



# Green inhibition effect of *Pyracantha coccinea* (Rosaceae) berries in assessing of acidic corrosion of iron

## Demirin asidik korozyonunu değerlendirmede *Pyracantha coccinea* (Rosaceae) meyvelerinin yeşil inhibisyon etkisi

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### Abstract

The purpose of this study is to explore the potential of *Pyracantha coccinea* berries extract as a sustainable and environmentally friendly corrosion inhibitor on iron electrode under ambient conditions. This green inhibitor's impact was examined using different electrochemical experiments such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). After a one-hour examination of the experiments with three different concentrations of *Pyracantha coccinea* berry extract, it was determined that the berry extract strongly inhibited the iron electrode in a solution containing 1.0 M HCl. The extract from *Pyracantha coccinea* berries revealed a strong inhibitor action, and iron electrode protection in HCl solutions increased as pyracantha extract concentrations increased. Finally, surface images were taken after an hour of immersion using a field-emission scanned electron microscope (FE-SEM) to analyse the surface morphology of the iron electrodes in aggressive HCl electrolyte with and without *Pyracantha coccinea* berry extract, and the surface containing the pyracantha extract was smoother than the blank one.

**Keywords:** Green extract, Red firethorn, Iron, Acidic corrosion, FE-SEM

### 1 Introduction

Iron is an essential material used in various industries due to its mechanical properties, availability and cost-effectiveness [1]. Iron, a fundamental material in numerous industrial applications, is prone to corrosion, especially under acidic conditions. This susceptibility poses significant challenges, particularly in industries that rely heavily on iron for machinery and infrastructure [2]. One such critical process is pickling, where metals are treated with acidic solutions to remove impurities, oxides, and scale. While essential for ensuring the quality and longevity of metal products, pickling exacerbates the problem of acid-induced corrosion [3].

The consequences of corrosion are manifold and severe. They include material degradation, loss of mechanical integrity, increased maintenance costs, and potential safety hazards. The application of corrosion inhibitors has become a standard practice to mitigate these adverse effects. These

### Öz

Bu çalışmanın amacı, *Pyracantha coccinea* meyvelerinin ekstrakt çözeltisinin ortam koşullarında bulunan demir elektrot üzerinde çevre dostu ve sürdürülebilir bir korozyon inhibitörü olarak potansiyelini araştırmaktır. Bu yeşil inhibitörün etkisi, potansiyodinamik polarizasyon ve elektrokimyasal impedans spektroskopisi (EIS) gibi farklı elektrokimyasal teknikler kullanılarak incelenmiştir. *P. coccinea* meyve ekstraktının üç farklı derişimleriyle yapılan deneylerin bir saatlik incelenmesinin ardından, meyve ekstraktının 1,0 M HCl çözeltisindeki demir elektrot üzerinde güçlü bir inhibisyon sergilediği belirlenmiştir. *P. coccinea* meyvelerinden elde edilen ekstrakt, güçlü bir inhibitör etki gösterdi ve pirakanta ekstraktı derişimindeki artışla birlikte, demir elektrotların HCl çözeltisindeki koruyucu etkisi de artmıştır. Son olarak, *P. coccinea* meyve ekstraktı içeren ve içermeyen agresif HCl elektrolitindeki demir elektrotlarının yüzey morfolojilerini analiz etmek için alan emisyon taramalı elektron mikroskobu (FE-SEM) kullanılarak bir saatlik daldırma sonrasında yüzey görüntüleri alınmış ve *P. coccinea* ekstresi içeren yüzeyin boş olandan daha pürüzsüz olduğu sonucuna varılmıştır.

**Anahtar kelimeler:** Yeşil ekstrakt, Kıvıll ateşdikeni, Demir, Asidik korozyon, FE-SEM

substances, when added in small quantities, can drastically reduce the rate of corrosion by forming protective barriers on the metal surface. Both organic and inorganic corrosion inhibitors are frequently referred to as corrosion inhibitors [4]. Due to its huge dosage and significant environmental contamination, the use of inorganic corrosion inhibitors has been severely limited [5, 6]. These special qualities can beneficially guarantee that the molecules acting as corrosion inhibitors efficiently adsorb onto the metal surface.

