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Unused Augmentin Drug as save corrosion inhibitor for α-brass in Nitric acid solution

ABSTRACT

Unused Augmentin was investigated as save corrosion inhibitor for α-brass in nitric acid solution by different monitoring techniques. The results showed the variation in inhibition performance of the drug with varying concentrations and temperatures. The maximum efficiency was found to be 93.6 % at 300 ppm concentration of the drug for the immersion period of 3 hours at 40 °C. Temkin was tested to describe the adsorption behavior of the drug on α-brass surface. Potentiodynamic polarization study clearly revealed that this drug acts as mixed type inhibitor. The results of the electrochemical impedance study showed a decrease in double layer capacitance and increase in charge transfer resistance. Chemical adsorption mechanism is proposed from the calculated thermodynamic parameters for the studied drug. The results of various techniques showed good agreements with each other.

Keywords: *Corrosion inhibition, α-brass, unused Augmentin, Temkin isotherm,* HNO_3

1. INTRODUCTION

Alpha brass has an excellent electrical and thermal conductivity, good corrosion resistance and mechanical workability. It is widely used in the construction of heat exchangers, condensers, and valve systems. They are mostly used in building fronts, rails, lock bodies, door knobs etc. Corrosive acid medium is generally utilized as a part of the industry. The most vital zones of use are acid pickling, industrial acid cleaning, acid decaling and oil well acidizing [1,2]. Corrosion inhibitors are introducing to lower the rates of corrosion on α-brass in this acidic solution [3-8]. An inhibitor is an substance that used to reduce the corrosion rate by the adsorption mechanism [9-10]. Many inhibitors have been prepared or selected from compounds existing, and the best inhibitors are those that contain π-electron donation while others might be obtain by naturally extracts from compounds occurring [11-13]. Many organic compounds are referred to be relevant as corrosion inhibitors for α-brass [14,15]. However, just a couple non-harmful and eco-friendly has been obtaining as inhibitors for corrosion. Succinic acid, Tryptamine, Sulfamethoxazole, Cefatrexyl and L-ascorbic acid were obtained to be good inhibitors for acidic medium. Dithiobiurets displayed the best execution towards the corrosion of mild steel in HCl arrangements indicated less poisonous quality [16-21]. The four antibacterial drugs, Amoxicillin, Flucloxacillin, Cloxacillin, and Ampicillin have investigated as inhibitors for the aluminum corrosion [22]. The inhibition action of the four antibacterial drugs was given by blocking the metal via presence of insoluble complexes on the surface of aluminum. Because of the fact that most of the chemical compounds that prevent the corrosion of metal and alloys are toxic, and thus pose threat both for human health and environment, their usage is limited. For this reason, several authors reported the use of natural products as corrosion inhibitors [23]. Also, some authors used drugs which are derivatives of natural substance like penicillin as a green corrosion inhibitors for various metals and alloys [24-32].

In the present work, authors investigate the corrosion protection activity of unused Augmentin by using chemical and electrochemical methods.

2. MATERIALS AND METHODS

2.1. Materials and solutions

The chemical composition of the used α-brass in weight % is: Pb 0.029, Fe 0.002, Zn 32.68, Cu

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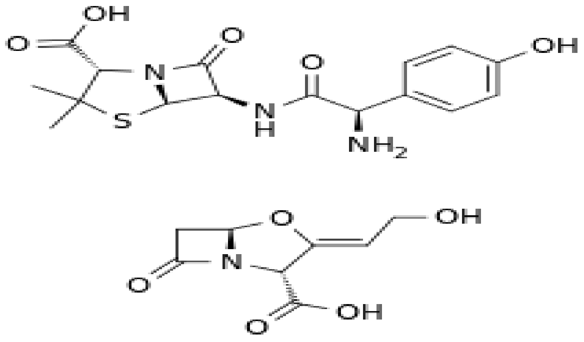
the rest. The solution of the corrosive medium 0.5 M HNO_3 was prepared by dilution of analytical reagent nitric acid (70 %) with bi-distilled water and its concentration was checked by restandarazied solution of NaOH. One gm of unused Augmentin was dissolved in one liter of bi-distilled water to yield 1000 ppm and the concentration used (50-300 ppm) was obtained by dilution by bi-distilled water. The structure of the unused Augmentin (Amoxicillin/ Clavulanic acid) drug is shown below with molecular structure $\mathbf{C_{24}H_{28}N_4O_{10}S}$ and molecular weight 564.5 g/mol:



(2S,5R,6R)-6-[[(2R)-2-amino-2-(4-hydroxyphenyl)acetyl]amino]-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid;(2R,3Z,5R)-3-(2-hydroxyethylidene)-7-oxo-4-oxa-1-azabicyclo[3.2.0]heptane-2-carboxylic acid.

2.2. Chemical measurements

Seven test pieces of α-brass were cut into 2 x 2 x 0.2 cm. They were abraded in presence of various grades of emery papers up to 1200 grit size (coarse grades was utilized first and then finer grades were final), washed with bi-distilled water then acetone and finally dried between filter papers and weighed. The specimens were immersed in test solution. Weight loss method was done for 3 hours at the temperature range 25 – 40°C by immersing α-brass pieces into 100 ml acid medium in presence and absence of unused Augmentin drug with different times, then weighed accurately again. The main weight loss at each time for seven samples was taken. The weight loss was obtained by:

$$\Delta W = W_B - W_A \quad (1)$$

where W_B and W_A is the weight of metal before and after exposure to the corrosive solution respectively. The percentage of inhibition efficiency (%IE) and the degree of surface coverage (θ) of the investigated compounds by the adsorbed molecules were calculated by the following equations:

$$\%IE = [1-(\Delta W_{inh}/\Delta W_{free})] \times 100 \quad (2)$$

$$\Theta = [1-(\Delta W_{inh}/\Delta W_{free})] \quad (3)$$

where ΔW_{free} and ΔW_{inh} is the weight loss of metal per unit area in the absence and presence of inhibitors respectively at given time period and temperature.

$$C.R.=\Delta W/ADT \quad (4)$$

where C.R is corrosion rate in mg cm^{-2} min^{-1}, A is area in cm^2, D= density of the metal in g cm^{-3} and T is the time in min.

