A COMPARISON OF THE ANTICORROSION POTENTIALS OF *Ceratonia siliqua* PLANT PARTS IN HCl MEDIUM

Supported by tetfund

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Received: May 13, 2020 **Accepted:** July 05, 2020

Abstract: Adsorptive and inhibitive properties of plant part extracts of *Ceratonia siliqua* was investigated in this study. The various extracts of the plant were assessed as acid-corrosion inhibitors. The corrosion inhibitive potentials of hexane, chloroform, and ethanol extracts of the bean (with gum and pod), leaves, and bark (with stem) of *C. siliqua* on zinc in 2M HCl was studied by measuring weight loss, inhibition efficiency, surface coverage, and corrosion rate. The weight loss studies showed the hexane extract of the bean (with gum and pod) to exhibit higher anti-corrosion property than the hexane fraction of the leaves and bark (with stem). Furthermore, the chloroform and ethanol extracts of the leaves were more efficient in retarding weight loss than the bean and bark. The ethanol extract of the leaves showed the highest inhibition efficiency of 96.67% and 0.9667 for surface coverage at 5 min for 50% v/v when compared with the other extracts of the plant. The chloroform extract of bark (with stem) and ethanol extract of leaves of *Ceratonia silique* has the best anticorrosion potentials in this study. *C. Siliqua* extracts can effectively serve as green inhibitors of zinc corrosion in acid medium.

Keywords: Anticorrosion, inhibition, *Ceratonia siliqua*, zinc, HCl

Introduction

There is increasing concern about the toxicity of most corrosion inhibitors in the industry. Most of the known corrosion inhibitors are synthetic chemicals or heavy metals such as chromate. They are expensive and very hazardous to living organisms and the environment. Hence current researches are directed towards the use of green inhibitors for the inhibition of the corrosion of metals (Paul *et al*. 2012).

Extracts of various parts of plants have been used as green inhibitors: leaves (Begum, 2011), barks (Okeniyi *et al*., 2014) stem (Singh *et al*., 2012) as they are biodegradable and do not contain heavy metals or other toxic compounds. The fruitful use of naturally occurring substances/molecules to inhibit the corrosion of metals in alkaline (Ramde *et al*., 2014; Suedile *et al*., 2014), acid (Al-Otaibia *et al*., 2014; Fadare *et al.,* 2016) and neutral medium (Beenakumari, 2013) has been reported by some research groups. Extracts of plant materials contain polar atoms such as S, N, O, P, etc. Because of this nature, the lone pair of electrons present on these atoms are pumped on to the metal surface; inhibitor molecules are adsorbed on the metal surface which forms protective film thereby inhibiting corrosion loss of electrons from the metal surface and corrosion is controlled (Karthiga *et al*., 2015).

Plant extracts of *Ceratonia siliqua* were chosen in this work because recent investigators had found out that some plant extracts could be used as corrosion inhibitors in some environments. This was corroborated by the fact that these plant extracts are in-expensive, ecologically friendly/acceptable, and posed no threat to the environment (Fadare *et al.,* 2016). The aim of this work is to compare the potentials of the extracts of the leaves, bean (plus the gum and pod), bark (plus stem) of *Ceratonia siliqua* as anti-corrosion agents in the corrosion of Zn metal in HCl acid medium using Weight-loss method.

Materials and Method

Sample collection

Ceratonia siliqua plant parts were collected from Tilla village, Keffi, Nasarawa State, Nigeria. The zinc coated roofing sheet was collected from a construction site in Keffi, Nasarawa State, Nigeria.

Sample preparation

Preparation of the parts of Ceratonia siliqua plant

The leaves of the *Ceratonia siliqua* were washed vigorously in distilled water to remove dust, stones, and other foreign materials and air dried at room temperature. The dried leaves were macerated and ground into powder using an electric blender (Kenwood). The powdered leaves were sieved using a sieve with a mesh size of 70 µm and kept in airtight already leached (with concentrated HCl) polyethene bags. The beans (plus gum and pod) and bark (with the stem) of *C. siliqua* were washed with distilled water, air-dried at room temperature, macerated, and ground into fine powder.