Most of corrosion inhibitors now in use pose a risk to living things. In light of the current emphasis on protecting the green environment, research on new eco-friendly corrosion inhibitors has been gaining great priority recently. In particular, plant extracts constitute a significant source of corrosion inhibitors that are safe for the environment in this field. Plant extracts are being preferred more frequently mainly because they may be easily and affordably obtained from various plant parts. These extracts are among the new

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types of green corrosion inhibitors due to their reasonable cost, renewability, sustainability, non-toxic nature, and eco-friendliness. [7, 8].

In some studies conducted in the literature, Sajadi et al. [9] comparatively investigated the preventive effect of *lemon verbena* (lemon v.) extract as a green corrosion inhibitor on the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M HCl solutions. Pai et al. [10] studied *Tabebuia heterophylla* plant leaves extract as corrosion inhibitor for low carbon steel in 1 M HCl solution. The main role in corrosion inhibition was due to Hexadecanoic acid 2-hydroxy-1-(hydroxymethyl) ethyl ester in it was analyzed by GC-MS. Muhammad et al. [11] investigated the capacity of *Kopsia teoi* (K. teoi) employing its stem extracts and three distinct extracts to prevent mild steel corrosion in 0.5 M HCl.

The increasing trend towards these inhibitors is driven by the need for sustainable and eco-friendly alternatives to traditional synthetic inhibitors, which often pose environmental and health risks. They include a range of chemical substances that have been demonstrated to have potent anti-corrosion activities, including tannins, alkaloids, and flavonoids, called secondary metabolites [12, 13].

This study aims to investigate the efficacy of *P. coccinea* berries extract collected from the central campus of Niğde Ömer Halisdemir University in inhibiting the acidic corrosion of iron, with a focus on their application by potentiodynamic polarization and EIS techniques. By exploring these natural inhibitors, it will be tried to contribute to the development of safer and more sustainable corrosion management practices in the industry. The berries of *P. coccinea* are tapped in traditional medicine for their cardiac, tonic, and diuretic qualities. Prior studies have demonstrated the existence of flavonoids in both the aerial and hypogea sections of adult plants, despite the significant differences in their qualitative contents [14, 15]. Nevertheless, there isn't a report on the technical study of applying and employing this type of *P. coccinea* aqueous extract as a green corrosion inhibitor on the iron in 1.0 M HCl solution among the publications that are now available. Finally, the surface morphology of iron electrodes in both inhibited and uninhibited solutions was evaluated analyzing field emission scanning electron microscopy (FE-SEM). As a result of support from these analyses, anti-corrosion performance of green inhibitor has been fully disclosed.

## 2 Material and method

### 2.1 Plant specimen

The *P. coccinea* berries utilized in this study were gathered in December 2023 from Niğde Ömer Halisdemir University's central campus (Figure 1).



Figure 1. Photographs of gathered *Pyracantha coccinea* berry specimens (original)

### 2.2 *Pyracantha coccinea* berries extract solutions

Approximately 10 g of dried *P. coccinea* berries (Figure 2) were embedded in a reaction flask (250 mL) and refluxed for 10 h with the contribution of adequate distilled water. The aqueous berry extract was filtered after the 10-hour reflux process, yielding an approximately 110 mL volume with a brick orange colour (Figure 3). Following the evaporation of 10 mL of *P. coccinea* berries extract, the concentration of the stock solution made from the berries was calculated to be 2.147% (w/v). This stock solution was diluted to prepare the other additional concentrations.



Figure 2. Dried *Pyracantha coccinea* berries



Figure 3. Schematic of *Pyracantha coccinea* berries extraction procedure

### 2.3 Electrochemical experiments

The iron electrodes used in corrosion tests have the following chemical composition (wt%): 0.21700 Cu, 0.00198 Co, 0.01100 P, 0.08400 C, 0.06030 Cr, 0.07890 Ni, 0.10200 Si, 0.00222 Nb, 0.01040 Mo, 0.01100 V, 0.01900 S, 0.01620 Sn, 0.40900 Mn, and the remaining Fe. Using the established three electrode method at ambient temperature and a CHI-660B model electrochemical analyzer, two electrochemical experiments were carried out. Iron was tapped with a cross-sectional area of 0.5024 cm<sup>2</sup> and utilized as the working electrode. The iron electrode's surface was mechanically sanded using emery papers with 150–600 grids to achieve the same level of surface roughness. The greasy residues were then removed with acetone and the electrode was cleaned with distilled-water. Ag/AgCl (3.0 M KCl) electrode served as the reference electrode, while a platinum sheet with a surface area of 2.0 cm<sup>2</sup> served as the counter electrode.

