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Corrosion Inhibition Study of Mild Steel in Acidic Medium by Antibiotic Drugs: A Comparative Study

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Abstract - A comparison of the inhibiting efficiency of antibiotic drugs (ciprofloxacin, cloxacillin, and amoxicillin) on the corrosion of mild steel in 1 mol·L^{-1} HCl were studied at room temperature using mass loss measurement. The main reason is probably be due to the formation of protective coverage by the inhibitor as other authors reported previously. Adsorption characteristics of the inhibitor has also been studied using simple equation and it was found that drugs inhibits the corrosion of mild steel by being adsorbed on the surface of mild steel by a physical adsorption mechanism. The adsorption of drugs on the mild steel surface was found to be spontaneous and obey the Langmuir adsorption isotherm model. It was observed that the test drug has a promising inhibitory action in acid medium against corrosion of mild steel. Moreover it was revealed that an inhibition efficiency of 80.1 % can be achieved with 3×10^{-3}M ciprofloxacin drug treatment on mild steel.
Keywords: Steel corrosion; Antibiotic drugs; Adsorption isotherm; Inhibition mechanism.

Introduction

Mild steel (MS) is an important category of materials most commonly employed as metallic material in open-air structure in a wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. MS are used in different industries as pipelines, storage tanks, and also for chemical batteries (Zhang *et al.*, 2010). Acid solutions are widely used in industrial processes, especially for the acid pickling of steel, chemical cleaning and processing etc. As acid solutions have aggressive properties, inhibitors are commonly used to reduce the corrosive attack on metallic materials (Singh *et al.*, 2011).

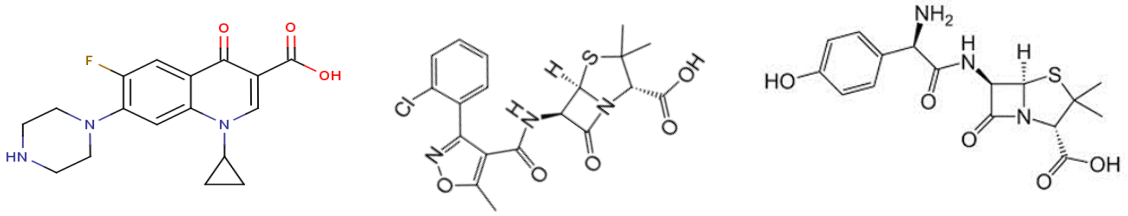
The inhibition efficiency of the inhibiting molecules is known to be effected by their molecular structure (Ashassi-Sorkhabi and Nabavi-Amri, 2000; El-Ouali *et al.*, 2010). It is well established that, organic compounds containing nitrogen, sulphur, oxygen, and phosphorus in their functional groups seems to have inhibition efficiency (Inemesit and Nnanake-Abasi, 2013; Umoren *et al.*, 2008; Kumar, 2008; Maayta *et al.*, 2010). Generally coatings, paints, and organic compounds are used for corrosion mitigation (Harikumar and Karthikeyan, 2012). Several compounds has been proposed to have their adsorption mechanism, by means of lone pairs of electron, of the organic functional groups on the metal surfaces (Niamien *et al.*, 2012). Several drugs are known to possess most of these qualities, and current research has been performed to in view of drug cost, and also which are environmentally safe as corrosion inhibitors (Ofoegbu and Ofoegbu, 2012; Harikumar and Karthikeyan, 2012).

Several drugs have been studied (Abdullah, 2004; Eddy and Odoemelam, 2008; Bouayed *et al.*, 1999) and found to be good corrosion inhibitors for the corrosion of metals. The main criteria of the drugs to be used as corrosion inhibitors are to have oxygen, nitrogen and sulphur

as active centers; should be less hazardous and environmentally friendly; can be easily produced and purified (Ebenso *et al.*, 2010). A chelate formation on the metal surface occurs by the corrosion inhibitors that form a covalent bond by transferring electrons from the organic compounds to the metal (Eddy et al., 2009b; Odiongenyi *et al.*, 2009; Ebenso *et al.*, 2010). The metal and the inhibitor acts as an electrophile and nucleophile, respectively in this adsorption process (Fang and Li, 2002). A wide use of quantum chemical calculations was justified by Eddy *et al.* (2009a) in this study by considering the charge transfer characteristics of the adsorption. But still no one elucidated the corrosion inhibition mechanism with drugs so far. It's an interesting subject to study in details considering the structure and properties of each drug.

