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## Corrosion Behavior of Titanium in the Presence of Some Drugs Based on Amino Groups

Rasha A. Jassim, Asmaa Kadim Ayal, Muna S. Sando, Ahlam Mohammed Farhan\*, Sameaa J. khammas

Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq

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### Abstract

This study evaluated the effect of two different types of amino group-containing pharmacological inhibitors on titanium corrosion under acidic conditions. The first inhibitor examined was the antibiotic trimethoprim. The second inhibitor studied was the nonsteroidal anti-inflammatory drug voltaren. The results showed that titanium had a high corrosion current in the absence of a corrosion inhibitor, however, trimethoprim notably enhanced corrosion resistance and protection percentages of titanium (%IE) at higher concentrations by adhering to the metal surface, as evidenced by improved protection percentages. Furthermore, the results showed that as Voltaren concentration was increased, both corrosion resistance and inhibition efficiency decreased. This demonstrates that less Voltaren was absorbed onto the metal surface as compared to trimethoprim.

**Keywords:** Acid media; Corrosion inhibitors; trimethoprim drug; voltaren drug; Titanium metal

### سلوك تاكل التيتانيوم بوجود بعض الادويه القائمه على مجموعات امينية

رشا عبد جاسم , اسماء كاظم عيال , منى سرحان صندو , احلام محمد فرحان\* , سميرة جمعه خماس  
قسم الكيمياء , كلية العلوم للبنات , جامعة بغداد , بغداد , العراق

### الخلاصة

قيمت هذه الدراسة تاثير نوعين مختلفين من المثبطات الدوائية المحتويه مجاميع امينية على تاكل التيتانيوم في الوسط الحامضي. كان المثبط الاول الذي تم فحصه هو المضاد الحيوي تريميثوبريم، والمثبط الثاني الذي تمت دراسته هو دواء الفولتارين المضاد للالتهابات. اظهرت النتائج ان تيار التاكل للتيتانيوم يكون عالي في حالة عدم وجود مثبط التاكل، ومع ذلك فان وجود تركيز عالي من دواء تريميثوبريم يزيد من مقاومه التاكل ومعدلات الحماية للتيتانيوم (%IE) وذلك من خلال التصاقه بسطح المعدن كما يتضح من تحسين معدلات الحماية، اضافة الى ذلك اوضحت النتائج بزياده تركيز الفولتارين تقل مقاومه التاكل وكفاءه التثبيط، وهذا يبين ان امتصاص الفولتارين اقل من التريميثوبريم على سطح المعدن.

## 1. Introduction

Titanium alloys are exposed to corrosion, which results in the accumulation of ions, species of metallic, and oxides in the tissues [1, 2]. Corrosion is one of the primary factors impacting the performance and longevity of orthopedic devices composed of titanium metal used as

