Communication in Physical Sciences 5(1): 1- 7 http://journalcps.com/

Adsorption studies on the inhibition of the corrosion of mild steel in 2 M NaCl by tetracycline and neomycin trisulphate drugs

B. Anand and S. Chitra

Received 24 November 2019/Accepted 2 March 2020/Published online: 04 April 2020

Abstract *Inhibition of mild steel corrosion in 2 M NaCl solution by tetracycline and neomycin trisulphate was studied using gravimetric, Fourier transformed infra red spectrophometry and scanning electron microscopy methods. Highest inhibition efficiencies were 82.90 and 75.10 % for tetracycline and neomycin trisulphate respectively. Inhibition efficiency was observed to increase with increase in the concentration of the inhibitor. Scanning electron micrographs of the metal surface reveals the formation of protective* inhibitor's *films in the presence of the inhibitor while Fourier transform infra red spectra indicated that some functional groups were useful for the adsorption of the inhibitor on the metal surface. The adsorption behaviour of the inhibitors was best described by the Temkin and Frumkin adsorption isotherm. The adsorption of the inhibitor was spontaneous and supported physiosorption mechanism.*

Key words: *Corrosion inhibition, adsorption, tetracycline, neomycin trisulphate*

B. Anand
Department of Chemistry,
Sir Theagaraya College,
Chennai. India

***S. Chitra**
Department of Chemistry,
SNS College of Engineering, Coimbatore, India
Email: chitrachem@gmail.com

List of symbols

CR	Corrosion rate
%IE	Inhibition efficiency
ΔW	Weight loss
i_{corr} c	Corrosion currents in the absence of the inhibitor
i_{inh}	Corrosion current in the presence of inhibitor
R_{ct}	Charge transfer uninhibited system
$R_{ct(inh)}$	Charge transfer for inhibited system
E_a	Activation energy
R	Gas constant
T	Temperature
ΔS^0_{ads}	Standard entropy change
ΔH^0_{ads}	Standard enthalpy change
ΔG^0_{ads}	Standard free energy change
'a'	Temkin interaction parameter
θ	Surface coverage
C	Concentration of the inhibitor
K_{ads}	Equilibrium constant of adsorption

1.0 Introduction:

In some industrial process, metals and alloys are often position to be in contact with acid, alkalis, and other aggressive media that can easily accelerate corrosion (Shukla *et al*., 2009). The use of corrosion inhibitors is one of the most effective options of protecting metals and alloys against corrosion (Shukla and Quraishi, 2009). Corrosion inhibitors are usually added to the aggressive solution to reduce the rate at which the exposed metal corrode. In the past few years, several researchers have successfully tested and confirm some drugs to be good corrosion inhibitors for metals including cefrazidine (Sing and Shulka, 2011), ceftobiprole dapsone (Singha *et al*., 2010; Quraishi, 2010), tetracycline (Eddy *et al*., 2010a), tarivid (Eddy *et al*., 2010b) , cloxacillin (Eddy and Ebenso, 2010), Penicillin (Eddy *et al.*, 2009), ampicillin (Eddy, 2010c; Siaka *et al*., 2014), etc. The main criteria that enhanced these drugs to be good corrosion inhibitors is the possession of heteroatoms (such as oxygen, nitrogen and sulfur, which function as active adsorption centers. Most of these drugs that are excellent corrosion inhibitors are also less toxic, less expensive, easily available and have known

chemical structure that can encourage computation of electronic parameters (Eddy *et al*., 2012.; Ahamad, 2010). A good corrosion inhibitor is capable of forming a chelate with the surface of the metal through charge transfer from charged inhibitor to charged metal surface (physiosorption mechanism) or through electron transfer from the inhibitor to the vacant d-orbital of the metal surface (chemisorption mechanism) (Fang and Li, 2002). Consequently, the metal and the inhibitor act as an electrophile and nucleophile respectively (Lalitha *et al.*, 2005). In acid medium, some drug exists as protonated species and may involves one of the hetero atoms (such as nitrogen, sulfur and oxygen atoms) present in the molecules to form adsorbed layer that can protects the metal against corrosion attack. These protonated species may be adsorbed on the cathodic sites of the mild steel and decrease the evolution of hydrogen (Eddy *et al*. 2010).