Ciprofloxacin, cloxacillin, and amoxicillin are well known antibiotic drugs. Ciprofloxacin compound belongs to fluoroquinolone group (Figure 1a) used against bacterial growth worldwide. Cloxacillin and amoxicillin are semi synthetic antibiotic with π-electrons, heteroatom's S, N and O. Those molecules are big enough and by adsorbing on the mild steel surface they block more surface area. The structure of the used drugs shown in the Figure 1.

The present study describes the corrosion protection action of several antibiotic drugs on mild steel in acidic medium using weight loss measurement. The inhibition efficiency of each drugs were investigated in acidic medium with different concentrations.



(a) b) (c)

Figure 1. Chemical structure of (a) Ciprofloxacin; (b) Cloxacillin; (c) Amoxicillin

Materials and Methods

Sample

The mild steel (purity= 98% Fe) sample was identified and obtained locally and used in this study. The coupons were cut mechanically from the sheets of MS in a size of 3 cm× 2 cm× 0.1 cm dimensions. A small hole of about 5mm diameter near the upper edge of the coupons was made to help hold them with hooks and suspend them into the measurement medium. The coupons were degreased in acetone, washed in distilled water, and stored in moisture-free box before use. The details sample preparation procedure was same as Akpan and Offiong (2012) described in their paper.

Inhibitors

We used three types of antibiotic drugs: (i) Ciprofloxacin; 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl) quinoline-3-carboxylic acid, with a molecular mass of 331.346g/mol., (b) Cloxacillin was purchased from medicine shop as a trade name Cloxacillin sodium capsules (Bioclox capsules), and (c) Amoxicillin. All drugs were used without further purification. From the mass of the drug samples and its molecular weight relation, appropriate concentrations of the drug were prepared by dilution. The corrosive medium used was 1N solution of hydrochloric acid. It was prepared by appropriate dilution of analytical grade of the acid reagent with distilled water without further purification. The range of the concentrations of inhibitor used for the inhibition is from $1x10^{-3}$ to $3x10^{-3}$ M.

Weight loss measurements

We have followed the theoretical weight loss measurement technique, where five plastic containers of 250mL capacity were labeled A to E, each containing 1N of HCl solution. The coupons were cleaned and immersed in the containers that contain acidic medium of known concentration. We used glass hooks to hold the coupons in the medium. All experiments were done at room temperature of 30 °C. All the specimens were weighted before immersion in acidic medium. After every experiments, the specimens were taken out from the container, dried with warm air, polished with emery papers, and reweighed after several washing with distilled water and aceton. From the initial and final weights of the specimens, the loss of weights was calculated, and the corrosion rate (inmpy^{-1}- millimeter penetration per year) was computed from the following equation:

$$\text{Corrosion rate, CR} = 534W/\text{DAt}, \quad \text{(i)}$$

Where W is the weight loss (g), D is the density of the specimen (7.85 g/cm^3), A is the surface area of specimen (cm^3) and t is the immersion time (days). The efficiency of the inhibitor was computed using the following equation (Akpan, 2012; Akpan and Offiong, 2012; Shylesha *et al.*, 2011):

$$\text{Inhibition efficiency, \%IE} = W_o - W_1/W_o \times 100, \quad \text{(ii)}$$

Where W_o is the weight loss without inhibitor and W_1 is the weight loss with inhibitor.

Results and Discussions

Weight loss measurements

Inhibition efficiency of antibiotic drugs that are commercially available and also environmentally safe were tested in 1N solution of hydrochloric acid solution against MS steel at room temperature by weight loss technique. Results for ciprofloxacin and its comparison with other drugs obtained from weight loss measurements are as shown in Figure 2 and Table 1. From the obtained result it is clear that the corrosion of mild steel significantly decreased by the introduction of antibiotic drug into the corrosive medium. The increase of inhibition efficiency seems to be proportional to its corresponding concentration. It can be suggest that the inhibition caused by the adsorption and coverage of the inhibitor molecules on the steel surface. The calculated values for the corrosion rates (CR) are shown in Figure 3. It has been observed that the corrosion rates of the mild steel in the corroding medium were reduced on addition of different concentrations of the inhibitor. From the Figure 3 it can be seen that the weight loss increase as the time of exposure increased.

