ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Effect of Cu on the Biocorrosion Inhibition of Ni-P coat based on Carbon Steel by the *Pseudomonas aeruginosa* Biofilm.

Mohsen Q[a,*], Sahar A Fadlallah[a,b], Sanaa MF Gad El-Rab [c,d], Montaser AA[a,e]

[a]Materials and Corrosion Lab (MCL), Faculty of Science, Taif University, Taif, Saudi Arabia.
[b] Chemistry Department, Faculty of Science, Cairo University, 12613Giza, Egypt [c]Biotechnology Department, Faculty of Science, Taif University, Taif, Saudi Arabia.
[d]Botany and Microbiology Department, Faculty of Science, Asuit University, 71516Asuit, Egypt.
[e]Chemistry Department, Faculty of Science, Aswan University, Egypt

ABSTRACT

The present study aims to illustrate the effect of *P. aeruginosa* (ATCC9027) to promote the biofilm formation on the modified Ni-Cu-P alloy coating supported on Aramco carbon steel C1018. The microbial biofilm formation of *P. aeruginosa* on C1018 and Ni-Cu-P alloy in artificial seawater and seawater containing crude oil was investegated. Scanning electron microscope (SEM), and energy dispersive X-ray surface analysis techniques were used to confirm the morphology and chemical composition of the alloy coating. On the other hand, the colony forming units of *P. aeruginosa* on carbon steel C1018, alloy coating and Heat treated Ni-Cu-P alloy coating was examined by the plate-counting method and the construction of the biofilm was distinguished by SEM analysis. Heat treated Ni-Cu-P alloy coating record the highest antibacterial efficiency via the formation of the thick biofilm layer. The produced modified alloy coating with the thick, spongy like biofilm layer are a high-quality protective cover for carbon steel to enhance its efficiency for petroleum industrial applications.

Keywords: Carbon steel, *Pseudomonas aeruginosa*, Biofilm, Microbial efficiency, Ni-Cu-P alloy, SEM/EDX.

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Pseudomonas aeruginosa (*P. aeruginosa*) is well thought-out one of the main microorganisms that show a physically powerful tendency to grow on the carbon steel surface and endorse the biofilm formation [1]. Biofilms are microbial populations from complex microbial structure composed of their metabolic products, cells and including extracellular polymeric substance (EPS), That may create both corrosive and inhibition actions and complex biofilm / protecting film interactions [2].

Carbon steel has been principally used in the manufacture pipelines that used for transporting hydrocarbon in seawater from one position to another, regard as the mainly professional and economic method [1]. Seawater has aggressive properties due to it richness of salt and microbial organisms that effect on the protection capacity of pipelines [3]. Accordingly the study of protecting carbon steel pipeline surface with a deep defensive coat is therefore quite considerable.

The ternary electroless nickel alloy has recently been proposed, by composing one or two metallic elements like Zn, Cu, Co, Fe, Sn, W, Mo, etc. in Ni-P matrix [4-7]. The accumulation of Cu to the electroless Ni-P alloy develops its properties, such as electrical conductivity, thermal stability, corrosion resistance and solder ability [8-16]. Additionally, in the electroless plating solution copper ions play a vital role as a stabilizer [8], smoothness [10, 11] and brightness [12] of the coat. Alternatively, the presence of the Cu enhances the anti-corrosion performance of the Ni-Cu-P for the reason that it slow down the dissolution of Ni and the transmission of Ni^{2+} toward the bulk solution [17,18]. Although, there are many reports focused on studying the impact of Cu on the physicochemical properties of Ni-Cu-P coat as; Zhao et al.[19] investigated the effects of the deposition of copper on the deposition rate and compositions of Ni–Cu–P coatings. Chen and Lin [20] investigated the deposition and crystallization performance of electroless Ni–Cu–P coatings on aluminium substrates. The effect of copper on electroless Ni–P matrix has been extensively studied on different substrates such as Al, Cu, AISI low carbon steel and stainless steel 304L [21-23]. However, few studies have paid attention the antibacterial activity of Ni-Cu-P [24].

In our previous work [17], the structure and the corrosion resistance of Ni-Cu-P coat with different Cu percentage was discussed. In this paper, the antibacterial activity of the Ni-Cu-P alloy coating with and without heat treatment was examined. It is aimed at the understanding of the influence of the novel biofilm / Ni-Cu-P ternary alloy coating on the microbial corrosion resistance efficiency of the carbon steel in seawater in the absence and in the presence of crude oil. The control of *P. aeruginosa* on the decay behavior of Ni-Cu-P will be expected.

EXPERIMENTAL

Materials and solutions

Cylindrical - shaped commercial carbon steel coupons with 15 mm thickness and 0.5cm height from Armco (Part Number:CO1113770204120, C1018), Serial Number: 2524 were used. C1018 carbon steel (CS) is composed of 0.26wt%C, 0.46wt%Mn, 0.27wt%Si, 0.035wt%S, 0.11wt%Cr, 0.09wt%Ni, 0.01wt %P and 0.15wt %Cu with the remainder Fe [1]. C1018 plate of 6 mm thickness was cut to 10 mm X 10 mm size coupons. Before every experiment, the coupons were mechanically polished using increasing better quality grades of silicon carbide papers from 400 up to 1200 grit. After polishing the coupons were ultrasonically agitated for 15 min and clean by immersion to pure ethanol for 1h [1].

Electroless deposition bath

The copper ternary alloy coating (Ni-Cu-P) was prepared from the sodium hypophosphite electrolyte bath by means of the chemical composition shown in Table1.Throughout the deposition process, the bath pH was adjusted at 8 value by sodium hydroxide[1]. Each and every one of the solutions was prepared through analytical grade reagents from Sigma-Aldrich and distilled water. The experimental conditions are given also as mentioned inside Table1[1].

ISSN: 0975-8585

Table 1. The Experimental conditions to prepare the Ni-Cu-P alloy coating.

