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Assessment of aqueous extract of Gypsophila aretioides for inhibitory effects on calcium carbonate formation

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Abstract: The aqueous extract of Gypsophila aretioides roots as a “green” or eco-friendly inhibitor of carbonate calcium formation was investigated. The presence of chelating factors such as polyphenol compounds and foaming agents in the plant extract was assessed. Atomic absorption spectroscopy (AAS) demonstrated the ability of G. aretioides extract for dissolution of the carbonate calcium precipitates. Moreover, conductivity measurements revealed that the G. aretioides extract could efficiently retard sedimentation of carbonate calcium from a brine solution of calcium ions exposed to carbonate ions by adding Na₂CO₃ to the system solution. In addition, chronoamperometry was performed for a period of 3 h by polarizing the steel electrode to -0.9 V (vs. SCE) at 40°C. The presence of G. aretioides extract at a concentration of 10% (w/v) in chronoamperometry prevented the precipitation of CaCO₃ on the steel electrode surface. This was confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses which showed an absence of precipitates and lack of calcium ions on the steel electrode after 3 h chronoamperometry, respectively. However, further studies are required in order to amend the characteristics of G. aretioides extract to render it more applicable as an eco-friendly, cost-effective, anti-scale agent for a wide range of industrial applications.

Keywords: scale inhibition; carbonate calcium; Gypsophila aretioides; root extract; chronoamperometry

1 Introduction

Surface and ground water supplies are exposed to different types of minerals. Some low soluble minerals, in particular, calcium carbonate, exhibit high potential for precipitation from water bodies on the water flow path or on surfaces that are exposed to water, particularly at high temperatures. Moreover, calcium carbonate precipitation occurs on surfaces which are exposed daily to hot or boiling water such as kettles or on bathroom tapware. Calcium carbonate precipitates are known as “scale” in industrial utilities. Scale appearing on heat transfer equipment is a common problem in many industrial processes which deal with high-temperature water such as heat exchangers, boilers and cooling towers [1,2]. The destructive effects of scale and technical problems including reduction of thermal and mechanical efficiencies, deposit-corrosion phenomenon and, foremost, billions of dollars in damage costs to related industries have attracted the attention of researchers in an effort to reduce these problems [2,3].

For the first time, Meyer [4] reported that a number of additives or impurities exhibited marked effects on the growth rate of the crystal facets even at very low concentrations. Subsequent research studies evaluated different chemical scale inhibitors to reduce the formation of calcium carbonate crystals and scales, as summarized by MacAdam et al. [2]. Despite the fact that calcium carbonate deposition can be ameliorated by chemical, physical or biological methods [2], chemical approaches are widely used in various fields of industry. The conventional method of controlling precipitate formations is through the use of chemical compounds known as scale inhibitors. The frequently used scale inhibitors are synthetic polymers such as polyphosphate, polyphosphonate, polycarboxylate and polyacrylic acid [5,6]. They can inhibit the formation of the calcium and magnesium precipitates at low concentrations if they are properly employed. However, the release of such chemical materials into the aquatic ecosystem has
been criticized. Some of the chemical scale inhibitors are not biodegradable and thus accumulate, leading to environmental risks. Moreover, some of the inorganic scale inhibitors released into the receiving water sources are consumed by aquatic plants (e.g. algal species) as nutrients. The subsequent growth of aquatic plants is intensified to the extent that the color of the seawater changes to green in some areas, a phenomenon known as “Eutrophication” or “green soup” disease [7]. Substituting alternative low-risk compounds to control the precipitate formation may greatly reduce these environmental risks. In this regard, non-nitrogenous, non-phosphorus, and biodegradable polymers and plant-derived inhibitors are of particular importance [3,8]. In the last decade, new green scale inhibitors have been synthesized which are more eco-friendly compared to conventional scale inhibitors [3,9]. Several reports have been made on green scale inhibitors that are environmentally acceptable compared to conventional inhibitors; for example, polyaspartic acid (PASP) [10], polyepoxysuccinic acid (PESA) [11,12], and carboxymethylinulin (CMI) [13] have shown to be the most promising green scale inhibitors to date.

