CORROSION RATES OF PIPELINE STEEL IN AGRICULTURAL PRODUCE/ HYDROCHLORIC ACID CORROSION SYSTEM

Makanjuola Oki[1]*, Adeolu A Adediran[1], Chiamaka P Ofili[1]
[1]Department of Mechanical Engineering
Landmark University, PMB 1001, Omu-Aran, Kwara State, Nigeria.
Email: Makanjuola.oki@lmu.edu.ng

Abstract
A preliminary investigation on the extracts of an agricultural produce, Onion (Allium Cepa), was studied for its corrosion inhibiting effects in a pipeline-steel/hydrochloric acid corrosion system using gravimetric and thermometric techniques in addition to optical microscopy examinations performed on specimens during natural exposure tests. The corrosion rate of steel increased with increase in time of immersion in HCl whereas it decreased as the concentration of the extract was increased in the corrosion system. In freely corroding state, the corrosion rates ranged from 2.15 mmpy to 1.08 mmpy in 10 M and 5 M hydrochloric acid respectively. Such difference in corrosion rates are attributable to large difference in concentrations of the corrodants. At an inhibitor concentration of 20 %, the corrosion rates decreased to $1.3x10^{-2}$ mmpy and $2.5x10^{-4}$ mmpy respectively corresponding to inhibition efficiencies of between 83 % and 92 %. The adsorption of active components in the extracts on the corroding surfaces obeyed the Langmuir adsorption isotherm. From examinations performed on painted steel specimens during natural exposure tests, the onion extracts, dispersed in a white colored alkyd paint system, prevented paint delamination over a period of 168 h. Whereas the specimens painted with uninhibited alkyd paint suffered major paint delamination over the same exposure period.

Keywords: Keywords: morphology, degradation; inhibition efficiency, concentration, adsorption

Submitted: 12.01.2017 Reviewed: 14.03.2017 Accepted: 02.05.2017

1. INTRODUCTION

Various acids, including hydrochloric acid are widely used in industries especially for descaling purposes on pipelines in food processing industries and down tube holes in the oil/gas industries (Oki *et al.* 2011; Solmaz *et al*. 2008; Fouda *et al*. 2016). Although useful for this purpose, it never the less corrodes metals in contact with it. Thus it becomes imperative to be able to predict its period of usefulness while in contact with the metal as regards the extent of acceptable corrosion it will inflict on pipelines at distances where corrosion gauges may be inaccessible.
In order to reduce metal wastages to a minimum, it is customary to employ inhibitors along with descaling chemicals for pipes and ancillary infrastructures in the food and oil/gas industries. Inhibitors can be classified in a variety of ways (Oki, 2013). Whereas a classification grouped inhibitors as acidic, alkaline or neutral inhibitors indicating the type of media in which they perform optimally, others classified them as anodic, cathodic or mixed inhibitors depending on their mode(s) of interaction and a resultant polarization geometry they attain on the Evans (E/log i) diagram. However, a more acceptable categorization differentiates them as organic or inorganic. Most inorganic and synthesized organic inhibitors have in recent times been implicated as environmental pollutants and may be injurious to human health. In view of this, researchers on corrosion inhibitors have focused attention on extracts of various parts of plants as viable alternatives. These are organic in nature and biodegradable which may be a limitation in corrosion systems where microbial actions are prevalent along with other forms of corrosion activities. They are referred to as “Green Inhibitors” (Satapathy *et al*. 2009; Sivaraju and Kannan, 2010; Abdallah, 2004; Mahmoud, 2006; Chaieb *et al*. 2009; Kesavan *et al*. 2012; Rani and Basu, 2012). In view of this and in addition to outcomes in a previous work by one of the authors and co-workers (Oki *et al*. 2011) in which extracted tannins from *Rizophora Racemosa* and onion skin achieved good