implants within the body. Titanium has been detected in both soft and hard tissues as well as submucosal plaques in people with peri-implantitis [3, 4]. In a postmortem study, titanium particles were discovered in the bone marrow tissue of the jaw near dental implants [1]. The presence of these metallic particles has the potential to cause tissue damage, which may provoke an atypical immune response in the body [2, 5]. To overcome this problem, the substances utilized must not bring any harmful biological reaction inside the body. In addition, these materials have to be stable and maintain their functional features [6, 7]. Titanium alloys are affected by fluctuations in the pH of the electrolyte, which can promote corrosion and challenge passivation [8, 9]. Titanium and its alloys are suitable for use in environments that can be from mildly reduced to highly oxidizing wherein protective oxide films spontaneously form and remain stable. Titanium exhibits excellent resistance to atmospheric corrosion in both marine and industrial environments. Titanium and its alloys also resist H<sub>2</sub>S and CO<sub>2</sub> gases at temperatures up to 260 °C [10]. Corrosion is one of the main issues that alloys and metals face in the industrial world. Corrosion brought on by chemical attack results in material loss and decomposition, which compromises the metal's dependability, structural integrity, and durability [11, 12]. A reaction known as corrosion occurs at the microscopic level of alloys and metals. Additionally, its macroscopic appearance is visual, which results in premature damage to metallic components, environmental pollution, financial waste, and/or injury or death [13]. Titanium and its alloys have corrosion resistance and high biocompatibility because of its ability to produce a passive oxide (TiO<sub>2</sub>) directly after reaching oxygen. This passive film is deemed stable when functioning inside the cavity of the oral, moreover, emerging data link inflammatory peri-implantitis to vastness raise in products of titanium corrosion around ill implants in contrast with healthy ones. Therefore, it is urgent to characterize which conditions in the peri-implant microenvironment may weaken titanium's resistance to corrosion [14]. Many techniques have been used to reduce or prevent corrosion of titanium alloys, and one of these methods is anodizing titanium [15–17] as the result was an improvement in the corrosion potential from -0.7 to -0.4 V [17]. It should be noted here that during the anodizing process, the electrolytic reaction on the surface of the substrate is possible to increase as a result of increased oxide rupture due to the evolution of oxygen during the process [18] [19]. Similarly, the current density of corrosion for Ti-6Al-4V decreased by twice when TiN was coated [20]. In addition, barrier protection, galvanization, and cathodic protection are among the methods that are used to prevent or protect from corrosion. For many years, corrosion-resistant coatings have received a lot of attention due to their efficiency and simplicity [21, 22]. Polymers, plant extracts, and drugs are utilized as inhibitors of corrosion as well as protective layers onto surfaces of carbon steel via the adsorption process. Trimethoprim drug is an antibiotic employed in the handling of diarrhea, middle ear infections, and bladder infections. Moreover, this drug is an effective inhibitor of steel corrosion in various media due to the presence of heterogeneous atoms such as oxygen and nitrogen, which have a high affinity for adsorption. Trimethoprim is adsorbed on the surface of carbon steel as a result of the interaction between the d orbitals of the metal and the electron pairs of the heteroatoms. [23]. Measurements confirmed that trimethoprim increased the inhibition efficiency of the complexes when the concentration was increased, and thus reduced surface corrosion of carbon steel. In addition, the metallic carbon steel was protected from corrosion by using Voltaren as an inhibitor as a result of the adsorption of its molecules on the surface of the metallic steel [24]. Actually confirmed and commonly applied mineral biomaterials include titanium, stainless steels, and cobalt-chromium-based alloys. One of the dangers of these current metal biomaterials is the liberation of toxic molecules or ions due to corrosion, which in turn will cause a series of inflammatory that cause tissue loss and reduce biocompatibility [25, 26]. Therefore, the aim of this study was to evaluate the corrosion resistance of both trimethoprim and voltaren in an acidic solution. According to the results, the two drugs can protect titanium from corrosion by adsorbing them on the titanium surface while

maintaining the electrochemical stability and structural integrity of the metal. Thus, this method is promising for protecting devices and implants from corrosion and degradation in humans.

## 2. Material and Method

### 2.1. Material

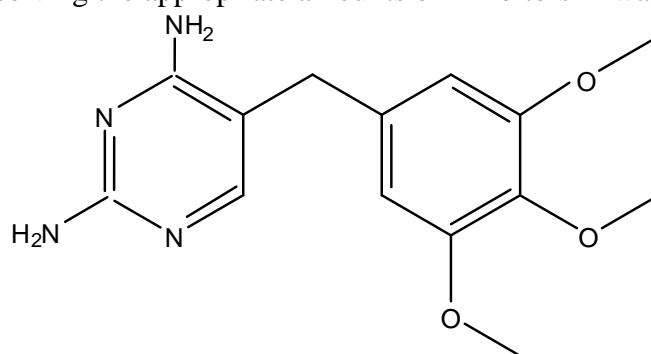
Table 1 illustrates the constituents of titanium metal, and the chemical composition of titanium metal was examined by X-ray fluorescence. Acid Media: 0.1 N Hydrochloric acid supplied by the company of BDH, and drugs of trimethoprim and voltaren as inhibitors as shown in Figures 1 and 2.