Corrosion and corrosion inhibition are surface processes, indicating that adsorption of the inhibitor occurs in the surface. Interesting information about the mechanism of inhibition of corrosion can be obtained through functional group analysis and examination of the microstructure of the surface. In spite of the large amount of work published on corrosion and corrosion inhibition, literature is relatively scanty on detail mechanistic study of the metal surface. Therefore, the present study is aimed at investigating the inhibition of the corrosion of mild steel through gravimetric, scanning electron microscopy and Fourier transformed infra-red spectrophotometry

Scanning electron microscopy (SEM) analysis has been used to characterize the microstructure of metal alloys and also for evaluation of corrosion attack (Montecinos, and Simison, 2011). Combination of this technique with Fourier transform infrared spectroscopy (FTIR) measurements (which allows the functional groups associated with the corrosion inhibition to be identified), it is possible to obtain information on the mechanism of corrosion inhibition and changes in the morphology of the metal during after corrosion inhibition.

The chemical structures of tetracycline and neomycin trisulphate are shown in Fig. 1 below. From the structures, it can be theoretically inferred that these drugs are expected to be good corrosion inhibitors because they possess several hetero atoms, useful functional groups, aromatic rings and π-electrons that can contribute to facilitate adsorption.

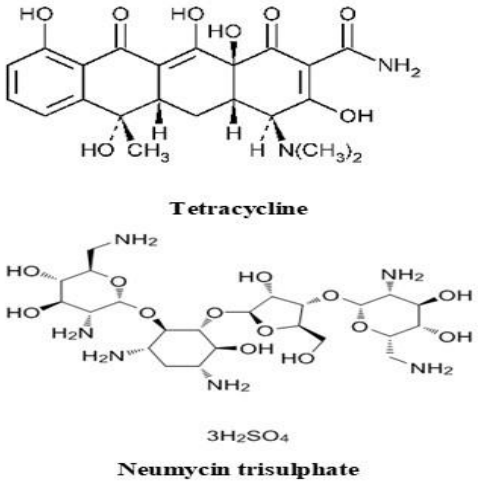

Fig. 1: Chemical structures of tetracycline and neomycin trisulphate

2. 0 Materials and methods

2.1 Preparation of Specimen

Mild steel sheet was cut into various coupons, each of dimension, 5 by 1 cm. The composition (weight %) of the mild steel were C (0.017), Si (0.007), Mn (0.196), S (0.014). P (0.009), Ni (0.013), Mo (0.015), Cr (0.043) and Fe (99.686). The samples were polished with various grades of SiC abrasive papers (from grits 120 to 1200) and degreased using acetone before allowing them to be air dried. The dried samples were preserved in a desiccator.

The antibiotics chosen for the study were tetracycline and neomycin trisulphate, Various inhibitors' solutions (with concentration ranging from 0.0001 to 0.0005 M) were prepared and dissolved in the salt solution (2 M NaCl). However, the blank solution was prepared without any additive except 2 M NaCl.

2.2 Weight loss measurement

Weight loss measurements were carried out as reported elsewhere (Eddy and Odiongenyi, 2010). Known weight of the metal coupon immersed in a 250 ml beaker containing the inhibitor's (and also in the blank solution) solution. Weight loss of mild steel after 96 hours of immersion was calculated as the difference in weight of the metal before and after 168 hours of immersion. Prior to the measurement, the mild steel was withdrawn, washed and dried. From weight loss measurement, inhibition

efficiency and corrosion rate of mild steel were calculated using equations 1 and 2 (Eddy *et al*., 2011)

$$\%\, IE = \frac{W_2 - W_1}{W_2} \times 100 \quad (1)$$

$$CR = 534\Delta W/DAT \quad (2)$$

where W_2 and W_1 are the weight losses (g) for mild steel in the absence and presence of the inhibitor respectively, D is the density of the metal, A is the area of the mild steel coupon (in cm^2), t is the period of immersion (in hours) and ΔW is the weight loss of mild steel after time, T.

