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Tetracycline: A Non-Toxic Corrosion Inhibitor for Mild Steel in Aqueous Environment

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Abstract: The inhibition efficiency of antimicrobial drug toward the corrosion behavior of mild steel using aqueous environment was studied using weight loss method and A.C. Impedence techniques. The obtained result revealed that the drug performed well as corrosion inhibitor in aqueous environment. The inhibition efficiency increased with increasing inhibitor concentration. The highest inhibition occurs through adsorption of the Inhibitor molecule on the metal surface without modifying the mechanism of corrosion process. The adsorption parameters were also used to evaluate the inhibitive property of drug. It was also found that the corrosion inhibition behaviour of tetracycline drug is more in sodium chloride.

Key words: Mild steel, corrosion, antimicrobial agent, tetracycline, potentiodynamic polarization

INTRODUCTION

Chemical inhibitors play an important role in the protection and mitigation strategies for retarding corrosion. The most effective and efficient inhibitors are the organic compounds that have p bonds, heteroatom (P, S, N and O) and inorganic compounds such as chromate, dichromate, nitrite and so on (Shukla *et al*., 2009). However, the use of these compounds has been questioned lately, due to the several negative effects they have caused in the environment (Shukla and Quraishi, 2009). Thus, the development of the novel corrosion inhibitors of natural source and non-toxic type has been considered to be more important and desirable (Naggar, 2007). Because of their natural origin as well as their non-toxic characteristics (Fouda *et al*., 2010) and negligible negative impacts on the aquatic environment (Ahamad and Quraishi, 2010), drugs (chemical medicines) seem to be ideal candidates to replace traditional toxic corrosion inhibitors. The inclination towards eco-friendly corrosion inhibitors development intersects across several goals of pharmaceutical research, one of which is to discover or develop molecules with desired biological activity. Efforts to attain this goal are strongly driven by the notion of molecular similarity because in general similar molecules tend to behave similarly (Anand, 2011). Five and six-membered rings are the most common but small ring systems occur with reasonable frequency (for example, the cyclopropane ring in ciprofloxacin and the aziridine ring in mitomycin C). Of the five and six-membered systems, the majority are aromatic or pseudo-aromatic. Hence, substituted benzene rings are very frequent and heterocycles such as pyridines, furans, thiophenes, imidazoles isoxazoles and others occur commonly in drug structure. Due to above-mentioned structural closeness, corrosion protection properties of many drugs have attracted too much attention in recent years.

MATERIALS AND METHODS

The present study is aimed at investigating the inhibitory effect of tetracycline for the corrosion of mild steel in aqueous environment. Tetracycline are a large family of compounds that were discovered by Benjamin Minge Duggar and first described in 1948. The primary use of tetracycline is for the treatment of acne and rosacea. From our knowledge, tetracycline has not been used as an inhibitor for the corrosion of mild steel in aqueous environment. The molar mass of tetracycline is 444.44 g mol^{-1} and its chemical formula is $C_{22}H_{24}N_2O_8$. It has five-OH bonds, three C = O bonds and one $-NH_2$ bond. Therefore, tetracycline is enriched with π-electrons and hetero atoms suggesting that the molecule may be a good corrosion inhibitor.

Experimental

Specimen preparation: According to ASTM method as reported already (Dubey and Potdar, 2009), cold rolled mild steel strips were cut into pieces of 5×1 cm having the following composition (percentage); C= 0.017; Si = 0.007; Mn = 0.196; S = 0.014; p = 0.009; Ni = 0.013; Mo = 0.015;

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Cr = 0.043 and Fe = 99.686 was used. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with various grades of SiC abrasive papers (from grits 120 -1200) and degreased using Acetone.

Preparation of solutions

Preparation of solutions: All the solutions were prepared using NICE brand analar grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 min to carry out de-aeration of the electrolytes.

Preparation of inhibitor: Various concentration of inhibitor was prepared on the basis Le Chatlier's principle.