**Table 1:** The constituents of Ti metal

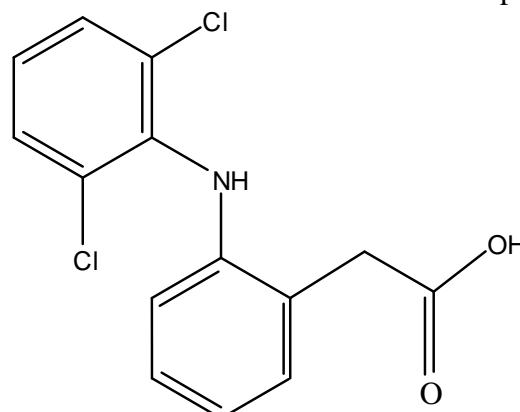
V%	Zn%	Cr%	Mg%	Mn%	Cu%	Fe%	Si%	Ti%	Others
<0.03	<0.05	<0.05	<0.05	<0.05	<0.05	<0.4	<0.25	98.09	<0.02

### 2.2. Inhibitor

To protect the titanium metal from corrosion, trimethoprim and voltaren were used as inhibitors, and their scientific names are 5-(3, 4, 5-Trimethoxybenzyl) pyrimidine-2,4 diamine and 2-(2-(2,6-dichlorophenylamino) phenyl) acetic, respectively. Figures 1 and 2 display the structural formulas of the inhibitors trimethoprim and voltaren, respectively. Both inhibitors were obtained from Samarra Drugs Industry (SDI) with a purity greater than 99%. Stock solutions of the inhibitors were prepared at concentrations of 10, 100, 200, and 300 parts per million (ppm) by dissolving the appropriate amounts of inhibitors in water.



**Figure 1:** The chemical Structure of trimethoprim drug



**Figure 2:** The chemical Structure of Voltaren drug

### 2.3 Preparation of Sample

Titanium was cut with thickness 0.5mm and dimensions of 2.5cm. The titanium sheets were then polished using emery paper of different grit sizes (300, 500, up to 2400) to create a consistent surface finish. The polished titanium sheets were then washed with acetone and distilled water to remove any residue. The cleaned titanium sheets were stored until used for testing.

2.4 .*Test Solution* : the test solution of hydrochloric acid (0.1N HCl)

2.5.*Method*

2.5.1. *Polarization potentiodynamic measurement*

Potentiostatic Set-Up were used calculated of parameter of electrochemical in different concentrations of trimethoprim drug and voltaren drug in 25°C in acid media, potentiostatic Set-Up consisted of magnetic stirrer, galvanostat-potentiostat M lab, host computer and the thermostat . The cell of corrosion was used to calculate the current and potential corrosion in absence and presence of the drugs. The corrosion cell that was made of pyrex with (1L) capacity consists of two outer vessels and an inner vessel that contains three electrodes. The potential of working electrode is determined according the potential of reference electrode, the reference electrode consists of two tubes outer and inner tubes, the solution of hydrochloric acid is filled outer tube while the inner tube contains Saturated calomel electrode. While platinum metal was used as an auxiliary electrode. The distance between the reference electrode and the working electrode to which the sample was attached was 2 cm. as show in Figure (3) [27].

