

# Surface Morphological and FTIR Spectroscopic information on the corrosion inhibition of drugs on Mild Steel in Chloride Environment

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## ABSTRACT

The disintegration of low carbon alloy in chloride environment was examined by surface morphological and FTIR spectroscopy methods. The retardation rises with increase drug concentration. The results achieved show that various concentrations of antibiotic drugs inhibited the oxidation in chloride solution through the adsorption of the inhibitor molecule on the superficial surface by obstructs its active sites. The results find from the FTIR are in excellent agreement. The use of antibiotic drugs as an inhibitor for corrosion of mild steel in chloride environment is advocated in this study.

**KEY WORDS:** Antibiotic drug, Chloride, Corrosion, SEM, Mild steel.

## 1. INTRODUCTION

The metallic materials are playing a key role in industrial process, so it is often exposed to the different environment, thereby prompting their deterioration (Shukla, 2009). The usage of drugs are one of the most effective means of shielding metals and alloys surfaces from corrosion in different environment. The drugs are usually added to the deterioration medium to minimize the material metal loss. In the few decades, several researchers reported the use of drugs for low carbon alloy corrosion (El-Naggar, 2007). Several environment friendly depressant have been studied and found to be effective inhibitors for the oxidation of metals because of forming insoluble complex on metal surface (Fouda, 2010). The main criteria of the drugs to be used as corrosion inhibitors are to have aromatic, long chain carbon compounds and selective functional groups as potent centers; should be less endangerment and environmentally friendly; and can be easily produced and decontaminated (Ahamad, 2010). A complex formed on the external surface by the corrosion inhibitors form a covalent bond to transfer electrons from the drug to metal surface (Fang, 2002). The metal and the stimulant act as a donors and acceptors in this adsorption process (Lalitha, 2005). In acid medium, stimulant adds a proton to the molecule. In both inhibitors, the hetero atoms present in the particle can be readily protonated in corroding medium. These protonated species are adsorbed on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adhesion on anodic site develops through electrons of aromatic rings and lone pair of electrons of nitrogen, sulfur and oxygen atoms existent in both the inhibitors, which decrease the anodic detachment of material. A vast use of quantum chemical calculations was accepted to consider the charge transfer characteristics of the adsorption process. But still, no one revealed the oxidation inhibition mechanism with drugs so far. It is a consequence subject to study in details, examining the surface morphology of mild steel after drug adsorption. Traditionally, scanning electron microscopy (SEM) analysis has been used to analyses the superficial morphology of metal alloys and also for evaluation of corrosion attack (Montecinos, 2011). Using this technique together with Fourier transform infrared spectroscopy (FTIR) measurements, which allows the detection of the corrosion products constitute on the metal surfaces. The aim of this investigation is to find the efficiency of aromatic drugs on mild steel corrosion using SEM and FTIR to obtain a clear understanding of the nature of drug adsorption. A detailed surface morphology study was done.

## 2. MATERIALS AND METHODS

**Preparation of Specimen:** According to ASTM method as stated already (Sathirachinda, 2010), the mild steel specimens were cut into pieces of 5cm × 1 cm having the following composition (in percentage) % C=0.014; Si=0.007; Mn=0.176; S=0.014; P=0.009; Ni=0.012; Mo=0.015; Cr=0.033 and Fe=99.686 was used. The constituent were polished and put hole at one end and numbered by punching. During the study the fragments were scratched with varied grades of SiC abrasive papers (from grits 120 to 1200) and degreased using Acetone.