margins of efficiencies as inhibitors for mild steel in hydrochloric acid and during natural atmospheric exposure, the current work focused on the extracts of the edible bulb of onion as inhibitor of interest. The extracts of onion, though contain some forms of tannins, is a mixture of various carbon compounds containing oxygen, sulphur and nitrogen which have electron rich centers and can adsorb on corroding metals (Okafor *et al*. 2010) where they interfere in one manner or the other to reduce rates of corrosion.
Various complementary techniques, such as gravimetric, gasometric and thermometric have been employed in studying corrosion rates of metals in different media in which results obtained showed good correlation. For the weight loss technique, relationships described in the literature by Oki *et al*.(2011) and others (Okafor *et al*. 2010) have been widely employed, these are:

Corrosion rate (mmpy) (CR)

$$= \frac{543 \text{ x } \Delta w}{\text{Area(A)x Time(t)xMetal density}(\rho)} \quad (1)$$

where, mass loss, ΔW, is in mg, area in cm^2, time in hours of exposure and metal density, expressed in gm/cm^3 . The degree of coverage, Θ, of the inhibitor is given by:

$$\Theta = \frac{\Delta Wu - \Delta Wi}{\Delta Wu} \quad (2)$$

where ΔW_u is the change in weight of specimen in uninhibited test solution and ΔW_i is the change in weight in the inhibited test solution. Also percentage inhibition efficiency, E% is given by:

$$E\% = \frac{CRu - CRi}{CRu} \text{ x } 100 \quad (3)$$

where CR_u and CR_i are the corrosion rates in uninhibited and inhibited test solutions respectively.

Prediction models, both numerical (Koch *et al*. 2015; Liao *et al*. 2012) and computer based (De waard and Williams, 1975, De waard and Williams, 1991) for the management of corrosion have gained enormous recognition in recent times and have been successfully utilised in oil/gas and other industries. In view of these, the current investigation forms a part of examinations to look into the use of a modification of the prolific Milliams and de-Waards model in predicting the corrosion rates of pipeline steel exposed to highly concentrated hydrochloric acid, although the model originally, was meant for CO_2 induced corrosion of steel.
Theoretically and partly on experimental basis, Dewaard and Millams developed a model that has been used frequently for determination of CO_2 corrosion rates on steel. A newer version of Dewaard- Millams equation is given as:

$$logVcorr = 5.8\frac{1710}{273+t} + 0.67\log(pCO2) \quad (4)$$

where, Vcorr = Corrosion Rate in mm/year
t = temp ^oC and pCO_2 = partial pressure of CO_2 in bar.

The factor, 0.67 indicates that the corrosion is not completely under cathodic control. If it was, the factor would be 1. In the equation, mass transfer limitation due to deposits of corrosion products was not taken into consideration. Therefore it represented a so-called worst case scenario which is associated with the reaction of pipeline steel in highly acidic environments.
Thus, from,

$$logVcorr = 5.8 - \frac{1710}{273+t} + 0.67 \log(pCO2)$$

we can rewrite the equation and have another version for pipeline steel in various concentrations of HCl as:

$$logVcorr = 5.8 - \frac{1710}{273+t} + 1 \log(pH) \quad (5)$$

Where, pH is the hydrogen ion concentration of HCl, and the factor, 0.67, had been replaced by 1, which indicates that for corrosion of steel in HCl solution, the corrosion is cathodically controlled; the mechanism for the H_2 evolution reaction is:

$$H^+ + e^- \rightarrow H \qquad (6)$$

followed by,

$$H + H \rightarrow H_2\uparrow \qquad (7)$$

While these reactions in equations (6) and (7) seem to be relatively simple, the rate at which H^+ are transformed into H_2 is a function of several factors, including the rate of electron, e^-, movement from metal, M to H^+.

From the literature, the exchange current density for hydrogen evolution on iron, Fe, $\log_{10} i_o$ (A/cm^2) = -6; whereas for Pt = -2. Thus these cathodic reactions on steel are extremely electrochemically slow and will be rate determining. Other extension of these investigations will be to use organic extracts from plants with viable corrosion inhibiting potentials as metal organic frameworks (MOFs). MOFs are porous Nano-coatings of immense potentials.