Preparation of zinc coated roofing sheet

The zinc sheets were mechanically cut into pieces (2 × 2 cm). The sheet's surface was washed with absolute ethanol. The washed sheets were then degreased with acetone and desiccated.

Extraction of plant parts

The extracts of the leaves, beans, and bark with stem were obtained using Soxhlet extractor according to the conventional method (Vashi and Champaneri, 1997). This involves refluxing about 50 g of dried powdered parts of *Ceratonia siliqua* with n- hexane, ethanol, and chloroform at 100°C for 8 h, respectively.

Preparation of reagents

A standard solution of 2M HCl was prepared by a simple dilution method in which 41.7 mL of the concentrated acid was made up to 1000 mL (1 dm^3) in a volumetric flask with distilled water.

Experimental procedure

Weight loss test

The weight-loss method was used in this study (Zhang *et al*., 2014). In the weight loss experiment, 100 mL beaker containing 50 mL of 2M HCl, was used as the corrodant. Zinc coupon was dipped into the corrodant solution. The coupon was retrieved from the corrodant solution at different time intervals i.e. (5, 10, 20 40, 60, 120 min, respectively). After each immersion time, it was dipped immediately into 20% NaOH to terminate the corrosion reaction and then washed with distilled water, dried in acetone, and then kept in a desiccator to be cooled and re-weighed. The weight loss, which is an average of triplicate measurements, is as given by Equation (1) below;

$$W = W_i - W_f \quad (1)$$

Where: W is the weight loss of the coupon in grams. W_i is the initial weight and W_f the weight after retrieval. The procedure was then repeated with the introduction of various concentrations (10, 20, 30, 40, 50% v/v, respectively) of the inhibitor (extracts of the leaves, bean (with gum and pod) and the bark (with stem) of *Ceratonia siliqua* into the acid solution maintained at the same temperature (31°C).

Inhibition efficiency and surface coverage

The inhibition efficiency (Adejo *et al.*, 2012; Adejo *et al.*, 2013), IE % was calculated using Equation (2);

$$IE\ \% = \left[1 - \frac{W_1}{W_2}\right] x\, 100 \qquad (2)$$

Where: W_1 and W_2 are the weight losses in grams of zinc coupon in the presence and absence of inhibitor, respectively.

The degree of surface coverage, ϴ, is given by Equation (3);

$$\theta = 1 - \frac{W_1}{W_2} \qquad (3)$$

The corrosion rate, CR, of the zinc was determined for the immersion period from weight loss using Equation (4);

$$CR = (gcm^{-2}h^{-1}) = \frac{W}{At} \qquad (4)$$

Where: *W* is the weight loss in grams (*g*), A is the coupon surface area in cm^2 and *t*, the immersion time in hours

Results and Discussion

Weight loss studies

The Figures (1 - 9) show the observed weight loss of zinc coupon immersed in 2M HCl. Hexane, chloroform, and ethanol extracts of leaves, beans (with gum and pod), and bark (with stem) of *Ceratonia siliqua* were added to inhibit the weight loss of zinc in the acid medium. The nine graphs showed similar trend. There was a decrease in weight loss with an increase in the concentration of the extract from 10 to 50% v/v.

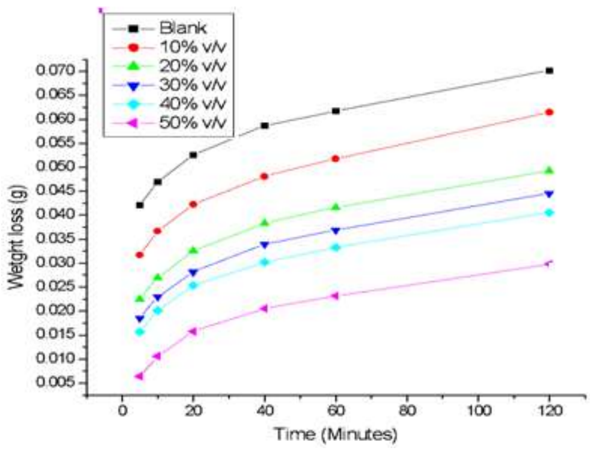

Fig. 1: Variation of weight loss with time for hexane extract bean (with gum and pod) of *Ceratonia siliqua*

