

Collaborative Education between Scientific Research and Production

-- An Example of Comprehensive Experiment of Green Corrosion Inhibitors based on Plant Materials

Yuchun Xia¹, Xia Wang², Aihua Liu¹, Yubo Lian¹, Chen Gang²

¹ Xi'an Changqing Chemical Group Co. Ltd of Changqing Oilfield, National Engineering Laboratory for Exploration and Development of Low Permeability Oil & Gas Fields, PetroChina Oilfield Company, Xi'an 710016, China

² Engineering Research Center of Oil and Gas Field Chemistry, Universities of Shaanxi Province, Xi'an Shiyu University, Xi'an, 710065, China

Abstract: Based on with the local abundant botany resource, a comprehensive experiment of the waste peel and leaf extract as the green corrosion inhibitor in the acid solution was designed. In this experiment, the effect of waste peel and leaf extract on steel plate in HCl solution was studied by weight loss method. This experimental project has a certain exploratory and practical, which is conducive to students to deepen the understanding of metal corrosion and protection theory, and gets the relevant experimental skills of comprehensive training, analytical skills and innovation ability. The use of waste peel and leaves as experiment raw materials could improve the concept of environmental protection students as well.

Keywords: Botany Material; Corrosion Inhibition; Comprehensive Experiment; Green Corrosion Inhibitor.

1. Introduction

School-enterprise cooperative education is an innovative and practical education model, which emphasizes the deep cooperation between schools and enterprises, aiming at jointly cultivating high-quality talents with both solid theoretical knowledge and rich practical experience. Under this mode, schools and enterprises establish a close cooperative relationship and participate in the whole process of talent training. The school is responsible for providing systematic theoretical teaching to cultivate students' professional quality and thinking ability; While the enterprise provides a practical platform for students to practice their skills and accumulate experience in a real working environment. This kind of education method combining theory and practice can not only enable students to better adapt to market demand and improve employment competitiveness, but also deliver talents with innovative thinking and practical ability for enterprises to promote the sustainable development of enterprises. In addition, school-enterprise cooperation in education can also promote the deep integration of education and industry, promote the optimal allocation of educational resources, and realize the positive interaction between education and economy. Therefore, school-enterprise cooperation in education is an educational model with broad prospects and far-reaching significance, which is worth further exploration and promotion. Changqing Chemical Group Company and Xi'an Shiyu University have long-term cooperation in scientific research and personnel training. The laboratory has been engaged in the research and application of green oilfield chemicals based on natural product materials for a long time, and has undertaken more than 20 national, provincial, municipal and enterprise cooperation projects in the fields of drilling fluid, fracturing fluid and oilfield water treatment, and has developed a large number of environmental protection treatment agents.

The corrosion problem of metal materials, especially steel materials, exists in almost every aspect of industrial

production and life, and the economic loss caused by it is very huge. In particular, in the process of oil field exploitation, it is necessary to inject acid in order to increase production, resulting in economic losses in all aspects. In order to reduce the corrosion of acid to metal pipelines and equipment, control the reaction rate of acid rock, improve the acidification effect, place the bottom pollution and reduce the construction cost, it is necessary to add corrosion inhibitors[1]. Acidizing corrosion inhibitor is the key content for applied chemistry students in the field of oilfield chemistry. For the students of petroleum related majors, "Principles of Oil and Gas Field Chemistry" is an essential professional course. "Principles of Oil and Gas Field Chemistry" requires students to understand the theory at the same time, combined with practice, to develop students' comprehensive problem analysis ability, experiment ability, data processing ability, literature review ability, problem solving ability and cooperation ability[2]. The task of engineering higher education is to cultivate engineering, practical and innovative high-quality talents needed by the society. In recent years, in order to meet the needs of college teaching reform under the new situation, a new experimental mode of cultivating students' scientific research and innovation ability, comprehensive experiment has become one[3] of the development trends of experimental teaching reform. Combined with the cooperative scientific research results of schools and enterprises, the establishment of vertical and horizontal close connection, grid structure, the scientific research results are applied to the experimental teaching, the design of a green comprehensive corrosion inhibition experiment requiring 4 class hours, to achieve the positive interaction between scientific research and teaching and scientific research to promote teaching practice activities. The green character of the experiment is reflected in the use of waste fruit peel (persimmon peel, orange peel, pomegranate peel, locust leaf, etc.) extract as corrosion inhibitor. The study showed that these peels contain phenols (tannins, flavonoids, etc.) which can coordinate with metal to form a protective