3.0 Results and discussion

3.1 Weight loss and inhibition efficiency

Table 1 contains average weight loss of mild steel in 2 M NaCl solution in the absence and presence of tetracycline and neomycin trisulphate. Inhibition efficiencies of the inhibitors at various concentrations. Weight loss of mild steel is seen to decrease with increasing concentration of the inhibitor while inhibition efficiency increases. Therefore, tetracycline and neomycin trisulphate are adsorption inhibitors because their efficiency increases with increase in concentration (Eddy *et al*.,2009).

Table 1: Weight loss of mild steel and inhibition efficiency of tetracycline and neomycin for mild steel in 2M NaCl.

C (M)	Tetracycline		Neomycin trisulphate	
	ΔW	IE%	ΔW	IE%
Blank	0.597	-	0.679	-
$1*10^{-4}$	0.465	22.1	0.601	11.5
$2*10^{-4}$	0.245	59.0	0.532	21.6
$3*10^{-4}$	0.205	65.7	0.436	35.8
$4*10^{-4}$	0.117	80.4	0.335	50.7
$5*10^{-4}$	0.102	82.9	0.169	75.1

3.2 Adsorption consideration

The adsorption behaviour of tetracycline and neomycin trisulphate at 303 K was investigated by establishing the best adsorption isotherms that fitted their behaviour. Langmuir isotherms were tested and it did comply with the adsorption of the drugs unto mild steel surface. However, their adsorption obeyed the Temkin and Frumkin isotherms with high degree of R^2.

The Temkin adsorption isotherm can be written as (Yurt *et al*., 2016),

$$e^{-2a\theta} = k_{ads}C \quad (3)$$

The above equation can be linearized to the following,

$$\theta = -\frac{1}{2a} lnk_{ads} + \left(-\frac{1}{2a}\right) lnC \quad (4)$$

where a is molecular interaction parameters, θ is the surface coverage of the inhibitor, C is the concentration and k_{ads} is the adsorption desorption equilibrium constant. Temkin isotherms for the adsorption of tetracycline and neomycin trisulphate are plotted in Fig. 2

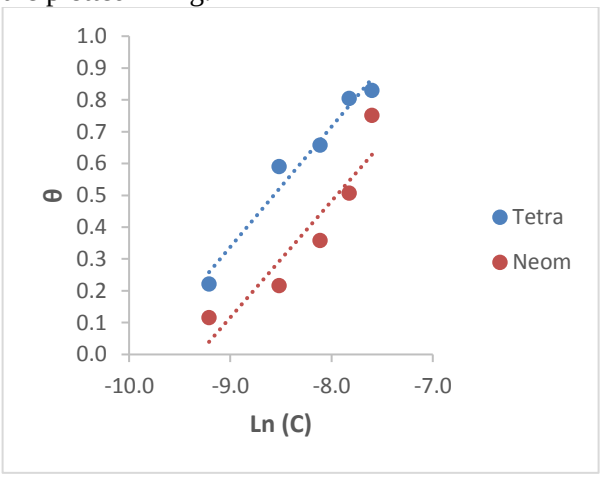

Fig. 2: Temkin isotherm for the adsorption of tetracycline and neomycin trisulphate on mild steel surface

Table 2: Adsorption parameters for tetracycline and neomycin trisuphate

Isotherm	lnk_{ads}	a/α	ΔG^0_{ads} (J/mol)	R^2
Temkin (Tetra)	3.7382	2.6467	-13.68	0.9648
Temkin (Neom)	3.4051	2.737	-13.25	0.8596
Frumkin (tetra)	-11.769	2.373	-19.53	0.9945
Frumkin (Neom)	-11.594	3.759	-19.09	0.9620

The results reveal strong adherence of the adsorption of neomycin trisulphate and tetracycline to the assumptions of Temkin. Excellent degree of linearity was obtained and the interaction parameters were positive indicating attractive behaviour of the inhibitors' molecules. Also, the adsorption constant for tetracycline was slightly higher than that of neomycin, indicating better

adsorption of tetracycline unto the surface of mild steel.