Chemical Composition	Wt (gram) in liter
Nickel Sulphate ($NiSO_4.6H_2O$)	28
Sodium hypophosphite(NaH_2PO2)	20
Sodium citrate($C_6H_8Na_3.2H_2O$)	35
Lactic Acid	5
Ammonium Sulphate(NH_4SO_4)	30
Copper sulphate ($CuSO_4.5H_2O$)	0.25
Operating Condition	
pH	8.0
Temperature	90± 2
Deposition rate (Δm/h)	8-10

Heat treatment

The prepared Ni-Cu-P alloy coating sample was then annealed in a muffle furnace (G-Therm) in in air at 450 ºC where the time of this stage was 1 hour.

Surface Analysis Studies

The surface morphology and chemical composition of C1018 and Ni-Cu-P alloy coating samples were examined and investigated by scanning electron microscope, SEM, with energy dispersive X-ray spectra, EDX, analysis by JEOL-840 electron prop micro analyzer [1].

Microbial Study

Inoculums cultivation

The entire tests were carried out using a nutrient-rich simulated seawater-based medium. The medium consists of 23.476 g/l NaCl; 3.917 g/l Na_2SO_4; 0.192 g/l $NaHCO_3$; 0.664 g/l KCl; 0.096 g/l KBr; 10.61 g/l $MgCl_2$; $6H_2O$; 1.469 g/l $CaCl_2$; $2H_2O$; 0.026 g/l H_3BO_3; 0.04 g/l $SrCl_2$; $6H_2O$, 3 g/l bacteriological peptone and 1.5 g/l yeast take out from Oxoid, UK. The value of pH of the medium was adjusted to 7.2 ± 0.1 by NaOH solution, and untainted by autoclaving for 20 min at 121 °C at low pressure. The *Pseudomonas aeruginosa* ATCC 9027 (*P. aeruginosa*) strain was supplied by INCQS/FIOCRUZ, RJ, and Brazil. A new culture was refreshing from ice-up-dried ampoule, and associate cultured two time in 5 ml of nutrient broth media before use [25]. The bacterium was cultivated for 3 days in a 125 ml Erlenmeyer flask containing 20 ml of the new culture medium on a rotary shaker (15 °C, 175 RPM) after the recovery. A total of 20 ml of the cultured bacteria stored in a -20 °C refrigerator is considered a substance used for inoculation in all the experiments to make sure the pure *P. aeruginosa* bacteria [1].

Bacterial attachment examination

The full amount of bacterial attachment was looked into by the plate-counting method [23]. The rate of bacteria attachment in the simulated repository environment was confirmed by counting up analysis of the media after 7, 14, 21 and 28 days of immersion. For all experimental conditions two samples were used for CFUs evaluation. The samples were taken away from the medium, softly washed to remove stick on bacterial cells on the samples were diffused into15 ml sterile phosphate buffer (0.0425 g KH_2PO_4 and 0.190 g $MgCl_2$ per liter) by forceful vortex mixing for 5 min [1]. Successive dilution of the bacterial cell suspensions was prepared and 0.1 ml of each concentration was plated onto nutrient agar to hold up the development of bacteria. The plates were incubated for 24h and the numbers of colonies are calculated. Suggested practical cells on each specimen were calculated and expressed as colony forming units per square centimeter (CFU cm^{-2})[1].

Biofim formation

In the present study the formation of biofilm was identified on Ni-Cu-P alloy coating before and after heat treatment by SEM after the specimens recapture from the inoculated medium after 28 days of exposure.

The samples were coated with gold by supporting method and examine with SEM. The location for SEM imaging were randomly chosen on the Ni-Cu-P alloy coating surface to be representative of their total surfaces [1].

RESULTS AND DISCUSSION

The difference between the morphology of carbon steel C1018, Ni-Cu-P and Ni-Cu-P alloy coating after heat treatment is presented inset in Fig.1. The mechanically polished C1018 appears homogenous and smooth with non-porous surface structure, Fig.1(A). SEM image of Ni- Cu-P coat deposited from bath with low Cu^{2+} concentration (0.001M) is shown in Fig.1(B) shows, the spherical nodular structure with low uniformity, no boundary which can be ascribed to ''nodule coalescence'' [26]. The SEM image of Ni-Cu-P alloy coating after heat treatment shows nodule of small size with homogenous structure, Fig 1(C). This result confirmed the fact that the heat treatment inducing crystallization of the amorphous coating [27].

The results of the EDX analysis of the surface of C1018 prove that the main elements present is Mn and Fe, Fig.2(A). In contrast, the EDX spectrum of Ni-Cu-P alloy coating before and after heat treatment, Fig.2(B & C) show that the peaks Ni and P that represent the bulk Ni-P coating are present. Moreover, peaks of Fe and Cu in between Ni and P peaks are seen that confirmed the incorporation of Cu into the Ni-P matrix.

Further effort in this study was appeared in Fig.3, where the surface morphology of the study samples; C1018, Ni-Cu-P and Ni-Cu-P after heat treatment alloy coating after immersion in the sterile renewing medium for 28 days is presented in Fig.3. The most important change was observed on the morphology of C1018 and Ni-Cu-P alloy coating before and after heat treatment. This figure, (Fig.3A-C), shows that all surfaces covered with biofilm, where the bacterial cells preferentially attached themselves to form patchy or blotchy biofilm on C1018 surface (Fig.3A) and to form an integral uniform biofilm layer on Ni-Cu-P alloy (Fig.3B), coating with thick biofilm layer on heat treated Ni-Cu-P alloy coating,Fig.3(C). The extensive biofilm formed on Ni-Cu-P alloy coating after heat treatment, we infer that the compact biofilm layer may provide extra protection to this alloy coating in seawater. On the other hand, the thickness of the biofilm layer on all samples increases in a continuous medium (biofilm on C1018 < Ni-Cu-P alloy < heat treated Ni-Cu-P alloy) as presented in Fig.4 (A-C). In continuous culture, the thickness of biofilm on steel and modified steel samples was lower than its parallel samples in renewing culture due to consumed of nutrients.