film[4-7] on the metal surface; The comprehensive type is reflected in the preparation of acidizing corrosion inhibitor, the processing and data recording of steel sheet, the performance evaluation and data processing of corrosion inhibitor, according to the UV-VIS spectrum and infrared spectrum analysis, speculate the mechanism of corrosion inhibitor. The experimental design of the "waste" reuse, reflecting the concept of green environmental protection, the design of the experiment is in line with the students more comprehensive understanding of the relevant knowledge of corrosion inhibition, but also help to train the comprehensive experimental ability of students and students scientific research, innovative thinking training and formation, but also can cultivate their environmental awareness in the actual work after.

2. Experimental Purpose

(1) To master a method for determining the corrosion rate of steel sheet (static weight loss method);

(2) Understand the corrosion inhibition mechanism of corrosion inhibitors;

(3) To understand the effective components of fruit peel extract that play the role of corrosion inhibition;

(4) Learn to further evaluate the corrosion inhibition effect of different corrosion inhibitors and analyze the reasons for the change of related parameters through data processing, analysis and calculation of related parameters;

(5) Understand the principle of UV-VIS photometer and infrared photometer, master the operation of UV-VIS photometer and infrared photometer, and be able to analyze their spectra.

3. Experimental Principle

Corrosion of steel sheet in acidic medium is electrochemical corrosion. If in hydrochloric acid, the corrosion reaction of steel sheet is:

Anode reaction: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}$

Cathode reaction: $2\text{HCl} + 2\text{e} \rightarrow \text{H}_2\uparrow + 2\text{Cl}^-$

Battery reaction: $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\uparrow$

In order to reduce the corrosion of the acid medium to the metal, the commonly used method is to add corrosion inhibitors to the acid medium. According to the mechanism of action, acid medium corrosion inhibitors can be divided into adsorption film type (such as formaldehyde) and "intermediate phase" type (such as butanol) two categories. The peel contains polyphenols, flavonoids, saponins and other compounds, which have phenolic hydroxyl groups that can coordinate with metals, and form a protective film on the metal surface through coordination. In order to quantitatively evaluate the corrosion inhibition effect of the inhibitor, the corrosion rate of the steel sheet in the medium with and without the inhibitor can be measured. In the determination of corrosion rate, the most commonly used method is the weight loss method.

4. Experimental Steps

4.1. Extraction of Effective Components of Plant Materials and Preparation of Corrosion Inhibition Solution

The natural dried peel and leaves (persimmon peel, orange peel, pomegranate peel, locust leaf, etc.) are crushed and ground into powder with a grinder, and sifted with a 120

purpose standard test screen to obtain a fine peel powder (prepared by the experimenter before the experiment). Different raw materials can be used for experiments according to the preparation of raw materials, and the corrosion inhibition effect of different raw materials can be compared.

Distilled water/anhydrous ethanol as the extraction agent, weigh a certain mass (10 g) of the peel, add 50 mL of distilled water/anhydrous ethanol into a 100mL flask, heat reflux for 30min, drop to room temperature, filter to obtain the peel extract solution. The obtained fruit peel extract aqueous solution was diluted with distilled water and configured into a 1mol/L corrosion inhibitor with hydrochloric acid concentration of 10, 20, 50, 100 and 200 dilution times, respectively. Add 120mL of diluted 5 concentrations of extract acid solution and hydrochloric acid blank solution into 150mL wide mouth bottle with bottle stopper respectively, label well, heat in 60°C water bath, wait for the corrosion solution temperature to reach the established temperature.