For the equilibrium of the system, the iron electrodes were immersed in the electrolyte extract solutions for an hour before the experiments started. EIS tests were conducted with an amplitude of 5 mV to prevent corrosion at

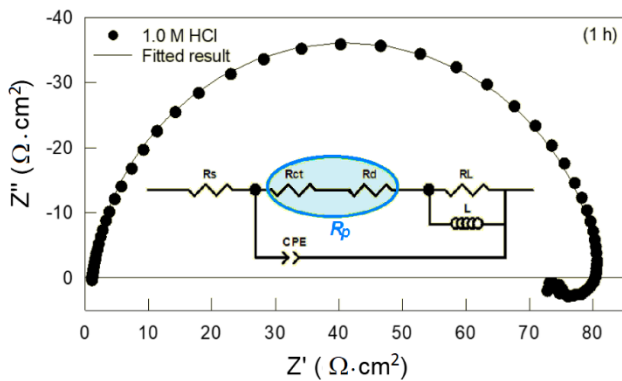
frequencies ranging from  $1.0 \times 10^5$  to  $5.0 \times 10^{-3}$  Hz. At anodic/cathodic potentials of  $\pm 0.350$  V in relation to  $E_{corr}$ , respectively, the potentiodynamic polarization tests were recorded. The scan rate used for this was  $1.0 \text{ mV s}^{-1}$ . Using the Tafel extrapolation method, the values of the corrosion process's current density ( $i_{corr}$ ) were found from the potentiodynamic polarization curves. All electrochemical experiments were fulfilled both with and without a 1.0 M HCl solution for three concentrations of *P. coccinea* berry extract.

Surface surveys were performed after the immersion of 1 h in a HCl electrolyte solution, both with and without highest concentration of *P. coccinea* berry extract, utilizing the analysis of FE-SEM with computer controlled (Zeiss GeminiSEM 500).

### 3 Results and discussion

#### 3.1 Green corrosion inhibition by EIS and potentiodynamic polarization experiments

The effects of *P. coccinea* berry extract, which has a green inhibitory effect on the iron surface, were measured using potentiodynamic polarization and impedance techniques throughout the course of an hour-long immersion at 298 K at three different concentrations. Whether organic or plant-based inhibitors are utilized, EIS is one of the most quickly, most straightforward techniques that is frequently chosen when examining the inhibitive qualities of all these compounds on materials in aggressive electrolyte solutions [16-18].

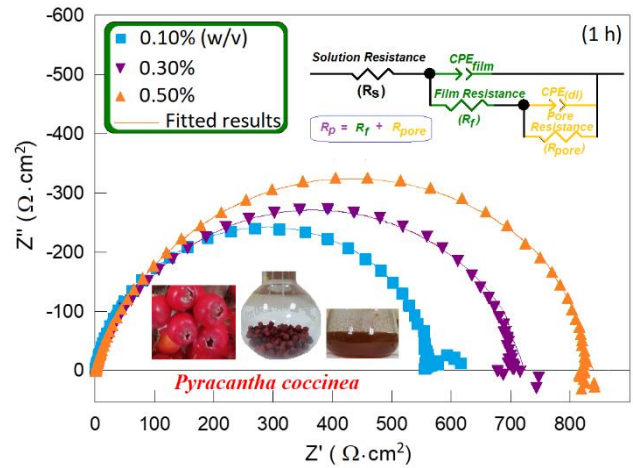


**Figure 4.** EIS diagram and proposed electrical equivalent circuit for 1.0 M HCl solution after immersion for 1 hour

In this procedure, two types of equivalent circuit models were put into use, one for the 1.0 M HCl solution inserted in the Nyquist diagram in Figure 4 and the other for the inhibited extract solutions inserted inside the Nyquist curves again in Figure 5.