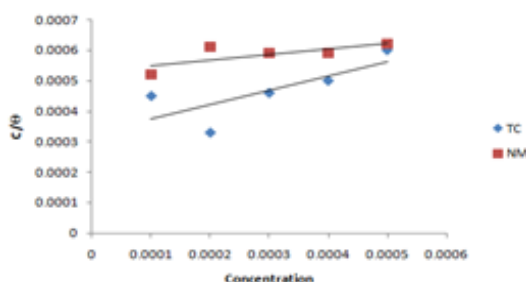
**Determination of Corrosion rate:** The commercially available drugs were purchased and used without more purification. From the molecular mass of the stimulant and its weight relation, proper concentrations of the drug were prepared (Sherine, 2010). The etching medium used was 2M solution of KCl. It was prepared by suitable dilution of analytical grade of the KCl with distilled water. The concentrations of inhibitor used for the inhibition is from  $1 \times 10^{-4}$  to  $5 \times 10^{-4}$ . The coupons were cleaned and immersed in the containers that contain chloride medium of known concentration. We used glass hooks to grip the coupons in the medium. All experiments were made at room temperature. All the mild steel fragments were weighted before immersion. After each one experiment, the specimens were taken away from the beaker, dried and polished with emery papers and reweighed after numerous washing with distilled water. From the initial and final weights of the specimens, the mass loss was calculated.

$$\text{Corrosion Rate} = 534 * W / D * A * T$$

Where W is the weight loss (g), D is the density of the specimen (7.85 g/cm<sup>3</sup>), A is the surface area of specimen (cm<sup>2</sup>) and t is the immersion time.

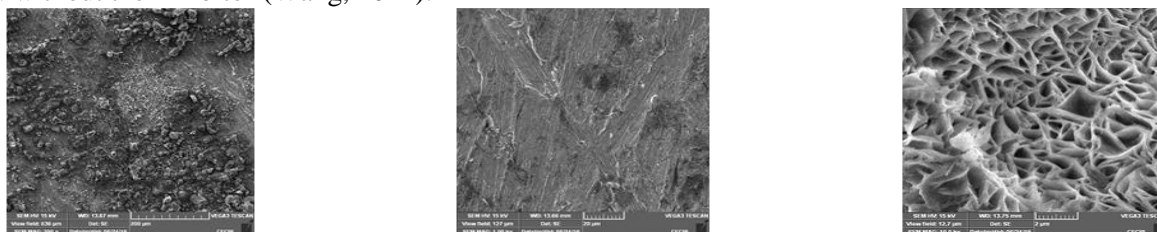
**Table.1. Weight loss values and calculated inhibition efficiency for mild steel corrosion in 2M KCl in the presence and absence of different concentration inhibitors antibiotic drugs**

| Inhibitor Concentration (M) | Tetracycline ( 4 hrs) |      | Neomycin tri Sulphate (4 hrs) |      |
|-----------------------------|-----------------------|------|-------------------------------|------|
|                             | Mass Loss             | IE%  | Mass Loss                     | IE%  |
| Blank                       | 0.597                 | -    | 0.679                         | -    |
| 1*10 <sup>-4</sup>          | 0.465                 | 22.1 | 0.601                         | 11.5 |
| 2*10 <sup>-4</sup>          | 0.245                 | 59.0 | 0.532                         | 21.6 |
| 3*10 <sup>-4</sup>          | 0.205                 | 65.7 | 0.436                         | 35.8 |
| 4*10 <sup>-4</sup>          | 0.117                 | 80.4 | 0.335                         | 50.7 |
| 5*10 <sup>-4</sup>          | 0.102                 | 82.9 | 0.169                         | 75.1 |

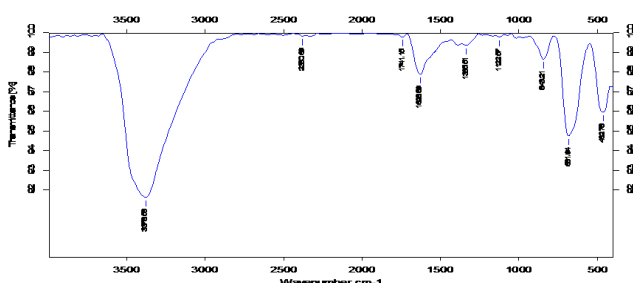


**Figure.1. Langmuir's adsorption isotherm for mild steel in 2M KCl containing various concentrations of antibiotic drugs as inhibitor**