4.2. Treatment Method of Static Hanging Film Weight Loss Method

4.2.1. Instrument

- (1) 4 enamel utensils;
- (2) vernier calipers, medical metal tweezers, absorbent cotton rope, scissors, etc., each 1;
- (3) 1 electric hair dryer;
- (4) 1 water bath;
- (5) 1 surface dish;
- (6) 1 package of steel sheet for corrosion evaluation.

4.2.2. Potions

- (1) Concentrated hydrochloric acid;
- (2) anhydrous ethanol;
- (3) Acetone;
- (4) petroleum ether.

4.2.3. Experimental Operation

- (1) Pre-treatment of hanging film
 - a. Grinding the steel sheet: grinding the steel sheet with 360 mesh, 600 mesh, 1200 purpose sandpaper, polishing to bright as a mirror; Use vernier caliper to measure its length, width, thickness and the inner diameter of the small hole, and calculate the surface area.
 - b. Degreasing: Put the polished steel sheet into the porcelain with petroleum ether, soak for 5 ~ 10min, degreasing and decontamination;
 - c. Put the defatted steel sheet into the porcelain with anhydrous ethanol, soak for 5 ~ 10min to dehydrate, and gently turn the steel sheet 2 ~ 3 times during the soaking process with tweezers;
 - d. Remove the steel sheet, put it on a clean quantitative filter paper, and dry it with a hair dryer;
 - e. The blown steel sheet will be weighed with an analytical balance, accurate to 0.0001g. Record the data;
 - f. The processed steel sheet shall not be used for direct touch or subjected to mechanical damage and contamination.
- (2) Hang the sheet

After the treated steel sheet is worn with a rope, hang it in the corrosive liquid that has reached the established temperature (60°C) in the water bath (action should be fast), pay attention to the steel sheet cannot touch the wall and the bottom of the bottle, completely soak in the solution, and soak in the water bath for 1 h.

- (3) Hang the sheet after processing

a. After removing the steel sheet from the corrosive liquid, wash it with water immediately to remove the corrosive liquid and loose corrosion products;

b. Put the washed steel sheet into acetone and anhydrous ethanol respectively, soak for 5 ~ 10min; Take out the hanging pieces on the quantitative paper, dry them with a hair dryer, and then weigh them with an analytical balance, accurate to 0.0001g. Record the data.

4.3. Determination of Infrared Spectrum and UV-visible Spectrum

4.3.1. Instruments

UV-2450 ultraviolet-Visible spectrometer (Shimadzu, Japan), Nicolet 5700 infrared spectrometer (Thermo Electron Corporation).

4.3.2. Experimental Operation

The peel extract from the above anhydrous ethanol is diluted 800 times with anhydrous ethanol to the test solution. The liquid sample of 1-10mg was placed between the two salt crystal slices and scanned by Nicolet 5700 infrared spectrometer to obtain the infrared spectrum of the corresponding peel extract.

The peel extract extracted by anhydrous ethanol was diluted by anhydrous ethanol to 800 times the liquid to be measured. The quartz colorimetric dish was scanned with UV-2450 UV-VIS spectrometer in the range of 190 ~ 800nm to obtain the UV spectrum of the corresponding peel extract.

5. Data Processing

The experiment adopts hanging 2 steel sheets, if the mass loss of 2 steel sheets is relatively close, the general rule is about 5%, then the average mass loss of 2 steel sheets is calculated; If the mass loss of the two steel sheets is quite different, this set of data is invalid, and it is necessary to re-experiment.

The calculation formula of corrosion rate W_{corr} is as follows (1):

$$W_{corr} = \frac{\Delta m}{St} \times 10^4 \quad (1)$$

Where: W_{corr} -- corrosion rate, $g \cdot m^{-2} \cdot h^{-1}$;

Δm -- quality of corroded steel sheet, g;

S -- total area of steel sheet, cm^2 ;

t -- test time, h.

(2) Calculation of corrosion inhibition rate E_w %

The definition of corrosion inhibition rate, the difference between the corrosion rate of steel sheet without adding and adding corrosion inhibitor and the ratio of corrosion rate of steel sheet without adding corrosion inhibitor, the calculation formula of corrosion inhibition rate E_w % is as follows:

$$E_w \% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \quad (2)$$

Where: E_w -- corrosion rate, %;

W_{corr} -- blank corrosion rate, $g \cdot m^{-2} \cdot h^{-1}$;

W'_{corr} -- corrosion rate with addition of corrosion inhibitor, $g \cdot m^{-2} \cdot h^{-1}$.