The adsorption of tetracycline and neomycin unto the surface of mild steel also agreed with the assumptions of Frumkin, whose isotherm equation is presented in equation 5 (Eddy and Odiongenyi, 2010)

$$ln\left([C].\left(\frac{\theta}{1-\theta}\right)\right) = lnk_{ads} + 2\alpha\theta \qquad (5)$$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the surface coverage of the inhibitor and α is the lateral interaction term describing the interaction in adsorbed layer. Plots of $ln\left([C].\left(\frac{\theta}{1-\theta}\right)\right)$ versus θ (Fig. 3) were linear for both tetracycline and neomycin trisulphate, which testified to the agreement between assumptions of Frumkin model and the adsorption of the drugs on the surface of the metal.

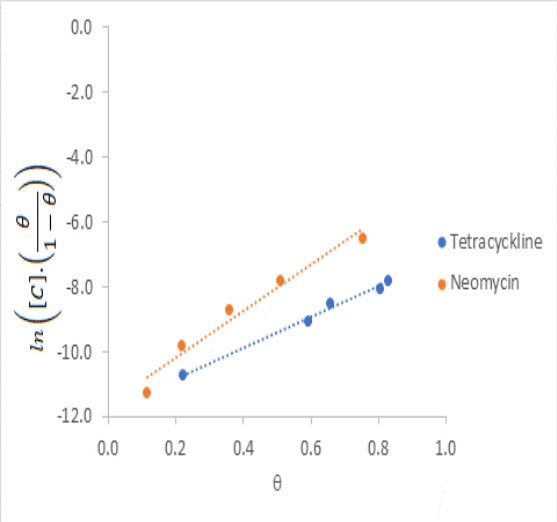

Fig. 3: Frumkin isotherm for the adsorption of tetracycline and neomycin trisulphate

Frumkin adsorption parameters were also recorded in Table 2. The interaction parameters were also positive for both inhibitors and also confirm the attractive behaviour of the inhibitors' molecules.

The equilibrium constant in the adsorption models is related to the standard free energy of adsorption, an index for measuring the feasibility of the adsorption process (equation 6) (El-Naggar, 2007)

$$\Delta G^0_{ads} = -RTln(55.5k_{ads}) \qquad (6)$$

Calculated values of the standard free energy change are also recorded in Table 2. Therefore, the adsorption of tetracycline and neomycin is spontaneous (because free energy change is negative) and supports the mechanism of physical adsorption (because the free energy change is less than the threshold value of – 40 kJ/mol).

3.3 *SEM and FTIR studies*

The scanning electron micrographs of mild steel in the absence and presence of inhibitor is shown in Fig. 4. The image reveals strong corroded surface of mild steel without the inhibitor. However, in the presence of tetracycline (Fig. 4b) and neomycin trisulphate (Fig. 4b), the surface is protected by the formation of a protective film which covers the entire metal surface. The FTIR spectra of the corrosion product of mild steel in the presence of tetracycline and neomycin are presented in Fig. 5 and 6 respectively. Table 3 present functional groups identified from FTIR spectrum of the drugs.

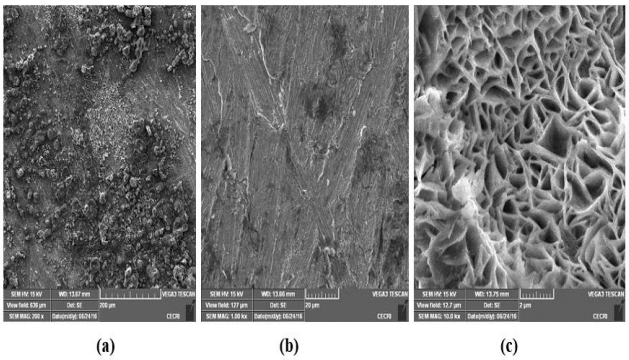

Fig. 4: Scanning electron micrograph of (a) mild steel in 2M NaCl (b) mild steel in 2 M NaCl containing tetracycline (c) mild steel in 2 M NaCl containing Neomycin trisulphate.

