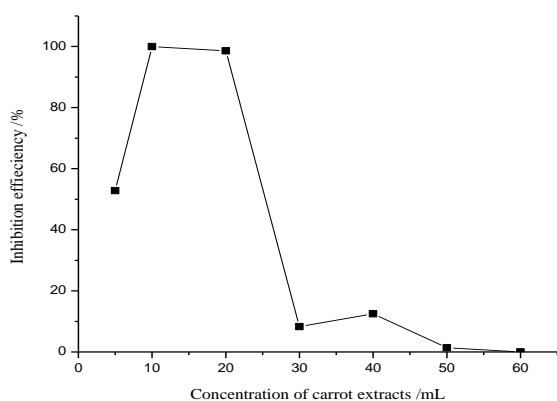


Figure 1. Influence of concentration of carrot extract on inhibition efficiency against CaCO₃ scale.

Figure 1 shows the variation of inhibition efficiency of carrot extract scale inhibitor against CaCO₃ scale with concentration. The inhibition efficiency against CaCO₃ scale increased with increasing concentration of carrot extract. The maximum inhibition efficiency, as high as 99.99%, was reached at an inhibitor concentration of 10 ml/L. With further increase of concentration of the scale inhibitor from 10 ml/L to 20 ml/L, the inhibition efficiency remained nearly unchanged. However, when the concentration of the scale inhibitor was beyond 20 ml/L, the inhibition efficiency decreased dramatically. This may be closely related to the chelating function of cellulose (14.74%), saccharides (23.05%), and ascorbic acid (33.77%) contained in the carrot extract for Ca²⁺. Resultant Ca²⁺-chelates can be adsorbed on the surface of the scale, leading to variation of scale inhibition efficiency with varying concentration. As the concentration of the scale inhibitor increases, the bond of the inhibitor with Ca²⁺ ions is enhanced, and the inhibition efficiencies increase[16]. When the concentration of the scale inhibitor is beyond the optimal value (e.g., 20 mg/L in the present research), Ca²⁺ ions in the solution

seemingly may be almost completely chelated, the inhibition efficiency, however, does not increase but decreases with further rising concentration of the scale inhibitor, largely due to the harmful interactions of various components in the carrot extract [17].

B. Influence of heating time of carrot extract on inhibition efficiency against CaCO₃ scale

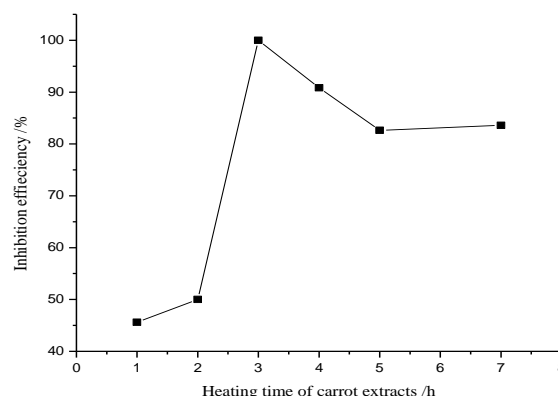
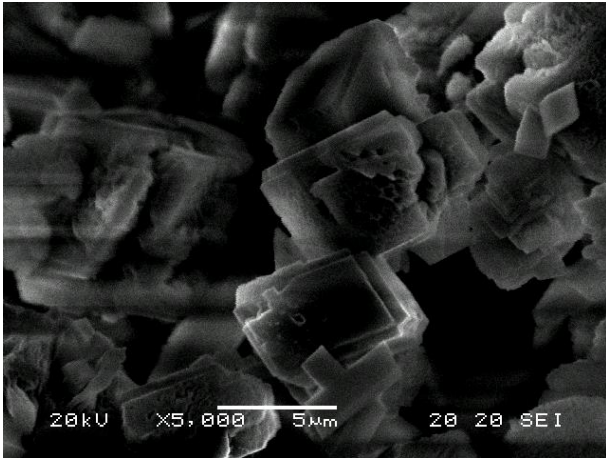