To confirm the efficiency of Ni-Cu-P alloy coating, supplementary study was completed. The surface morphology of the study samples; C1018, Ni-Cu-P and Ni-Cu-P after heat treatment alloy coating after immersion in the sterile renewing medium for 28 days with crude oil is presented in Fig.5 (A-C). The thickness of biofilm of *P. aeruginosa* in continuous culture with crude oil was less than that formed in renewing culture with crude oil Fig.6A-C due to consumed of nutrients in culture medium. The broad bulky biofilm formed on Ni-Cu-P alloy coating either with heat treatment or without heat treatment, we infer that the compact biofilm layer may provide extra protection to this alloy coating in seawater. Conversely, the condensed biofilm layer are formed in seawater with crude oil.

In the present study, Figs.7& 8 show the *P. aeruginosa* colonies on Nutrient agar plates for antibacterial activity evaluation in the absence and in the presence of crude oil, respectively. This result exhibited decreases in the colony forming units of *P. aeruginosa* colonies on C1018, while exhibited increases in the colony forming units of *P. aeruginosa* colonies on Ni-Cu-P and Ni-Cu-P alloy coating after heat treatment samples. Possible explanations of the best antibacterial properties of Ni-Cu-P alloy coating after heat treatment is due to the coverage area of the sample by biofilm is larger than that area of the other sample (Table 2).This result shows that the strategy of coating and heat treatment play an important role to increasing the corrosion resistance.

ISSN: 0975-8585

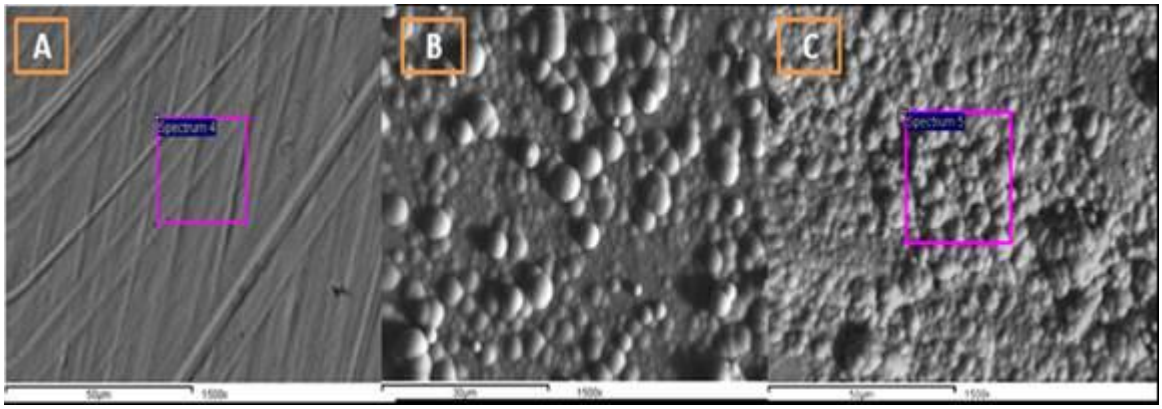

Fig.1 SEM images of the morphology of (A) C1018, (B) Ni-Cu-P Coat and (C) Ni-Cu-P after heat treatment.

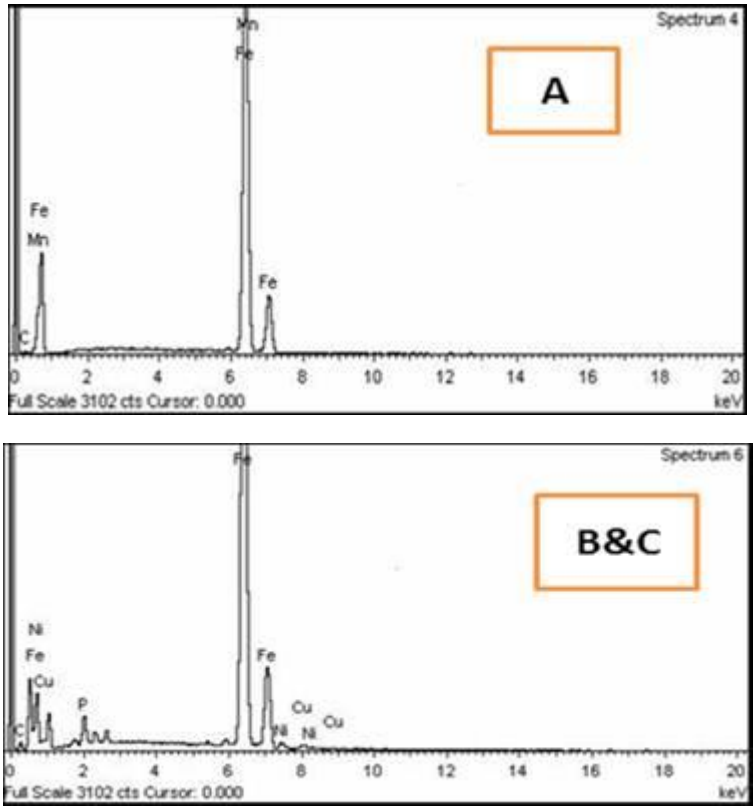

Fig.2. EDX analysis of the chemical composition of (A) C1018, (B) Ni-Cu-P Coat and (C) Ni-Cu-P after Heat treatment.

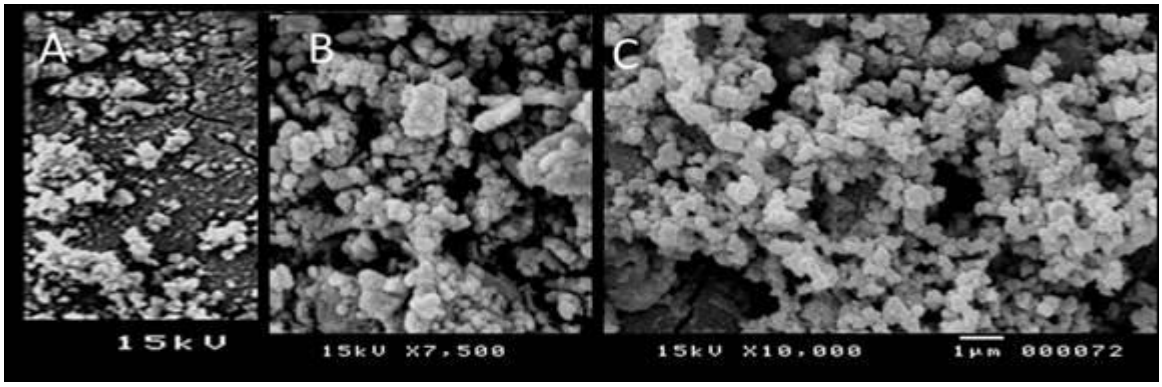

Fig. 3. Morphology of Biofilm on Carbon steel C1018 (A) and Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat(C) after 28 days of immersion in renewing culture of *Pseudomonas aeruginosa*