2.3. Electrochemical measurements

Electrochemical measurements were done by using typical three electrodes cell, first working electrode (1 cm^2) of the α-brass, second (SCE) saturated calomel electrode as a reference electrode and a platinum foil (1 cm^2) as a counter electrode. All the experiments were done in open system. All potential values were reported versus SCE. Tafel polarization curves were obtained by the electrode potential changing from - 0.6 to 0.5 V vs. SCE at open potential circuit with a scan rate of 1 mVs^{-1}. The corrosion current is done by extrapolation of cathodic and anodic Tafel lines to obtain log i_{corr} and (E_{corr}). The impedance method was done and interpreted depend on the equivalent circuit. The data which obtained from the analysis of Nyquist curves are (R_{ct}) the charge transfer resistance and the double layer capacity C_{dl}. Electrochemical frequency modulation (EFM) was carried out using two frequencies 2 and 5 Hz. The larger peaks were used to measure the Tafel slopes ($ß_c$, $ß_a$), causality factors CF-2&CF-3 and i_{corr}.

All the electrochemical studies were performed using Gamry Instrument Series G750™ Potentiostat/Galvanostat/ZRA with Gamry applications include DC105 software for potentiodynamic measurements, EFM140 software for EFM measurements, and EIS300 software for EIS measurements. Echem Analyst 5.5 Software installed in a laptop computer was used for graphing, plotting and fitting data.

3. RESULTS AND DISCUSSION

3.1. Weight loss tests

Figure1 shows plot of weight loss-time curves for α-brass corrosion in 0.5 M HNO_3 containing different concentrations of unused Augmentin at 25°C. From the plots, it is evident that the weight loss of α-brass was decreased with increasing the concentration of the drug. The data of Table 1 represent the corrosion rates of α-brass, % IE and degree of surface coverage of unused Augmentin in HNO_3 solution. The % IE raises with higher concentration of the unused Augmentin [33] and the drug showed more than 87 % inhibition efficiency and lowest corrosion rate at optimum concentration 300 ppm. This result is due to the co-ordination between the hetero atoms and α-brass in the drug. Also it is obvious that the weight loss of α-brass in the presence of this inhibitor varies linearly with time. This indicates the absence of oxide film on α-brass surface. The inhibitory action of Augmentin against α-brass corrosion can be attributed to the adsorption of drug molecules on α-brass surface, which limits the dissolution of the latter by blocking its corrosion sites and hence decreasing the weight loss [34].

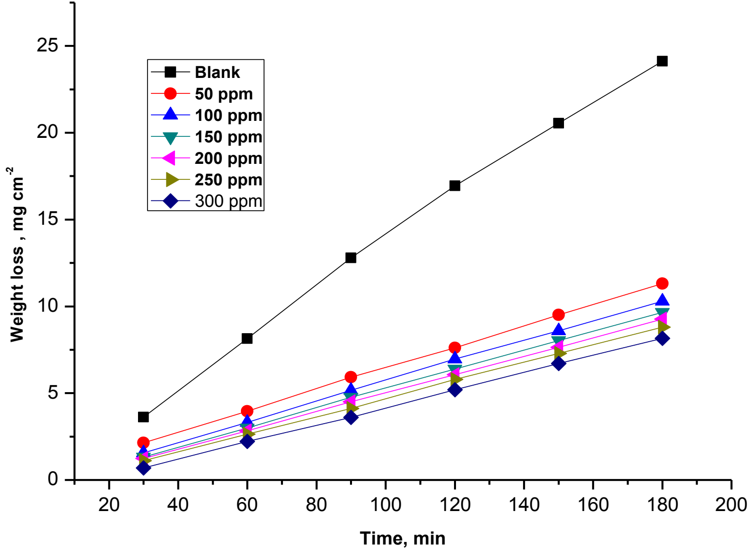


Figure 1 - Weight loss-time curves of α-brass in 0.5 M HNO_3 in the absence and presence of various concentrations of unused Augmentin at 25°C

3.2. Temperature effect on inhibition efficiency

The data obtained in Table 1 showed the effect of temperature on % IE and C.R. The obtained data revealed that, the inhibition efficiency increased with rise in temperature. This suggested that drug molecule is adsorbed on the α-brass surface chemically. The data of Tables 1 revealed that weight loss of α-brass decreases with increasing the temperature indicating that the rate of corrosion of metal decreases with increasing the temperature. It is also clear that rate of corrosion of α-brass without and with Augmentin obeys Arrhenius type equation as it increases with raising solution temperature. The dependence of the rate of corrosion (k_{corr}) on the temperature can be expressed by Arhenius equation 2:

$$i_{corr} = A \exp(-E_a^*/RT) \qquad (5)$$

where A = pre-exponential factor and E_a^* = apparent activation energy for corrosion process.

Arrhenius plots (Figure 2) show the corrosion of α-brass in 0.5 M HNO_3 solution with and without different concentrations of unused Augmentin. The linear regression (R^2) is close to 1 which led to that the corrosion of α-brass in 0.5 M acidic medium can be determined by using the kinetic model. Table 2 gives the data of E_a^*, for inhibited Augmentin solution.

Table 1 - Corrosion Rate (C.R.) and inhibition efficiency (% IE) at different concentrations and temperatures of unused Augmentin for the corrosion of α-brass after 120 min immersion in 0.5 M HNO_3

Temp. °C	Conc. ppm	Augmentin	
		CR (mg cm^{-2} min^{-1}) x 10^3	%IE
25	50	30	78.4
	100	26	81.1
	150	25	82.5
	200	23	83.9
	250	20	85.9
	300	17	87.7
30	50	39	81.1
	100	35	83.4
	150	33	84.2
	200	30	85.1
	250	25	88.2
	300	20	90.4
35	50	45	83.1
	100	39	85.4
	150	35	87.0
	200	32	88.1
	250	26	90.5
	300	21	92.0
40	50	54	86.0
	100	45	88.5
	150	40	89.6
	200	35	91.1
	250	28	92.8
	300	25	93.6

Table 2 - Activation parameters for α-brass corrosion in the absence and presence of various concentrations of drug in 0.5 M HNO_3

ΔS^*,- $J\ mol^{-1}K^{-1}$	ΔH^*, $kJ\ mol^{-1}$	E_a^*, $kJ\ mol^{-1}$	Conc., Ppm
97.2	49.2	51.4	**0**
183.2	25.7	29.5	50
195.1	24.3	26.3	100
201.9	22.5	24.4	150
214.8	17.9	20.7	200
225.6	16.9	18.4	250
228.5	16.3	17.1	300