Figures 4 and 5 display the EIS results, which are Nyquist plots used to further examine the *P. coccinea* berry extract's ability to suppress green corrosion. Zview2 software was utilized to fit the equivalent circuits for the inhibition and corrosion processes from the EIS data. Remarkably, a unique inhibitor layer forms on the iron surface in solutions containing *P. coccinea* berry extract, and this leads to a proportional increase in resistance. A better understanding is

given by Figure 5, which shows that the addition of *P. coccinea* berry extract in different concentrations reduces the corrosion of iron electrodes in a 1.0 M HCl solution. The *P. coccinea* berry extract takes place a preservative film on the iron surface, which helps to prevent corrosion. Moreover, the EIS diagram in Figure 5 clearly shows that as the concentration of the *P. coccinea* berry extract enhances, the capacitive loops become larger.



**Figure 5.** Proposed electrical equivalent circuits and EIS diagrams with varying *P. coccinea* berry extract concentrations

Table 1 provides a summary of the relevant potentiodynamic polarization parameters and EIS. Two separate frequency zones can be seen in the impedance plots: the high frequency area is related to the diffusion layer ( $R_d$ ) and charge transfer ( $R_{ct}$ ) during the corrosion process. Inhibition happens in the low frequency range, which is controlled by the film resistance ( $R_f$ ) that occurs on the iron surface from the berry extract of *P. coccinea*. In addition, as seen in Figure 5, the fire thorn berry extract solution procedure has two constant phase components ( $CPE$ ). The first one is the double layer capacitance ( $CPE_{dl}$ ), and the second one is the film layer capacitance ( $CPE_{film}$ ) occurred on iron surface.

The impact of *P. coccinea* berry aqueous extract on iron corrosion inhibition in 1.0 M HCl is demonstrated in this study by computing the values of percent inhibition efficiency ( $\eta\%$ ) at all concentration using the EIS method in the following manner [19]:

$$\eta(\%) = \left( \frac{R'_p - R_p}{R'_p} \right) \times 100 \quad (1)$$

Where  $R'_p$  and  $R_p$  are the fire thorn berry extract solutions and uninhibited polarization resistance values, respectively. It was clear from looking at the polarization resistance data obtained from the EIS experiments in Table 1 that adding the fire thorn berry extract to the aggressive solution raised the  $\eta\%$  values. The EIS method's data were used to derive inhibitory efficiency values, which varied from 87.63% to 91.45%.

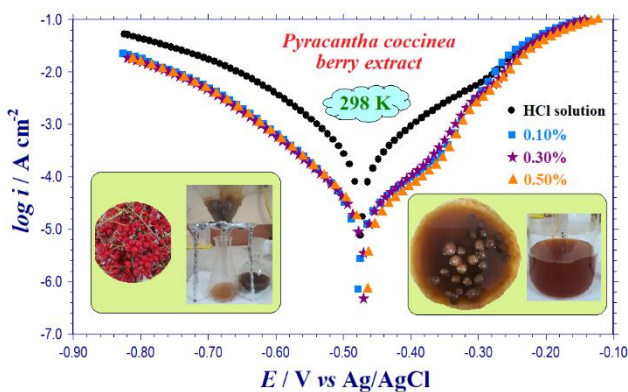
**Table 1.** Impedance and potentiodynamic polarization results described from the measurements in solutions with and without *P. coccinea* berry extract

C (w/v %)		EIS						
<i>P. coccinea</i> berry extract	$E_{ocp}$ (V/Ag/AgCl)	$R_s$ ( $\Omega \text{ cm}^2$ )	CPE ( $\mu\text{F cm}^2$ )	$n$	$R_L$ ( $\Omega \text{ cm}^2$ )	$L$ (H)	$R_p$ ( $\Omega \text{ cm}^2$ )	$\eta$ (%)
1.0 M HCl	-0.474	1.2	110	0.94	8	4	72	-
0.10	-0.475	1.3	80	0.87	-	-	582	87.63
0.30	-0.468	1.1	61	0.80	-	-	730	90.14
0.50	-0.462	1.2	52	0.79	-	-	842	91.45
*Potentiodynamic polarization								
<i>P. coccinea</i> berry extract	$E_{corr}$ (V/Ag/AgCl)	$-\beta_c$ (mV dec <sup>-1</sup> )	$i_{corr}$ ( $\mu\text{A cm}^2$ )	$\eta$ (%)				
1.0 M HCl	-0.475	108	265	-				
0.10	-0.464	93	32	87.92				
0.30	-0.470	93	24	90.94				
0.50	-0.478	92	21	92.08				

The capacitance data in the aggressive solution was recorded at 110  $\mu\text{F/cm}^2$ . Nevertheless, it was noted that adding *P. coccinea* berry extract to the HCl solution caused this value to drastically drop, with CPE values ranging between 80 and 52  $\mu\text{F/cm}^2$  [20].