ISSN: 0975-8585

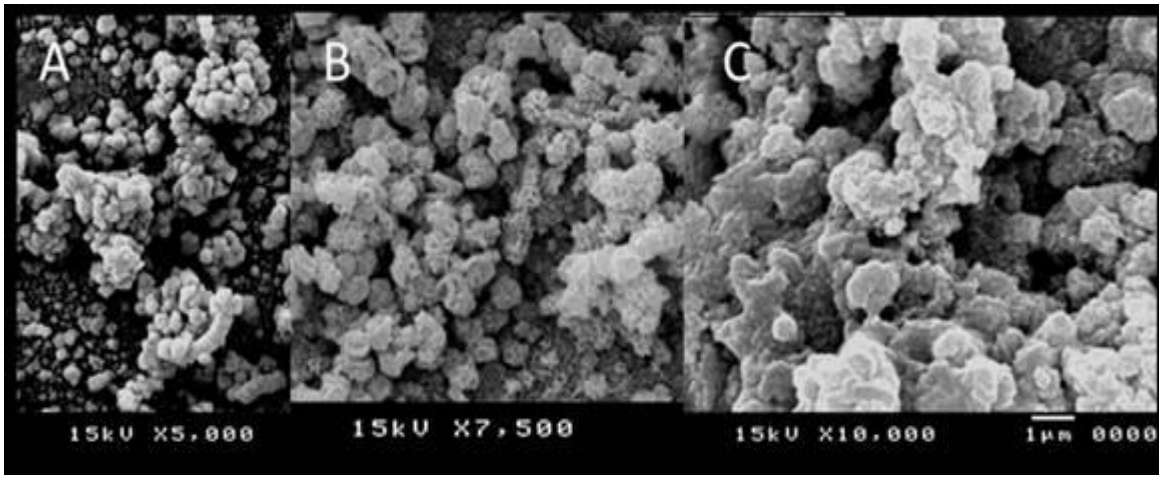

Fig. 4. Morphology of Biofilm on Carbon steel C1018 (A) and Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat(C) after 28 days of immersion in continuous culture of *Pseudomonas aeruginosa.*

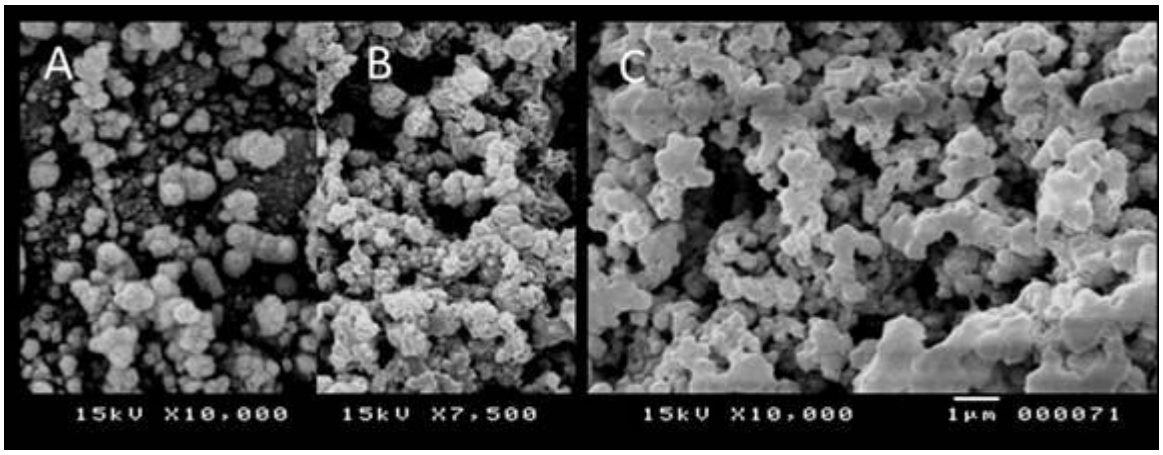

Fig.5. Morphology of Biofilm on Carbon steel C1018 (A) and Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat (C) after 28 days of immersion in renewing culture of *Pseudomonas aeruginosa* with crude oil.

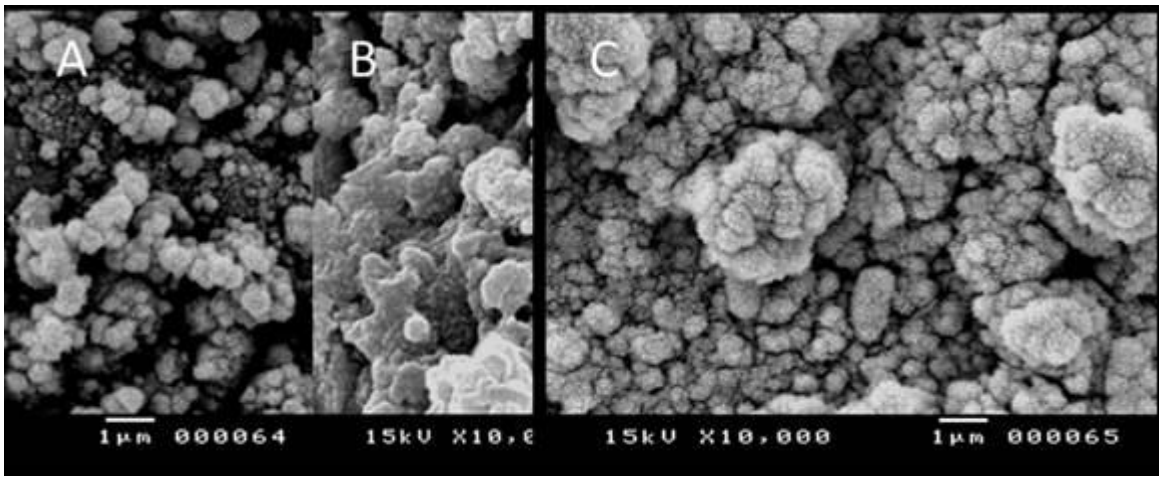

Fig. 6. Morphology of Biofilm on Carbon steel C1018 (A), Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat (C) after 28 days of immersion in continuous culture of *Pseudomonas aeruginosa* with crude oil.