6. Think About the Question

(1) Explain the corrosion inhibition mechanism of the tested fruit peel extract, and explain the reasons for poor

corrosion inhibition effect at low temperature;

(2) Explain the effect of the finish of the steel sheet on the corrosion;

(3) The corrosion inhibition effect of alcohol extract and water extract of the same peel was compared in the group, and the reasons were explained;

(4) The corrosion inhibition effects of different peel extracts as corrosion inhibitors were compared between groups, and the reasons were explained;

(5) What interference should be removed before analyzing the infrared spectrum and ultraviolet spectrum of extracts? What functional groups does the infrared spectrum and ultraviolet spectrum indicate in the extract? The inhibition mechanism of compounds in the extract was discussed.

7. Summary

In the design of this experiment, the knowledge of organic chemistry and oilfield chemistry was applied to evaluate the corrosion inhibition effect of fruit peel extract on steel sheet in acidic solution. In the experiment, waste fruit peel is used as raw material to extract organic matter as corrosion inhibitor, which can exercise students' ability to extract experimental operation, improve students' awareness of environmental protection, measure the corrosion inhibition rate of steel sheet by static weight loss method, and enable students to master the basic operation of corrosion inhibition experiment, especially practice the operation and reading of vernier calipers. The improvement of the follow-up processing ability of experimental data, as well as the deepening of the understanding of infrared spectrum and UV-visible spectrum and the enhancement of the ability to analyze the spectrum. The experiment is carried out in small groups, which is conducive to improving the students' cooperation ability and team spirit.

References

- [1] Gang Chen, Min Zhang, Jingrui Zhao, Rui Zhou, Zuchao Meng, Jie Zhang, Investigation of Ginkgo biloba leave extracts as corrosion and oil field microorganism inhibitors[J], Chemistry Central Journal, 2013, 7: 83.
- [2] Gang Chen, Min Zhang, Min Pang, Xiao-qing Hou, Huijun Su, Jie Zhang, Xiao-jiang Hao, Extracts of Punica granatum Linne husk as green and eco-friendly corrosion inhibitors for mild steel in oil fields[J], Research on Chemical Intermediates, 2013, 39: 3545-3552.
- [3] Jie Zhang, Yingpan Song, Huijun Su, Li Zhang, Gang Chen*, Jingrui Zhao, Investigation of Diospyros Kaki L.f husk extracts as corrosion inhibitors and bactericide in oil field[J], Chemistry Central Journal, 2013, 7: 109-114.
- [4] Jie Zhang, Jing Tian, Haiyang Wang, Li Zhang, Gang Chen*, Jingrui Zhao, Hong Li, Synthesis and evaluation of lignosulphonate Mannich base as eco-friendly corrosion inhibitors[J], Asian Journal of Chemistry, 2014, 26(22): 7643-7646.
- [5] Gang Chen, Xiaoqing Hou, Qilong Gao, Li Zhang, Jie Zhang, Jingrui Zhao, Research on Diospyros Kaki L.f leaf extracts as green and eco-friendly corrosion and oil field microorganism inhibitors[J], Research on Chemical Intermediates, 2015, 41: 83-92.
- [6] [Xuefan Gu, Ke Dong, Jing Tian, Hong Li, Jie Zhang, Chentun Qu, Gang Chen*, Investigation of modified Ginkgo biloba leaves extract as eco-friendly inhibitor for the corrosion of N80

steel in 5% HCl[J], Desalination and Water Treatment, 2018, 107: 118-126.

[7] Qiang Deng, Jie Zhang, Xuefan Gu, Weichao Du, Yun Ma, Gang Chen*, Environmental education in applied chemistry—A comprehensive experiment of corrosion inhibition by overdue medicines[J], Basic & Clinical Pharmacology & Toxicology, 2018, 123(Supplement 3): 82.