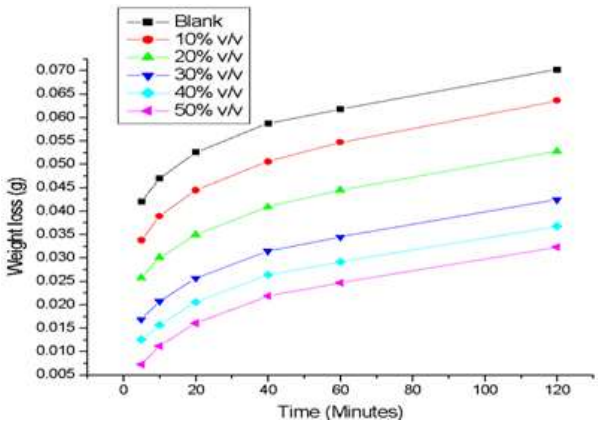

Fig. 2: Variation of weight loss with time for chloroform extract of bean (with gum and pod) of *Ceratonia siliqua*

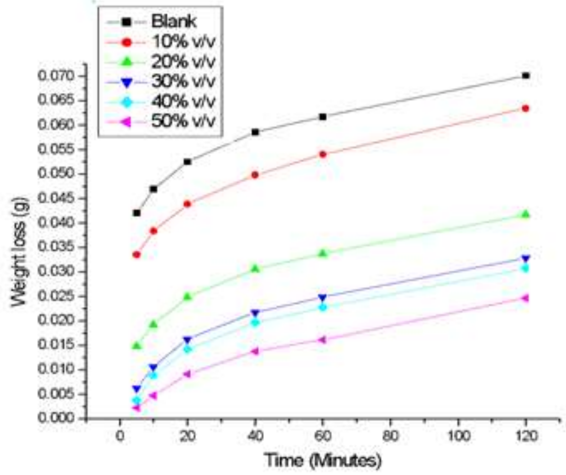

Fig. 3: Variation of weight loss with time for ethanol of bean (with gum and pod) of *Ceratonia silique*

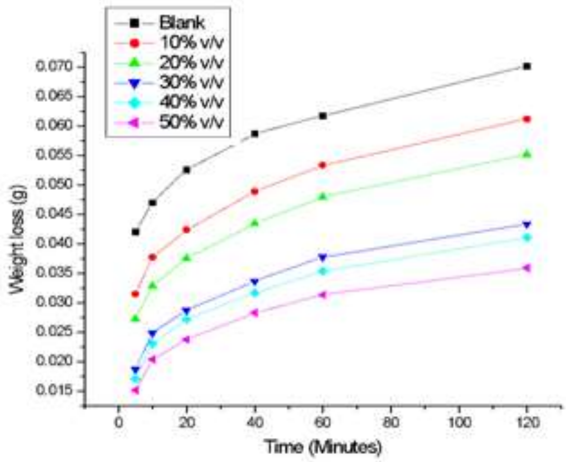

Fig. 4: Variation of weight loss with time for hexane extract of bark (with stem) of *Ceratonia silique*

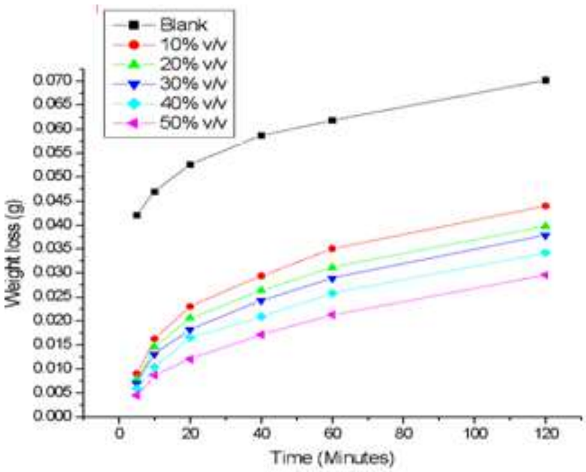

Fig. 5: Variation of weight loss with time for chloroform extract of bark (with stem) of *Ceratonia silique*