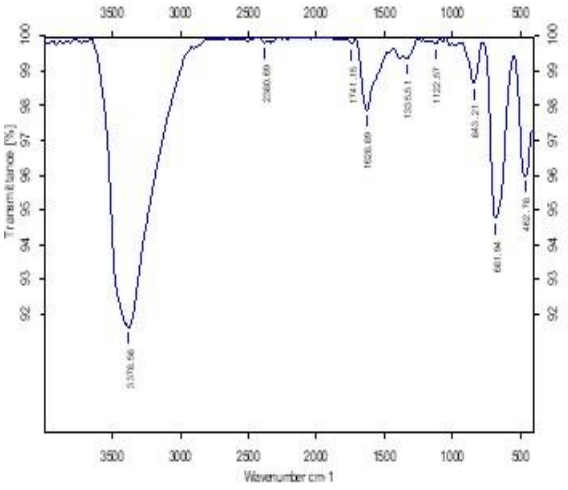

Fig. 5: FTIR spectrum of corrosion product of mild steel in the presence of tetracycline drug.

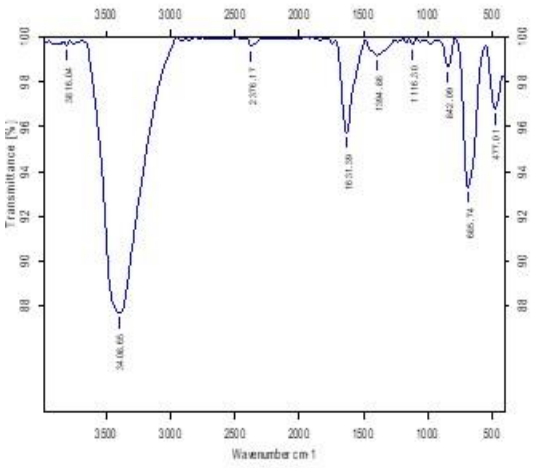

Fig. 6: FTIR spectrum of corrosion product of mild steel in the presence of Neomycin trisulphate drug

Table 3: Peaks, Assignments of IR adsorption by mild steel corrosion product (Containing tetracycline and Neomycin trisulphate

Corrosion product containing tetracycline		**Corrosion product containing Neomycin trisulphate**	
Peak (cm^{-1})	**Assignment**	**Peak (cm^{-1})**	**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	1122	C-N Stretching

It is evident from the FTRIR of tetracycline (Fig. 4) that the phenolic O-H stretch has shifted from 3805 cm^{-1} to 3408 cm^{-1}. The C-H stretching frequency of methyl group shifted from 2684 cm^{-1} to 2380 cm^{-1}. The C=C bond has shifted from 1635 cm^{-1} to 1631 cm^{-1}. The C-O stretching frequency shifted from 1338 cm^{-1} to 1394 cm^{-1}. The aromatic in plane and out plane deformation peak was observed at 1116 cm^{-1}. The shift in frequency is attributed to existent of interaction. However, from the observed changes, tetracycline might have been coordinated to the metal surface through the phenolic oxygen. The FTIR spectrum of the protective film formed on the metal after immersion in the 2M NaCl solution in the presence of neomycin trisulphate for four hours is shown in Fig. 5 .It is evident that vibration due to phenolic O-H stretch was shifted from 3805cm^{-1} to 3378 cm^{-1} ·The C-H stretching methyl group was shifted from 2684 cm^{-1} to 2376 cm^{-1}·The C=C bond shifted from 1635 cm^{-1} to 1628 cm^{-1}.The C-O stretch shifted from 1338 cm^{-1} to 1335 cm^{-1}. However, a new bond attributed to C-N stretching vibration was observed at 122 cm^{-1}. Therefore, there is interaction between the inhibitor and the metal surface and new bond was formed to facilitate the adsorption of the drug to the surface of mild steel.

4.0 Conclusion

Tetracycline and neomycin trisulphate are good corrosion inhibitors for mild steel in solution of NaCl. They possess suitable functional groups, aromatic system, hetero atoms, π-electron system and have higher molecular weight, among other properties that enhance their good corrosion inhibitor. The drugs are adsorption inhibitors because their inhibition efficiencies increase with concentration while the corrosion rate decreased with concentration. Frumkin and Temkin models are best suited isotherms that best describe the adsorption behaviour of the inhibitors.