Furthermore, the open circuit potential ( $E_{ocp}$ ), which was originally measured at -0.474 V in the hydrochloric acid electrolyte, altered to more anodic potentials when *P. coccinea* berry extract was added to the solution (Table 1). The metal's surface inhomogeneity coefficient is represented by the "n" value that is discovered by curve fitting using the Zview2 software. These values declined as the inhibitor concentration enhanced. It can be suggested as a proof of the adsorption of more phytochemical compounds on the iron by declining the active surface area, by virtue of enhancing the green inhibitor concentration and the "n" values minimized. Table 1 also displays the iron electrode's dissolution treatment parameters, which were ascertained by the use of a second electrochemical approach called the \*Tafel extrapolation method.

The potentiodynamic polarization graphs for the iron electrodes in aggressive solution with three different *P. coccinea* berry extract concentrations at 298 K are shown in Figure 6.



**Figure 6.** Potentiodynamic polarization plots of iron electrodes in hydrochloric acid for three concentrations of *P. coccinea* berry extract

Without the extract, the corrosion current density ( $i_{corr}$ ) was found at 265  $\mu\text{A/cm}^2$ . The Equation (2) that follows provides the percent inhibition efficiencies ( $\eta\%$ ) derived from the Tafel plots [21].

$$(\%) = \left( \frac{i_{corr} - i'_{corr}}{i_{corr}} \right) \times 100 \quad (2)$$

In this context,  $\eta\%$ ,  $i_{corr}$ , and  $i'_{corr}$  represent the inhibition efficiency derived from Tafel plots, as well as the corrosion current density values for both 1.0 M HCl and containing extract solutions, respectively.

Nevertheless, the  $i_{corr}$  values progressively dropped after the fire thorn berry extract was added to the HCl solution (\*Table 1). In contrast to the declining  $i_{corr}$  values, the increasing concentration was accompanied by an increase in the  $\eta\%$  values, which became 87.92%, 90.94%, and 92.08%, respectively. The cathodic Tafel constant ( $-\beta_c$ ) in the green inhibitor-containing solutions ranged from 92  $\text{mV dec}^{-1}$  to 93  $\text{mV dec}^{-1}$ , whereas it was 108  $\text{mV dec}^{-1}$  in the 1.0 M HCl medium. The comparatively stable cathodic Tafel constants in solutions containing and excluding *P. coccinea* berry extract indicate that the inhibitor under study had little effect on the mechanism of hydrogen evolution [22]. Figure 6 and Table 1 show that the  $E_{corr}$  value was recorded at -0.475 V in aggressive solution for the iron electrode by Tafel extrapolation of cathodic curve at 298 K. But the  $E_{corr}$  values moved toward more anodic potentials when *P. coccinea* berry extract solutions were added.

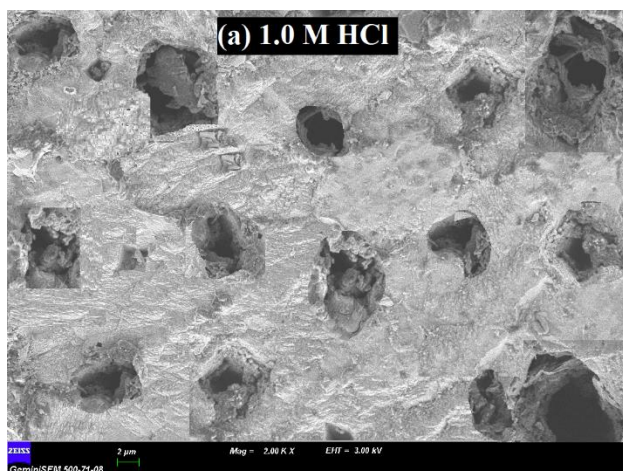
As can be seen clearly from Figure 6 and Table 1, current density values declined drastically in solutions containing fire thorn extract compared to the aggressive solution without extract. At the same time, when *P. coccinea* berry extract was added to hydrochloric acid medium, almost the same rate current decreases were observed in both anodic and cathodic curves, which can be attributed to the mixed-type inhibitor behaviour of *P. coccinea* berry extract for the iron electrode in 1.0 M HCl medium [23-25]. The conclusion that *P. coccinea* berry extract adsorption on the metal surface is an unavoidable phenomenon was reached based on the complementary data from the two testing methods. Furthermore, because this extract has no negative impacts on

the environment, it can be regarded as a non-toxic green inhibitor.

