Anti-corrosion and Anti-bacteria Property of Modified Pomegranate Peel Extract

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Abstract. Using weight loss method, the pomegranate peel extract (PPE), that is a green corrosion inhibitors, have been studied in the corrosion inhibition of Q235A steel in 1M hydrochloric acid solution at 30°C, 45°C, 60°C, respectively. The inhibition rate of extract varies with the extraction concentration in the range of 10 ~ 1000mg / L, up to 92.7%. Extract inhibits corrosion through adsorption mechanisms. Besides polyphenols hydroxyl and ether groups can slow down corrosion by capturing H⁺. Polyphenols can remove the dissolved O₂, and curb oxygen reducing corrosion. PPE is antifungal active against TGB and FB, but not so active against SRB.

1. Introduction

Acidic fluids such as hydrochloric acid etched the fracture walls irregularly during the field acidification operation, resulting in highly conductive channels [1]. More attentions have been paid to enhance it’s the resistance corrosion by changing the chemical composition. However, the added corrosion inhibitor is the most useful method for the aggressiveness of acidic media [2-3]. It has been found that compounds containing p and/or π-electrons in the electronegative groups and triple or conjugated double bonds are effective as inhibitors against metal corrosion [4-6]. Organic inhibitors generally promote the formation of chelates on metal surfaces by the transfer of p and/or π-electrons in the electronegative groups and triple or conjugated double bonds are effective as inhibitors against metal corrosion [4-6]. Organic inhibitors generally promote the formation of chelates on metal surfaces by the transfer of p and/or π-electrons in the electronegative groups and triple or conjugated double bonds are effective as inhibitors against metal corrosion [4-6]. Organic inhibitors generally promote the formation of chelates on metal surfaces by the transfer of p and/or π-electrons in the electronegative groups and triple or conjugated double bonds are effective as inhibitors against metal corrosion [4-6]. Organic inhibitors generally promote the formation of chelates on metal surfaces by the transfer of p and/or π-electrons in the electronegative groups and triple or conjugated double bonds are effective as inhibitors against metal corrosion [4-6].

Pomegranates grow on the China, Persia and other Asian countries and have been localized in the warm latitudes of the West Indies and other civilized nations. It has brilliant, crimson flowers that tend to double and flowering in July and August. Called the ancients’ burnish flowers, flavors are a little bit tasteless and odorless, and their extract produces a dark blue-black sediment with iron salts. Sputum was purple when chewing. Tannins and gallic acid are all in their composition. In some foreign pharmacopoeia, they are considered official along with seeds. The bark of the rhizome is the only part used in this country. The skin is also our former official. It is different in all respects of the fruit, and
the fruits of the West Indies have become well developed (Figure 1). The pomegranate tree grew up outside the north side of Washington, D.C in this country.\cite{16}

![Fig. 1 The tree, flower and peel of pomegranate](image)

The dry peel is brownish-yellow in exterior, yellow in interior, thick in lines, firm and smooth or small, hard, dry, fragile, irregularly shaved, odorless, astringent and slightly bitter. Its infusion provides a rich, dark blue precipitate with iron salts. The analysis showed that it mainly contains 29.9% of trace resin, 18.8% of tannin, 10.8% of extract, 17.1% of mucus, 30% of lignin. (U. S. P.)

About 20 per cent of tannin is contained in pomegranate bark. Rembold thinks that it has two astringent principles, one is gallotannic acid (it is shown in Fig. 2), the other punicotannic acid ($C_{20}H_{16}O_{13}$) which is peculiar to the bark. It is hydrolyzed into sugar and ellagic acid ($C_{14}H_{8}O_{9}$) by Sulfuric sulphuric acid. The bark contains 10.5% to 16.5% ash. It also has a yellow pigment. The pest-killing properties of the bark are due to the presence of several alkaloids found by Tanget in 1878 and 1880, in honor of the famous French chemist Pelletier, who gave the name Pelletierine. C.J.Bender proposed the more pleasing name punicine. A solution of 4 alkaloids was obtained by mixing the powdered bark with the milk of lime, venting with water, shaking with chloroform, and extracting the solution with dilute acid. Sodium bicarbonate releases methyldivinylpyridine and pseudocystine which are removed by chloroform, after addition of caustic potash, free pelletierine and isopelletierine are obtained from this solution \cite{17}. The purpose of paper is to inspect the inhibition in pomegranate peel extraction as a corrosion inhibitor and bacteriostat.

