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Sodium Chromate and Diethylene Amine as Corrosion Inhibitors for Mild Steel in Cassava Fluid

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Abstract: This report presents the investigation of sodium chromate and diethylene amine as inhibitors of corrosion of a mild steel in cassava fluid. The inhibition study was carried out using the weight loss immersion technique. The inhibitive potentials of the two inhibitors was evaluated based on a determination of the corrosion rates in the presence and absence of the inhibitors, determination of the pH of various cassava fluids and a calculation of the inhibition efficiencies of the two inhibitors at different levels of concentrations. The results of this study show that diethylene amine is a much better inhibitor of the corrosion of mild steel in cassava fluid than sodium chromate. The inhibition efficiencies by diethylene amine are higher than 85% for the 0.5, 1.0 and 1.5 M concentrations investigated. In the case of sodium chromate, inhibition efficiencies only become significant for 1.0 M and 1.5 M concentrations. Generally, the pH of all cassava fluid with and without inhibitors increased with duration of exposure and the corrosion rates of the mild steel decreased with increase in the pH of the cassava fluid.

Key words: Corrosion, inhibitors, diethylene amine, sodium chromate, cassava, efficiency

INTRODUCTION

NST-44 mild steel is one of the Nigeria made steel that is often used as a constructional material because of its mechanical strength and ease of fabrication. The agro-allied industries in Nigeria make use of this steel for the production of machines such as grater, hammer mills, etc. Sadly, the life span of these machines has been reduced considerably because of the corrosive effect of cassava. The cyanide content of cassava has been identified by many investigators as the main species responsible for corrosion (Fontana and Greene, 1987; Alagbe *et al.*, 2005). Several studies have investigated the inhibition of metal corrosion by various types of organic and inorganic compounds (Trethewey and Chamberlain, 1995). Inhibition by these compounds is mainly as a result of adsorption of molecules or ions at the metal surface forming a protective layer. The extent of inhibition depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor and the type of corrosion media (Thomas, 1981; Maayta, 2002). Corrosion inhibition of iron and steel in various media has been the subject of numerous studies (Umoru *et al.*, 2005; Loto, 2003, Loto and Mohammed, 2000).

The inhibitive effect of chromate and nitrite on the corrosion of iron has been extensively studied since 1950 (Azambuja *et al.*, 2003). The inhibitive effect of molybdate and tungstate ions, which are weaker oxidizing agents than chromate anion, on the corrosion of iron have also been investigated (Pryor and Cohen, 1953). It is noted in these previous works that the inhibitive behaviour of the molybdate and tungstate ions greatly depend on the presence of dissolved oxygen.

Among the various inorganic inhibitors so far studied, it is well known that chromate is one of the most effective even though little is known about its activities in cassava environments.

The inhibitive effects of numerous organic inhibitors on the corrosion of iron and steel have also been carried out (Loto and Muhammad, 2000; Loto, 2003; Alagbe *et al.*, 2005; Umoru *et al.*, 2005; Rajappa and Venkatesha, 2003). A literature survey showed only limited systematic work done to the corrosion inhibition of NST-44 mild steel in various media.

The purpose of the present research is to study the inhibitive effect of sodium chromate (inorganic compound) and diethylene amine (organic compound) on the corrosion of NST-44 mild steel in cassava fluid. There is yet to be any reported study on the effect of these additives as corrosion inhibitors for NST-44 mild steel in cassava medium.

MATERIALS AND METHODS

The NST-44 mild steel rods used for this work were obtained from Oshogbo Steel Rolling Mill, Oshogbo, Osun State, Nigeria. And the experimental work was carried out in the Materials Laboratory of the Department of Metallurgical and Materials Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria. The mild steel rods' dimensions are 25 mm diameter and 10 mm thickness. The chemical composition of the steel is: - C- 0.33; Mn- 0.09. P-0.02. S- 0.02; Ni- 0.03; Cr- 0.45; Mo -0.02; Sn- 0.01 ; Fe (balance).

Corrosion coupons were cut from the steel obtained and machined appropriately to reduce the cold working effect of the sheared edges. Subsequently, each of the coupons was subjected to grinding on emery papers 240, 320, 400 and 600 grits. The oil and grease stains on the specimens were removed with petroleum spirit. Afterwards, the coupons were weighed on a PB 153 Mettler Toledo digital weighing balance and then kept in desiccators prior to exposure. Peeled cassava tubers were crushed and squeezed to extract the cassava fluid used for the experiment. As soon as the cassava fluid was ready, different media containing 0.5, 1.0 and 1.5M concentrations of sodium chromate and diethylene amine inhibitors were prepared. The seventh medium without any inhibitor was used as the control experiment. Finally, the corrosion coupons were exposed to the various media. Specimens were later withdrawn periodically at intervals of 48 h and washed thoroughly under running tap. Thereafter, they were dried, reweighed and the corrosion rates calculated in millimeter per year (mmpy). The corrosion rates have been calculated in mmpy using the expression.

$$\text{mm/yr} = 87.6 W / \text{DAT}$$

where, W is the weight loss in mg, D is the density of the specimen in g cm^{-3} , A is the total exposed surface area of the specimen in cm^2 and T is the exposed time in hours.