5.0 References:

Ahamad, M.A. (2010)Quraishi, Mebendazole: new and efficient corrosion inhibitor for mild steel in acid medium. Corrosion Science, 52, pp. 651-658.

Eddy, N. O. & Ebenso, E. E. (2010). Adsorption and quantum chemical studies on cloxacillin and halides for the corrosion of mild steel in acidic medium. *International Journal of Electrochemical Science*, 5, 6, pp. 731-750.

Eddy, N. O. & Ebenso, E. E. (2010). Corrosion inhibition and adsorption characteristics of tarivid on mild steel in H_2SO_4. *E Journal of Chemistry*, 7, S1, pp. S442-S448.

Eddy, N. O. & Odiongenyi, A. O. (2010). Corrosion inhibition and adsorption properties of ethanol extract of *Heinsia crinata* on mild steel in H_2SO_4. *Pigment and Resin Technology*, 38, 5, pp. 288-295.

Eddy, N. O., Ibok, U. J. & Ebenso, E. E. (2010). Adsorption and quantum chemical studies of the inhibitive properties of tetracycline for the corrosion of mild steel in 0.1 M H_2SO_4. *Anales des la Asociacion Quimica Argentina* (*The Journal of the Argentine Chemical Society)*, 97, 2, pp. 178-194.

Eddy, N. O., Odoemelam, S. A. & Ekwumemgbo, P. (2009). Inhibition of the corrosion of mild steel in H_2SO_4 by penicillin G. *Scientific Research & Essay*, 4, 1, pp. 033-038.

Eddy, N. O., Ebanos, E. E. & Ibok, U. J. (2010). Adsorption, synergistic inhibitive effect and quantum chemical studies on ampicillin and halides for the corrosion of mild Steel. *Journal of Applied Electrochemistry* ,40, pp. 445-456.

El-Naggar, M. M. (2007). Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds. *Corrosion Science*, 49, pp. 2226–2236.

Fang, J. & Li, J. (2002). Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides. *Journal of Molecular Structure (Theochem*), 593, 1/3, pp. 179-185.

Lalitha, A. Ramesh, S. & Rajeswari, S. (2005), "Surface protection of copper in acid medium by azoles and surfactants. Electrochimica Acta, 51, 1, pp. 47-55.

Montecinos, S. & Simison, S.N. (2011). 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, pp. 7732-7738.

Quraishi, A. M. (2010). Dapsone: A novel corrosion inhibitor for mild steel in acidic medium. *The Open Electrochemistry Journal*, 2, 1, pp. 43-51.

Shukla, S. K & Quraishi, M. A. (2009). Ceftriaxone: a novel corrosion inhibitor for mild steel in hydrochloric acid. *Journal of Applied Electrochemistry*, 39, pp. 1517–1523.

Shukla, S. K., Singh, A. K., Ahamad, I. & Quraishi, M. A. (2009). Streptomycin: A commercially available drug as corrosion inhibitor for mild steel in hydrochloric acid solution. *Materials Letters*, 63, pp.819–822.

Siaka, A., Eddy, N. O., Idris, O. S. & Magaji, L. (2014). Ampicillin potentials as Corrosion Inhibitor: Fukui function calculations using B3-YLP exchange correlation. *Nigerian Journal of Chemical Research*, 19, pp.12-23.

Singh, A. K. & Quraishi, M. A. (2011). Adsorption properties and inhibition of mild steel corrosion in hydrochloric acid solution by ceftobiprole. *Journal of Applied Electrochemistry*, 41, pp. 7–18.

Singh, A.K. & Quraishi, M.A. (2011). investigation of the effect of disulfiram on corrosion of mild steel in hydrochloric acid solution. *Corrosion Science*, 53,4, pp. 1288-1297.

Yurt, A., Duran, B & Dal, H. (2016). An experimental and theoretical investigation on adsorption properties of some diphenolic Schiff bases as corrosion inhibitors at acidic solution/mild steel interface. Arabian Journal of Chemistry, 7, pp. 732-740.