The data of this Table indicate that E_a^* values decreases in presence of drug than in its absence, this indicates that the drug molecules are adsorbed on α-brass surface chemically [35]. Entropy and Enthalpy of activation (ΔH^*, ΔS^*) of the process of corrosion were calculated from the transition state theory as given from eq.6 (Table 2):

$$k_{corr} = (RT/ Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \qquad (6)$$

Where h is Planck's constant and N is Avogadro's number. A plot of log (k_{corr}/T) vs. 1/T for α-brass with different concentrations of unused Augmentin gives straight lines as shown in Figure 3. Values of $\Delta H^*$are negative. This means that the activation process is an exothermic corrosion process. The entropy of activation $\Delta S^*$is large and negative. This implies that the activated complex represents association rather than dissociation step, i.e. decrease in disorder occurs when moving from reactants to the activated complex [36]. Figure 3 Transition-state for α-brass corrosion (k_{corr}/T) in 0.5 M HNO_3 with and without unused different drug concentrations. Table 2 reported the parameters (ΔH^*, ΔS^*) of Activation for α-brass corrosion without and with various concentrations of unused drug.

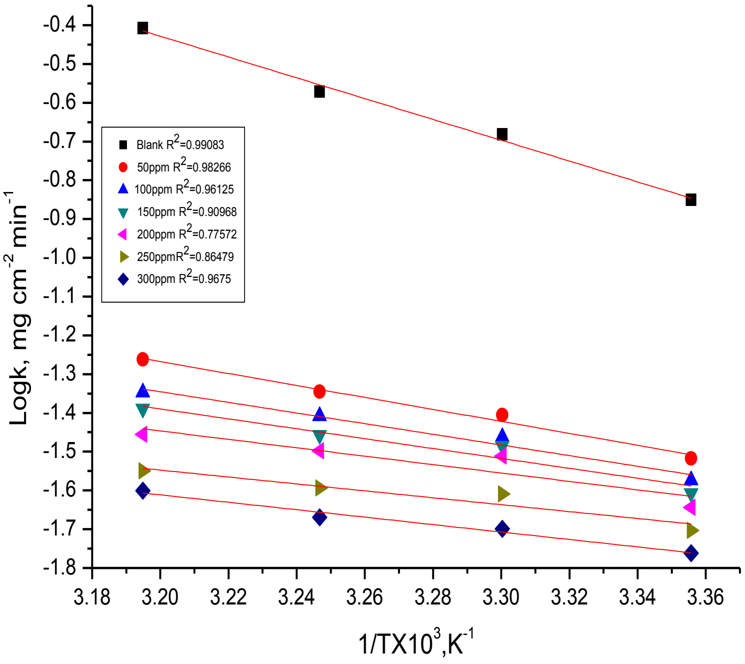


Figure 2 - Arrhenius plots for α-brass corrosion rates ($k_{corr.}$) after 120 minute of immersion in 0.5 M HNO_3 in the absence and presence of various concentrations of the Augmentin

3.3. Adsorption isotherms

Adsorption isotherm values are vital to explain the mechanism of corrosion inhibition of organo electrochemical reactions. The all frequently used isotherms are Temkin isotherm (Figure 4). Thermodynamic parameters for the adsorption of investigated drug on α-brass surface at various temperatures were reported in Table 3. From Table 3 it was found that: The negative data of $\Delta G°_{ads}$ reflect that the adsorption of studied drug on α-brass in 0.5 M HNO_3 solution is spontaneous process [37]. The obtained values of $\Delta G°_{ads}$ (27.5-29.8 $kJ\ mol^{-1}$) lead to the absorption of the drug on the α-brass surface is mixed one (physisorption and chemisorptions).

Table 3 - Thermodynamic adsorption parameters from Temkin isotherm model for α-brass in 0.5 M HNO3for unused Augmentin

Temp., K	K_{ads}, M^{-1}	$-\Delta G°_{ads}$ $kJ\ mol^{-1}$	$-\Delta H°_{ads}$ $kJ\ mol^{-1}$	$\Delta S°_{ads}$ $J\ mol^{-1}\ k^{-}$
298	1175	27.5	24.2	173.4
308	1187	29.4		176.8
318	1676	29.3		173.7
328	1680	29.8		172.5

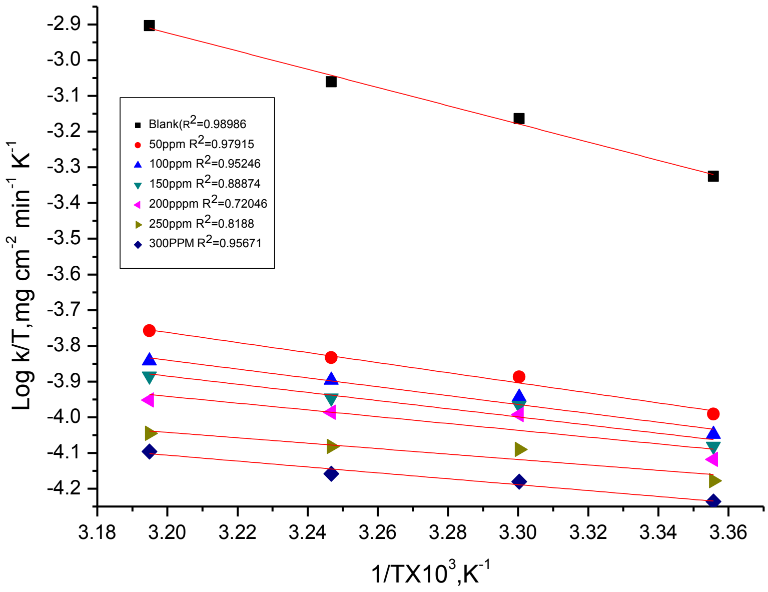


Figure 3 - Transition-state for α-brass corrosion (k_{corr}/T) in 0.5 M HNO_3 in the absence and presence of various concentrations of the Augmentin