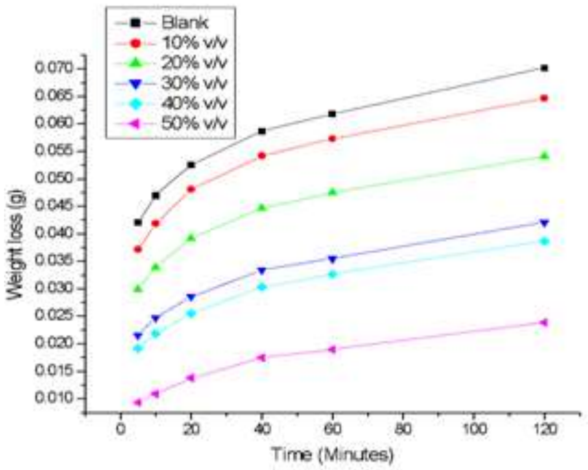

Fig. 6: Variation of weight loss with time for ethanol extract of bark (with stem) of *Ceratonia silique*

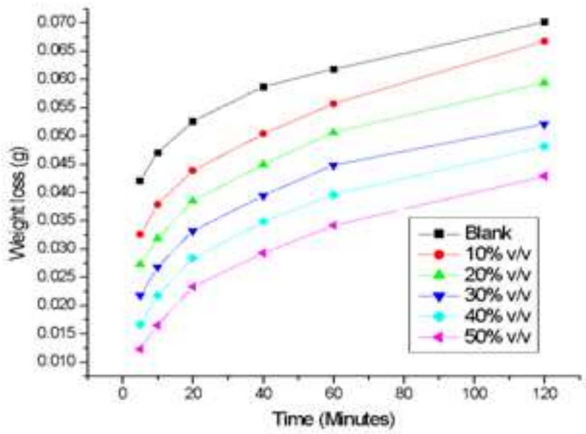

Fig. 7: Variation of weight loss with time for hexane extract of leaves of *Ceratonia silique*

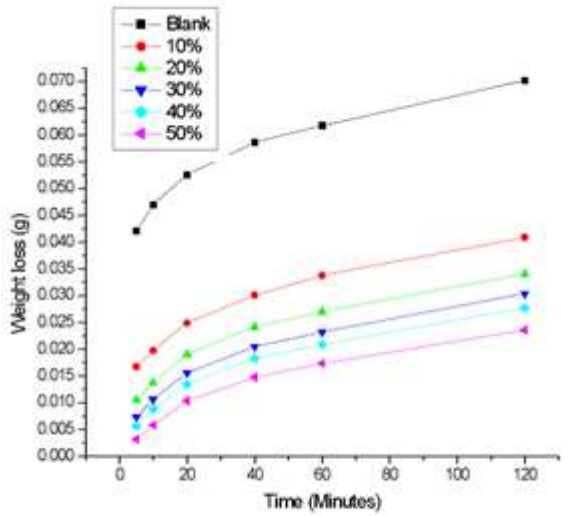

Fig. 8: Variation of weight loss with time for chloroform extract of leaves of *Ceratonia siliqua*

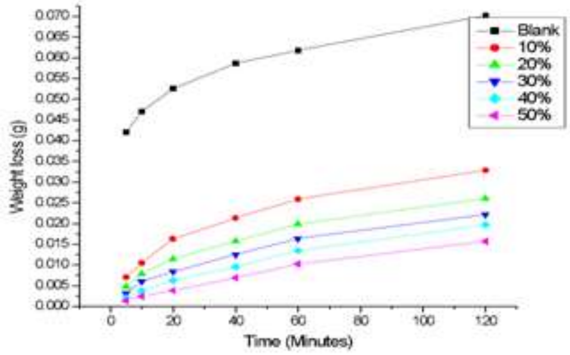

Fig. 9: Variation of weight loss with time for ethanol extract of leaves of *Ceratonia silique*

The observed weight loss of zinc coupon immersed in 2M HCl was investigated. Hexane, chloroform and ethanol extracts of leaves, beans (with gum and pod) and bark (with stem) of *Ceratonia siliqua* inhibited the weight loss of zinc in the acid medium (Figs. 1 – 9) which supports earlier research conclusions (Okeniyi *et al.*, 2014; Fouda *et al.*, 2014; Elbouchtaoui *et al.*, 2014; Fadare*et al.*, 2016) that plant extracts inhibit corrosion. As observed in previous studies on plant extract corrosion inhibitor potential in acidic medium (Al-Otaibia *et al*., 2014; Fadare *et al.*, 2016).

