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Corrosion inhibition performance of a metallic zinc corrosion inhibitor in chemical cleaning

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ABSTRACT

The corrosion inhibition effect of the extract (i.e., SPLE) of sweet potato leaf on metallic zinc in hydrochloric acid solution was studied by weight loss method. The results showed that SPLE had a good corrosion inhibition effect on metallic zinc in hydrochloric acid solution with a concentration of 0.1–0.5 mol L^{-1}, and the adsorption on the surface of metallic zinc conforms to the Langmuir adsorption isotherm. The corrosion inhibition rate increased with the increase of SPLE concentration but decreased with the increase of temperature and hydrochloric acid concentration. The adsorption enthalpy ΔH_{ads} and corrosion kinetic parameters (rate constant k, kinetic constant B) were obtained by Van't Hoff equation and Mathur empirical formula, the corrosion inhibition behavior of SPLE was discussed based on this parameter.

Keywords: zinc; sweet potato leaf; extract; hydrochloric acid; corrosion inhibition; adsorption

1. Introduction

Metallic zinc has good corrosion resistance since it easily forms oxide film on the surface, so it is widely used as a heat transfer equipment of industrial circulating water in industries such as electric power, petrochemical industry, pharmaceutical, food, and compressed natural gas production, etc. But after using for a certain period of time, the surface of the galvanized layer is prone to scale formation, which affects heat transfer performance and energy-saving effect, it needs to be chemically cleaned. In the cleaning process, since zinc is a very active amphoteric metallic, it basically reacts with all acids and bases. Therefore, the use of corrosion inhibitors is an important means to prevent corrosion of metallic zinc. However, inorganic corrosion inhibitors such as chromate, nitrite, heavy metallic ions, etc., are restricted or prohibited due to their toxicity and environmental pollution, while organic zinc corrosion inhibitors [1] also have their shortcomings such as toxicity, complicated synthetic routes and high cost, which are not conducive to popularization. In recent years, natural plant extracts have become a popular research hotspot as a green plant corrosion inhibitor because they are harmless to the environment [2–7]. Based on the related plant extracts in inorganic acid having excellent corrosion inhibition performance on cold-rolled steel and the adsorption on the steel surface conforming to the Langmuir model [8,9], This paper studied the inhibition effect of sweet potato leaf extract, SPLE, on metallic zinc in 0.1–0.5 mol L^{-1} hydrochloric acid. The corresponding corrosion kinetics parameters (rate constant k, kinetic constant B) of adsorption enthalpy ΔH_{ads} were obtained by Van't Hoff equation and Mathur empirical formula, then corrosion inhibition behavior of SPLE were discussed according to this parameter, this could provide some theoretical basis for the sweet potato leaf extract as a corrosion inhibitor for metallic zinc in acid medium.

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2. Materials and methods

2.1. Materials and reagents

Sweet potato leaves, pure zinc test tablets with purity ≥99.9%, petroleum ether (boiling range 60°C–90°C), absolute ethanol, acetone, and hydrochloric acid were all analytical reagents.

2.2. Preparation of SPLE

First, the natural sweet potato leaves were decontaminated, the surface dust was washed away with water, after drained and placed in an oven and dried at 60°C for 48 h, then they were naturally cooled at room temperature, pulverized, passed through a 350 μm sieve, and placed in a jar for extraction.

Taking an appropriate amount of sweet potato leaf powder into a three-neck round-bottom flask, 80% ethanol solution was added into the flask and a water bath was adjusted to 75°C. After dipped for 2 h, the extract was filtered and the filtrate part was taken out to be extracted by petroleum ether and remove the ester. Eventually, it was processed by a rotary evaporator to be a concentrated liquid and finally dried under vacuum.