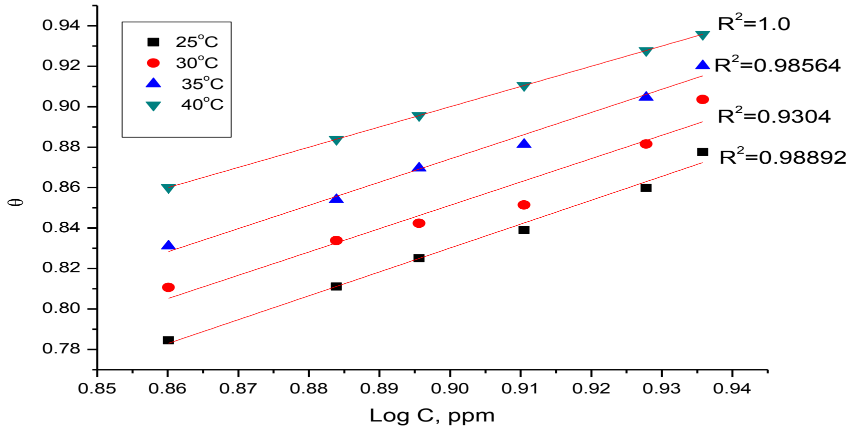


Figure 4 - Temkin isotherm of augmentin on α-brass surface in 0.5 M HNO_3 at different temperatures

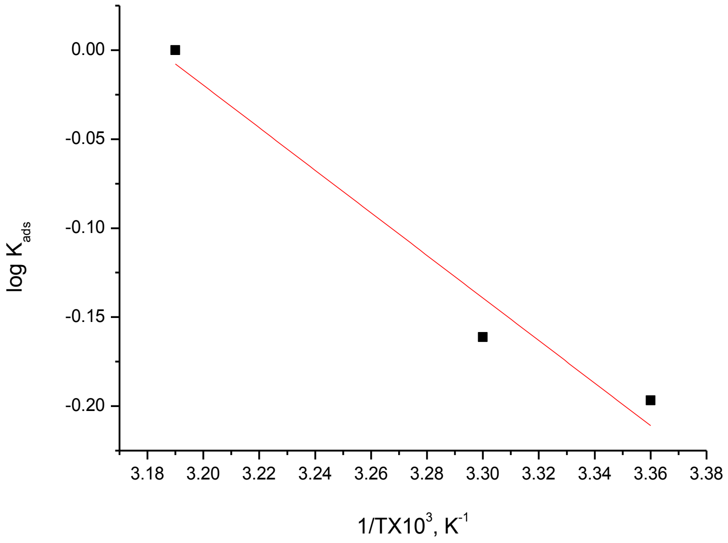


Figure 5 - Log K_{ads} vs (1/T) for the corrosion of unused drug on α-brass surface in 0.5 M HNO_3 at different temperatures

Figure 5 shows the plot of log K_{ads} vs.1/T, $\Delta H°_{ads}$ was obtained from the slope of this line. $\Delta S°_{ads}$ values were obtained from the basic equation ($\Delta G°_{ads} = \Delta H°_{ads} - T\Delta S°_{ads}$) The negative sign of $\Delta H°_{ads}$ reveals, an exothermic adsorption process which suggested either chemisorptions or physisorption while endothermic is attributed to chemisorption [38]. The positive values of $\Delta S°_{ads}$ can be related to the lower in the entropy of the solvent and this led to more entropy positive. It is also discussed that the rise of the disorderness in presence of the drug, this is may be due to more water molecules, which can be desorbed from the α-brass surface by one drug molecule. The experimental data give good curves fitting for the applied adsorption isotherm. K_{ads} value increases with the increase of temperature from 25 to 40°C.

3.4. Potentiodynamic polarization tests

Polarization methods were done in order to gain knowledge of the kinetics of the cathodic and anodic reactions. Figure 5 presents the data of the effect of Augmentin on the cathodic and anodic polarization curves of α-brass in 0.5 HNO_3. Both the cathodic and anodic reactions were suppressed in presence of investigated drug, which led to lowering the anodic dissolution of α-brass and also retarded the evolution of hydrogen reaction. Electrochemical corrosion kinetics parameters, i.e. corrosion potential (E_{corr}), Tafel slopes ($ß_a$, $ß_c$) and (i_{corr}) given from the extrapolation of the polarization curves, were given in Table 4. The parallel cathodic Tafel lines in Figure 6 lead to the evolution of hydrogen is activation controlled and the lower mechanism is not affected with inhibitor. The region between linear part of cathodic and anodic branch of polarization diagrams becomes wider as put the Augmentin to the acid solution. Similar results were obtained in the literature [39]. The data of $ß_a$ and $ß_c$ changed slightly with rise inhibitor concentration indicated the influence of these compounds on the kinetics of metal dissolution and of hydrogen evolution.

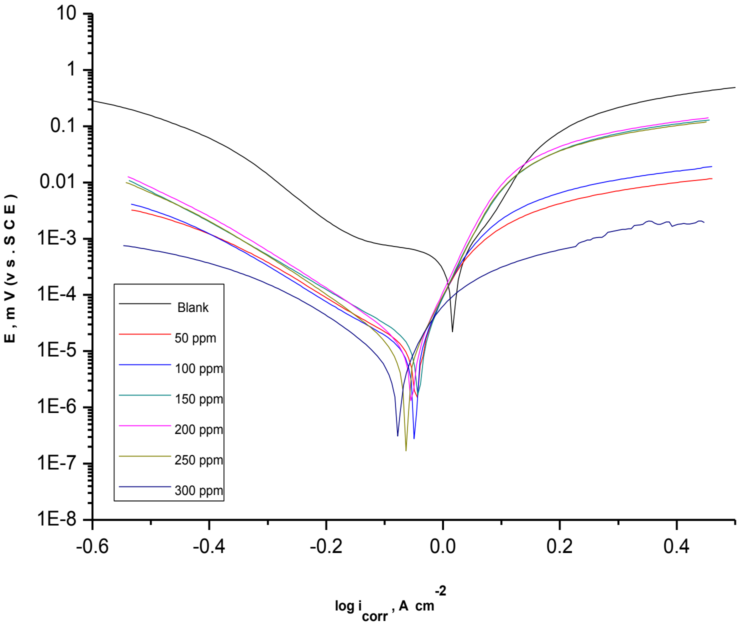


Figure 6 - Potentiodynamic polarization curves for the dissolution of α-brass in 0.5 M HNO_3 in the absence and presence of different concentrations of Augmentin at 25^oC