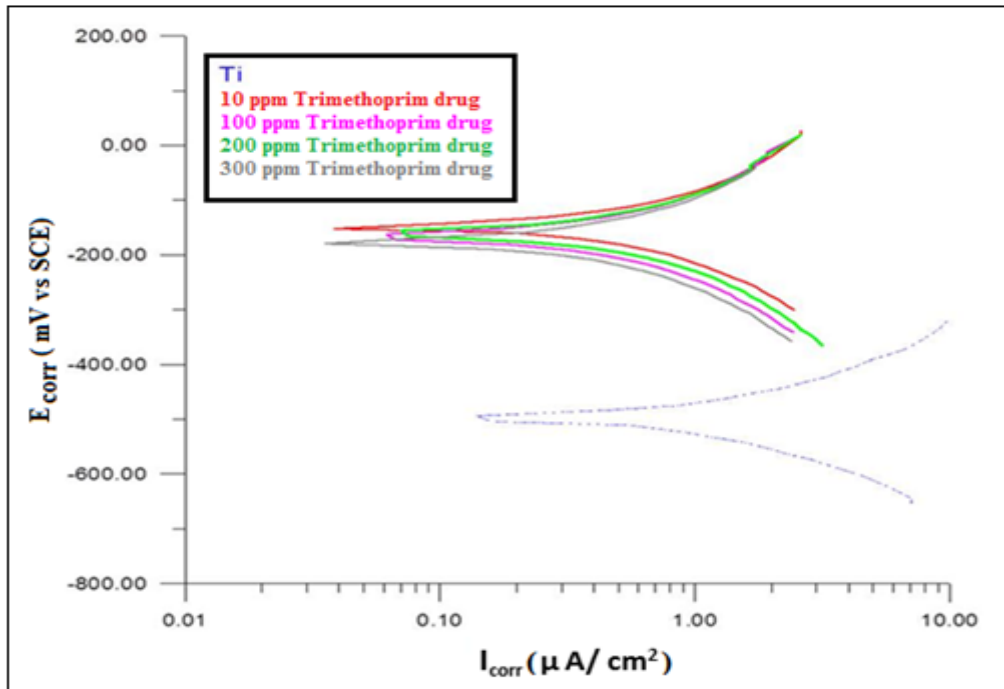


**Figure 3:** The corrosion cell used during the current study

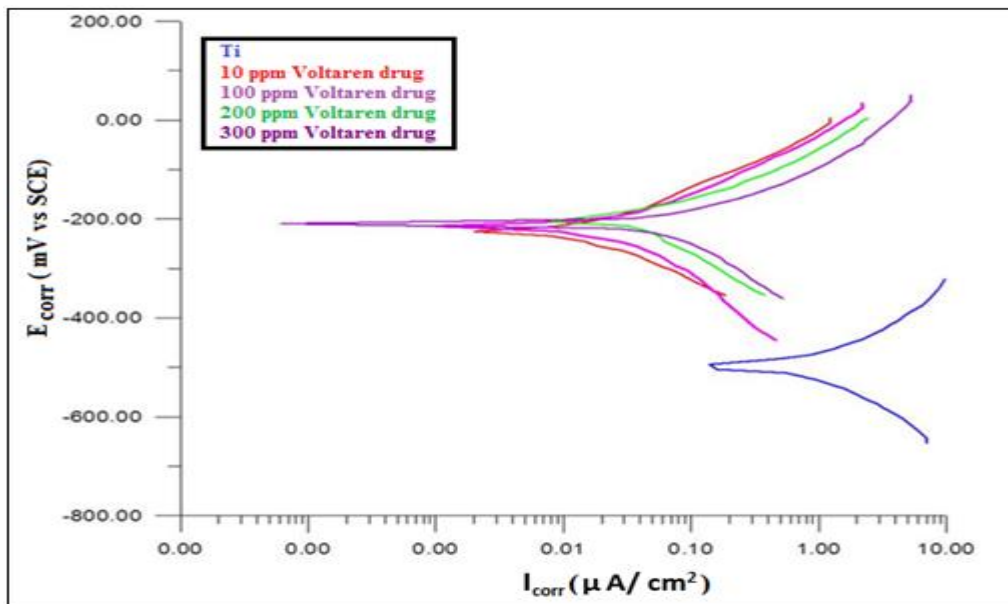
### 3. Results and discussion

Data on corrosion current densities, corrosion potential, polarization resistance ( $R_p$ ), cathodic and anodic Tafel slopes ( $b_c$ ,  $b_a$ ), and inhibition effectiveness (IE) are shown in Table 2. The presence of the substances did not change the cathodic response, as evidenced by the parallel cathodic Tafel lines observed with and without the drugs trimethoprim and voltaren [28]. Additionally, the  $b_a$  and  $b_c$  values varied in the presence of the inhibitors due to the inhibitor particles adhering to the titanium surface and forming a protective layer, as has been reported previously [29, 30]. According to Table 2 examination of polarization resistance and Figures 4 and 5, when titanium was added, the polarization curves shifted to the low current areas and the corrosion potentials increased [31]. The inhibition in the acidic medium was observed to be increasingly obvious when medication concentration is increased. Additionally,