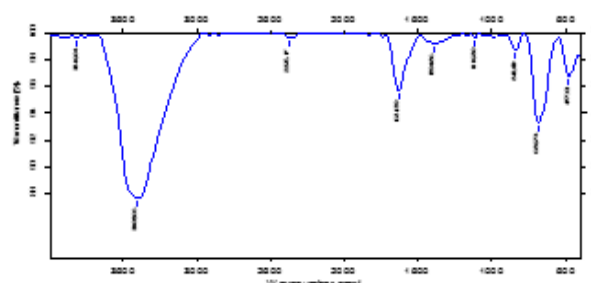
**Surface characterization:** The mild steel immersed in blank solution and in the inhibitor solution for a period of 4 hour was removed, rinsed with double-distilled water, dried and observed in a scanning electron microscope to examine the surface morphology (Silverstein, 2002). The surface morphology measurements of mild steel specimen were determined using scanning electron microscope. To observe the surface attachment of drug molecules, the insoluble complex formed on the corroded steel specimens were scrapped, collected and subjected to IR spectral studies (Singh, 2011). FTIR study reveals the new bonding information and the product formed on metal surface with and without the inhibitor (Wang, 2011).



**Figure.2. SEM images of (a) mild steel immersed in 2M KCl and (b) mild steel immersed in tetracycline Solution (c) mild steel immersed in Neomycin tri sulphate solution**



**Figure.3. (a) FTIR spectrum of corrosion product of mild steel in the presence of Tetracycline drug**



**Figure.3. (b) FTIR spectrum of corrosion product of mild steel in the presence of Neomycin trisulphate drug**

**Table.2. Peaks, Assignments of IR adsorption by mild steel corrosion product (Containing tetracycline and Neomycin tri sulphate as inhibitor)**

| Corrosion product containing tetracycline |  | Corrosion product containing Neomycin trisulphate |                                |
|---|--|---|--------------------------------|
| Peak (cm <sup>-1</sup> )                  | Assignment   | Peak (cm <sup>-1</sup> )                          | Assignment                     |
| 3408                                      | O-H stretching / N-H stretching                      | 3378  | O-H stretching                 |
| 2376                                      | C-H stretching of Methyl group                       | 2380  | C-H stretching of Methyl group |
| 1631                                      | C=C bond   | 1628  | C=C bond                       |
| 1394                                      | C-O Stretching                                       | 1335  | C-O Stretching                 |
| 1116                                      | The aromatic in plane and out plane deformation peak | 1122  | C-N Stretching                 |

### 3. RESULTS AND DISCUSSION

**Weight loss study:** Inhibition competence of non-toxic environment friendly antibiotic drug was tested in 2M solution of KCl solution in opposition to mild steel at room temperature by weight loss technique. Results for drugs attained from weight loss measurements are as shown in Table.1. From the obtained result, it is clear that the oxidation of mild steel significantly suppressed by the introduction of antibiotic drug into the KCl medium (Yasakau, 2008). The increase of IE seems to be equal to its subsequent concentration. It was conceding that the superficial coverage of stimulant molecule on surface actively inhibits the oxidation of metal (Anand, 2011). It has been found that the corrosion rates of the mild steel in the corroding medium were decreased on inclusion of distinct concentrations of the inhibitor. As it is believed that the action of drugs follows by adsorption on the external surface of metal by using their active centers, it is important to find out the possible adsorption mechanism by examining the experimental data with possible adsorption isotherms (Singh, 2011). The adhesion behavior of antimicrobial drug in KCl solution was explained by measuring the surface coverage using weight loss data. The linear-relationship can be achieved on plotting  $C/\theta$  as a function of  $c$ , with a slope of unity (Dubey, 2009; Pang, 2008). It was found that the linear correlation coefficients clearly shows that the adsorption of antibiotic drugs from 2M KCl solutions on the Mild steel obeys the Langmuir isotherm, as shown in Figure.1.