Table 4 - Effect of concentrations of various compounds on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}),Tafel slopes (β_c, β_a), corrosion rate (k_{corr}), degree of surface coverage (θ), and inhibition efficiency (%IE) of α-brass in 0.5 M of HNO_3 at 25ºC

% IE	Θ	C.R. mmy^{-1}	β_c, mV dec^{-1}	β_a, mV dec^{-1}	i_{corr} mA cm^{-2}	$-E_{corr}$ mVvs SCE	Conc. ppm
-----	----	133.3	19	99	136	17	0.0
87.7	0.877	7.527	19	84	16.7	47	50
88.8	0.888	7.498	17	52	15.3	42	100
89.7	0.897	6.885	17	54	14.0	53	150
92.3	0.923	5.186	17	63	10.4	49	200
92.9	0.929	4.564	20	74	9.61	77	250
93.8	0.938	4.117	14	56	8.38	63	300

Due to the found of some active sites, such as hetero-atoms, aromatic rings in the Augmentin for making adsorption, they may work as adsorption inhibitors. Being absorbed on the alloys, Augmentin controlled the cathodic and anodic reactions during corrosion process. The structure and functional groups of the Augmentin play important roles during the adsorption process. On the other hand, an electron transfer obtains during adsorption of the neutral organic compounds at surface of alloy [40]. As in the Table 5, the studied inhibitor lowers both cathodic and anodic currents with a slow shift in potential of corrosion (47 mV). According to Ferreira and others [41], the studied inhibitor is mixed-type inhibitor. The results which were given from Tafel polarization yield good agreement with the data given from mass reduction method. The % IE and coverage surface (θ) were measure utilized Equation.6:

$$\%IE = \theta \times 100 = [1-(i_{corr}/i°_{corr})] \times 100 \qquad (6)$$

where i_{corr} and $i°_{corr}$ are the current densities without and with inhibitor, respectively.

Table 5 - EIS parameters for the corrosion of α-brass in 0.5 M HNO_3 in the absence and presence of different concentrations of investigated drug at 25°C

Conc., ppm	C_{dl}, μF cm^{-2}	R_{ct}, ohm cm^2	Θ	% IE
Blank	9.7410	116	-----	----
50	6.5000	714	0.838	83.8
100	0.3259	717	0.839	83.9
150	0.1682	915	0.874	87.4
200	0.1389	939	0.877	87.7
250	0.1249	1160	0.900	90.0
300	0.0627	1320	0.912	91.2

3.5. EIS Tests

Tests Nyquist curves of metal in inhibited and uninhibited acid solutions containing different concentrations of unused augmentin are presented in Figure 7. EIS spectra data consists of one depressed capacitive loop. The higher diameter of loop given in acidic medium with Augmentin indicated the inhibition of corrosion of α-brass. The high frequency capacitive loop may give the charge transfer reaction.

Corrosion kinetic parameters derived from EIS method are given in Table 6. (R_{ct}) charge transfer resistance and (C_{dl}) given from EIS method as described elsewhere [42]. It is apparent from Table 7 that the impedance of the inhibited system amplified with the inhibitor the C_{dl} data lower with augmentin. This lower in C_{dl} data from a lower in local dielectric constant and/or an higher in the thickness of the double layer, given that inhibitor molecules inhibit the iron corrosion by adsorption on metal/acid interface [43]. The lower in Nyquist loop is a feature for solid electrodes and often lead to as frequency remove and given the roughness and other inhomogeneities of the solid electrode [44]. Figure 8 showed the electrical equivalent circuit employed to analyze the impedance spectra. Excellent fit with this model was obtained for all experimental data. The surface coverage (θ) and % IE were measure utilized Equation. 7:

$$\%IE = \theta \times 100 = [1-(R_{ct}/R_{ct}°)] \times 100 \qquad (7)$$

where $R°_{ct}$ and R_{ct} are the charge transfer resistances without and with Augmentin inhibitor, respectively.

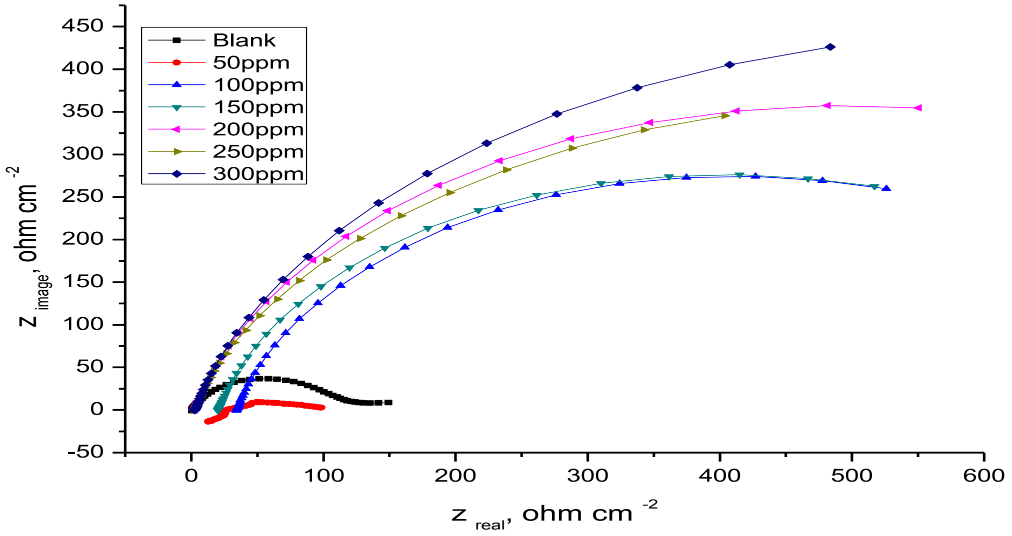


Fig. 7a)