Inhibition efficiency (IE)

The inhibition efficiency (IE) of the various plant parts are shown in Figs. 10 – 18. All the graphs followed the same trend.

Inhibition efficiency increases as the concentration of the plant extracts were increased and maximum efficiency was observed at 50% v/v (Figs. 10-18). There was a relatively very small variation of IE with an increase in the concentration of ethanol extract of the bark (with stem) sample as shown in Fig. 16. Figs. 1- 3 show the graphs of the weight loss with time for hexane, chloroform and ethanol extracts of the beans (with gum and pod) sample. Reduction in the weight loss of the zinc coupon was observed with an increase in the concentration of the beans (with gum and pod) samples. At 120 min using 50% v/v, hexane extract of the beans (with gum and pod) showed a weight loss of about 0.0298 g with IE of 57.55% (Fig. 15), chloroform extract of the beans (with gum and pod) had a weight loss of 0.0323 g with IE of 53.99% (Fig. 14), while a weight loss of 0.0247 g with IE of 64.32% (Fig. 13) was recorded for the ethanol extract of the beans (with gum and pod). The ethanol extract of the beans (with gum and pod) showed a lower weight loss value/higher IE. This suggests that the phytoconstituents are more soluble in polar solvents like ethanol.

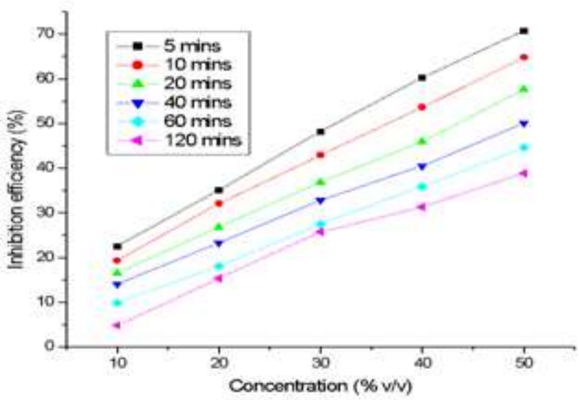

Fig. 10: Variation of IE with concentration of hexane extract of the leaves of *Ceratonia silique*

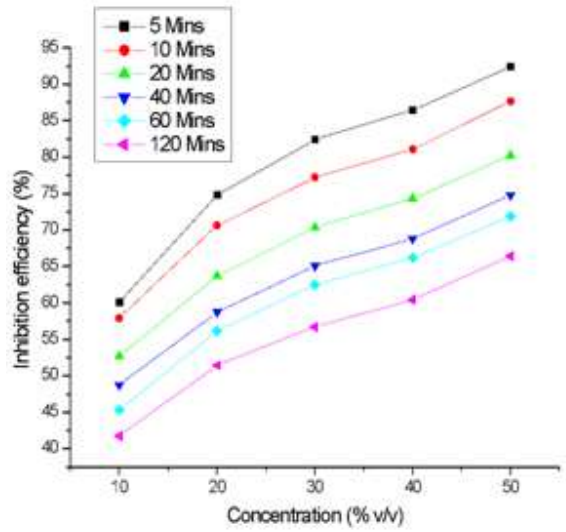

Fig. 11: Variation of IE with concentration of chloroform extract of the leaves of *Ceratonia siliqua*

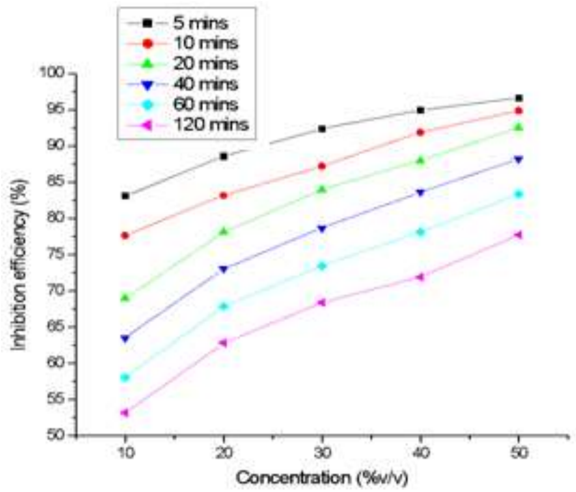

Fig. 12: Variation of IE with concentration of ethanol extract of the leaves of *Ceratonia siliqua*