ISSN: 0975-8585

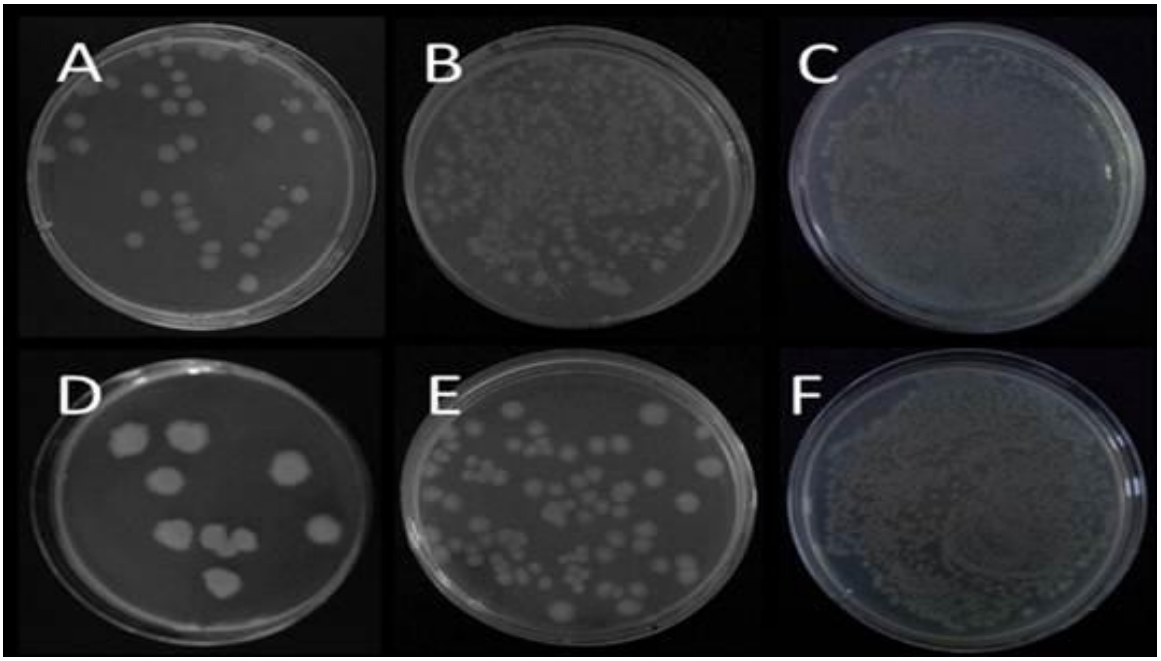

Fig.7. *Pseudomonas aeruginosa* biofilm colonies on Nutrient agar plates. 1-the Biofilm collected from surface of samples put in renewing culture (A) Colony forming units of Carbon steel C1018, (B) colony forming units of Ni-Cu-P alloy coating and (C) colony forming units of Ni-Cu-P alloy coating with heat. 2-The biofilm collected from continuous culture (D)colony forming units of Carbon steel C1018 , (E) colony forming units of Ni-Cu-P alloy coating without heat and (F) colony forming units of Ni-Cu-P alloy coating with heat.