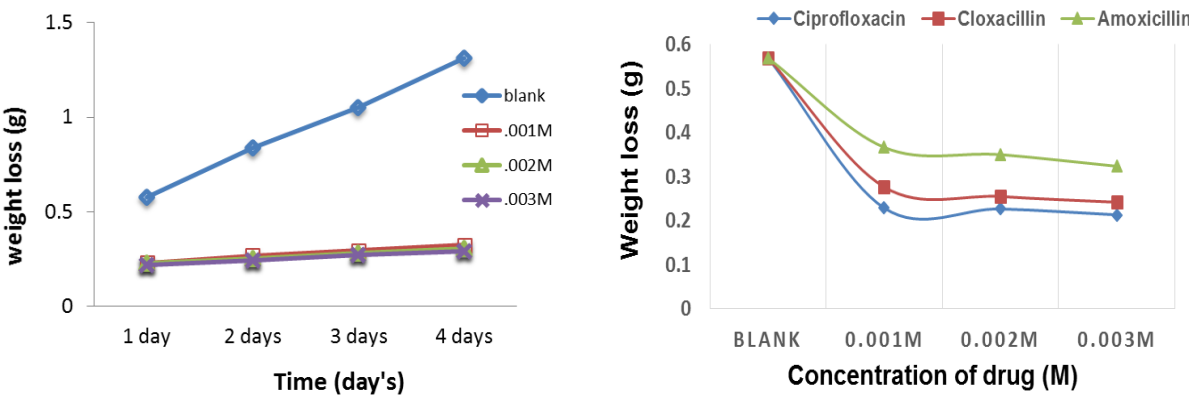


Figure 2. Variation of weight loss with time and drug concentrations. Weight loss measurement after days of ciprofloxacin treatment (left) and a comparison between both drugs at different concentrations vs weight loss measurement (right).

The values of inhibition efficiency (IE %) and the corrosion rate (CR) obtained from weight loss method at different concentrations of cloxacillin are summarized in Table 2 and Figure 3, respectively. It is evident from the table that cloxacillin inhibits the corrosion of mild steel in HCl solution at all the concentrations used in the study i.e. $1x10^{-3}$ to $3x10^{-3}$. Maximum inhibition efficiency was obtained at the concentration $3x10^{-3}$.

Table 1. Weight loss values and calculated inhibition efficiency for mild steel corrosion in 1N HCl in the presence and absence of different concentration inhibitors (ciprofloxacin drug)

Inhibitor conc.	1 day		2 days		3 days		4 days		5 days	
	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%
Blank	0.5764	-	0.8400	-	1.05	-	1.312	-	1.533	-
1×10^{-3}M	0.2288	60.30	0.2683	68.05	0.2958	71.82	0.3230	75.38	0.369	75.92
2×10^{-3}M	0.2267	60.67	0.2506	70.16	0.2809	73.24	0.3045	76.79	0.3277	78.62
3×10^{-3}M	0.2197	61.88	0.2441	70.94	0.2700	74.28	0.2906	77.85	0.3050	80.10