![Fig. 2 Gallotannic acid in the pomegranate peel](image)
2. Experimental

2.1 Gravimetric measurements
A corrosion test was carried out on Q235A at a part (in wt.%) of Mn: 1.40, C: 0.22, S: 0.05, Fe: 0.045 and Si: 0.35 balance. The solution of electrolyte was 1 M HCl, which is manufactured from the distilled water and HCl (38%). The concentrations of the extract in pomegranate pericarp (PPE) range from 10 mg/L to 1000 mg/L. All the tests were done in the degassing solution through the National oil industry standards for weight test, and made some changes. Three tests per test are performed simultaneously to provide reproducible results.

2.2 Microbial monitoring
The counts of FB, TGB and SRB of the produced water which were collected from Chuankou Oilfield, were measured through the national oil industry standards, SY/T 5890-1993.

3. Results and discussion

3.1 Acidic corrosion inhibition
The inhibition efficiency of the pomegranate peel extract (PPE) was within the scope of 10 to 1000 mg/L, and the change of it (%) with the concentration of the inhibitor is counted in Table 1.

| Extract | Concentration(mg/L) | Inhibition efficiency(%) |
|---------|---------------------|--------------------------|
| PPE     | 0                   | (30˚C) 0.72               |
|         |                     | (45˚C) 0.70               |
|         |                     | (60˚C) 0.80               |
|         |                     | (30˚C) 11.8               |
| PPE     | 10                  | (45˚C) 21.0               |
|         |                     | (60˚C) 33.9               |
|         |                     | (30˚C) 24.0               |
| PPE     | 50                  | (45˚C) 32.9               |
|         |                     | (60˚C) 44.8               |
|         |                     | (30˚C) 41.8               |
| PPE     | 100                 | (45˚C) 56.3               |
|         |                     | (60˚C) 51.0               |
|         |                     | (30˚C) 55.8               |
| PPE     | 200                 | (45˚C) 79.0               |
|         |                     | (60˚C) 57.8               |
|         |                     | (30˚C) 82.9               |
| PPE     | 500                 | (45˚C) 83.7               |
|         |                     | (60˚C) 64.3               |
|         |                     | (30˚C) 93.0               |
| PPE     | 1000                | (45˚C) 86.8               |
|         |                     | (60˚C) 78.6               |

It can be inferred from the Table 1 that PPE had a significant inhibition on the Q235A steel, and the inhibition efficiency (IE) showed an upward trend with the increase of concentration. The inhibitory effect shows that inhibition may be due to the PPE concentration increased. The changes of IE (%) in HCl at different temperatures and different concentrations are shown in Fig. 3. As the temperature
increases, the inhibitory efficiency subjoins, reaching 92.7% at 60°C in 1% hydrochloric acid at a concentration of 1000 mg/L. However, concentrations below 100 mg/L show a difference. The result means that the concentration and temperature of the inhibitor should be changed in the experiment.

![Inhibition of PPE at different temperatures and HCl concentrations](image)

Fig. 3 Inhibition of PPE at different temperatures and HCl concentrations

Besides, the stability of PPE was also invested. It was found that PPE was fermented within a week in a closed vases, so the PPE was modified by hydroxymethylation and Mannich. The five systems included PPE, formaldehyde and ethylenediamine; PPE, formaldehyde and diethanolamine; PPE and formaldehyde; PPE, formaldehyde and morpholino; PPE, formaldehyde and piperazine. Experiments showed that the stability of these modified PPEs were all obviously improved, especially after PPE was modified by hydroxymethylation adding formaldehyde. Furthermore, the inhibition efficiency of modified PPE in the different temperature was invested as shown in Fig. 4.

