

Investigation of *Ligustrum lucidum* Ait. Seeds Extract as Green Corrosion Inhibitors and Bacteriostatic Agent

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Keywords: *Ligustrum lucidum* Ait., extract, inhibitor, inhibition efficiency

Abstract. The extract of *Ligustrum lucidum* Ait. seeds, as green and eco-friendly corrosion inhibitors, have been investigated on the corrosion inhibition of Q235A steel in 1M hydrochloric acid solution at 60°C by weight loss and potentiodynamic polarisation techniques. The inhibition efficiency of the extracts varies with extract concentration from 10 mg/L to 1000 mg/L and the highest one reaches to 95.0%. The extracts inhibit corrosion mainly by adsorption mechanism. Besides the hydroxyl and ether groups of polyphenols can capture the H^+ to reduce the corrosion, and the polyphenols can eliminate the dissolved O_2 to inhibit the oxygen-adsorption corrosion. Potentiodynamic polarisation studies show that extracts are mixed type inhibitors.

Introduction

During the acidification operation in oilfield, hydrochloric acidic fluid is pumped into wells, which etches the fracture walls irregularly to create highly conductive channels[1]. So it is a challenge for the metal instruments involved. Great attentions have been drawn to heat treatment and changing chemical composition to improve its corrosion resistance. But, for the aggressiveness of acidic media, the use of corrosion inhibitors is considered as the most effective method for the protection of many metals against such acid attack [2,3]. Compounds, containing functional electronegative groups and p and/or π -electron in triple or conjugated double bonds, are found to be efficient as inhibitors against metal corrosion [3-6]. It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring p and/or π -electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption[7-10]. Organic compounds, containing heteroatoms, such as sulfur, phosphorus, nitrogen and oxygen, together with aromatic rings in their structure are the major adsorption centers, and the Schiff bases, a condensation product of an amine and a ketone/aldehyde, are such typical molecules [3-10]. Some polydentate Schiff base compounds (PSCs) have been reported as effective corrosion inhibitors for various metals in acid media [11-15].

Ligustrum lucidum (broad-leaf privet, Chinese privet, glossy privet, tree privet or wax-leaf privet) is a species of privet (*Ligustrum* genus), a flowering plant in the olive family, Oleaceae, native to the southern half of China and naturalized in many places: Spain, Italy, Algeria, Canary Islands, New Zealand, Lesotho, South Africa, Japan, Korea, Australia, Norfolk Island, Chiapas, Central America, Argentina, and the southern United States. The name "Chinese privet" is more frequently used for *Ligustrum sinense*[16-18].



Figure 1 The tree, flower and seeds of *Ligustrum lucidum*

The seeds are known as Nu-zhen-zi (female chastity seed) in traditional Chinese medicine and are believed to nourish liver and kidney Yin and Jing in the treatment of tinnitus (ringing in the ears), vertigo (dizziness), premature graying of the hair, and soreness/weakness of the lower back and knees. *Ligustrum lucidum* Ait. has been used in traditional Chinese medicine for over 1000 years because of its anti-tumor, antimutagenic, antidiabetic, and hepatoprotective properties. Due to the belief in the seeds' ability to nourish the liver, they are also used in the treatment of disorders of the eye involving red or dry eyes, blurred vision, and pain. Chemical constituents of the seeds include oleanolic acid(a), nuzhenide(b), and ligustroside(c), as shown in Figure 2 [16-20]. The aim of this work is to investigate the inhibition of *Ligustrum sinense* seeds extraction as corrosion inhibitors and bacteriostatic agent in oil field.

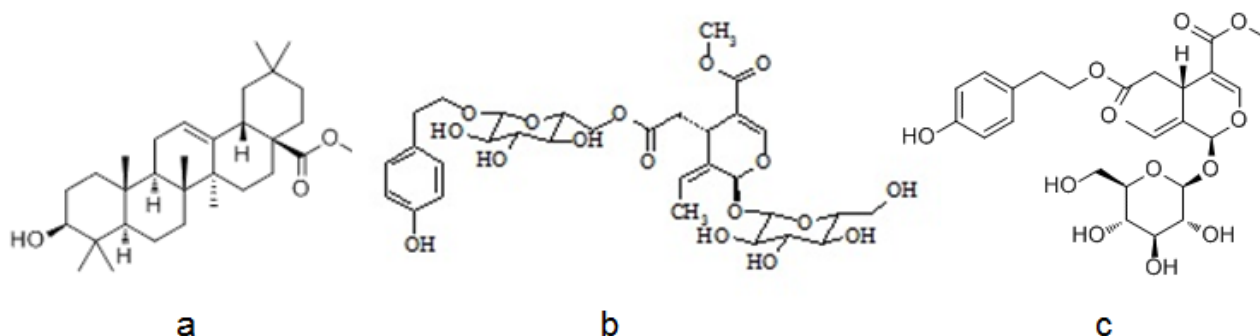


Figure 2 Chemical constituents of the *Ligustrum sinense* seeds

Experiment

Gravimetric measurements.