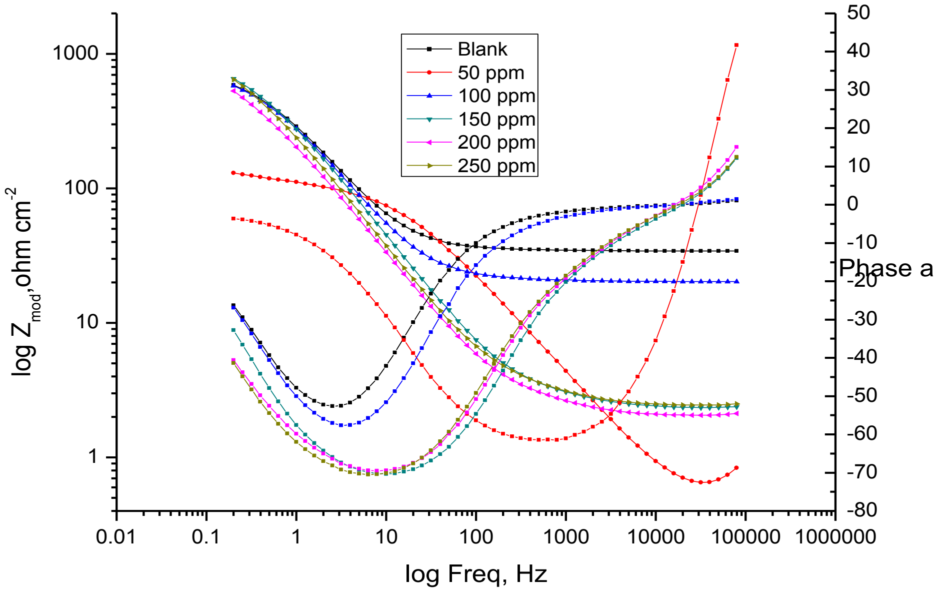


Fig 7b)

Figure 7 - EIS Nyquist plots (a) and Bode plots (b) for alpha brass in 0.5 M HNO$_3$ in the absence and presence of different concentrations of augmentin at 25^{o}C

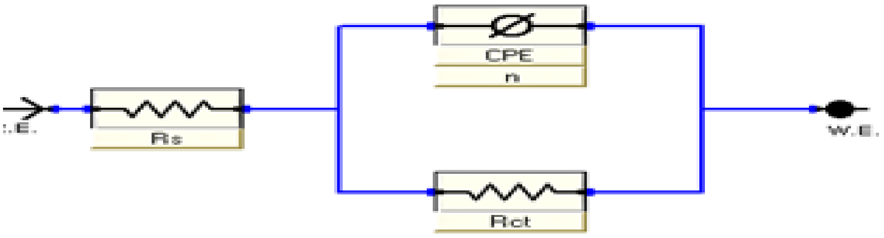


Figure 8 - Electrochemical equivalent circuits used to fit the impedance measurements that include a solution resistance (R$_s$), a constant phase element (CPE) and a polarization resistance or charge transfer (R$_{ct}$).

Table 6 - Electrochemical kinetic parameters obtained from EFM technique for α-brass in 0.5 M HNO$_3$ in the absence and presence of different concentrations of unused augmentin drug

Conc ppm	i_{corr}, µAcm^{-2}	βc, mVdec^{-1}	βa, mVdec^{-1}	CF-2	CF-3	C.R, mpy	Θ	% IE
0.0	175.8	110	170	1.926	3.12	69.5	-	-
50	41.98	60	130	2.087	3.593	20.47	0.761	76.1
100	37.71	60	140	1.969	3.113	17.01	0.785	78.5
150	34.88	60	130	1.961	3.588	16.07	0.802	80.2
200	31.95	60	130	1.991	2.284	15.46	0.818	81.8
250	26.14	60	120	1.940	2.775	13.72	0.851	85.1
300	20.91	110	170	1.877	2.692	13.12	0.881	88.1

Table 7 - Surface composition (wt %) of alpha brass before and after immersion in 0.5 M HNO$_3$ without and with 300 ppm of Augmentin at 25°C

(Mass %)	Cu	Zn	Fe	C	O	Al	As	Si
Free	60.78	32.72	0.79	3.48	1.13	0.70	0.40	----
Blank	54.57	25.78	0.78	10.41	7.85	----	0.61	----
Augmentin	38.10	20.21	------	28.82	12.53	----	----	0.35

3.6. EFM Tests

A nondestructive corrosion method likes EIS; it is a small signal technique. Unlike EIS, two waves (at various frequencies) are occurring to the cell simultaneously. The causality factors which given a check internal on the quality of the EFM method, given verified of data lead to higher EFM strength [45]. The spectrum of EFM is named the intermediation in figure 9. The spectra contain current responses assigned for harmonical and intermediation peaks of current. The biggest peaks were utilized to measure the current corrosion. The % IE measured by Equation 6 rise with higher the inhibitor concentrations studied. Intermodulation spectra obtained from EFM measurements were constructed for α-brass acidic solution as a function of 300 ppm of Augmentin at 25°C. Each spectrum is a current response as a frequency. Data not shown here. Corrosion kinetic parameters, namely current corrosion density (i_{corr}, Tafel constants ($ß_a$, $ß_c$) and causality factors (CF-2, CF-3) were listed Table 6 as a function of concentrations of investigated drug at 25ºC. The causality factors in Table 7, which are very close to theoretical data towards to the EFM theory, The standard values for CF-2 and CF-3 are 2 and 3 [46]. The data obtained from mass reduction, electrochemical frequency, potentiodynamic polarization and impedance techniques are in a good agreement but it is of interest to note that, the data of % IE given by electrochemical techniques are bigger than those obtained by mass reduction measurements; this may be due to the fact that the electrochemical methods were obtain by freshly prepared solutions.