![The inhibition efficiency of modified PPEs under different temperature](image)

Fig. 4 The inhibition efficiency of modified PPEs under different temperature

The corrosion inhibition can be illustrated by the additive adsorption. It is well known that the inhibitor with the organic molecules establish inhibitory effect through inhibitor adsorption in the metal/dissolution surface. The chemical structure in the inhibitor affects the adsorption process, nature of the metal and the charged surface and the charge distribution across the inhibitor molecule. That
there are S, O, N atoms and conjugated double bonds at the organic structure allows the conformation of the bonds at p-d by p-electron doping into 3d empty orbitals of iron atom, that improves the complex at the surface of the metal. Usually, molecules of inhibitor can be adsorbed at the surface of metal in the following different ways:

(a) The electrostatic interactions between charged metals and charged molecules;
(b) The unshared electrons and metals in the molecule interact;
(c) p electron-metal interaction;
(d) a combination of types (a-c).

Aromatic rings in phenolic-rich phenols and pomegranate polyphenol extracts mean that they are compatible with iron to form a protective film. There are many p-electron ether groups in polyphenols and hydroxyls that trap H+ and cut back the concentration and corrosivity of the HCl solution. By dissolving O3 in the solution, the polyphenol can be oxidized into benzoquinone, thereby inhibiting oxygen absorption corrosion.

3.2 Bioactivity
It is estimated that 30-50% of the corrosion that is the result of microbial activity. The so-called microbial corrosion (MIC), is a microbial activity leads to or accelerate the deterioration of the electrochemical process materials. MICs resulting from the breeding of total bacteria (TGB), iron bacteria (IB) and sulfate-reducing bacteria (SRB) in the oil transport are deemed to be main problems in the petroleum industry water treatment. MICs could cause different categories of attacks that are pitting, cracking, rationalization and corrosion in pipes. Corrosion caused by microorganisms is hydrogen sulfide, hydrogen molecular, unstable metal oxide film. Additionally, crude oil's degradation by microbial leads to increases of acidity at the oil phase, which is a problem of pipeline corrosion. The results show that the interaction between TGB, SRB and IB accelerates the rate of corrosion and the mixture of the three is more corrosive than the single microorganism. If so, different corrosion inhibition systems should be considered, of which fungicides have been the most widely recognized. At present, oxidants, aldehydes, quaternary ammonium salts and heterocyclic compounds such as trichloroisocyanuric acid (TCCA), formaldehyde, ClO2, pentane-1,5-diol and Cl2 have been used as microicides and pharmaceuticals. Antifungal activity of PPE on oilfields microorganism was tested under the concentration of 0.1 g/L to 2 g/L, and the results were summarized in Table 1. From the table, it can be found that PPE is antifungal active against TGB and FB, but not so active against SRB.

| Concentration(g/L) | SRB | TGB | FB |
|-------------------|-----|-----|----|
| —                 | 110.0 | 70.0 | 70.0 |
| 0.1               | 110.0 | 25.0 | 1.3 |
| 1.0               | 70.0 | 20.0 | 1.3 |
| 2.0               | 2.0  | 2.0  | 1.3 |

3.3 Conclusion
The inhibitory effect of pomegranate peel extract and its mechanism of corrosion on highly protected Q235A steel in HCl solution were investigated. In 1% HCl solution, the concentration of 1000mg/L can inhibit the corrosion, under different conditions, the best inhibition, up to 92.7%. In addition, it has strong activity on oilfield aquatic bacteria, especially on TGB and FB.