2.3. Corrosion inhibition performance test

The 25 mm × 20 mm × 0.25 mm pure zinc test tablets were polished to the mirror-like surface with sandpaper, it was washed with distilled water and dried by a hair dryer. After degreased the acetone and accurately weighed it with an electronic balance, it was suspended on the glass hook and soaked in 100 mL of a 0.1 mol L^{-1} hydrochloric acid solution containing a certain concentration of SPLE at 30°C. After stored in a constant temperature water bath for 6 h, the zinc tablets were taken out, cleaned, dried, after accurately weighed it, the weight loss of the zinc tablets, ΔW, was obtained. The above experiment was then repeated by changing the hydrochloric acid concentration and temperature. The corrosion rate (V) was calculated using the following Eq. [10]:

$$V = \frac{\Delta W}{(S \times t)} \tag{1}$$

$$E = \left[\frac{(V_0 - V)}{V}\right] \times 100\% \tag{2}$$

In the equation: ΔW was the weight loss of the zinc tablets (g); S was the test surface area of the metallic zinc (m^2); t was the corrosion time (h); V_0 and V, respectively were the corrosion rates of the metallic zinc tablets without and with the corrosion inhibitor (%); E was the corrosion inhibition rate (%) [1].

3. Results and Discussion

3.1. Corrosion inhibition effect of SPLE on zinc

The corrosion rate of metallic zinc in 0.1 mol L^{-1} hydrochloric acid and the corrosion inhibition rate of SPLE to metallic zinc at each concentration were shown in Table 1.

Table 1
Corrosion rate of zinc in 0.1 mol L^{-1} HCl and corrosion inhibition rate of SPLE toward zinc

SPLE concentration (mg L^{-1})	Corrosion rate V/(g m^{-2} h^{-1})		Corrosion inhibition rate E/%	
	30°C	40°C	30°C	40°C
0	3.38	7.74	–	–
100	1.35	5.36	60.1	28.3
300	0.85	4.00	74.8	46.5
500	0.74	3.53	78.2	52.8
700	0.70	3.14	79.3	57.9
1,000	0.68	2.82	80.0	62.7

It can be seen from Table 1 that the corrosion rate of metallic zinc decreased significantly after the addition of sweet potato leaf corrosion inhibitor, SPLE, indicating that SPLE had a corrosion inhibition effect on metallic zinc, and as the concentration of SPLE increased, the corrosion inhibition effect increased continuously; The maximum corrosion inhibition rate at a concentration of 1,000 mg L^{-1} reached 80.0% and 62.7% at 30°C and 40°C, respectively.

The corrosion inhibition mechanism of SPLE on metallic zinc was presumed as follows. In literature [11], the plant extract contained a mixture of flavonoids, vitamins, amino acids, nicotinic acid, phosphorus, etc., which were polar groups containing O and N. (–NH_2, –COOH, –OH, O=C, etc.), and were also the main functional groups in sweet potato leaf extract, they were excellent chelating agents with lone pair electrons and π electrons, so they can form chelation with Zn or Zn^{2+}, then it generated adsorption [1] to forms an adsorption film layer with corrosion inhibition on the surface of the metal zinc, which exerted a good corrosion inhibition effect.

It was worth noting that the corrosion inhibition rate of SPLE to metallic zinc decreased with the increasing of temperature. The reason may be that increasing the temperature accelerated the corrosion of the metallic zinc by the acid, and generates a large number of bubbles on the surface of the metallic zinc, making it difficult to adsorb the corrosion inhibitor molecules on the zinc surface; besides, it also caused that the corrosion inhibitor molecules were also desorbed from the surface of the metallic zinc.

3.2. Adsorption model of PLE and adsorption enthalpy ΔH_{ads}

In order to further study, the adsorption behavior of SPLE on the surface of metallic zinc, it was assumed that the adsorption of corrosion inhibitor on the surface of metallic zinc conformed to the Langmuir adsorption equation, then it is shown by Eq. (3) [10]:

$$\frac{c}{\theta} = \frac{1}{K} + c \tag{3}$$

In Eq. (3): c was the corrosion inhibitor concentration, (mg L^{-1}); K was the adsorption equilibrium constant; θ is the surface coverage, and the θ value can be calculated by the following Eq. [10]:

$$\theta = \frac{(\Delta W_0 - \Delta W)}{(\Delta W_0 - \Delta W_m)} \quad (4)$$

In Eq. (4): ΔW_m was the weight loss when the corrosion inhibition rate was maximum (minimum weight loss of zinc tablets), g; $c/\theta - c$ linear regression was conduct by computer, the results are listed in Table 2, and $c/\theta - c$ linear correlation diagram was drawn (Fig. 1).