RESULTS

Figure 1 shows that the corrosion rates of the steel in cassava after inhibiting with 0.5 M sodium chromate did not vary much from those without inhibition. However, with 1.0 and 1.5 M inhibition the corrosion rates were significantly lowered.

The results contained in Fig. 2 show that the corrosion rates of mild steel were much lower in the diethylene amine inhibited cassava fluid than in the uninhibited medium at 0.5, 1.0 and 1.5 M concentrations.

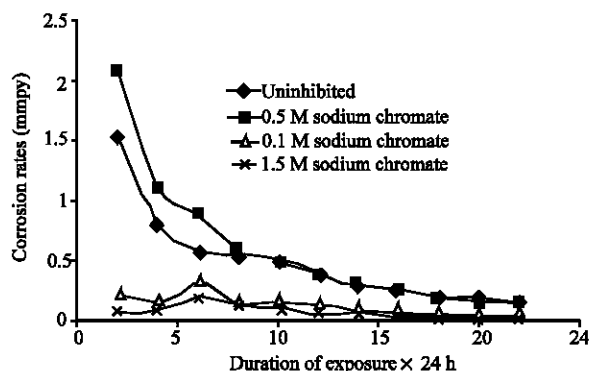


Fig. 1: Effect of sodium chromate on the corrosion inhibition of a mild steel in cassava fluid

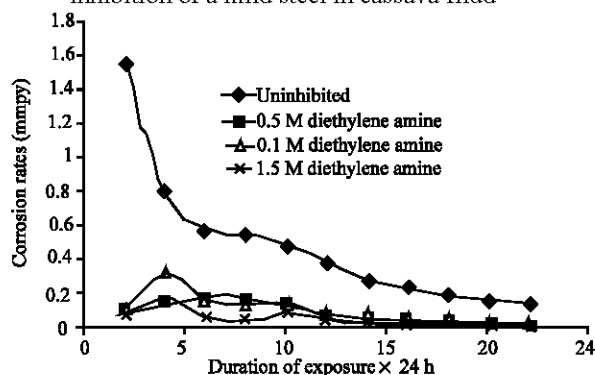


Fig. 2: Effect of diethylene amine on the corrosion inhibition of a mild steel in cassava fluid

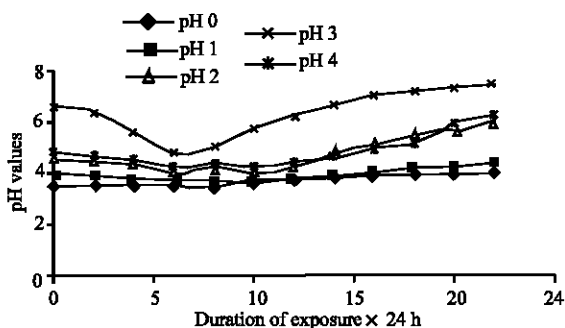


Fig. 3: Variation of pH values of cassava fluid with or without sodium chromate

Figure 3 and 4 show the effects of corrosion products and inhibitor presence on the pH of corrosion media. It is clear from these figures that the pH of the cassava (pH 0) without steel specimens and inhibitor changes linearly but at a low rate. The pH of the cassava medium (pH 1) with immersed steel specimens but without inhibitor was greater than pH 0 though only slightly.

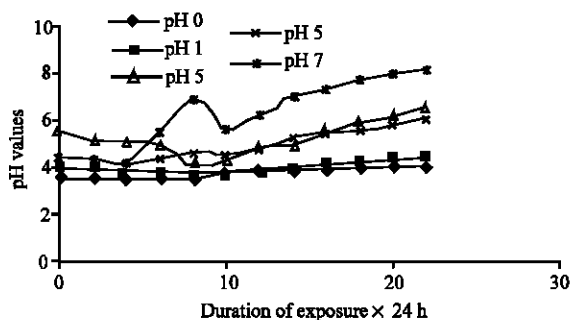


Fig. 4: Variation of pH values of cassava fluid with or without diethylene amine

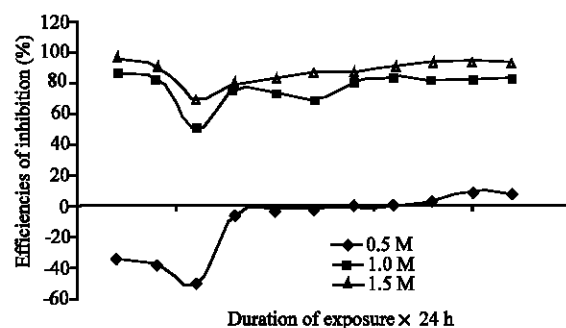


Fig. 7: Variation of the inhibition efficiencies of sodium chromate with concentration and duration of exposure