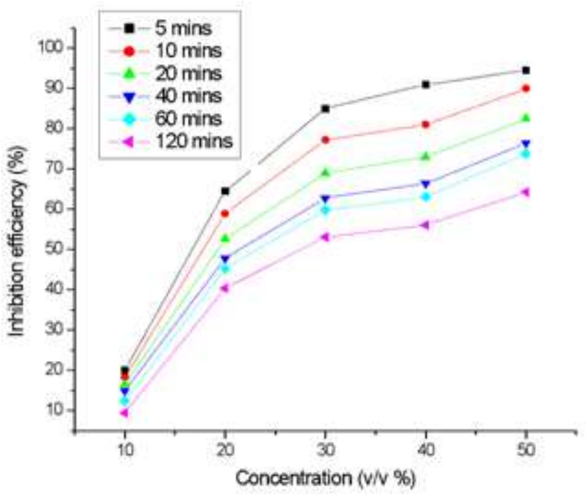

Fig. 13: Variation of IE with concentration of ethanol extract of bean (plus gum and pod) of *Ceratonia siliqua*

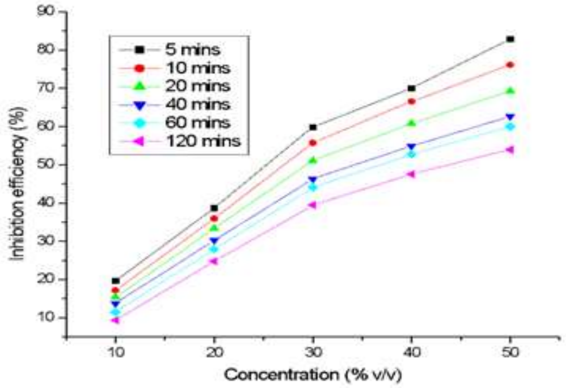

Fig. 14: Variation of IE with concentration of chloroform extract of bean (plus gum and pod) of *Ceratonia siliqua*

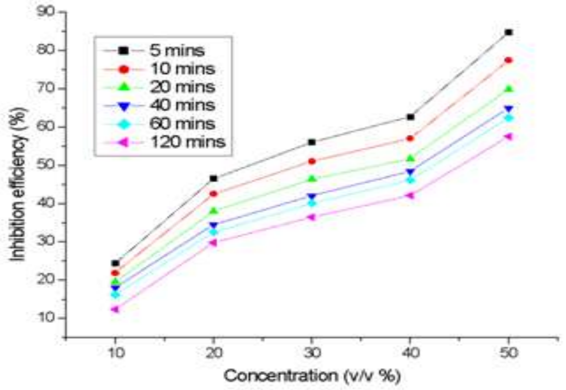

Fig. 15: Variation of IE with concentration of hexane extract of bean (plus gum and pod) of *Ceratonia siliqua*

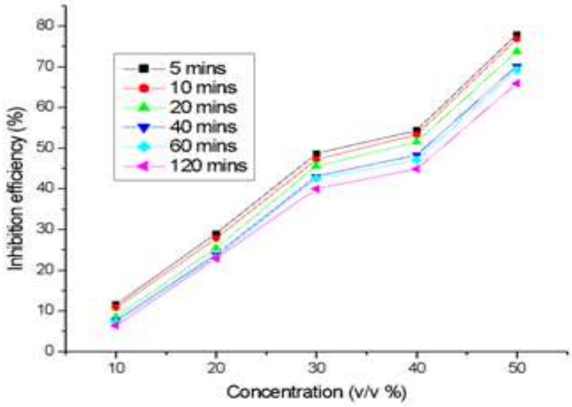

Fig. 16: Variation of IE with concentration of ethanol extract of the Bark (with stem) of *Ceratonia siliqua*