The results showed that $c/\theta - c$ had a good linear relationship; the linear slope at 30° was close to 1, indicating that the adsorption of SPLE on the surface of metallic zinc conformed to the Langmuir adsorption model. It was worth noting that the slope of the line at 40° deviated from 1, indicating a large interaction force between the SPLE molecules adsorbed on the surface of the metal zinc [12–15].

The calculation of adsorption enthalpy can be obtained by the Van't Hoff equation [15]:

$$\Delta H_{\text{ads}} = \left[\frac{(RT_2 - T_1)}{(T_2 - T_1)}\right] \ln\left(\frac{K_2}{K_1}\right) \quad (5)$$

In Eq. (5): ΔH_{ads} and K were adsorption enthalpy and adsorption equilibrium constant, respectively, R was the gas constant (8.314 J K^{-1} mol^{-1}), and T was the absolute temperature (K).

From Eq. (5), it can be calculated that $\Delta H_{\text{ads}} = -115.2$ KJ mol^{-1}, indicating that the adsorption process of SPLE on the zinc surface was an exothermic process, that was, the increase of temperature was not conducive to the adsorption of corrosion inhibitor on the surface of metallic zinc.

Table 2
c/θ—c, Linear regression parameters

Temperature/°C	Correlation coefficient	Slope	Intercept	K (L/mg)
30	0.9999	0.9639	33.0990	0.03021
40	0.9986	0.8666	142.4255	0.00702

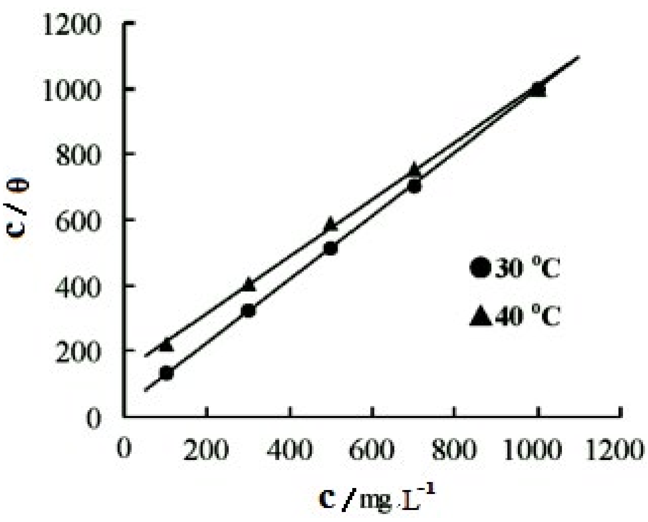

Fig. 1. The $c/\theta - c$ line in 0.1 mol L^{-1} HCl.

3.3. Effect of hydrochloric acid concentration on corrosion inhibition performance

At 30°C, the concentration of hydrochloric acid was in the range of 0.1–0.5 mol L^{-1}, and the corrosion rate of metallic zinc and the corrosion inhibition rate of SPLE toward zinc are shown in Table 3.

It can be seen from Table 3 that the corrosion rate of metallic zinc increased with the concentration of the hydrochloric acid medium, but the addition of SPLE corrosion inhibitor reduced the corrosion rate. That was, within the range of hydrochloric acid concentration in the paper, SPLE generated corrosion inhibition toward metallic zinc, the corrosion inhibition rate decreased significantly with the increase of hydrochloric acid concentration. This was because the concentration of hydrochloric acid increased, and the adsorption film layer of SPLE on the surface of the metallic zinc was damaged by the medium, and the corrosion inhibition effect was lowered. Table 3 also demonstrates that the corrosion inhibition rate increased with the increase of SPLE concentration in the whole concentration range of 0.1–0.5 mol L^{-1} hydrochloric acid. Therefore, in practice, the concentration of corrosion inhibitor can be further increased to increase the corrosion inhibition performance toward metallic zinc in concentrated hydrochloric acid.

It was assumed that the corrosion rate V (g m^{-2} h^{-1}) of metallic zinc and the concentration of hydrochloric acid (C) were in accordance with Mathur's empirical formula [16]:

$$\ln V = \ln k + BC \quad (6)$$

In Eq. (6): B was the kinetic constant, k was the rate constant, and the line of ln$V$-C at each inhibitor concentration is shown in Fig. 2:

According to Eq. (6), each kinetic parameter was obtained from the slope and intercept of the lines, and the results are shown in Table 4.