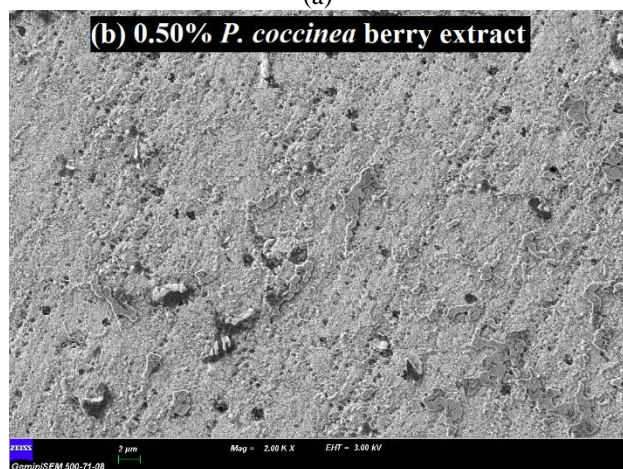
### 3.2 Morphological characterization by FE-SEM analysis

Field emission scanning electron microscope is widely preferred in corrosion inhibition studies because it provides much higher resolution surface images. Figure 7 depicts the surface morphology of iron electrodes immersed for 1 h in HCl medium, both with and without the presence of 0.50% *P. coccinea* berry extract concentration at 298 K.

As illustrated in Figure 7(a), the entire iron surface was extensively corroded, with eroded pits that were incredibly dense and irregular, after immersion in HCl medium under uninhibited solution. The surface morphology is shown in Figure 7(b) with the addition of 0.50% (w/v) *P. coccinea* berry extract. It is apparent that the entire iron surface gets smoother and that the amount of corroded cavities significantly decreases [26]. It can be said that the berry extract of *P. coccinea* almost acts as a sort of cover for the iron surface. It demonstrates that the berry extract of *P. coccinea* may effectively inhibit the iron corrosion brought on by the HCl solution.



(a)



(b)

**Figure 7.** FE-SEM morphologies of iron electrodes for 1 h immersion

## 4 Conclusions

Two electrochemical techniques were used in this study to analyse the impact of *P. coccinea* berry extract—a green inhibitor that is ecologically friendly—on the corrosion behaviour of Fe in HCl medium. The *P. coccinea* berry extract was demonstrated to be substantially adsorbed on the metallic surface and to exhibit an impressive 90% inhibition rate at all extract concentrations. When two distinct experimental procedures were applied, rising the concentration of *P. coccinea* berry extract resulted in a boost in the inhibition efficiencies. This finding suggests that a boost in the concentration of the fire thorn extract corresponds with an elevation in the amount of organic compounds adhered to the iron surface.

The key to attaining such an excellent inhibition efficiency against iron corrosion is the chemical makeup of phytochemicals, or secondary metabolites, present in *P. coccinea* berry. These compounds are distinguished by double bonds between phenolic molecules,  $\pi$  electrons and aromatic rings among other properties. Consequently, these characteristics are primarily responsible for their great inhibitor efficiency in controlling iron corrosion in this regard. As these naturally found, non-toxic compounds in plant extracts are biodegradable and involve no hazardous materials, their inhibitory impact is exceptionally critical for industrial processes as well as the environment. The surface observations in the fire thorn extract solution was seen to be rather smooth and the holes were apparently covered compared to the observation in the uninhibited one, in order to more thoroughly analyze the impact of the *P. coccinea* berry extract on the iron. The experimental methods' data are in excellent line with the surface observations.

### Conflict of interest

The author claims that there is no conflict of interest.

**Similarity rate (iThenticate):** 12%

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