2. MATERIALS AND METHODS

Mild steel specimen which contained, Carbon, 0.16 %; Magnesium 0.53 %; Silicon 0.16 % and Iron 99.25 % was made out into spade-like electrodes with total exposed surface area of 10.4 cm^2. Prior to exposure to various corrosive media, the specimens were abraded with emery paper after which they were individually rinsed in distilled water and degreased in acetone, dried in air and stored in desiccators prior to use in the investigations.

Acid extracts of onion was obtained by initial drying of sliced onion in an oven set at 31^o C for 17 h. After pulverizing, 40 grams of the powdered onion was added to 400 ml of 5 M and 10 M HCl respectively. Filtered solutions from these were subsequently employed through serial dilution to obtain different percentages of inhibitor (5, 10, 15 and 20 % respectively) of interest in the corrosion systems. All chemicals employed were of laboratory grades. The experiments were carried out in triplicates for reproducibility.

2.1 Gravimetric Measurements.

Weight loss measurements were carried out by immersion of each cleaned and pre-weighed electrode in 100 ml of 5 M or 10 M HCl for various periods of time to act as control. Other electrodes were similarly exposed in 5 M and 10 M HCl media containing various concentrations of onion extracts. Duplicate experiments were performed in each case and the mean values of the weight loss recorded for further evaluations. The corrosion rates were obtained in millimetre penetration per year (mmpy) with the relationship in equation 1 as described by Oki *et al.* (2015); Ekpe *et al.* (1995) and other researchers (Umoren *et al.* 2008).

2.2 Thermometric Measurements

The reaction number, RN, which gives a measure of corrosion rate, is defined by Oki and others (2015) as:

$$RN = \frac{Tm - To}{t} \qquad (8)$$

where, T_m and T_o are the maximum and the initial reaction temperatures respectively and **t** the time taken to attain the maximum temperature.

The various specimens were immersed in 100ml of test solutions of interest. The temperatures at immersion and the time to maximum temperature attained were noted.

2.3 Atmospheric Exposure

Two 100 ml of white alkyd paints were prepared in 200 ml beakers. One blank and the other mixed with inhibitor extracted with deodorized kerosene. Both paint specimens were thinned to approximately similar viscosities. Four electrodes were immersed in the blank and inhibited paint. Two samples were prepared for each and air-dried for 48 h. The two painted specimens (blank and inhibited) and an untreated specimen were exposed vertically to the outside environment at Omu-Aran, Kwara State. These specimens were observed regularly and at the end of 168 h, the specimens were examined and photographed.

2.4 Exposure in 3.5% Sodium chloride solution

Two specimens treated as in the case of atmospheric exposure tests were immersed in

100 ml of 3.5% sodium chloride solutions at a nominal pH of about 7.5 and observed daily over a period of 168 h. Photographs of the specimens were taken before, during and after the immersion periods.

3. RESULTS AND DISCUSSIONS

3.1 Corrosion rates from weight loss measurements

Figure 1 graphically portrays the variation of the corrosion rates with time of immersion in the various concentrations of hydrochloric acid. The corrosion rates obviously increased with time of immersion in the acid. However, the corrosion rate increased more rapidly in the highly concentrated 10 M than in 5 M HCl. This was expected as the higher the concentration of acids, the higher the intensity of their reactions with metal surfaces.