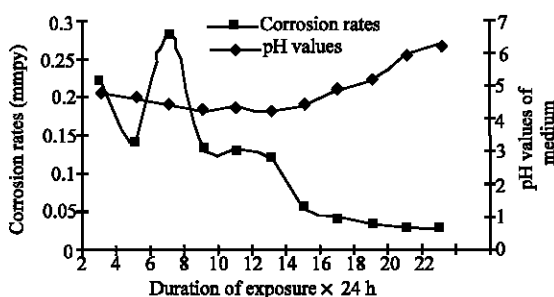


Fig. 5: Relationship between corrosion rates and the pH values of cassava fluid inhibited with 1.0 M sodium

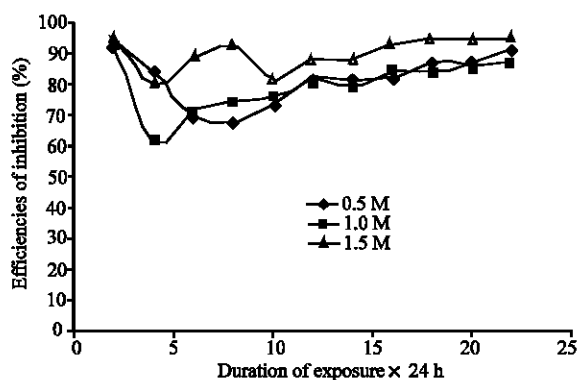


Fig. 8: Variation of the inhibition efficiencies of diethylene amine with concentration and duration of exposure

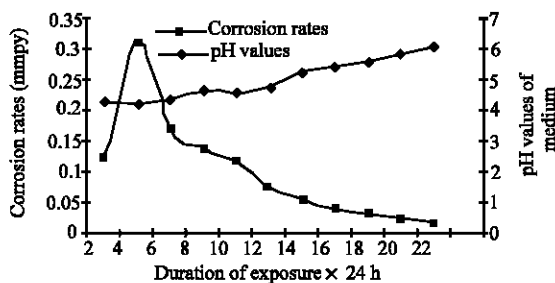


Fig. 6: Relationship between corrosion rates and the pH values of cassava fluid inhibited with 1.0 M diethylene

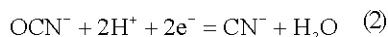
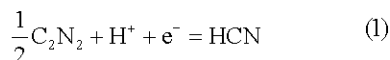
From Fig. 3, the effects of sodium chromate on the pH (pH 2, pH 3 and pH 4) can be said to decrease slightly initially to a minimum after about 6 to 8 days of exposure and later increased almost linearly. The three curves respectively represent the influence of the three concentrations; 0.5 M, 1.0 M and 1.5 M of sodium chromate investigated.

The effect of diethylene amine on the pH is similar to those of sodium chromate (Fig.4) except that the pH curves, pH 5 and pH 6 representing 1.0 M and 1.5 M diethylene amine did not vary as much as the curve of pH 7 representing 1.5 M diethylene amine.

From these Figs. 5 and 6 it can be said that the pH of the inhibited cassava media varies inversely with the corrosion rates of mild steel. Figure 7 shows that sodium chromate only become significantly efficient at 1.0 M concentration and beyond. It exhibited little or no efficiency at 0.5 M concentration. Unlike the former, diethylene amine shows an efficiency greater than 85% at concentration of 0.5 M. This efficiency according to Fig.8 is similar to those exhibited by 1.0 M sodium chromate inhibited cassava fluid. The increase in the inhibition efficiencies of the two inhibitors with increase in their concentrations is similar to an earlier research on inhibition of mild steel corrosion in seawater by *Theobroma cacao* and *Cola acuminata* leaves extracts (Umoru *et al.*, 2005).

DISCUSSION

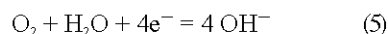
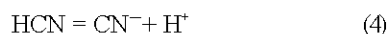
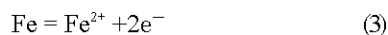
One of the most aggressive ions in cassava fluid is the cyanide ion (CN^-). Cassava contains cyanogens and cyanates both of which are easily reduced to form hydrogen cyanide acid, HCN and cyanate ion, CN^- respectively during fermentation according to Eqs. 1 and 2 (Fontana and Greene, 1987).