In addition, plant-derived compounds from various plant genera have been studied as possible scale precipitation inhibitors. The use of plant extracts such as olive leaf [14], fig leaf [15], tobacco [16], Paronychia argentea extract [17], palm leaf extract [18] and soybean oil [19] as effective scale inhibitors has been reported. The inhibitory effect of plant extractions on scale deposits has recently been investigated using both dynamic and static tests in experimental studies [3]. Plants are invaluable sources for obtaining natural green materials. Typically, green or eco-friendly compounds have three outstanding properties which include biodegradability, low toxicity for living organisms and extractability from renewable resources [19]. The extraction process is typically simple and inexpensive using easily accessible and widely available plant species [9,20]. Therefore, the continued study, development and utilization of plant extracts as effective, eco-friendly sources for debilitating scale formations is very promising.

This study aims to evaluate the capability of aqueous extract of G. aretioides to reduce the deposition of calcium carbonate scale. Gypsophila is a widely available, perennial herb [21] which typically grows in calcareous soils and therefore appears to synthesize compounds that can dissolve calcium salts and accumulate them in aerial organs. G. aretioides is a common species of the genus which is widely distributed in northern Iran.

2 Experimental

All chemicals and reagents were of analytical grade and prepared by Merck Co., Germany. Plant extract was obtained from G. aretioides. The steel sheeting and its analysis were prepared by Fouladrizan Co., Iran, according to the American Iron and Steel Institute (AISI) standards.

2.1 Gypsophila aretioides roots, collection and aqueous extraction

The roots of Gypsophila aretioides were collected from steppe regions of Mahdishahr located in Semnan Province, Iran, in July 2015, and identified by Dr. Atefeh Pirani, a plant taxonomist at the Faculty of Science, Department of Biology, Ferdowsi University in Mashhad, Iran. The voucher specimen (3881-TMRC) is deposited at the Herbarium of Traditional Medicine and Materials, Medical Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran. G. aretioides, its habitat, aerial parts as well as roots are shown in Figure 1. In order to obtain an aqueous extract from the roots of G. aretioides, the roots were washed and then oven-dried at 70°C for two hours. Subsequently, they were grated and weighed for 5 g dried mass which was then transferred to a vessel containing 100 ml distilled water at boiling point and incubated for 15 min, then the solid phase was removed using filter paper (Whatman Grade No. 42). The liquid phase was concentrated and dried to obtain the crude extract of the plant roots.

2.2 Determination of dominant metals in soil

Soil samples were collected from the habitat of the roots of G. aretioides and analyzed to determine the dominant

Figure 1: A display of Gypsophila aretioides: (a) habitat (b) aerial parts and (c) the roots.
existing metal ions. \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+ \) and \( \text{K}^+ \) were quantified in soil saturated extract by the Mechanical Soil Laboratory of Tehran Transportation Department according to standard methods.

### 2.3 Assessment of polyphenol compounds and foaming agents in root extract

Polyphenols are predominately found in plant-derived substances. They are considered chelating agents which form a complex with calcium cations via their carboxyl and hydroxyl groups, thereby inhibiting the nucleation step and thus the formation of precipitates [3]. The total content of polyphenols was measured using the Folin-Ciocalteu method according to slight modifications by Biju et al. [22]. To carry out the test, \( G. \ aretioides \) extract (0.2\% (w/v)) and Gallic acid solutions (20, 40, 60, 80 and 100 \( \mu \text{g/ml} \)) were prepared in distilled water as the sample and standard solutions, respectively. In each experiment, 1ml extract or standard solution was added to a 25-ml volumetric flask, containing 9 ml distilled water. A blank sample was prepared using distilled water. One ml Folin-Ciocalteu phenol reagent was added to each flask and shaken for 5 min. Subsequently, 10 ml 7\% (w/v) \( \text{Na}_2\text{CO}_3 \) solution was added to each mixture and the volume was then augmented up to the mark. The mixtures were incubated at room temperature for 90 minutes and the absorbance against the blank sample was determined at 550 nm with a UV-Visible spectrophotometer. The total content of polyphenols was expressed as \( \mu \text{g} \) Gallic acid Equivalents (GAE).