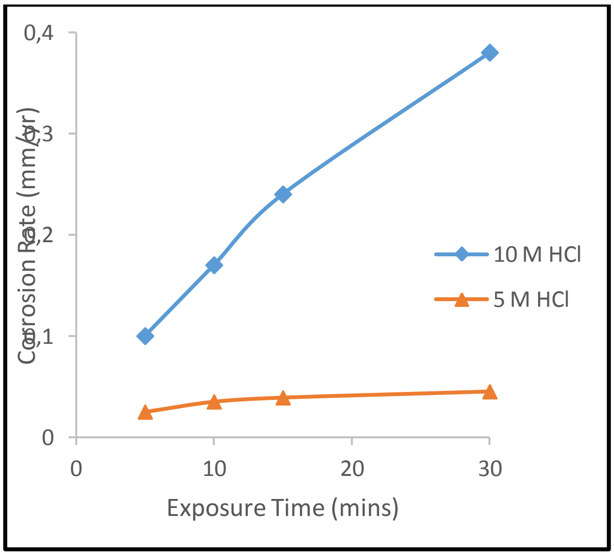


Fig.1: Corrosion rates with time of pipeline steel in 5 M and 10 M of HCl from gravimetric measurements.

Fig. 2 summarizes the corrosion rates of pipeline steel in inhibited 10 M and 5 M hydrochloric acid where it can be observed that as the concentration of the inhibitor increased, there was a corresponding decrease in corrosion rates which reflected as increases in inhibitor efficiencies from about 72 % at a concentration of 5 % to around 83 % at an inhibitor concentration of 20 % for 10 M acid.

Whereas a similar trend was observed for the corrosion rates of pipeline steel in 5 M HCl with various concentrations of the inhibitor; albeit, higher inhibitor efficiency was observed. This may be related to the observed lower corrosion rates than in 10 M hydrochloric acid. The inhibition efficiency in both concentrations of the acid increased initially rapidly with a rate that decreased with increase in the concentration of the inhibitor as its coverage on the corroding surface gradually increased.

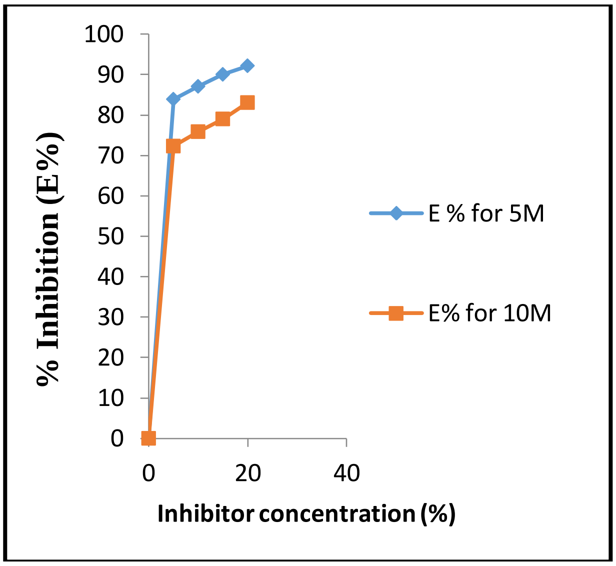


Fig. 2– Variation of inhibition efficiencies of onion extracts for pipeline steel in 5 M and 10 M HCl over a period of 15 minutes from gravimetric measurements

From Figs. 2 and 3 which showed the relationships between corrosion rates and inhibitor concentration on the one hand and inhibition efficiency and inhibitor concentration respectively, it is obvious that a reduction in corrosion rates with increase in inhibitor concentrations resulted in increases in inhibition efficiency. This was envisaged as organic inhibitors usually perform by adsorbing on corroding surfaces (Umoren et al. 2008) and the degree of coverage when coupled with other parameters can indicate the adsorption isotherm relevant to the adsorbing species (Ekpe *et al*. 1995; Umoren *et al*. 2008).