**FTIR study:** FTIR spectra have been used to evaluate the protective film developed on metal surface to resolve the type of bonding for organic inhibitor adsorbed on the metal surface (El-Naggar, 2007). The FTIR spectrum of the protective film formed on the metal after immersion in the 2M KCl solution in the occurrence of drug for four hours is shown in Figure 3(a). It is evident that phenolic O-H stretching has shifted from 3805cm<sup>-1</sup> to 3408 cm<sup>-1</sup>. The C-H stretching frequency of methyl group has shifted from 2684 cm<sup>-1</sup> to 2380 cm<sup>-1</sup>. The C=C bond has shifted from 1635 cm<sup>-1</sup> to 1631 cm<sup>-1</sup>. The C-O stretching frequency shifted from 1338 cm<sup>-1</sup> to 1394 cm<sup>-1</sup>. The aromatic in plane and out plane deformation peak occurred at 1116 cm<sup>-1</sup>.

It was concluded that tetracycline has coordinate with metal through the phenolic oxygen (Bouklah, 2006). The FTIR spectrum of the protective layer formed on the fragment after immersion in the 2M KCl solution in the existence of neomycin tri sulphate for four hours is shown in Figure 3(b). It is evident that phenolic O-H stretching has shifted from 3805cm<sup>-1</sup> to 3378 cm<sup>-1</sup>. The C-H stretching frequency of methyl group has shifted from 2684 cm<sup>-1</sup> to 2376 cm<sup>-1</sup>. The C=C bond has shifted from 1635 cm<sup>-1</sup> to 1628 cm<sup>-1</sup>. The C-O stretching frequency shifted from 1338 cm<sup>-1</sup> to 1335 cm<sup>-1</sup>. The C-N stretching frequency occurred at 1122 cm<sup>-1</sup>. Thus, FTIR spectral study leads to the conclusion that the protective deposit consists of metal – drug complex.

**Scanning electron microscopy analysis of metal surface:** The SEM micrographs of mild steel surface in Figure.2a, show the coarseness of the fragment surface, which suggest the corrosion of surface in chloride medium. The surface observed was very rough and densely damaged due to metal dissolution (Bouyanzer, 2007). Clear cracks were noticed on the corroded surface. However, the presence of inhibitor restrain the rate of deterioration, and surface damage has been lessen substantially. Figure.2b and c, as correlated to the blank solution Figure.2a, suggesting formation of a protective inhibitor film at the mild steel surface. It can be clarified that the surface coverage increases, which in turn bring about the accumulation of insoluble complex on the exterior part of the metal - inhibitor complex, and the surface is covered by a delicate layer of inhibitors which control the erosion of mild steel.

### 4. CONCLUSION

- The IE of antibiotic drugs tetracycline and Neomycin tri sulphate in controlling corrosion of mild steel immersed in chloride medium has been evaluated by weight loss method.
- It was found that suppression efficiency of tetracycline is more than Neomycin tri sulphate by obeying Langmuir adsorption isotherm.
- The adsorption of drug at the mild steel surface has been substantiated by FTIR study. FTIR spectra affirm that the protective film involved insoluble metal-inhibitor complex on surface.
- The sequence of microscopy measurements and weight loss test validated that drug adsorbs on the steel surface, and its inhibition performance is dependent on the concentration of drugs.

- The morphological investigation also confirms the effective protection of mild steel, through the less damaged and minimum pits found in the inhibited surface.