In addition, foaming agents are amphiphilic molecules which form aggregates or micelles at increased concentrations in which calcium ions are entrapped and thus rendered unavailable to carbonate anions, thereby inhibiting formation of precipitates. The presence of foaming agents in the aqueous extract content was qualitatively investigated. Aqueous solution of \( G. \ aretioides \) extract was vigorously vortexed for 2 min and foam formation was detected.

### 2.4 Effect of \( G. \ aretioides \) extract on dissolution of the precipitates

Dissolution of calcium carbonate precipitates was evaluated in the presence of \( G. \ aretioides \) extract. To this end, 33 mg \( \text{CaCO}_3 \) was transferred to different Erlenmeyer flasks and a specified volume of extract stock solution was added to each flask, the volume of each being augmented to 100 ml to make a supersaturated solution at room temperature [17]. Flasks were shaken for 120 min at 150 rpm. Subsequently, the contents of each flask were filtered using Whatman paper to separate the undissolved portion. The filtrate was analyzed for calcium ion concentration by atomic absorption spectroscopy. Calcium ion concentration in each sample was quantified by an atomic absorption spectrometer (varian AA240) equipped with a calcium lamp (\( \lambda = 239.9 \text{ nm} \)). Calcium ion concentrations were calculated from a standard curve for absorption versus calcium ion concentration in a range of 0 to 350 ppm prepared by serial dilutions of the aqueous calcium chloride solution.

The dissolving percentage was estimated for each test as shown in Eq. 1:

\[
\text{Dissolving efficiency (\%)} = \frac{C_i}{C_0} \times 100
\]

where, \( C_0 \) is total mg of calcium ion in supersaturate solution (120 mg/l), \( C_i \) is the concentration of calcium ion in solution after treatment with plant extract. Due to the fact that calcium ions are naturally present in root extract, the amount of \( \text{Ca}^{2+} \) ions in aqueous extract solution was determined and considered for calculations of the dissolving efficiency in each sample.

### 2.5 Effect of \( G. \ aretioides \) extract on inhibition of sedimentation in solution

In order to determine the inhibitory impact of \( G. \ aretioides \) extract on sedimentation of calcium carbonate precipitates from solution, conductivity tests were performed according to Drela et al. [23]. Firstly, all parts of the conductometry set-up including the glass container, mechanical stirrer and conductivity sensor were rinsed with \( \text{H}_2\text{SO}_4 \) (1 M), followed by double-distilled water, to remove any deposits which could lead to measurement error.

To begin the experiment, different volumes of the stock solution of root extract were added to each acid-cleaned flask containing 5 ml of \( \text{CaCl}_2 \) solution (0.1 M). The content of each flask was augmented with double-distilled water up to 100 ml. Each mixture was stirred during the titration with \( \text{Na}_2\text{CO}_3 \) (0.1 M). For all experiments, conductivity was measured continuously after each addition of 0.2 ml titrant solution to stirring mixture until a constant value of conductivity was attained [23].
2.6 Effect of *G. aretioides* extract on inhibition of scale formation on steel surface

The ability of *G. aretioides* extract to reduce the calcium carbonate deposition on the surface of a steel electrode was investigated by chronoamperometry techniques. According to [14], calcium carbonate precipitations on metal surfaces at cathodic potential (-0.9 V versus SCE) were measured. This method was based on several oxidation-reduction reactions in the vicinity of the electrodes. When potential is applied, oxygen molecules (O$_2$) are reduced to hydroxyl groups (OH$^{-}$) through the reaction 1.