Acknowledgement
This research was financially supported by the grants from National Science Foundation of China (No.50874092), Industrial Science and Technology Research Projects of Shaanxi Provincial (No. 2016GY-218) and Science and Technology Local Service Special Project of Shaanxi Education Department (Industrialization Cultivation Project) (No. 17JF025).
References

[1] J.K. Borchardt, T.F. Yen, Oil-field chemistry—enhanced recovery and production stimulation, Toronto, 1988.

[2] Y.R. Liu, Z.M. Gao, Z. Zhang, D.F. Shi, Electrochemically aided deposition of TiO2 films on Ni-P pre-plated A3 carbon steel, Corrosion Science and Protection Technology, 19 (2007) 323-325.

[3] J.H. Jiang, L. Li, J.X. Hu, J.Q. Jiang, A.B. Ma, New Zinc-phosphating process with RE catalyzer at low temperature for painting pretreatment of cold-rolling A3 steel sheet, Surface Technology, 36 (2007) 79-81.

[4] V.S. Sastr, Corrosion inhibitors principle and application, John Willey & Sons, New York, 1998, pp.198-202.

[5] A. Raman, P. Labine, M.A. Quraish, Reviews on corrosion inhibitor science and technology, NACE International, Houstan, 2004, 3.

[6] A. Cizek, Acidizing inhibitors, Materials Performance, 33 (1994) 56-61.

[7] J. Cruz, R. Martinez, J. Genesca, E.G. Ochoa, Experimental and theoretical study of 1-(2-ethylamino)-2-methylimidazoline as an inhibitor of carbon steel corrosion in acid media, Journal of Electroanalytical Chemistry, 566 (2004) 111-121.

[8] Y.X. Huang, J. Cai, J.M. Zhou, Corrosion inhibition of magnolia leaf extracts in acid medium for A3 steel, Applied Chemistry Industrial, 39 (2010) 538-540.

[9] M.Z. Pan, J. Cai, M. Yu, Corrosion inhibition of Gum leaves extracts in acid medium for A3 steel, Chemical Engineering, 2 (2012) 70-72.

[10] S.R. Zhao, G.D. Xu, X.Q. Liao, Preliminary study on the extracts of pine apple waste as corrosion inhibitor and their inhibiting properties to A3 steel in H2SO4 solution, Chemical Cleaning, 12 (1996) 4-6.

[11] Y.P. Tang, F.C. Lou, J.H. Wang, Y.F. Li, Zhuang S.F.: Coumaroyl flavonol glycosides from the leaves of Ginkgo biloba, Phytochemistry, 58 (2001) 1251-1256.

[12] C. vanDijk, A.J. Driessen, K. Recourt, The uncoupling efficiency and affinity of flavonoids for vesicles, Biochemical Pharmacology, 60 (2000) 1593-1600.

[13] E. Varga, The protective effect of EGB 761 in isolated isochemical/ reperfused rat hearts, Acta Pharmaceutica Hungarica, 72 (2002) 265-271.

[14] J. Stanislav, M. Shahid, N. Koji, Isolation of ginkgolides A, B, C and bilobalide from G. biloba extracts, Phytochemistry, 65 (2004) 2897-2902.

[15] S. Issaadi, T. Douadi, A. Zouaoui, S. Chaif, M.A. Khan, G. Bouet, Novel thiophene symmetrical Schiff base compounds as corrosion inhibitor for mild steel in acidic media, Corrosion Science, 53 (2011) 1484-1488.

[16] M.A. Hegazy, A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution, Corrosion Science, 51(2009) 2610-2168.

[17] D.W. Gao, Q.W. Li, Y. Li, Z.H. Liu, Z.W. Liu, Y.S. Fan, Z.S. Han, J. Li, K. Li. Antidiabetic potential of oleanolic acid from Ligustrum lucidum Ait. Canadian Journal of Physiology and Pharmacology, 85 (2015) 1076-1083.