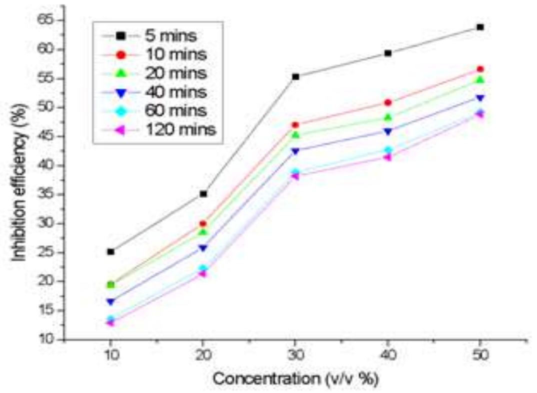

Fig. 17: Variation of IE with concentration of hexane extract of the Bark (with stem) of *Ceratonia silique*

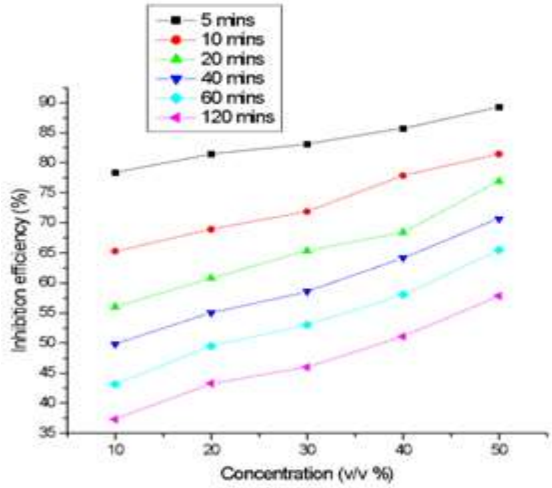

Fig. 18: Variation of IE with concentration of chloroform extract of the bark (with stem) of *Ceratonia silique*

At 120 min, using 50% v/v, the reduction in the weight loss for zinc coupon and IE in all the different solvents used for the bark (with stem) varied from 0.0423 g with IE of 48.86% for hexane extract (Figs. 4 & 17), 0.0296 g with IE of 57.83% for chloroform extract (Figs. 5 & 18) and 0.0239 g with IE of 65.95% for ethanol extract (Figs. 6 & 16). This same trend was observed for the beans (with gum and pod) samples. The leaves extracts of *Ceratonia siliqua* at 120 minutes using 50% v/v had the weight loss of 0.0156 g with IE of 77.78% for ethanol extract (Figs. 7 & 12) in the acid medium, 0.0236 g with IE of 66.38% was recorded when the chloroform extract (Figs. 8 & 11) was used, while 0.0429g of the zinc coupon was lost in the acid medium with IE of 38.89% when hexane extract (Figs. 9 & 10) was used.

The inhibition efficiency was highest at 5 min for all the extract of the plant parts of *C. siliqua* where it varied from 20.19% at 10% v/v to 94.54% at 50% v/v for ethanol extract of bean (with gum & pod) as shown in Fig. 13. For the bark (with stem), chloroform extract was highest with 78.38% at 10% v/v to 89.31% at 50% v/v (Fig. 18), while for the leaves, ethanol extract recorded the highest IE with 83.13 % at 10% v/v to 96.67% at 50% v/v (Fig. 12). Less than 45 mg was lost in 120 min at all concentrations (10 – 50% v/v) of chloroform extract of bark (with stem) with least loss of 27.5 mg (50% v/v) and Less than 35 mg lost for ethanol extract of leaves of *Ceratonia silique* with least loss of 15 mg (50% v/v) as shown in Figs. 5 & 9, respectively.

Conclusion

Ceratonia siliqua extracts can effectively serve as green inhibitors of zinc corrosion in acid medium. The variations in the inhibitive properties of the leaves, beans (with gum and pod) and the bark (with stem) of *C. siliqua* is based on the abundance of phytochemicals in each plant parts and the polarity of the solvents used. The electron densities around the functional groups in these phytochemicals are the key structural features that determine the effectiveness of inhibition. Chloroform extract of bark (with stem) and ethanol extract of leaves of *C. silique* has the best anticorrosion potentials in this study and should be further researched. This study suggests that the active anticorrosion constituents are more soluble in polar solvents like ethanol, so a more polar solvent like methanol should be tried in further research.

Conflict of Interest

Authors declare that there is no conflict of interest reported in this work.

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