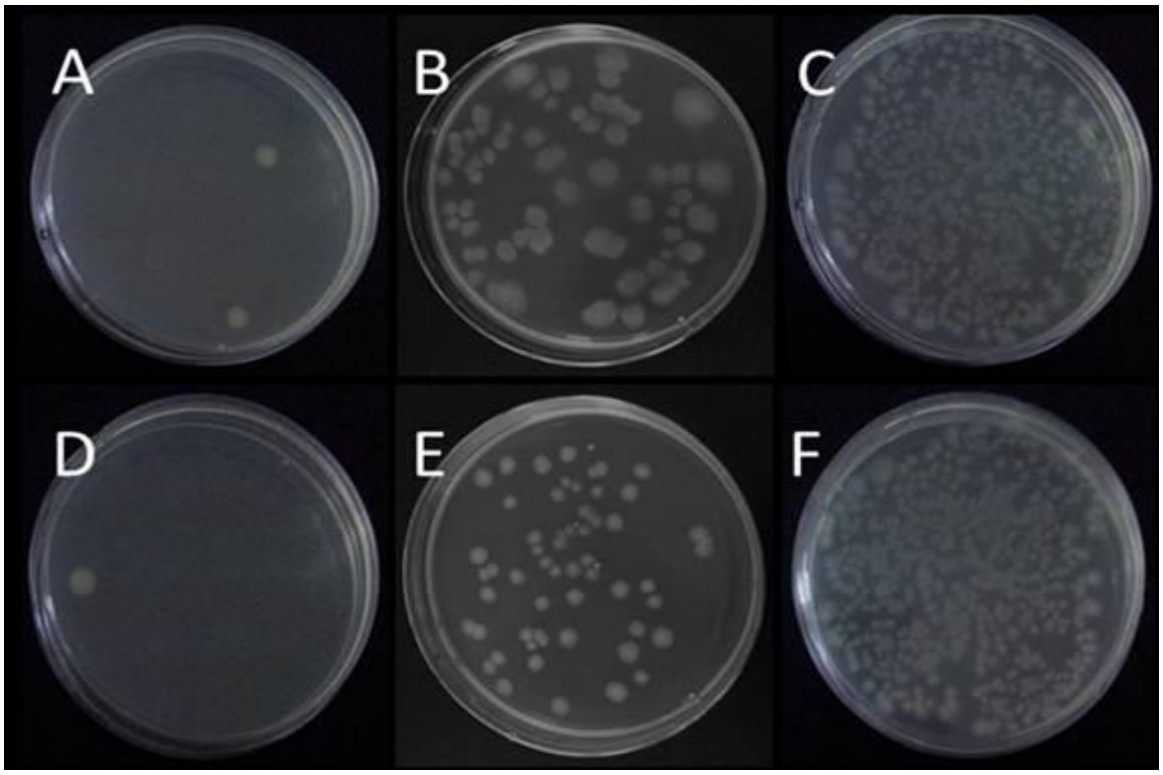

Fig.8. *Pseudomonas aeruginosa* biofilm colonies on Nutrient agar plates. 1-Biofilm collected from surface of samples put in renewing culture with crude oil (A) Colony forming units of Carbon steel C1018, (B) colony forming units of Ni-Cu-P alloy coating and (C) colony forming units of Ni-Cu-P alloy coating with heat. 2- The biofilm collected from continuous culture with crude oil (D)colony forming units of Carbon steel C1018 , (E) colony forming units of Ni-Cu-P alloy coating and (F) colony forming units of Ni-Cu-P alloy coating with heat.

ISSN: 0975-8585

Table 2. Percentage of antimicrobial biofilm coverage

Type of cultivation	Percentage of antimicrobial biofilm coverage	
	Ni-Cu-P alloy without heat	Ni-Cu-P alloy with heat
seawater inoculated with *P. aeruginosa* (renewing culture)	127.27%	163.63%
seawater inoculated with *P. aeruginosa* (continuous culture)	104%	136%
seawater inoculated with *P. aeruginosa* with crude oil (renewing culture)	48.27%	79.93%
seawater inoculated with *P. aeruginosa* with crude oil (continuous culture)	34.37%	53.32%

In the present work, the *P. aeruginosa* culture colonies evaluation after 28 days of coupons exposure was studied. The carbon steel coupons showed the lowest number of attached bacteria while Ni-Cu-P alloy coating after heat treatment showed a significant highest number of bacteria that enhance the formation of a thick biofilm layer on it. Fig. 9-12 shows the CFU/ml values of C1018 sample which was significantly lower than Ni-Cu-P alloy coating sample.This result supports the result deduced from Figs.7, 8, which illustrate that the thick biofilm layer formed on Ni-Cu-P alloy coat act as a protective antimicrobial auxiliaery coat [28]. The present results agreement with another further results that pointed to the existence of extra-cellular polymers (EPS) which extracted from the cells of bacteria and formed on the alloy surface. EPS retarded the corrosion process or impaired the protective nature of the alloy through the formation of passive layer from died cells [28]. Commonly, biofilm is considered as a coagulate collected 95% from water with EPS, which adjust the material goods at the interface between the metal or alloy surface and bulkiness of the solution.

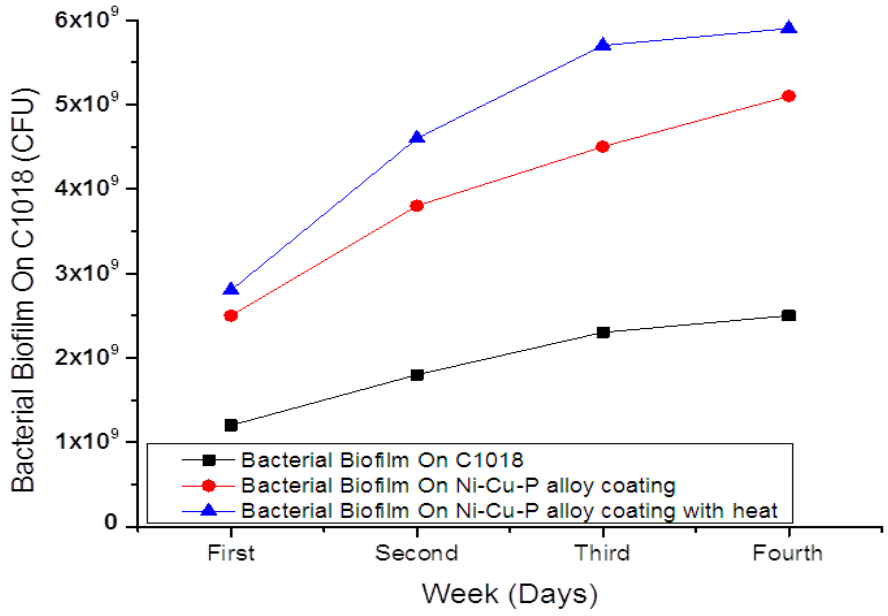

Fig.9. Growth curve of Biofilm on Carbon steel C1018 (A), Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat(C) after 28 days of immersion in renewing culture of *Pseudomonas aeruginosa.*

ISSN: 0975-8585

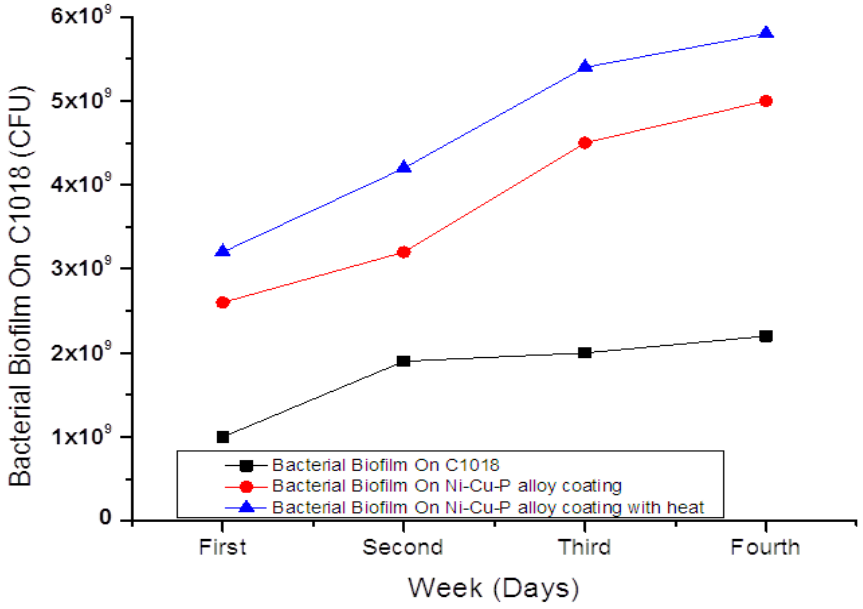

Fig.10. Growth curve of Biofilm on Carbon steel C1018 (A), Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat(C) after 28 days of immersion in continuous culture of *Pseudomonas aeruginosa.*