when inhibitor concentration increased, both cathodic (hydrogen evolution) and anodic (titanium) processes were suppressed, though the anodic impact was more pronounced [32]. This is because the medication acts as an anodic inhibitor [33, 34]. Furthermore, the corrosion current density ( $i_{corr}$ ) values increased with higher concentrations of the voltaren drug, whereas they decreased with rising concentrations of the trimethoprim drug. This can be attributed to the cathodic branches only exhibiting modest diffusion-limited currents as a result of hydrogen gas reduction occurring on the titanium surface [35].



**Figure 4:** Polarization plots of Titanium with different concentrations of trimethoprim drug in (0.1N) hydrochloric acid .



**Figure 5:** Polarization plots of titanium with different concentrations of Voltaren drug in (0.1 N) hydrochloric acid

**Table 2:** A comparison of titanium corrosion in hydrochloric acid regarding various concentrations and in the presence and absence of drugs

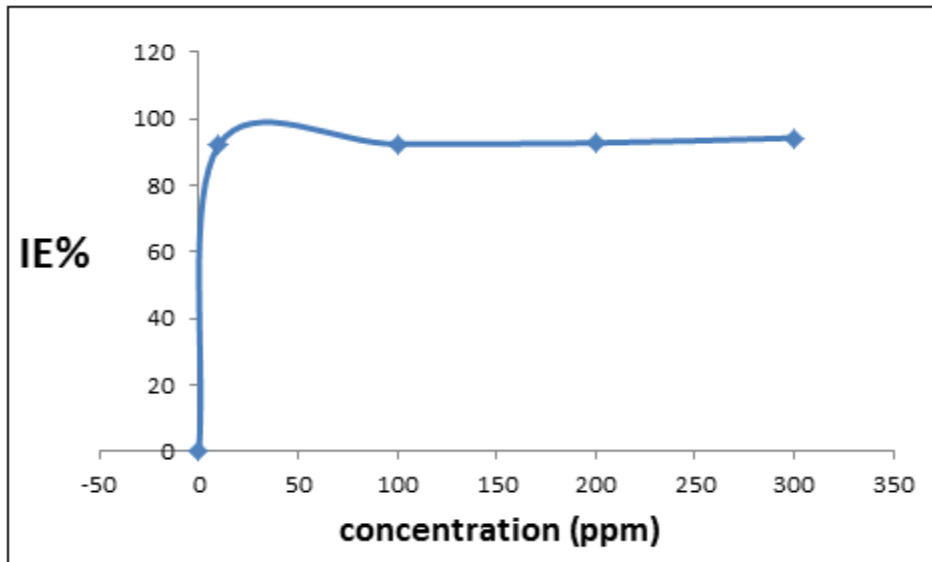
Drug (Inhibitor)	Concentration (ppm)	$i_{corr}$ ( $\mu Acm^{-2}$ )	$-E_{corr}$ (mv)	ba	-bc	IE%	Rp
Trimethoprim drug	Ti	1580	505.3	212.6	220.4	-	-
	10	125.94	145.5	60.7	58.4	92.08	236.3
	100	120	150.8	61.7	59.3	92.4	251.4
	200	115.88	156.6	62.4	60.8	92.72	533.7
	300	91.32	172.6	59.3	50.6	94.22	548.9
Voltaren drug	10	375.73	475.8	127	87.3	76.21	137.963
	100	491.92	490.9	109.6	132.9	68.86	122.1
	200	510.95	491	114.9	112.3	67.66	111.262
	300	555.92	117.9	122.7	117.9	64.81	108.335

The inhibitory efficiency was determined using Equation 1 [36] from the polarization curves.