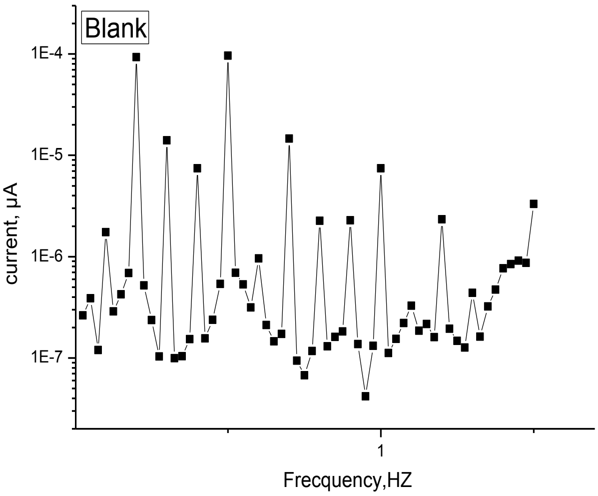


Figure 9 - Intermodulation spectra for α-brass in 0.5 M HNO_3

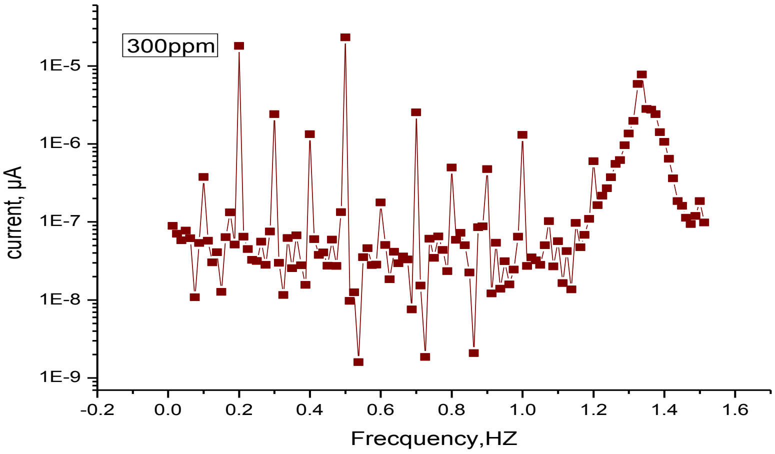
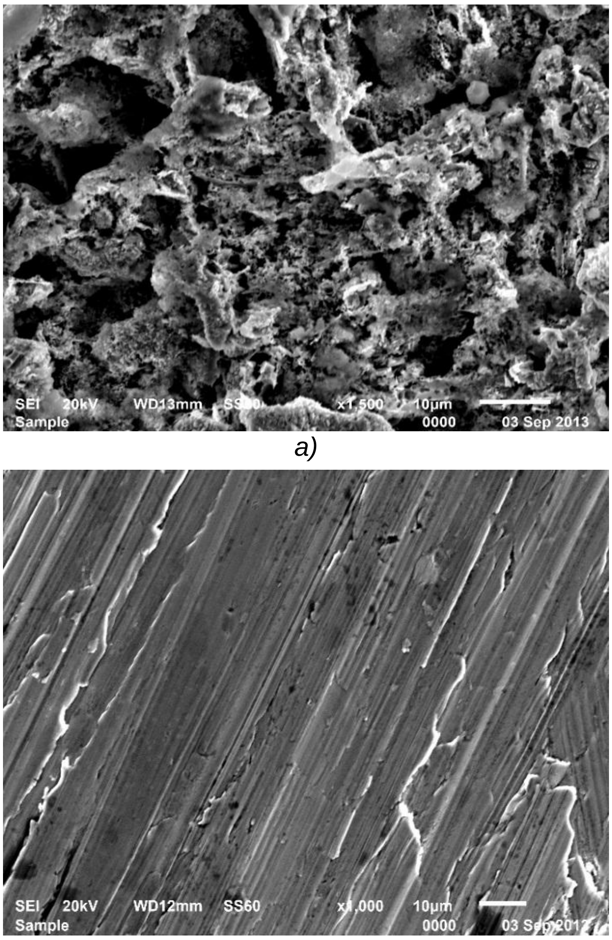


Figure 10 - Intermodulation spectra for alpha brass alloy in 0.5 M HNO_3+ 300 ppm of unused Augmentin

3.7. Surface Examinations

3.7.1. Scanning electron microscopy (SEM) studies

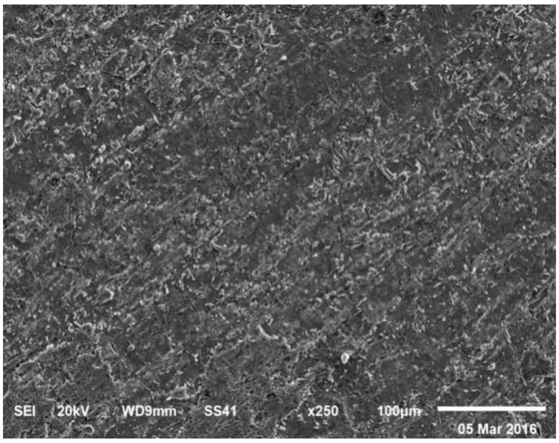
Figure 11 represents the micrograph obtained of α-brass samples after exposure to 0.5 M HNO_3 for one day immersion. It is clear that alpha brass alloy surfaces suffer from severe corrosion attack. Figure 12 reveals the surface on alpha brass alloy after exposure to 0.5 M HNO_3 solution containing 300 ppm drug compound. It is important to stress out that when the compound is present in the solution, the morphology of alpha brass alloy surfaces are quite different from the previous one, the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the alpha brass alloy. This may be interpreted as due to the adsorption of the drug compound on the alpha brass alloy surface incorporating into the passive film in order to block the active site present on the alpha brass alloy surfaces. Or due to the involvement of inhibitor molecules in the interaction with the reaction sites of alpha brass alloy surface, resulting in a decrease in the contact between alpha brass and the aggressive medium and sequentially exhibited excellent inhibition effect.



a)

b)

Figure 11 - SEM micrographs of alpha brass surface (a) before of immersion in 0.5 M HNO$_3$, (b) after 24 h of immersion in 0.5 M HNO$_3$.

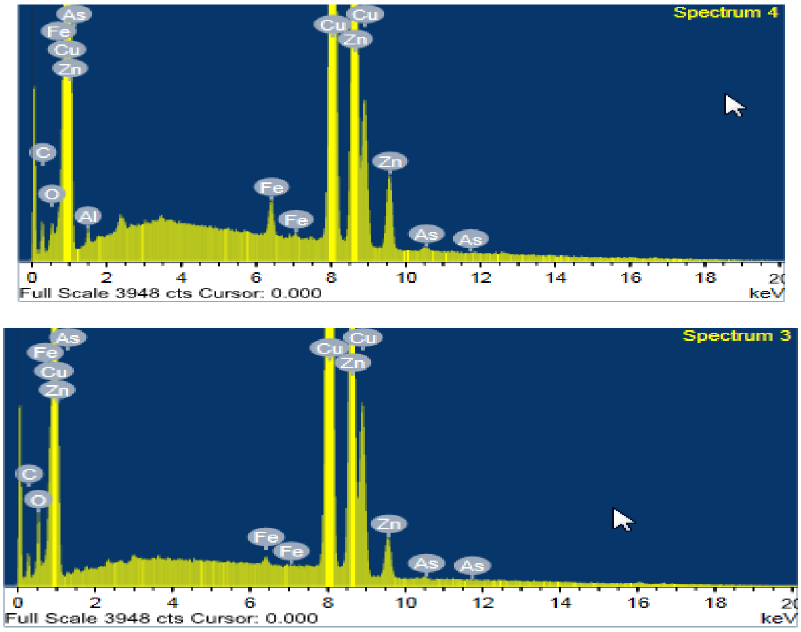


c)

Figure 12 - (C) after 24 h of immersion in 0.5M HNO$_3$+300 ppm augmentin.