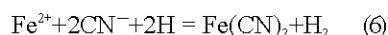
The pH variation of cassava fluid with time of exposure without any sample immersed in it can be traced to Eq. 1 during which acidity of the juice is increased. That is the decrease in the pH values of the juice for the first few days (i.e., the first 192 h) could be associated with the release of the HCN above.

When all the linamarin (C_2N_2) has been hydrolyzed, the release of HCN is stopped and the acidity of the juice reached its peak (Fig. 3 and 4). This result corroborates the findings in an investigation of the inhibitive potential of some amino acid derivatives in cassava fluid (Alagbe *et al.*, 2005). Beyond this point, the cassava fluid begins to experience an increase in pH probably because of increasing dilution of the fluid without corresponding production of HCN.

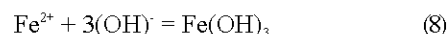
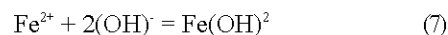
With the immersion of a mild steel in the cassava fluid it is most probable that corrosion sets in with dissolution of iron at the anode (Eq. 3), dissociation of HCN (Eq. 4) and consumption of dissolved oxygen and the electrons produced at the anode according to Eq. 5



The overall reaction initially is suspected to be that of equation (vi) when $\text{Fe}(\text{CN})_2$ is formed.



However, as soon as all the cyanogens have been consumed and the production of HCN is halted, the overall reaction is expected to have changed to those of Eq. 7 and 8 leading to the release of ferrous hydroxide, $\text{Fe}(\text{OH})_2$ or in the presence of surplus oxygen ferric hydroxide, $\text{Fe}(\text{OH})_3$ as the corrosion products.



These products are probably responsible for the increase in the alkalinity of the cassava medium resulting in subsequent increase in pH (Fig. 3 and 4). The increased pH reduced the attacks of the mild steel by the cassava medium as shown in Fig. 5 and 6. This trend is supported by Pourbaix diagram for iron-water system where $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are the products of corrosion in alkaline environment (Umoru *et al.*, 2003). The inhibition produced by sodium chromate in this work supports earlier reports of its potential in aqueous environment (Trethewey and Chamberlain, 1995).

Sodium chromate according to the literature (Roberge, 2000) is a passivating inhibitor that is capable of causing a large anodic shift of corrosion potential thereby forcing a metallic surface into the passivating range. It is an oxidizing anion that passivates steel in the absence of oxygen. This perhaps explains its active role as an inhibitor of steel in cassava at higher concentrations. It is important to point out the characteristic of anode inhibitors to accentuate corrosion when used in insufficient quantity because of unfavourable anode-cathode area effect. From the results of this work, it is clear that sodium chromate exhibited to follow at 0.5 M this characteristic as it was unable to inhibit mild steel corrosion in cassava fluid (Fig. 7). When it was however applied in excess of 1.0 M concentration, inhibition of mild steel corrosion in cassava slurry increased significantly.

Inhibition of metal corrosion by organic compounds is a result of adsorption of molecules or ions at the metal surface forming a protective layer. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor and the type of corrosive media (Thomas, 1981). Heteroatoms such as oxygen, nitrogen, phosphorus, sulphur and the presence of aromatic rings or triple bonds in the structure of organic inhibitors enhance the adsorption process (Rajappa and Venkatesha, 2003 and Bentiss *et al.*, 2000). They do so by acting as chemisorptions centers. The protective properties of these compounds depend on the electron densities at the chemisorptions center. The effectiveness of the inhibitor increases with higher electron densities at the center (Rajappa and Venkatesha, 2003). Diethylene amine, $(\text{C}_2\text{H}_5)_2\text{NH}$ only contains nitrogen as a heteroatom. It is thus explainable that the inhibitive protection from diethylene amine is dependent on the electron density

around nitrogen chemisorption centers. The NH group must have interacted with the steel surface to increase the corrosion resistance of NST-44 mild steel in the diethylene amine inhibited cassava fluid.

CONCLUSIONS

It may be concluded therefore that although mild steel in cassava fluid environment suffered corrosive attack the addition of diethylene amine and sodium chromate as inhibitors reduce the corrosion rates substantially. The inhibitive efficiencies of sodium chromate and diethylene amine increases with increase in concentrations of the inhibitors.

The results of this study also show that diethylene amine is a more active inhibitor of the corrosion of mild steel in cassava fluid than sodium chromate the reason being that its efficiencies of inhibition was greater than 85% for all the concentrations investigated unlike the case of sodium chromate at lower concentrations.

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