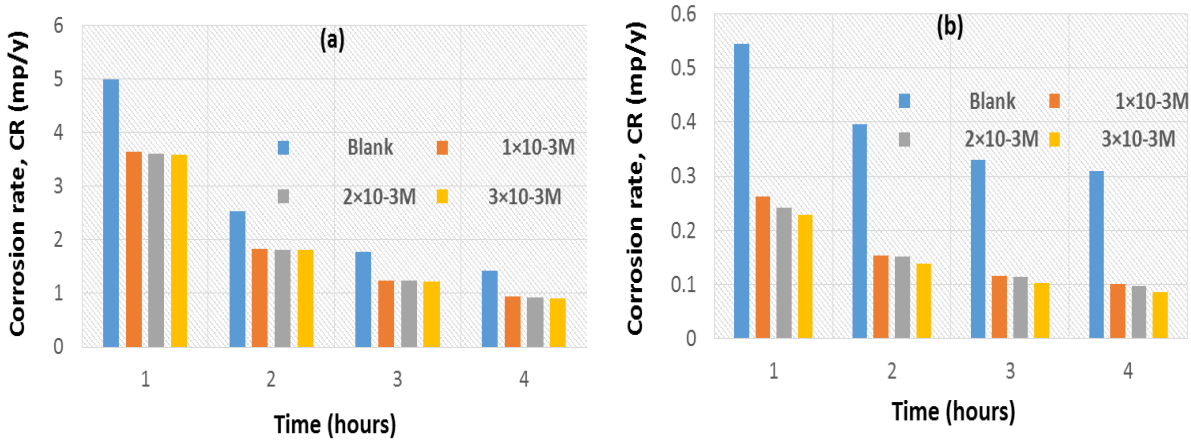


Figure 3. Calculated values of corrosion rate of mild steel in 1N HCl solution in absence and presence of different concentration of inhibitors, a) Ciprofloxacin drug; b) Cloxacillin drug.

Table 2. Weight loss values and calculated inhibition efficiency for mild steel corrosion in 1N HCl in the presence and absence of different concentration inhibitors (Cloxacillin drug)

Inhibitor conc.	1 day		2 days		3 days		4 days		5 days	
	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%	Weight loss	IE %	Weight loss	IE %
Blank	0.5764	-	0.8400	-	1.05	-	1.3120	-	1.533	-
1×10^{-3}M	0.2775	51.85	0.3245	61.36	0.3684	64.91	0.4228	67.27	0.4630	69.79
2×10^{-3}M	0.2557	55.63	0.3190	62.02	0.3608	65.63	0.4063	69.03	0.4470	70.84
3×10^{-3}M	0.2413	58.13	0.2920	65.23	0.3246	69.08	0.3644	72.22	0.4080	73.38

Adsorption Isotherm

Since it is believed that the action of corrosion inhibitors follows by adsorption on the metal surface by the inhibitor molecules using their adsorption centers, it is important to find out the possible adsorption mechanism by examining the experimental data with possible adsorption isotherms. The surface coverage (θ) was measured for all inhibitor concentrations in HCl solution that was assessed by weight loss data and the detail adsorption behavior was explained. It was in target to fit different isotherms including Frumkin, Temkin, and Langmuir, respectively with the

degree of surface coverage values (θ) and thereby all data were tested graphically. We obtained a straight line by plotting (C/θ) vs θ for Langmuir isotherm with regression coefficient (R2=0.9961) and confirmed this approach as the case of Langmuir isotherm shown in Figure 4.

The degree of surface coverage (θ) at different concentrations of the inhibitor is one of the factors considered in this test and was computed from weight loss measurements using formula (iii) (Cang *et al.*, 2013; Mistry *et al.*, 2011).

$$\theta = \frac{W_o - W}{W_o}, \quad \text{(iii)}$$

where W_o is the weight loss without inhibitor and W is the weight loss with inhibitor:

$$\frac{C}{\theta} = \frac{1}{k} + C, \quad \text{(iv)}$$

where C is the concentration of the corrosion inhibitor, $\theta$is the degree of surface coverage, and k is the adsorption equilibrium constant.

On consideration of the Langmuir adsorption isotherm, which is well described by formula (iv) (Mobin *et al.*, 2011; Quraishi and Sardar, 2004; Nnanna *et al.*, 2012; Khadom *et al.*, 2009; Khalifa *et al.*, 2010), it has been found that the experimental data gave a straight line graph on a plot ofC/θ versus C and fitted the adsorption isotherm showing in Figure 4a and Figure 4b.The Langmuir isotherm assumes a monolayer adsorption of the inhibitor molecules on the metal surface (Joseph *et al.*, 2010). Not only the structure and functional groups, but also their nature affects the action of the inhibitor compounds (Chitra *et al.*, 2010; Saliyan and Adhikari, 2009). The one electron donor group of each organic inhibitors usually regarded as reaction center for adsorption on metal surface (Bentiss *et al.*, 1999; Dubey and Potdar, 2009).