3.7.2 Energy Dispersion Spectroscopy (EDX) Studies

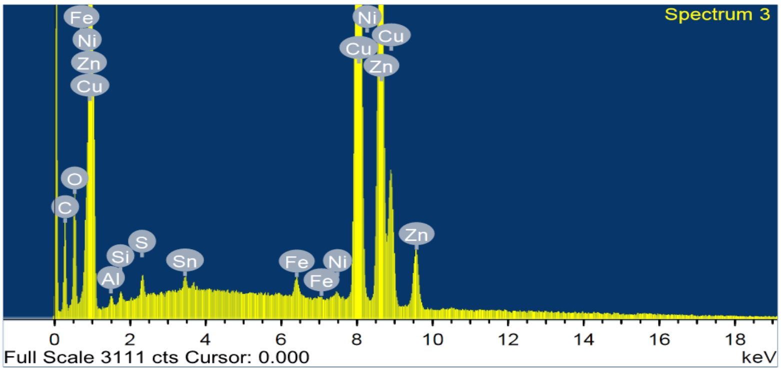
The EDS spectra were used to determine the elements present on the surface of α-brass and after one day of exposure to the uninhibited and inhibited 0.5 M HNO$_3$. Figure13 shows the EDX analysis result on the composition of alpha brass only without the acid and inhibitor treatment. The EDX analysis indicates that only carbon and oxygen were detected, which shows that the passive film contained CaCo$_3$ and SiO$_3$. Figure14 portrays the EDX analysis of α-brass in 0.5M HNO$_3$only and in the presence of 300 ppm M of drug compounds. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of drug compound). These data shows that the carbon and N materials covered the specimen surface.



a)

b)

Figure 13 - EDX spectra of alpha brass surface (a) before of immersion in 0.5 M HNO$_3$, (b) after 24 h of immersion in 0.5 M HNO$_3$.



c)

Figure 14 - EDX spectra of alpha brass (c) After 24 h of immersion in 0.5 M HNO_3+ 300 ppm Augmentin

3.8. Mechanism of corrosion inhibition

It is generally, assumed that the adsorption of the inhibitors at the metal / solution interface is the first step in the action mechanism of the inhibitors in aggressive acid media. Four types of adsorption may take place during inhibition involving drug molecules at the metal / solution interface: i) Electrostatic attraction between charged molecules and charged metal ii) Interaction of unshared electrons pairs in the molecule with the metal iii) Interaction of π electrons with the metal vi) A combination of the above [47].

In acidic solutions, transition of metal/solution interface is attributed to the adsorption of the inhibitor molecules at the metal/solution interface, forming a protective film. The rate of adsorption is usually rapid and hence, the reactive metal surface is shielded from the acid solutions [48]. The adsorption of an inhibitor depends on its chemical structure, its molecular size, the nature and charged surface of the metal and distribution of charge over the whole inhibitor molecule**.** The exact nature of the interaction between a metal surface and a drug compound depends on the relative coordinating strength towards the given metal of the particular groups present [49] generally, two modes of adsorption were considered. In one mode, the neutral molecules of drug can be adsorbed on the surface of α-brass through the chemisorption mechanism, involving the displacement of water molecules from the α-brass surface and the sharing electrons between the hetero-atoms and α-brass. The inhibitor molecules can also adsorb on the α-brass surface on the basis of donor–acceptor interactions between π- electrons of the hetero-cyclic ring and vacant d-orbitals of copper surface. In another mode, since it is well known that the α-brass surface bears positive charge in acidic solutions [50], so it is difficult for the protonated drugs adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface covered with NO^-_3 ions**.**

4. CONCLUSIONS

The unused Augmentin drug establishes a very good inhibition for α-brass in HNO_3 solution. Unused Augmentin drug inhibits α-brass corrosion by adsorption on its surface. Adsorption of the unused Augmentin drug fits a Temkin isotherm model. The effect of temperature on corrosion inhibition efficiency of the inhibitor has been investigated, showing that the inhibition efficiency increases with increasing temperature. Double layer capacitance decreases with respect to blank solution when the drug is added. Polarization data showed that the investigated drug acts as mixed-type inhibitor in 0.5 M HNO_3. The negative values of ΔG^o_{ads} show the spontaneity and strongly adsorbed of this drug on the α-brass surface. The values of inhibition efficiencies obtained from the different independent quantitative techniques used are in good agreement and showed the validity of the results.

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IZVOD

NEOBIČNO KORIŠĆENJE LEKA AUGMENTIN KAO INHIBITORA KOROZIJE α-MESINGA U RASTVORU HNO_3

Nekorišćeni lek Augmentin je ispitivan kao inhibitor korozije α-mesinga u rastvoru azotne kiseline različitim tehnikama praćenja. Rezultati su pokazali da postoje varijacije u inhibiciji pri korišćenju leka pri različitim koncentracijama i temperaturama. Maksimalna efikasnost od 93.6% je dobijena pri koncentraciji od 300ppm leka, pri temperaturi od 40^0C *i pri potapanju od 3 sata. Temkinova izoterma je korišćena da opiše adsorpciju leka na površini α-mesinga . Potenciodinamička ispitivanja su pokazala da ovaj lek deluje kao mešoviti tip inhibitora. Rezultati elektrohemijske impedance pokazali su smanjenje kapacitivnosti dvojnog sloja i povećanje otpornosti prenosa naelektrisanja. Mehanizam hemijske adsorpcije je predložen na osnovu izračunatih termodinamičkih parametara za ispitivani lek. Rezultati ispitivanja različitim tehnikama pokazali su dobre međusobne uporedne podatke.*

Ključne reči*: Inhibicija korozije, α-mesing, lek augmentin, Temkinova izoterma,* HNO_3*.*

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