The corrosion tests were performed on Q235A with a composition (in wt.%) C: 0.22, P: 0.045, Si: 0.35, S: 0.05, Mn: 1.40, and Fe balance. The electrolyte solution was 1M HCl, prepared from analytical grade 38% HCl and distilled water. The concentration range of *Ligustrum lucidum* Ait. seeds extract (LSE) was employed as 50 mg/L to 1000 mg/L. All tests have been performed in deaerated solutions. The gravimetric tests were carried out according to the People's Republic of China Standard of Petroleum and Natural Gas Industry (Evaluation method for behavior of corrosion inhibitor for produced water of oilfield, SY/T5273-2000) with a few modifications. Each test was done with three specimens at the same time to give reproducible results.

Microbiological monitoring.

Viable counts of SRB, TGB and FB were determined with the "most probable number" method, People's Republic of China Standard of Petroleum and Natural Gas Industry, the national method of the bactericidal agent's performance, SY/T 5890-1993). The produced water containing the three kinds of bacteria was gathered from Zichang Oilfield Factory, Yanchang Oilfield.

Results and Discussion

Acidic corrosion inhibition.

The inhibition efficiency (IE) of *Ligustrum lucidum* Ait. seeds extract (LSE) was investigated in the concentration range from 10 mg/L to 500 mg/L in 1 M HCl; changes of IE (%) with the inhibitor concentration are summarized in Table 1. It can be inferred from the Table 1 that LSE exhibits obviously good corrosion-inhibition effect on Q235A steel, and the inhibition efficiency (IE) is rising as the concentration increasing. Increase in inhibition efficiencies with the concentration of LSE shows that the inhibition actions may due to its adsorption on the steel surface [11,12].

Table 1 The inhibition efficiency of LSE measured by weight loss

Extract	Concentration (mg/L)	Inhibition Efficiency (%)
LSE	10	20.1
LSE	20	44.5
LSE	50	62.5
LSE	100	85.0
LSE	200	86.4
LSE	500	88.5

Changes of the IE (%) under different temperature with different concentration are shown in Figure 3. For the concentration 1000mg/L, the inhibition efficiency increase with the temperature, which reach to 88.5% in 1M HCl under 30°C. But it shows different for the concentration lower than 100 mg/L. The results imply that we should change the concentration of the inhibitor with the temperature.

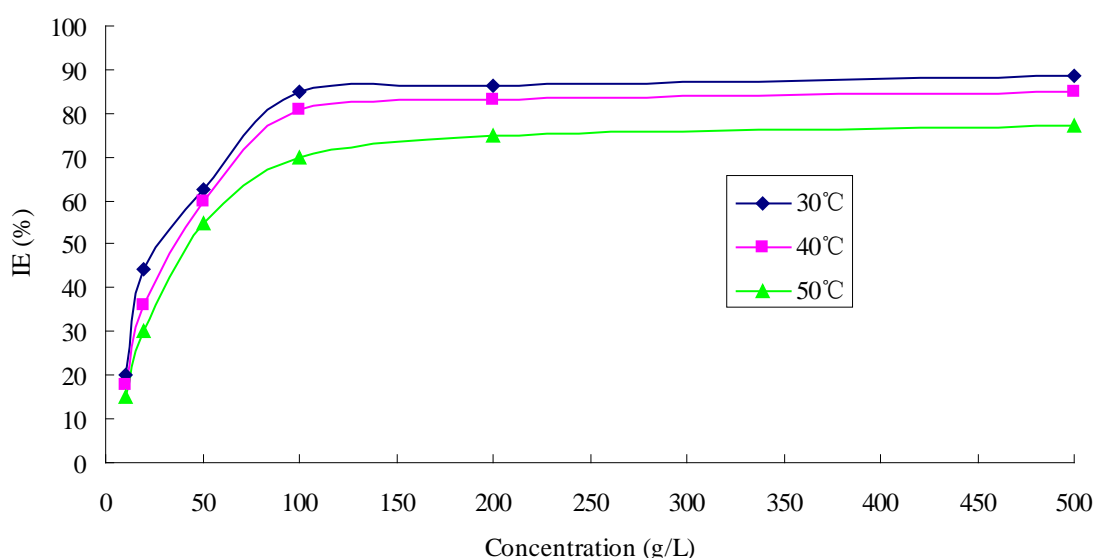


Figure 3 The inhibition efficiency of LSE under different temperature

The corrosion-inhibition effect can be explained on the basis of additive adsorption. It is well recognized that organic inhibitor molecules set up their inhibition action via the adsorption onto the metal/solution interface. The adsorption process is affected by the chemical structures of the inhibitors, the nature and charged surface of the metal and the distribution of charge over the whole inhibitor molecule. The presence of N, O, S atoms and conjugated double bonds in the organic structures makes the formation of p-d bonds resulting from overlap of p-electrons to the 3d vacant

orbital of iron atoms, which enhances the adsorption of the compounds on the metal surface [13-16]. In general, organic inhibitor molecules may be adsorbed on the metal surface in one or more of the following ways [13-16]:

- (a) electrostatic interaction between the charged molecules and the charged metal;
- (b) interaction of unshared electron pairs in the molecule with the metal;
- (c) interaction of p-electrons with the metal;
- (d) a combination of types (a–c).

The electron rich phenol groups and aromatic rings of polyphenols extract from pomegranate means it is easy to coordinate with the iron and form a protective film (as shown in Figure 4). The hydroxyl groups and ether groups of polyphenols, with abundant *p*-electrons, can capture the H^+ , which reduce the concentration and corrosive of HCl solution. The polyphenols can be oxidized to benzoquinone by the O_2 resolved in the solution, by which inhibit the oxygen-adsorption corrosion

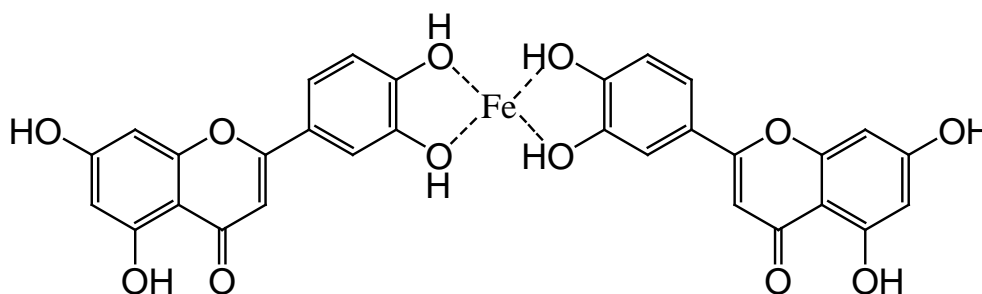


Figure 4 The absorption of ellagic acid on the ion surface by coordination

Bioactivity.

Corrosion is an electrochemical process leading to the deterioration of materials that can be caused or accelerated by microbiological activity, so called Microbiologically Influenced Corrosion (MIC). It is estimated that 30-50% of the corrosion cases are a result of microbial activity. MIC caused by growth of sulfate reducing bacteria (SRB), iron bacteria (IB) and total general bacteria (TGB) in oil pipelines, is considered a major problem for water treatment in the oil industry. MIC can result in different types of attack: pitting, crevices, dealloying and erosion in pipelines[25]. Corrosion products produced by microorganisms are production of hydrogen sulfide, molecular hydrogen, hydrogen ions and destabilization of metal oxide films. In addition, microbial degradation of crude oil can lead to increased acidity in the oil phase, and oil containing acids is a problem concerning corrosion of pipelines. The reported results showed that the interaction of IB, SRB and TGB accelerated the corrosion rate, and the corrosion in the mixture of IB, SRB and TGB was more serious than in a single microbial system. If this is the case, different treatment system to inhibit corrosion should be considered, among which bactericide agent has received the greatest acceptance. Currently, oxidizer, aldehyde, quaternary ammonium salt and heterocycle compounds has been used as bactericide agents, and Cl_2 , ClO_2 , formaldehyde, pentane-1,5-dial, trichloroisocyanuric acid (TCCA) and ect, but the toxicity tests have been conducted on a limited selection. The antifungal activity of LSE against oilfield microorganism was tested under the concentration of 50 mg/L to 1000mg/L, and the results were summarized in Table 2. From the table, it can be found that LSE is antifungal active against TGB and IB, but not so active against SRB.

Table 2 The antifungal activity of LSE against oil field MIC

Concentration mg/L	Microbiotic Concentration /mL		
	SRB	IB	TGB
—	110.0	110.0	110.0
50	70	70	70
100	70	25	25
200	25	6	6
500	25	6	6
1000	25	6	6

Conclusion

The inhibition of *Ligustrum lucidum* Ait. seeds extract and the mechanism on the corrosion of high protective Q235A steel in HCl solution were screened and discussed. It can inhibit the corrosion with moderate inhibition efficiency in different conditions and the highest reaches to 83.2% with the concentration of 1000 mg/L in 1M HCl solution. Besides, it displays potent activity against the oilfield water-borne bacteria, especially for SRB and IB.

Acknowledgment

This work was financially supported by the grants from National Science Foundation of China (21376189) and Scientific and Technological Plan Projects of Shaanxi Province (2014TG-09).

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