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## REFERENCES

- Ahamad M.A, Quraishi, Mebendazole, new and efficient corrosion inhibitor for mild steel in acid medium, *Corros. Sci.*, 52, 2010, 651.
- Anand B, Balasubramanian V, Corrosion behaviour of mild steel in acidic medium in presence of aqueous extract of *Allamanda blanchetii*, *E-Journal of Chemistry*, 8 (1), 2011, 226.
- Bouklah M, Hammouti B, Thermodynamic characterization of steel corrosion for the corrosion inhibition of steel in sulphuric acid solution by Artemisia, *Port Electrochim Acta*, 24, 2006, 457.
- Bouyanzer A, Majidi L, Hammouti B, Inhibition of steel corrosion in 1M HCl by essential oil of Cedre, *Phys Chem News*, 37, 2007, 70.
- Dubey RS, Potdar Y, Corrosion inhibition of 304 stainless steel in sodium chloride by ciprofloxacin and norfloxacin, *Indian J. Chem Tech*, 16, 2009, 334–338.
- El-Naggar MM, Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds, *Corrosion Science*, 49, 2007, 2226–2236.
- Fang J and Li J, Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides, *Journal of Molecular Structure (Theochem)*, 593 (1/3), 2002, 179-185.
- Fouda AS, Mostafa HA, El-Abbasy HM, Antibacterial drugs as inhibitors for the corrosion of stainless steel type 304 in HCl solution, *J Appl, Electrochem*, 40, 2010, 163.
- Lalitha A, Ramesh S and Rajeswari S, Surface protection of copper in acid medium by azoles and surfactants, *Electrochimica Acta*, 51 (1), 2005, 47-55.
- Leblanc P and Frankel GS, A study of corrosion and pitting initiation of AA2024- T3 using atomic force microscopy, *Journal of Electrochemical Society*, 149 (6), 2002, B239-B247.
- Montecinos S and Simison SN, Study of the corrosion products formed on a multiphase CuAlBe alloy in a sodium chloride solution by micro-Raman and in situ AFM measurements, *Applied Surface Science*, 257 (17), 2011, 7732-7738.
- Pang XH, Guo WJ, Li WH, Xie JD, Hou BR, Electrochemical, quantum chemical and SEM investigation of the inhibiting effect and mechanism of ciprofloxacin, norfloxacin and ofloxacin on the corrosion for mild steel in hydrochloric acid, *Sci China Ser, B-Chem*, 51, 2008, 928–936.
- Sathirachinda N, Pettersson R, Wessman S and Pan J, Study of nobility of chromium nitrides in isothermally aged duplex stainless steels by using SKPFM and SEM/EDS, *Corrosion Science*, 52 (1), 2010, 179-186.
- Sherine B, Nasser AJA and Rajendran S, Inhibitive action of hydroquinone – Zn<sub>2</sub> system in controlling the corrosion of carbon steel in well water, *International Journal of Engineering Science and Technology*, 2 (4), 2010, 341-357.
- Shukla SK and Quraishi MA, Ceftriaxone, a novel corrosion inhibitor for mild steel in hydrochloric acid, *Journal of Applied Electrochemistry*, 39, 2009, 1517–1523.
- Shukla SK, Singh AK, Ahamad I and Quraishi MA, Streptomycin, A commercially available drug as corrosion inhibitor for mild steel in hydrochloric acid solution, *Materials Letters*, 63, 2009, 819–822.
- Silverstein RM and Webster FX, *Spectrometric Identification of Organic Compounds*, 6th ed, Jhon Wiley and Sons, New York, NY, 2002.
- Singh AK and Quraishi MA, Investigation of the effect of disulfiram on corrosion of mild steel in hydrochloric acid solution, *Corrosion Science*, 53 (4), 2011, 1288-1297.
- Singh AK, Quraishi MA, Adsorption properties and inhibition of mild steel corrosion in hydrochloric acid solution by ceftobiprole, *J Appl Electrochem*, 41, 2011, 7–18.
- Wang B, Du M, Zhang J and Gao CJ, Electrochemical and surface analysis studies on corrosion inhibition of Q235 steel by imidazoline derivative against CO<sub>2</sub> corrosion, *Corrosion Science*, 53 (1), 2011, 353-361.
- Yasakau KA, Zheludkevich ML and Ferreira MGS, Study of the corrosion mechanism and corrosion inhibition of 2024 aluminum alloy by SKPFM technique, *Advanced Materials Forum IV*, 587/588 (1), 2008, 405-409.