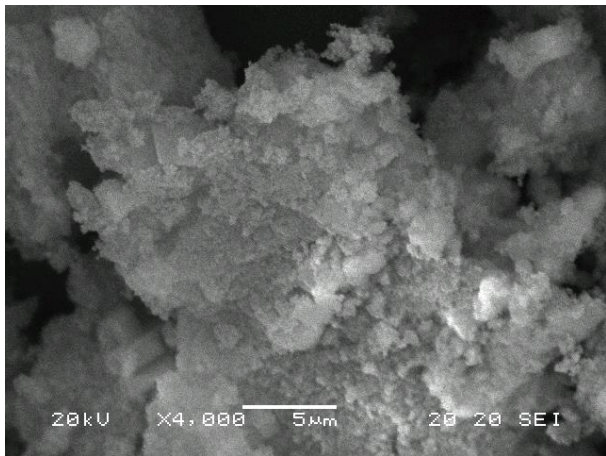
Figure 2. Influence of heating time of carrot extract on inhibition efficiency against CaCO₃ scale.

Figure 2 shows the effect of heating time of the scale inhibitor on its scale inhibition efficiency. In general, the scale inhibition efficiency increased with extending heating time. The maximum inhibition efficiency, as high as 99.99%, was reached at an inhibitor heating time of 3 h. Beyond 3 h, the scale inhibition efficiency decreased gradually with further extension of heating time up to 5 h at which an inhibition efficiency of 84.5% was obtained. Above 5 h, the inhibition efficiency leveled off with further increase of heating time. Thus it can be inferred that appropriate heat treatment of the carrot extract helps to enhance the chemical bonding of the functional groups such as OH⁻ and -COOH in cellulose, saccharides, and ascorbic acid with Ca²⁺. However, the adsorption of the scale inhibitor to scale is exothermic. As a result, the adsorption capacity is weakened and the adsorbed quantity is reduced with extending heating time, leading to decreased scale inhibition efficiency at a too large heating time (above 3 h).

C. FESEM observation of CaCO_3 scales formed in the absence and presence of carrot extract as a scale inhibitor



(a) CaCO_3 deposit formed in the absence of carrot extract inhibitor



(b) CaCO_3 deposit formed in the presence of carrot extract inhibitor

Figure 3. SEM images of CaCO_3 deposits in the absence (a) and presence (b) of carrot extract inhibitor.

Figure 3 shows the SEM images of CaCO_3 scale deposits formed in the absence and presence of carrot extract as the scale inhibitor. CaCO_3 deposit with regular shape, glossy surface, and compact arrangement was formed when no carrot extract was used [figure 3(a)][18]. On the contrary, when the carrot extract was added into the solution as a scale inhibitor, flower-like floppy CaCO_3 deposit was formed [figure 3(b)][19]. The reason may lie in that the carrot extract is able to block the crystal growth habits of CaCO_3 , resulting in irregularly shaped (flower) floppy CaCO_3 scale which can be removed easily[20].

D. Influence of concentration of carrot extract on dispersion of ferric oxide

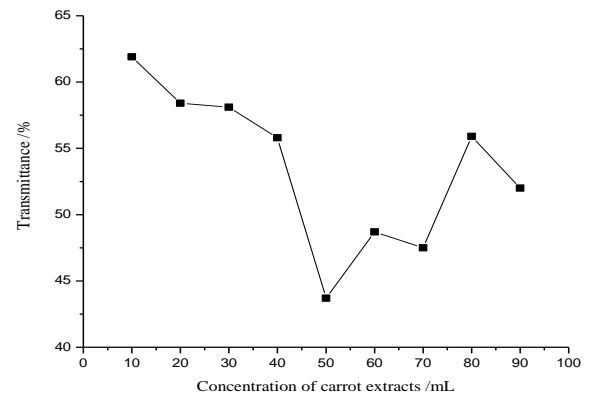


Figure 4. Influence of carrot extract concentration on dispersion of ferric oxide.