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^-
\]  

(Reaction 1)

Consequently, accumulation of OH$^{-}$ around the electrode results in pH increase which, in turn, causes the calcium carbonate precipitation on the electrode [24] according to the reactions 2 and 3:

\[
HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \text{ (in bulk)}
\]  

(Reaction 2)

\[
Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \text{ (at the interface)}
\]  

(Reaction 3)

where, the carbonate anions and calcium cations participating in these two reactions are provided by the ions present in brine solution in which the chronoamperometry experiment is carried out.

In this regard, *G. aretioides* extract was evaluated for decreasing the last reaction and therefore restraining or retarding the electrode fouling. A three-electrode cell system was employed for all electrochemical experiments; platinum sheet and saturated calomel electrodes were utilized as the counter and reference electrodes, respectively. The working electrode was steel with a weight percent composition of C, 0.081; Si, 0.020; Mn, 0.4; P, 0.0098; S, 0.0094; Al, 0.056; Ni, 0.031; Co, 0.0061; Cu, 0.028; balance Fe. The steel was embedded in epoxy resin in a manner that left one side uncovered (approx. 1cm$^2$) as the exposed surface (Figure 2). Prior to experiments, electrodes were serially washed with DD-water, analar grade (A.R.) ethanol and DD-water to provide a clean surface. Chronoamperometry measurements were performed through a potentiostat PARSTAT 2273 in brine solution (NaCl, 0.7 M; NaHCO$_3$, 0.0025 M; Na$_2$SO$_4$, 0.028 M and CaCl$_2$, 0.01 M, pH = 7 ± 0.5) including 0, 5, 10 and 20% (w/v) *G. aretioides* extract [14]. Chronoamperometry records were graphed during a period of 3 h by polarizing the steel electrode to −0.9 V (vs. SCE) at 40°C in each test solution. The graphs express

![Figure 2: The steel embedded in the epoxy resin used for chronoamperometry experiments.](image)
3 Results and discussion

3.1 Aqueous extract of G. aretioides roots, extraction yield, polyphenol assessment and foaming agents

*G. aretioides* in various steps of extraction from root powder to extract form is shown in Figure 3. Results show that 200 ± 10 mg dried extract was obtained from 5 g root powder. This means a 4% extract production yield.

The presence of polyphenols was evaluated using the Folin-Ciocalteu method. In this method, a standard graph was plotted to show the absorption at 550 nm against the concentration for different Gallic acid solutions (Figure 4). A regression line with R-squared more than 0.99 demonstrated that the standard graph was suitable for estimation of polyphenol concentration from absorption data. A 0.2% (w/v) solution of *G. aretioides* extract in distilled water showed absorption of 0.5063 at 550 nm which is equivalent to approximately 198 ± 20 µg/ml of polyphenol. Calculations estimated that polyphenol constitutes approximately 10 ± 1 percent of *G. aretioides* extract. The presence of polyphenolic substances is expected to be a scheme for capturing the calcium ions and keeping them bound to $\text{CO}_3^{2-}$, thus inhibiting calcium carbonate precipitation [14]. Chaussemier et al. claimed that phenolic molecules may inhibit the nucleation step by formation of a complex with calcium cations via their carboxyl and hydroxyl groups [3]. This hypothesis is strengthened when the calcium ions are found both in soils collected from the *G. aretioides* habitat (Table 1) and an aqueous solution of *G. aretioides* extract detected using atomic absorption spectroscopy (data not shown). This may be due to the fact that *G. aretioides* contains active agents such as polyphenolic substances which may enhance absorption of calcium ions from the habitat soil. This phenomenon is further supported by Abdel-Gaber [15] where *Ficus carica* L. grown in calcareous soil conditions showed calcium accumulation in the leaves, and fig leaf extract revealed scale inhibition activity in an alkaline CaCl2 brine solution.

In addition, formation of stable foam with a 2 cm height in aqueous solution of root powder demonstrated the presence of foaming agents in *G. aretioides* extract solution. The foaming agents present in plants are usually saponins which may also improve the dispersant properties of the extract which would, in turn, help reduce precipitation of calcium carbonate. The presence of saponin compounds in the *Gypsophila* genus has been studied and demonstrated previously by Krasteva et al. [21]. These foaming agents are amphipathic substances which form micelles at increased concentrations which, in turn, entrap the calcium cations and restrict their precipitation.