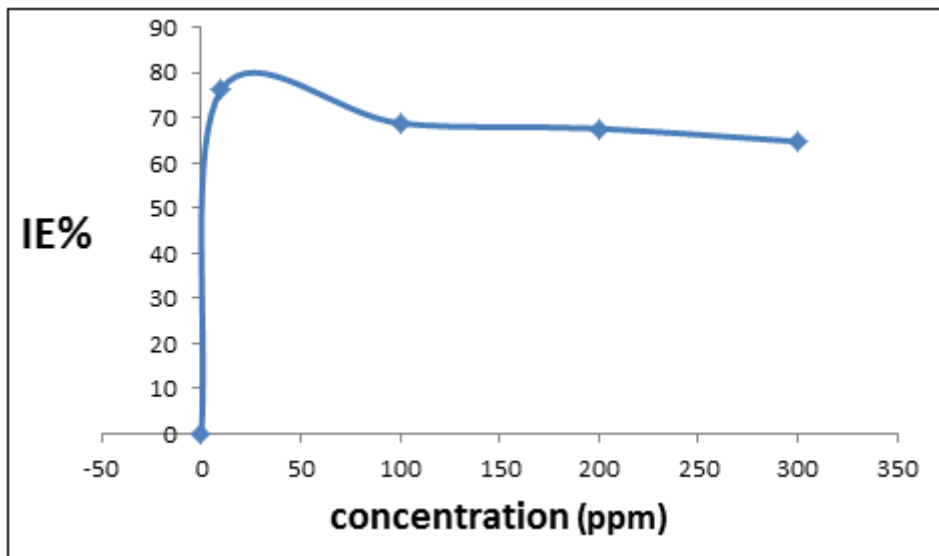
$$IE\% = \frac{i_{corr(i)} - i_{corr}}{i_{corr(i)}} \times 100 \dots\dots\dots (1)$$

where the abbreviations for the current density of corrosion for titanium with absent and present pharmaceuticals, respectively, are  $i_{corr}$  and  $i_{corr(i)}$ .

The results in Table 2 and Figures 6-7 show that trimethoprim at a concentration of 300 ppm achieved a higher level of inhibitory efficiency (94.22%) compared to voltaren at 300 ppm (64.81%) in 0.1N HCl. The synergistic adsorption mechanism, whereby the drug molecule (inhibitor) and acid anion cooperatively adsorb to the metal surface, provides evidence that these pharmaceuticals can effectively function as corrosion inhibitors for titanium protection in acidic environments due to formation of a protective layer. Therefore, trimethoprim is better than voltaren as an inhibitor on the titanium metal surface.[7], due to trimethoprim contains in its structure heteroatoms (N, O) in its molecules, having lone pair electrons or electrons in aromatic rings or multiple bonds. It enables relatively strong interactions between metal atoms and organic molecules, resulting in a protective layer of organic molecules adsorbed at the corrosive-mineral-solution interface [37]. Greater concentrations result in higher inhibition efficiency values, which prove that the titanium is pure and that the adsorption is of the physical kind [7].