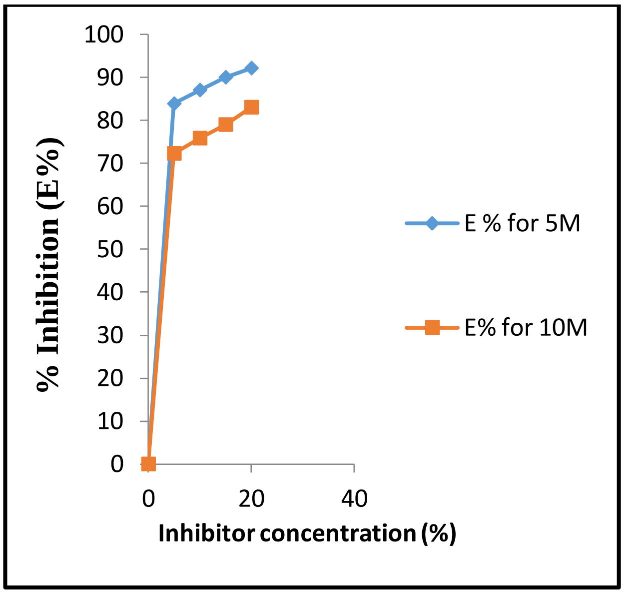


Fig 3– Corrosion rate of pipeline steel in 5 M and 10 M HCl in various concentrations of onion extracts from gravimetric measurements

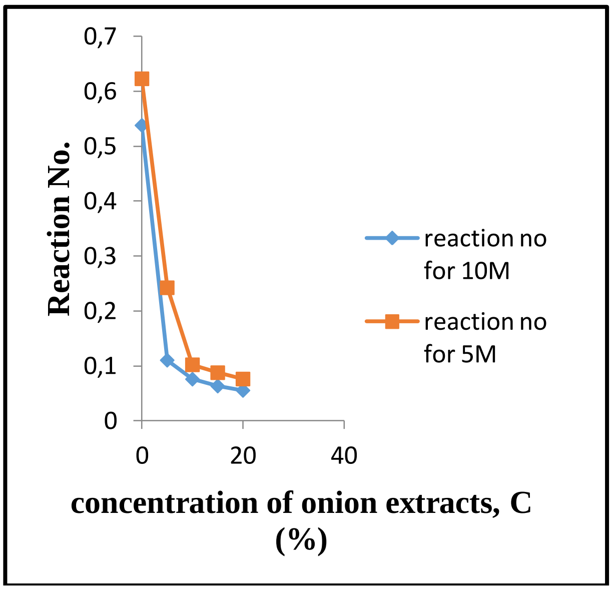


Fig. 4 Variation of reaction number for pipeline steel in 10 M and 5 M HCl with various concentrations of onion extracts

Thus onion extracts which contain tannins, sulphur and nitrogen containing organic components will reduce the corrosion rates of pipeline steel by adsorption. This was further corroborated by the straight line curve obtained from the plot of surface coverage (ɵ)/concentration(c) versus concentration of inhibitor i.e. ɵ/c versus c; where the degree of coverage, Ө, of the inhibitor is given by equation 2 as:

$$\Theta = \frac{\Delta Wu - \Delta Wi}{\Delta Wu} \qquad (2)$$

where all the symbols have their usual meanings. This clearly indicated that the adsorption of the active components on the metal surface obeyed the Langmuir adsorption isotherm which indicated that there were no interactions among adsorbed moieties on the metal surface.

3.2 Thermometric measurements

As displayed in Fig.4, reaction number, RN, decreased with increase in inhibitor concentration.

In addition, the calculated inhibitor efficiencies obtained, as shown in Fig. 5, are within the same range as the values obtained from the weight measurements.

The graphical representation of the variation of reaction number and percentage inhibition efficiencies with increases in inhibitor concentrations is displayed in figure 5 where it can be observed that the values showed a close correlation with those obtained from weight loss measurements.