![Figure 3: An illustration for different stages of Gypsophila aretioides extraction](image)

![Figure 4: Standard graph for Folin-Ciocalteu method](image)

![Table 1: Metal ion analysis of soil samples collected from the habitat of Gypsophila aretioides](image)
3.2 Dissolution of the precipitates by *G. aretioides* extract

The calcium ion concentration in the presence of different amounts of root extract was determined using the atomic absorption method. Regarding the initial concentration of calcium ions in supersaturated solution, the dissolving efficiency of *G. aretioides* extract is calculated in Eq. 1. A standard graph for absorption versus calcium ion concentration is depicted using calcium chloride solutions (Figure 5a). \( R^2 \) near the 1 demonstrates the linear correlation of absorption and concentration in ranges of 0-350 ppm of calcium ion. The impact of different amounts of root extract on percentage of solubilized calcium ions is shown in Figure 5b. The highest efficiency occurred when the concentration of *G. aretioides* extract fell between 45 to 60% (w/v). Increase in extract concentration to more than 60% (w/v) reduced dissolution of calcium. This may be due to the fact that once the extract concentration exceeds 60% (w/v), calcium ions existing in the root extract reach the equilibrium with solid phase ions and therefore further solubilization of Ca\(^{2+}\) is inhibited in the system.

3.3 Inhibition of sedimentation in solution by *G. aretioides* extract

Conductivity measurements in calcium chloride solution in the presence and the absence of different *G. aretioides* extract concentrations were carried out by means of a sodium carbonate titration method to determine the ability of root extract to retard precipitate formations. This rapid method was developed by Drela et al. [23] for the first time. This method is based on the assumption that the adding of Na\(_2\)CO\(_3\) causes an increase in conductivity. This behavior continues up to supersaturation state where CaCO\(_3\) begins to precipitate and thus salting out of Ca\(^{2+}\) from solution occurs which results in decreased conductivity. When precipitation of CaCO\(_3\) is completed, adding Na\(_2\)CO\(_3\) causes Na\(^{+}\) ions and a raise in conductivity. In this way, the presence of inhibitor substances can postpone the formation of CaCO\(_3\) and therefore leads to a drop in conductivity levels.

Figure 6 demonstrates that different amounts of *G. aretioides* extract can inhibit the formation of calcium
carbonate in such a way that conductivity reduction is delayed in comparison to experiments performed in the absence of root extract. Similar observations were reported for *Punica granatum* extracts indicating that the presence of *P. granatum* extract impedes the supersaturation [25]. Furthermore, when the concentration of *G. aretioides* compound exceeded 45% (w/v), increasing the extract concentration increased the level of precipitation of CaCO$_3$. This outcome may be due to the existence of calcium ions in the *G. aretioides* extract which can lead to a disturbance in the system and ion equilibrium and consequently render sufficient calcium ions to begin calcium carbonate precipitation.

### 3.4 Inhibition of scale formation on steel surface by *G. aretioides* extract

Chronoamperometry is the most commonly used technique to investigate scaling processes. According to the fundamentals of this technique described in detail in the Experimental section, in the chronoamperometry method, when the potential is applied, the hydroxyl groups are released into the solution and result in precipitation of CaCO$_3$ on the steel electrode. A precipitate layer of CaCO$_3$ forms progressively on the electrode surface, leading to a decrease of current intensity. When the surface of the working electrode is totally covered by scale, the current density reaches a steady-state called the residual current, the value of which depends on the porosity of the scale layer [3].