From Eq. (6), the physical meaning of k was the corrosion rate when the hydrochloric acid concentration tended to zero, so k represents the corrosion ability of hydrochloric acid to metallic zinc [16–18]. B was the slope of the ln$V$-C line, and the B value indicated the change range of the corrosion rate of the metallic zinc after the concentration of hydrochloric acid was changed.

The data in Fig. 2 and Table 4 show that the ln$V$-C line had a good linear relationship between the blank hydrochloric acid solution and the hydrochloric acid solution added with SPLE, which represented that the corrosion law of the metallic zinc conformed to the Mathur empirical formula. The data in Table 4 showed that the rate constant, k, decreased by an order of magnitude after the addition of SPLE, and decreased with the increase of corrosion inhibitor concentration; this meant that SPLE had a corrosion inhibition effect on metallic zinc in the whole hydrochloric acid concentration range. The other kinetic constant B increased over the entire concentration range of hydrochloric acid, which indicated that the rangeability of corrosion rate of metallic zinc with the change of the concentration of hydrochloric acid after

Table 3
Corrosion rate of zinc in 0.1–0.5 mol L^{-1} HCl and corrosion inhibition rate of SPLE toward zinc

HCL concentration/ mol L^{-1}	Corrosion rate *V*/(g m^{-2} h^{-1})			Corrosion inhibition rate *E*/%		
	Blank	500/mg L^{-1}	1,000/mg L^{-1}	Blank	500/mg L^{-1}	1,000/mg L^{-1}
0.1	3.38	0.74	0.68	–	78.2	80.0
0.2	5.32	1.82	1.51	–	65.8	71.6
0.3	7.82	3.38	2.70	–	56.7	65.4
0.4	11.45	6.03	5.05	–	47.3	55.9
0.5	16.08	12.72	11.02	–	20.9	31.5

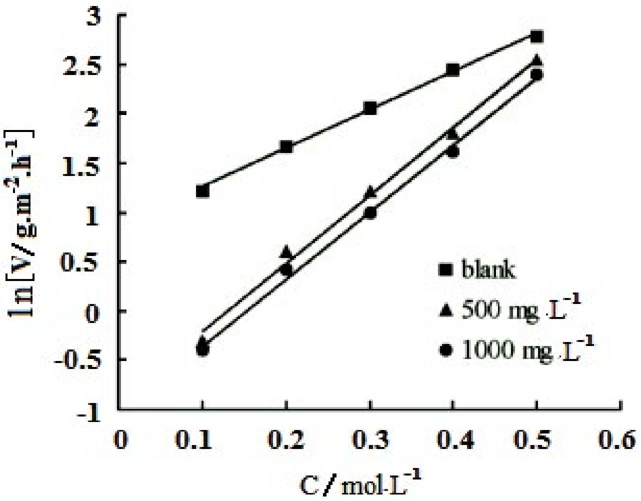

Fig. 2. 30° ln*V*-*C* line.

Table 4
ln*V*-*C* linear regression parameters of metallic zinc in HCl solution at 30°

SPLE/mg L^{-1}	Correlation coefficient	*B*/g m^{-2} h^{-1} L mol^{-1}	*k*/g m^{-2} h^{-1}
0	0.9965	38.85	2.38
500	0.9919	68.85	0.41
1,000	0.9958	67.87	0.36

addition of SPLE was higher than that without corrosion inhibitor, which indicated SPLE at the same concentration had different corrosion inhibition ability for metallic zinc in different concentrations of hydrochloric acid. That was, the corrosion inhibition ability was significantly reduced with the increase of hydrochloric acid concentration, which is consistent with the results in Fig. 2 [19–23].

4. Conclusions

The plant corrosion inhibitor (i.e., SPLE) extracted from sweet potato leaves has good corrosion inhibition effect on metallic zinc in 0.1 mol L^{-1} hydrochloric acid solution, and has broad application prospects in industrial applications. The adsorption of SPLE on the surface of metallic zinc conforms to the Langmuir adsorption model.

The corrosion inhibition rate increases with the increase of corrosion inhibitor concentration but decreases with the increase of temperature and hydrochloric acid concentration. The corrosion law of metallic zinc without SPLE corrosion inhibitor conforms to the Mathur empirical formula. After adding SPLE, the rate constant k decreases significantly, while the kinetic constant B increases.

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