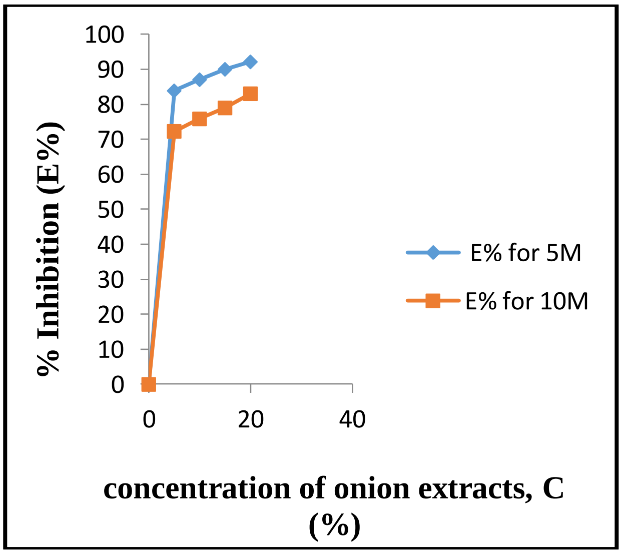


Fig.5. The variation of % inhibition efficiency of onion extracts for mild steel in 5 M and 10 M of HCl from thermometric studies

3.3 Atmospheric exposure

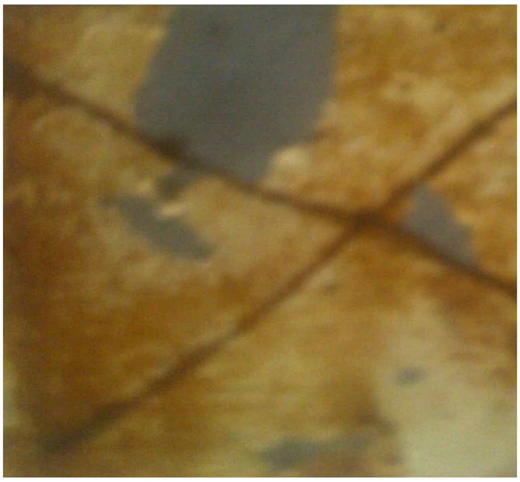
The various specimens after atmospheric exposure displayed various degrees of corrosion. To the naked eye, untreated mild steel specimens showed some red-brown patches of rust on the first day of exposure to the atmosphere. These are the corrosion products of iron which was exposed to moist air, ferrous hydroxide and was further oxidized to the hydrated oxide within the 24 h of exposure period. However, the painted specimens did not reveal evidence of corrosion. The paints protected the substrates for the limited exposure time, 168 h, although the specimens without inhibitor showed a brownish background under the white alkyd paint. Despite the deliberately inflicted scratches on the substrates prior to atmospheric exposure regimes, there were no other discernible differences between the specimens coated with inhibited and uninhibited paints.

3.4 Exposure of specimens to 3.5% NaCl.

From the optical macrograph obtained, Figs 6a and b for the inhibited and uninhibited specimens respectively, the specimen coated with inhibited alkyd paint prevented paint delamination over the exposure period of 168 h. Tannin, a component of the onion extract have been demonstrated to be a good atmospheric corrosion inhibitor of steel (Oki et al. 2011) and as it contains oxygen while other components of the extracts which possess sulphur and nitrogen with lone pairs of electrons will effectively interfere with corrosion reactions to reduce the effects at the steel electrode/environment interphase.

From Fig 6a, the inhibited specimen, although it showed a rust-stained at the top right-hand corner, the paint was not disrupted after adhesive tape test. However, as displayed in Fig. 6 b, the top coating of uninhibited paint was removed on most parts of the surface of the specimen after the adhesion test. Thus, it can be safely inferred that the inhibiting pigments from onion was largely responsible for the better corrosion performance of the former.

(a)



(b)

Fig 6. Pipeline steel (a) coated with inhibited and (b) plain alkyd paints after immersion in 3.5% NaCl for 168 h after adhesion tape tests

4. CONCLUSION

The extracts of onion are effective inhibitors of the corrosion of pipeline steel in 5 M and 10 M hydrochloric acid. The percent inhibition efficiency increased with increased inhibitor concentration giving efficiencies of 92 % and 83 % respectively in 5 M and 10 M HCl at an inhibitor concentration of 20 %.

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