The relationship between the carrot extract concentration and the transmittance of the tested solutions is shown in Figure 4. It seems that the transmittance of the tested solutions change complicatedly and irregularly with varying concentration of the carrot extract. The light transmittance of the tested solutions decreased with increasing concentration of carrot extract up to 15 ml/L, corresponding to improved dispersion efficiency for Fe_2O_3 . The best dispersion efficiency for Fe_2O_3 was reached when 50 ml/L of carrot extract was introduced into the tested solution, corresponding to 43.7% of light transmittance of the solution. When the concentration of the carrot extract was increased to 50~70 ml/L, the dispersion efficiency for Fe_2O_3 varied slightly; then it tended to decline to some extent with increasing dosage of the scale inhibitor from 70 ml/L to 90 ml/L. This can be ascribed to the fact that the scale inhibitor can be absorbed on the surface of microcrystal grains or scale nucleus via physical and chemical adsorptions. As a result, a double electron layer is formed to change the radical charge status of the particles and avoid the formation of scale via inter-particles exclusiveness [21], leading to easy dispersion and hence greatly increased dispersion capacity of ferric oxide particles in water[22].

E. Corrosion inhibition efficiency of carrot extract for carbon steel in saline water

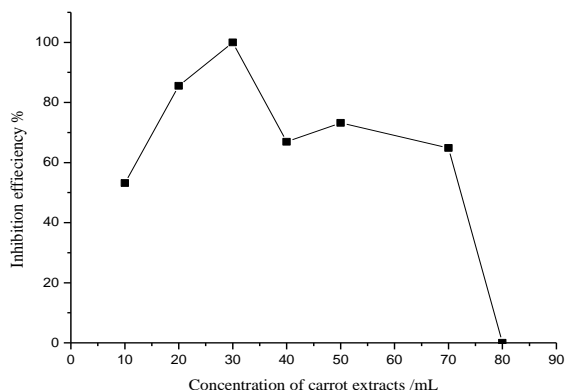


Figure 5. Influence of carrot extract concentration on corrosion inhibition efficiency.

Figure 5 shows the influence of carrot extract concentration on corrosion inhibition efficiency. The anticorrosion efficiency of the carrot extract increased with rising concentration, and the maximum corrosion inhibition efficiency, as high as 99.99%, was reached at a carrot extract concentration of 30 mg/L. The corrosion-inhibition rate decreased lightly when the concentration of the carrot extract was increased from 30 ml/L to 40 ml/L. And it remained nearly unchanged in a concentration range of 40~70 ml/L. Beyond 70 ml/L, the corrosion-inhibition rate almost linearly decreased with further increasing concentration. In general, a corrosion-inhibition rate of more than 50% was reached at various concentrations of the carrot extract, pointing to good corrosion inhibition performance of the carrot extract as a corrosion inhibitor. The reason lies in that the carrot extract consists of cellulose, saccharides, and ascorbic acid whose hydroxyl and carboxyl groups contain oxygen atoms with lone-pair electrons [23]; as a result, those organic components can form covalent bonds with metal and/or be chemisorbed onto the metal surface forming a protective film thereon, thereby preventing metal from being corroded [24].

IV. CONCLUSION

Carrot extract was obtained *via* facile extraction of powdered carrot in water at a moderate temperature of 80 °C and follow-up filtration in response to the requirement for “green chemistry”. The scale- and corrosion-inhibition performances as well as dispersion capacity for ferric oxide of as-obtained carrot extract were investigated. It has been found that as-prepared carrot extract is able to efficiently inhibit CaCO₃ scale and has good dispersion capacity for Fe₂O₃ as well as good corrosion inhibition ability for carbon steel in saline water. The performances of the carrot extract highly depend on the time for heating the carrot roots in water and on concentration of the extract as well. When

the powdered carrot-water mixture is heated at 80 °C for 3 h and the concentration of resultant carrot extract is fixed at 10 ml/L, the inhibition efficiency against CaCO₃ scale can reach as high as 99.99%. Besides, when 50 ml/L of carrot extract is introduced into the to-be-tested solution, the best dispersion capacity for Fe₂O₃ is reached, corresponding to a light transmittance of 43.7% of the solution. Further, the maximum corrosion inhibition efficiency, as high as 99.99%, is reached at a carrot extract concentration of 30 mg/L, and the corrosion inhibition rate of the carrot extract at various tested concentrations is all above 50%. In one word, as-prepared carrot extract may be used as a potential green water treatment agent.

ACKNOWLEDGMENT

The authors wish to thank Henan University. This work was supported in part by a grant from Henan Province Science and Technology Office..

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