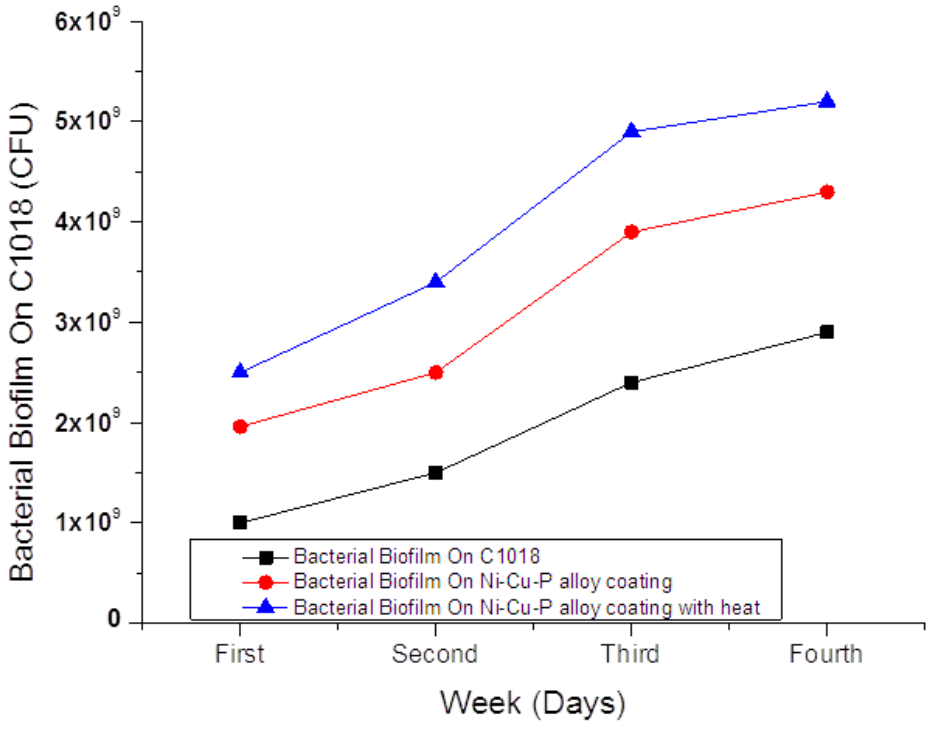

Fig.11. Growth curve of Biofilm on Carbon steel C1018 (A), Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat(C) after 28 days of immersion in renewing culture of *Pseudomonas aeruginosa* with crude oil.

ISSN: 0975-8585

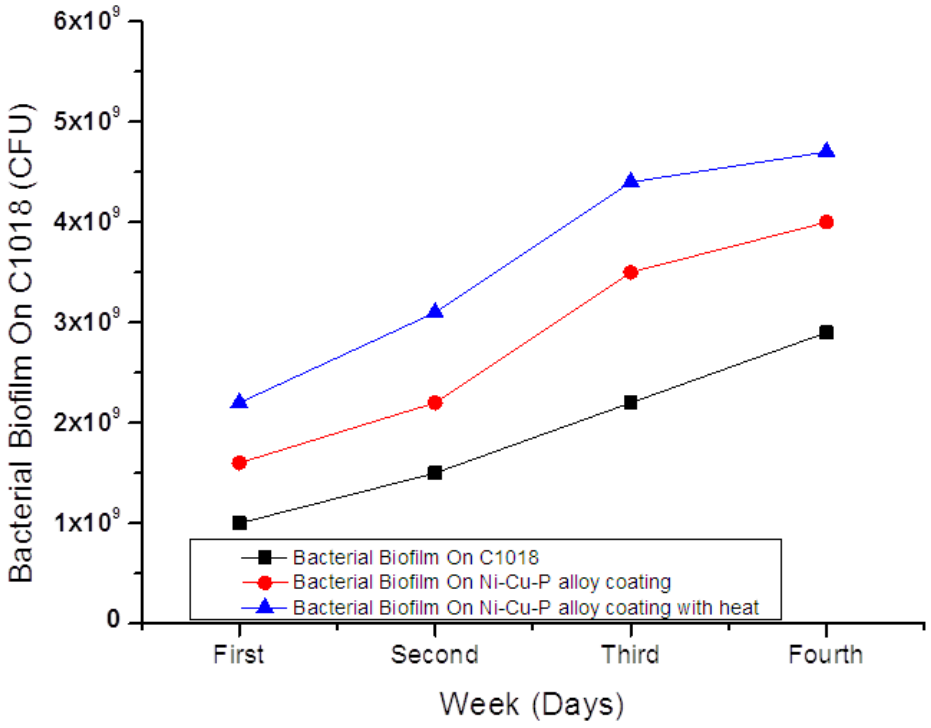

Fig.12. Growth curve of Biofilm on Carbon steel C1018 (A), Ni-Cu-P alloy coating (B) and Ni-Cu-P alloy coating with heat(C) after 28 days of immersion in continuous culture of *Pseudomonas aeruginosa* with crude oil.

4. CONCLUSION

Our previous work [17] is concluded that, the presence of low concentrations of Cu (0.001M) in electroless plating bath improved the corrosion resistance of mild steel in acid medium. In this work, Ni-Cu-P alloy coating was prepared via the identical electroless plating conditions and was modified by heat treatment (at 450ºC for 1h) to examine their microbial resistance against *P. aeruginosa* bacteria in seawater free and containing crude oil (1ml/50 ml of seawater). The heat treated Ni-Cu-P alloy coating showed the higher CFU/ml value than unheated Ni-Cu-P after 28 immersion in sterile continuous and renewing cultures with or without crude oil, this refers to the thick consistent biofilm configuration was formed on heat treated Ni-Cu-P alloy coating and proved by SEM analysis. The highest percent of the biofilm coverage layer in seawater renewing culture with and without crude oil was proofed for the heat treated Ni-Cu-P (79% and 163%, respectively). Our future work will directed to check up and measure the corrosion resistance of the present modified prepared coat in microbial solutions.