**Figure 6:** shows the effectiveness of inhibition (IE%) of Ti metal at different trimethoprim drug.

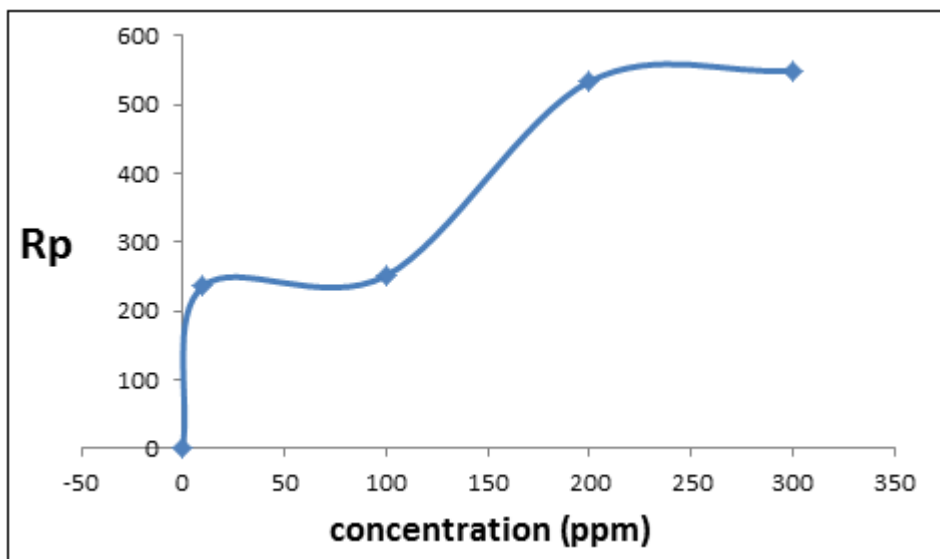


**Figure 7:** shows the effectiveness of inhibition (IE%) of Ti metal at various Voltaren drug

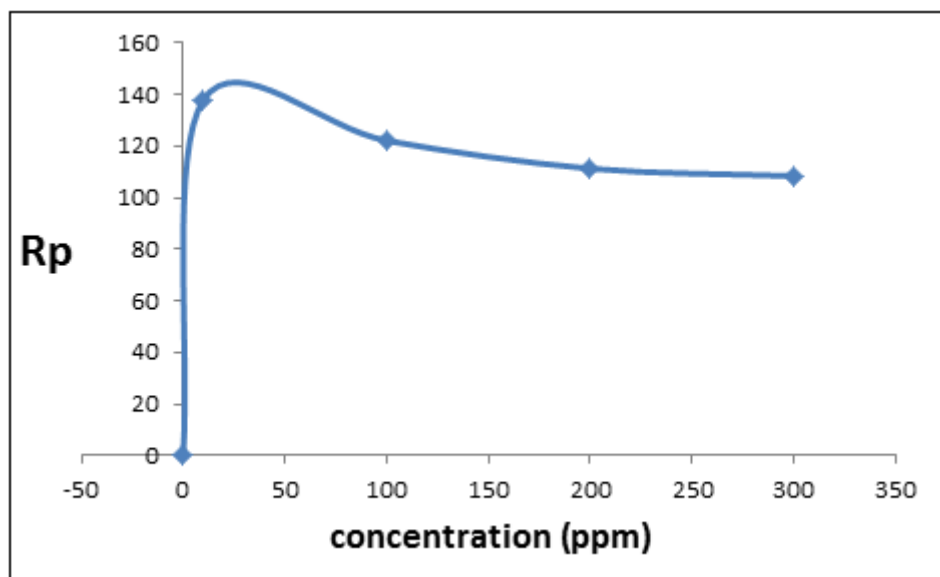
The polarization resistance ( $R_p$ ) from equation (2) [37] can be calculated with the aid of these parameters' valuation.

$$R_p = \frac{babc}{2.303 (ba+bc)i_{corr}} \quad \text{-----} \quad (2)$$

As indicated in Table 2 and Figures (8, 9), when the polarization resistance ( $R_p$ ) was calculated using Equation 2, it was discovered that it was high at the high concentration of trimethoprim and the low concentration of voltaren[38, 39].



**Figure 8:** Polarization resistance of titanium metal at different concentrations of trimethoprim drug



**Figure 9:** Polarization resistance of titanium metal at different concentrations of Voltaren drug

### Conclusion

In conclusion, this study described how trimethoprim and voltaren prevent Ti from corrosion. Testing at different concentration levels showed that both drugs functioned as corrosion inhibitors for titanium immersed in 0.1N HCl solution. In particular, trimethoprim at a concentration of 300 ppm achieved an inhibition efficiency of 94.22%, successfully lowering the corrosion current density from an initial value of  $1580 \mu\text{A}/\text{cm}^2$  down to a reduced level of  $91.32 \mu\text{A}/\text{cm}^2$ . In addition, the inhibition efficiency reached 94.22% as a result of an increase in adsorption on the titanium surface as the concentration of trimethoprim in an acidic solution increased. Additionally, as the concentration of Voltaren increased, the resistance to corrosion and the effectiveness of inhibition (IE%) decreased because Voltaren adsorption on titanium surface was less than trimethoprim at high concentrations.

### Conflicts of Interest

The author declares that they have no conflicts of interest.



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