Weight loss measurement: Mild steel specimens were immersed 1M NaCl and 1M KCl for 2 h at room temperature (28±2°C) for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen was determined. From this, the inhibition efficiency (IE %) was calculated using Equation:

$$IE\% = \frac{W_0 - W_i}{W_0} \times 100$$

where, W_O and Wi (g) are the values of the weight loss observed of mild steel in the absence and presence of inhibitor, respectively.

Impedance studies: A well polished mild steel electrode was introduced into 100 mL of test solution and allowed to attain a steady potential value A.C. signal of amplitude of 10 mV was applied and the frequency was varied from 10 MHz 10 kHz using Solartron Electrochemical measurement unit (1280 B). The real and imaginary parts of the impedance were plotted in Nyquist plots. From the Nyquist plot, the charge transfer Resistance (Rct) and double layer Capacitance (C_{dl}) values were calculated:

$$IE\% = \frac{R_{et(i)} - R_{et}}{R_{et(i)}} \times 100$$

Where:

R_{ct} = Charge transfer resistance in the absence of inhibito

$R_{ct(I)}$ = Charge transfer resistance in the presence of inhibitor

RESULTS AND DISCUSSION

Weight loss method: From Table 1, it is clear that the corrosion rate was decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency of Tetracycline for Mild Steel in 1M NaCl was 80.8% and in 1M KCl 70.18%, respectively at 5×10^{-4} of the inhibitor solution for 2 h at room temperature.

It was also suggested that the inhibitor was best inhibitor in preventing the mild steel corrosion in 1M NaCl and 1M KCl. But when comparing the inhibitor efficiency was more in 1M NaCl than 1M KCl. The comparison graph of corrosion behaviour and inhibitor efficiency of Mild Steel in 1M NaCl and 1M KCl with Tetracycline which was studied by weight loss method at 2 h at room temperatures was given in Fig. 1a.

Adsorption isotherm: In aqueous solution, the metal surface was always covered with absorbed molecule.

Table 1: Corrosion parameters in absence and presence tetracycline with 1M NaCl and 2M, NaCl at 2 h

Inhibitor	Concentration of Inhibitor M	Corrosion rate 1M NaCl	Corrosion rate 1M KCl	Inhibition efficiency (%) 1M NaCl	Inhibition efficiency (%) 1M KCl
Tetracycline	Blank	27.7	21.6	-	-
	1×10^{-4}	24.1	13.5	37.6	13.0
	2×10^{-4}	18.7	9.8	54.9	32.4
	3×10^{-4}	15.8	7.7	64.3	42.9
	4×10^{-4}	10.9	5.1	76.3	60.7
	5×10^{-4}	8.3	4.1	80.8	70.1

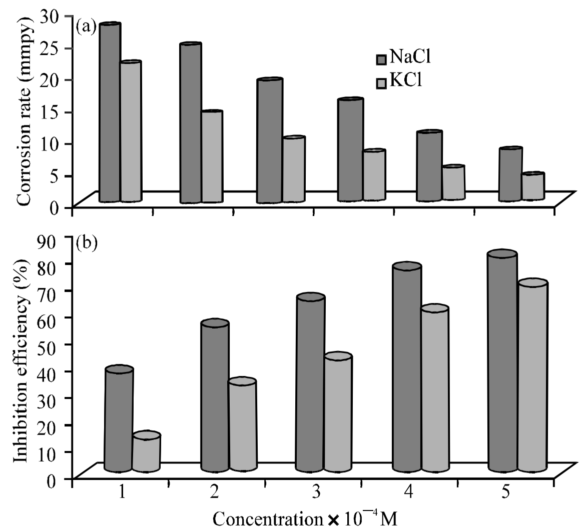

Fig. 1: a) Comparison of Corrosion Rate (CR) with concentration of Tetracycline in 1M NaCl and lM KCl solution at 2 h at room temperature; b) Comparison of Inhibition Efficiency (IE) with concentration of concentration of Tetracycline in 1M NaCl and lM KCl solution at 2 h at room temperature