Inhibitory compounds can prevent the reaction of CaCO$_3$ formation on the electrode. *G. aretioides* extract at different concentrations was added to the brine used in chronoamperometry experiments. In Figure 7, root extract exhibited inhibitory activity against deposition of CaCO$_3$ on the electrode in such a way that current intensity increased once the *G. aretioides* extract was added to the brine. However, effective performance of extract was detected at concentrations below 20% (w/v). Abdel-Gaber et al. [25] reported similar results when they evaluated the scale inhibition activity of *Punica granatum* extract. Chronoamperometry measurements showed that *P. granatum* extract impedes the crystal growth stage by retarding the nucleation step, so that the current density increased when the concentration of the *P. granatum* extract increased from 10 to 100 mg/L. Moreover, Belarbi et al. [17] carried out chronoamperometry experiments to test the scale inhibition performance of aqueous *Paronychia*

![Figure 7](image-url)

*Figure 7: Chronoamperometry curves for steel electrode in the brine solution in the absence and the presence of different concentrations of *Gypsophila aretioides* extract at 40°C.*
Figure 8: Scanning electron microscopy (SEM) and energy dispersive X-rays spectroscopy (EDX) images of steel electrode after 3 h chronoamperometry in (a) the absence, and the presence of (b) 5%, (c) 10 and (d) 20% Gypsophila aretioides extract.
argentea extract which showed effective scale inhibition properties at a concentration of 70 ppm. Similar observations were recorded for tobacco rob extract [16] and Paronychia argentea [17].

Furthermore, when the concentration of G. aretioides extract exceeded 20% (w/v), increasing the extract concentration increased the level of CaCO$_3$ precipitation and therefore the current density reduced. In fact, the presence of Ca$^{2+}$ ions in the extract leads to accumulation of calcium ions in the system and provides a counterforce against inhibitory tendencies; thus at plant extract concentrations of more than 20% (w/v), the amount of precipitate on the electrode is actually more than the amount formed in the presence of 5% (w/v) or 10% (w/v) extract of G. aretioides.

To further investigate precipitation on the electrode surface, SEM and EDX analyses were prepared for steel electrodes used in each experiment which included 0, 5, 10 and 20% (w/v) extract in brine solution, respectively (Figure 8). SEM and EDX data in Figure 8a demonstrate that in the absence of G. aretioides extract, a complete surface coverage of scale crystals takes place on the steel electrode. The calcium carbonate crystals decrease with increasing extract concentrations up to 10% (w/v) (Figures 8b and 8c). Moreover, EDX analysis : (Figure 8c-right) revealed that calcium ions are absent on the steel surface when the concentration of G. aretioides extract reached 10% (w/v) in the brine solution, the concentration at which no precipitates were found on the steel electrode in SEM imaging (Figure 8c-left). However, Figure 8d shows that in the presence of extract at a concentration of 20% (w/v), CaCO$_3$ crystals appeared on the electrode surface. The X-ray diffraction pattern for precipitates scraped from the steel surface at the end of chronoamperometry is presented in Figure 9a. The most intense peak (104) in the diffraction pattern of precipitates reflected pure calcite (most stable form of calcium carbonate) according to JCPDS CARD No. 05-0586 [26]. However, a main broad peak at the vicinity of $2\theta = 20-24^\circ$ (Figure 9b) showed an amorphous form (least stable form of calcium carbonate) [27] for calcium carbonates existing in the plant extract. This discrepancy shows that the crystals on the steel electrode surface in electrochemical experiments have a chemical, not plant, origin. In other words, the precipitates deposited on the steel electrode originated from the reaction of calcium and carbonate ions present in brine when potential was applied in chronoamperometry experiments.

4 Conclusions

A number of analyses of G. aretioides extract have shown that this extract contains polyphenol and foaming agent compounds. These compounds may be responsible for the scale inhibitory role of G. aretioides extract on the formation of calcium carbonate sediment. The inhibitory effect on calcium carbonate scale formation depends on the concentration of G. aretioides extract in the brine solution. According to chronoamperometry experiments, an effective scale inhibition performance in brine solution was obtained at a concentration of 10% (w/v). These results were also confirmed by atomic absorption and conductivity measurements. In addition, SEM and EDX analyses implied that calcium carbonate scale formation was affected by the concentration of G. aretioides extract. These results indicate the potential of G. aretioides extract as an eco-friendly, cost-effective scale inhibitor for the treatment of industrial brine solutions.
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