5. ACKNOWLEDGEMENT

The authors thank Taif university for financial support under serial No 1-433-1994 and advance to thank Mrs Reem Al-Santali for her participation in the experimental work of this paper.

6.REFERENCES

[1] Sahar A. Fadl-allah, A.A. Montaser, Sanaa M.F. Gad El-Rab, *Int. J. Electrochem. Sci.,* 11 **(2016)** 5490 – 5506.

[2] N.O. San, H.Nazır , G. Donmez, *Corros. Sci*., 79 (2014) 177.

[3] V. Scotto, R.D. Cintio and G. Marcenaro, *Corros.Sci*., 25 (1985) 18.

[4] A. Aal, H.B. Hassan. M.A. Abdel Rahim; Nanostructured Ni–P–TiO2 composite coatings for electrocatalytic oxidation of small organic molecules, *J. Electroanal. Chem.* 619 (2008) 17.

[5] M. Palaniyappa, S.K. Seshadri; Hardness and structural correlation for electroless Ni alloy deposits *J. Mater. Sci.* 42 (2007) 6600.
[6] R. C. Agarwala, V. Agarwala; Electroless alloy/composite coatings: A review, Sadhana 28(parts 3&4 June/August) (2003) 475.
[7] K. Hari Krishnan, S. John, K.N. Srinivasan, J. Praveen, M. Ganesan, P.M. Kavinani; An overall aspect of electroless Ni-P depositions—A review article, *Metall. Mater. Trans.* A 37 A(2006) 1917.
[8] S. Armyanov, J. Georgeiva, D. Tachev, E. Valova, N. Nyagolova, S. Mehta, D. Leibman, A. Ruffini; *Electrochem. Solid- State Lett.* 2 (1999) 323.
[9] E.Valova, J. Dille, S. Armyanov, J. Georgieva, D. Tatchev, M. Marinov, J.L. Delpancke, O. Steenhaut, A. Hubin; *Surf. Sci.* 255 (2009) 6652.
[10] J.N. Balaraju, K.S. Rajam; Electroless deposition of Ni–Cu–P, Ni–W–P and Ni–W–Cu–P alloys, *Surf. Coat. Technol.* 195 (2005) 154.
[11] R. Tarazaite, A. Selskis; Trans. Inst. Met. Finish 84(2006) 105.
[12] C.H. Chen, B.H. Chen, L. Hong, Role of Cu^{2+} as an Additive in an Electroless Nickel−Phosphorus Plating System: A Stabilizer or a Codeposit?; *Chem. Mat.* 18 (2006) 2959.
[13] J. Georgieva, S. Armyanov, Electroless deposition and some properties of Ni–Cu–P and Ni–Sn–P coatings *J. Solid state Electrochem.* 11 (2007) 869.
[14] L.L. Zhong, C.C. Liu, Nickel coating electrolessly deposited using a bath containing aluminum and/or copper ions; magnetic recording material; US Pat 6 106- 927 (2000)
[15] L.L. Zhong, C.C. Liu, St. John, D. Jeff, Electroless nickel-phosphorous coatings with high thermal stability; US Pat 6 410-104 (2002).
[16] R.H. Guo, S.Q. Jiang, C.W.M. Yuen, M.C.F. Ng, Effect of copper content on the properties of Ni–Cu–P plated polyester fabric; *J. Appl. Electrochem* 39 (2009) 907.
[17] Ahlam M. Fathia, Sahar A. Fadl-allah, Deposition Behavior and Corrosion Properties of Ni-P and Ni-Cu-P Amorphous Alloys, 3rd International Conference (31st annual) Conference on Corrosion Mitigation and Surface Protection Technologies, , 8-11 December 2014, Luxor, Egypt.
[18] Y. Liu, Q. Zhao, Study of electroless Ni–Cu–P coatings and their anti-corrosion properties; *Appl. Surf. Sci.* 228 (2004) 57–62.
[19] Zhao Q, Liu Y, Abel EW. Effect of Cu content in electroless Ni–Cu–P–PTFE composite coatings on their anti-corrosion properties. *Mat.Chem. Phys.* 2004; 87: 332–335.
[20] S. Ranganatha, T.V. Venkatesha, K. Vathsala, Process and properties of electroless Ni–Cu–P–ZrO2 nanocomposite coatings; *Materials Research Bulletin* 47 (2012) 635–645.
[21] S. Armyanov, J. Georgeiva, D. Tachev, E. Valova, N. Nyagolova, S. Mehta, D. Leibman, A. Ruffini; *Electrochem. Solid- State Lett*. 2 (1999) 323.
[22] E. Valova, J. Dille, S. Armyanov, J. Georgieva, D. Tatchev, M. Marinov, J.L. Delpancke, O. Steenhaut, A. Hubin; *Surf. Sci.* 255 (2009) 6652.
[23] G. Liu, L. Yang, L. Wang, S. Wang, L. Chongyang, J. Wang, Corrosion behavior of electroless deposited Ni–Cu–P coating in flue gas condensate; Surf. Coat. Technol. 204 (2010) 3382–3386.
[24] S.M.F. Gad El-Rab, S.A. Fadl-allah, A.A. Montaser, *Appl.Surf.Sci*., 261 (2012) 1.
[25] W.A. Badawy, A.M. Fathi, R.M. El-sherief, S.A. Fadl-allah, *J. Alloys Compd*., 475 (2009) 911.
[26] Sherar, I.M. Power, P.G. Keech, S. Mitlin, G. Southam, D.W. Shoesmith, *Corros. Sci*., 53 (2011) 955.
[27] F.Garcia, A.L.R. Lopez, J.C. Guille, L.H. Sandoval, C.R. Gonzalez, V. Castano, *Anti-Corros.Methods Mater.,* 59 (2012) 10.