Therefore, the adsorption of inhibitor molecule from an aqueous solution is a quasi substituted process and the inhibitor that have the ability to adsorb strongly on the metal surface will hinder the dissolution reaction of such metal in the corrosive medium (Singh and Quraishi, 2011). The degree of surface coverage is considered as the determining factor which plays the main role in inhibition efficiency (Dubey and Potdar, 2009). The extend of adsorption depends on many factors such as the nature of metal, condition of metal surface ,the chemical structure of inhibitor molecule, the nature of its functional groups, pH and type of corrosion medium (Pang *et al.*, 2008). Basic information on the interaction between the inhibitor and the Mild steel metal surface can be proved by the adsorption isotherm and in general, inhibitor can function either by physical (electrostatic) adsorption or chemisorption with the metal surface . Actually, the adsorbed molecule may cause some difficulty for the surface to adsorb further molecule from neighboring sites. To acquire more information about the interaction between the inhibitor molecules and the metal surface, a number of mathematical adsorption expressions have been developed to fit the degree of surface coverage through different adsorption isotherms in order to provide some knowledge on the nature of interaction of the adsorbed molecule (Naggar, 2007). The fractional surface coverage θ at different concentrations of inhibitors in 1M NaCl and 2M NaCl solutions were determined from the weight loss measurements data using Equation:

$$(\theta) = \frac{W_0 - W_i}{W_0} \quad (1)$$

where, W_0 and W_i are the values of weight loss of uninhibited and inhibited specimens, respectively:

$$Kc = \frac{\theta}{1-\theta} \quad (2)$$

Where c is the concentration of the inhibitor, è is the fractional surface coverage. The Langmuir isotherm, Eq. 4 which is based on the assumption that all adsorption sites are equivalent and that molecular binding, occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant K is related to the free energy of adsorption ΔG_{ads} as:

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (3)$$

where, $C_{solvent}$ represents the molar concentration of the solvent which in the case of water is 55.5 mol dm^{-3}, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. 5 can be rearranged to obtain the following expression:

$$\frac{c}{\theta} = \frac{1}{K} + c \quad (4)$$

so that a linear-relationship can be obtained on plotting c/θ as a function of c with a slope of unity. The thermodynamic parameters K and ΔG_{ads} for the adsorption of the studied inhibitors on Mild steel is obtained by Langmuir's adsorption isotherm are plotted in Fig. 2 and the obtained values are given in Table 2. It was found that the linear correlation coefficients clearly prove that the adsorption of tetracycline from 1M NaCl and 1M KCl solutions on the Mild steel corrosion obeys the Langmuir adsorption isotherm. The negative values of (ΔG^0_{ads}) for the addition of inhibitors indicate that the process of adsorption of studied inhibitors is spontaneous in nature. The free energy of adsorption of (ΔG_{ads}) for mild steel in 1M NaCl was found to be -10.18 kJ mol^{-1} while for 1M KCl it was found to be -8.056 kJ mol^{-1}, respectively.

It is well known that the values of ΔG_{ads} in the order of -20 kJ mol^{-1} or lower indicate a physisorption while those about -40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond.

The calculated adsorption values for the studied inhibitor show that the adsorption is of physical in nature and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the

Table 2: Thermodynamic parameters for the adsorption in of tetracycline 1M NaCl and 1M KCl on the mild steel

Medium	Concentration (M)	Surface coverage (θ)	Δgads KJ mol^{-1}	K (10^{-2} M^{-1})
M NaCl	5×10^{-4}	0.808	-10.18	1.80
1M KCl	5×10^{-4}	0.701	-8.056	1.80

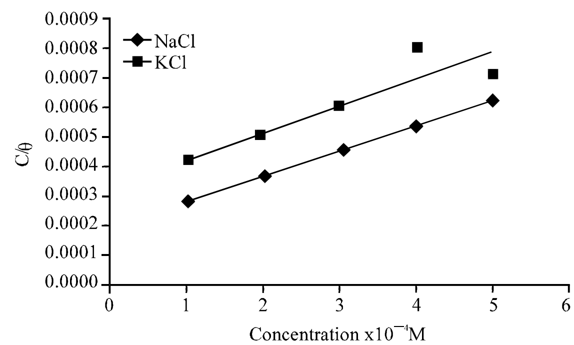

Fig. 2: Langmuir isotherm for adsorption of of tetracycline on the mild steel surface studied at 1M NaCl and 1M KCl