Ciprofloxacin, cloxacillin, and amoxicillin contain oxygen atoms, nitrogen atoms, homo and heterocyclic rings with conjugated and isolated double bonds which may get effectively adsorbed on the surface of mild steel and protects the surface from aggressive acid medium. The single inhibitor displaces a large number of water molecules and chloride ions; and forms complex with the metal (Dubey and Potdar, 2009).

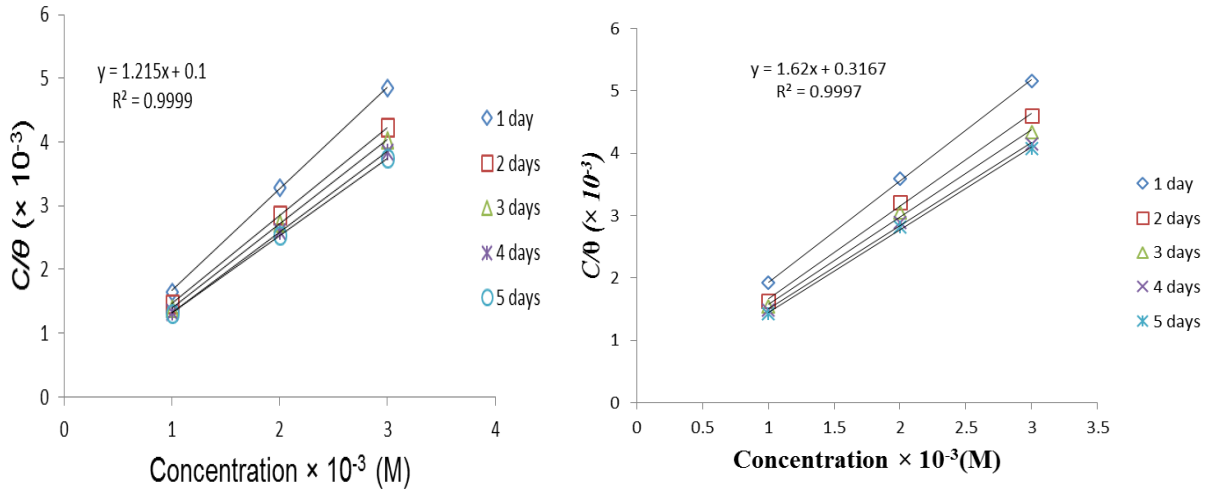


Figure 4. (Left side) Langmuir's adsorption isotherm for mild steel in 1N HCl containing various concentrations of cloxacillin as inhibitor. (Right side) Langmuir's adsorption isotherm for mild steel in 1N HCl containing various concentrations of ciprofloxacin as inhibitor.

Corrosion inhibition of drugs depends on the adsorption of the molecules on the metal surface i.e. the metal/solution interface, interactions between protonated atoms and aromatic rings π-electrons that may also interact with the vacant d-orbitals of the atom/metal interface. It is established that the steel surface always bears positive charge in acid medium. The antibiotic

drugs being protonated in acidic solution and played an electrostatic interaction with Cl^- by attaching to the mild steel surface. Inhibition can be effected by the wider surface covered by large molecules of the inhibitor due to the large molecular weight of a drug compound (Inemesit and Nnanake-Abasi, 2013). This phenomena forms a complex on the steel surface and thus inhibits corrosion. The adsorbed layer effectively protects the steel surface from the aggressive nature of acid medium. To know the details mechanism and to clarify the better inhibition efficiency of ciprofloxacin over cloxacillin, we are considering doing FTIR and SEM study that is now undergoing.

Conclusions

We observed that ciprofloxacin, cloxacillin, and amoxicillin are good inhibitors for mild steel in solution of hydrochloric acid. Comparing the inhibition efficiency of the test drugs, ciprofloxacin seems to have the highest efficiency. It was revealed that the inhibition efficiency increased with an increase in the concentration of the inhibitor. The adsorption behavior on mild steel surface favors the mechanism of physical adsorption and is best described by the Langmuir adsorption model.

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