Table 3: Impedance parameters for the corrosion of mild steel in 1M NaCl and 1M KCl containing different concentration of tetracycling

Concentration of inhibitor (M)	Rct (Ω cm^2)		Cdl (μF cm^{-2})		I.E (%)	
	1M NaCl	1M KCl	1M NaCl	1M KCl	1M NaCl	1M KCl
Blank	70.120	64.34	4.618	4.831	-	-
1×10^{-4}	107.91	72.72	2.235	4.118	35.01	11.52
2×10^{-4}	130.24	87.90	2.054	2.669	46.16	26.80
3×10^{-4}	167.24	107.9	1.772	1.966	58.07	40.37
4×10^{-4}	280.00	159.4	1.514	1.872	74.95	59.63
5×10^{-4}	299.56	206.2	1.396	1.817	76.59	68.79

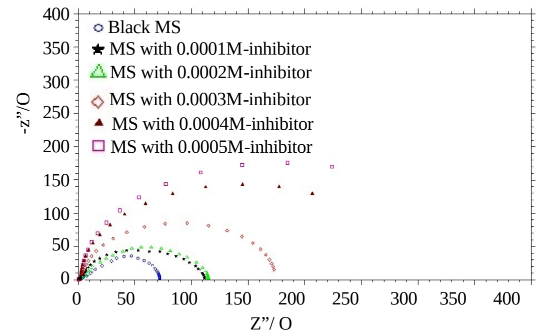

Fig. 3: Nyquist plots for mild steel in 1M NaCl with Tetracycline

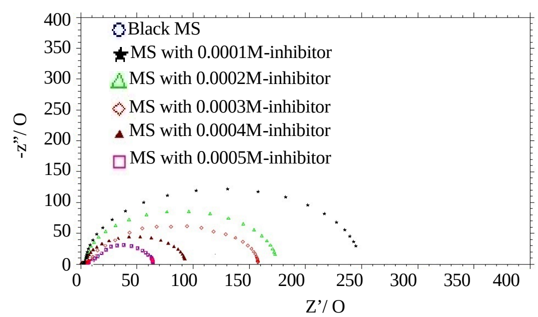

Fig. 4: Nyquist plots for mild steel in 1M KCl with Tetracycline

adsorption of tetracycline at 2 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

Electrochemical impedance spectroscopy results: Impedance diagram (Nyquist plot) obtained for mild steel in 1M NaCl has been depicted in Fig. 3 and 1M KCl in the presence of various concentrations of the inhibitor is depicted in Fig. 4. They are prefect semicircles and this was attributed to charge transfer reaction. Impedance parameters derived from Nyquist plot are tabulated in Table 3. It can be seen that as the concentration of inhibitor increases, C_{dl} value decrease. Decrease in C_{dl} which can result from an increase in thickness of electrical double layer, suggests that the inhibitor molecules function by adsorption at the metal-solution interface.

CONCLUSION

The tetracycline was found to be effective inhibitor in the aqueous medium giving up to 80.8 % in 1M NaCl. The inhibition efficiency increased with increase in concentration of inhibitors at 2 h at room temperature. From the comparative studies of weight loss method, it was concluded that the inhibitor efficiency is better in 1M NaCl than 1M KCl. Weight loss data were confirmed by impedance method. The corrosion rate of mild steel in NaCl was higher than that of KCl. The drug was very good inhibitors because of the presence of ð-electrons and hetero atoms that cause effective adsorption process. The adsorption of the drug is exothermic spontaneous as suggested by the negative values of $\Delta G_{ads\ and}$ obeys Langmuir's adsorption isotherm. The adherence of the data to Langmuir's adsorption isotherm support physical adsorption process.

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