

Study on Effect of Benzotriazole and Surfactants on Corrosion Inhibition of Copper Alloys in Sulphuric Acid

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This research investigated the corrosion inhibition and corrosion rates of copper alloys in sulphuric acid by benzotriazole (BTAH) and surfactants. Three types of surfactants namely sodium dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB) and X-Triton were used in the given research work. From the results, it was noticed that the rate of corrosion of copper decreased with an increase in concentration of inhibitor. Excellent results on corrosion inhibition of the copper alloys, in the tested acids, were achieved in the presence of benzotriazole and surfactants. It was observed that benzotriazole and surfactants inhibit the corrosion of copper significantly. The highest corrosion inhibition was materialized in post micellar concentration (PMC) of Triton X-100 and CTAB with 0.75 ppm benzotriazole in 1.5 M H₂SO₄. The maximum corrosion inhibition achieved with Triton X-100 and CTAB was 5.41 and 5.44 mpy, respectively. Finally, the Linear Polarization Resistance (LPR) was used to investigate the corrosion resistance of optimized concentrations of surfactants and BTAH. The LPR results revealed that Triton X-100 causes significantly higher corrosion inhibition performance as compared to CTAB.

Keywords: Corrosion inhibitor; surfactants, copper alloys, scaling, sulphuric acid and benzotriazole.

1. INTRODUCTION

Copper is broadly used in various industrial processes and the study of its corrosion inhibition has great significant [1]. The improvement of corrosion inhibitor based on organic compounds has numerous industrial applications. The organic inhibitor has the ability to produce a protective coating on a metal surface due to adsorption of organic molecules or ions. This coating minimies the metal

corrosión and surface damages. The scope of adsorption largely depends upon type of the metal, condition of the metal surface, adsorption method, inhibitor structure and nature of the caustic media [1]. The adsorption process can be enhanced by using the heteroatoms in the inhibitor. The presence of triple bonds or aromatic rings, sulphur, nitrogen, oxygen and phosphorous enhances the adsorption process [2-5]. The inhibition efficiency of hydrocarbons is greatly influenced by size and mode of interaction at molecular level with the metal surface [6]. Surfactants have sulphur and nitrogen atoms in their structure, these are prospective corrosion inhibitors due to these two atoms [7]. However, small part of the past studies on corrosion inhibition was devoted to the use of chelating agents as corrosion inhibitors, particularly, those posture sulphur and nitrogen atoms for coordinating [8, 9]. The awareness in these ingredients ascends due to their significance in the past and present advancement. Copper and its alloys are among the earliest metals known to man. They have been used from pre historic times and their importance at the present time is probably greater than ever. However, the corrosion inhibition of copper has remained the hot research subject [10, 11]. A literature review indicated merely fractional organised research work of copper corrosion inhibition and its alloys in numerous corrosive environments [12-14].

The mechanism of corrosion of copper is that when it comes in contact with water (as in industrial boilers and cooling towers), minute spots of lower and higher potentials are formed on its surface in arbitrary manner due to non-uniformity of the surface [15, 16]. When non-condensed gases such as ammonia and oxygen are present in the steam, they are highly concentrated near the air extraction section and corrode copper by the following reaction [15]:



The corrosion rate can be checked on inhibitor by coating the surface of metal by different inhibitors in the presence of surfactants. Corrosion inhibitor is a chemical ingredient in the solution which when added, generally in minor concentration, successfully reduce the corrosion rate. Inhibitors often get adsorbed themselves on the surface of metal and protect the metallic surface by forming a protective layer. Inhibitors may slowdown the corrosion process by any one of the processes: (a) by developing the cathodic or anodic polarization performance, (b) by dropping the diffusion of ions to the surface of metal and (c) by improving the electrical resistance of the metal surface.

The past literature lists only one test for copper corrosion inhibitors in archaeological management. Industrial corrosion examinations were consequently pursued in American society for testing material (ASTM) and the international organization (ISO). For the duration of pitting corrosion, the central area of pits are vigorously corroded in anodic region of metal cathode [17]. In observation of passively rusting copper, the metallic portions act as an anode and the formation of corrosion layers primarily act as a cathode. The innards of corrosion pits are excessively create anodic region. The margins of anodic and cathodic portions in rusted metal are commonly not vibrant in the heteroatomic structure of compound and its pits corrosion products Benzotriazole was found darkening the appearance of the corrosion products, particularly in repetitive use, as some time required [18].

In the present research, corrosion inhibition of copper in sulphuric acid in the presence of non-ionic surfactant, anionic surfactant, cationic surfactant (Cetyle trimethyl ammonium bromide) and

organic inhibitor benzotriazole were studied using weight loss method. From the optimized concentrations of surfactants and organic inhibitor, synergistic effect was also investigated. Linear Polarization Resistance (LPR) was used to investigate further the corrosion resistance of optimized concentrations of surfactants and BTAH.

2. MATERIALS AND METHODS

The assessment of metal using corrosion coupons is a consistent physical proof to estimate corrosion. These coupons produce precise data on the origin of ordinary mass loss; amount and spreading the confined corrosion and it can further deliver the information on nature and yield of corrosion. In this era of science lot of attention has been given to the investigation of various causes of corrosion and their remedy by the development of new environment friendly products/chemical coatings.

Herein, the corrosion coupons of identified weight were immersed in sulfuric acid as shown in Fig.1 (having the molarity 0.5 M, 1 M, 1.5 M, respectively) for a period of 20–15 days. The corrosion rates were calculated under various conditions, e.g. chemical treatment with acid and corrosion inhibitor without surfactant and chemical treatment with anionic, cationic and non-ionic surfactants at pre-micelle, critical and post-micelle concentrations by adopting the weight loss method after each 24 hours [9]. Three different concentration of benzotriazole (BTAH) (0.25 ppm, 0.50 ppm, 0.75 ppm) were also prepared to study the corrosion rate under organic inhibitor. All components were of analytical grade.

Fig. 1 shows the copper coupons dipped in the prepared solutions of 0.5 M, 1 M and 1.5 M H_2SO_4 at 25°C. The first set of coupons was exposed to acidic environment for 21 days. The corroded coupons were then washed in 20% (w/v) NaOH and zinc powder for removal of corrosion contents. Thereafter, the treated coupons were cleaned, dried and weighed for deliberation of weight loss. Each measurement was repeated three times and averaged by using an analytical balance. The difference in pre and post treatment weights of the coupons was taken as weight loss. Experiments were performed using three different concentrations of the surfactants at pre, critical and post micellar concentrations and 0.25 ppm, 0.50 ppm and 0.75 ppm of BTAH in optimized 1.5 M H_2SO_4 at room temperature. The optimized concentration of surfactants and BTAH were chosen to study the synergistic effect on corrosion inhibition. The corrosion rate was calculated using the relation:

$$\text{Corrosion rate} = 354M/ADT \quad (4)$$

Where, M is the mass loss in mg, A is the surface area of the coupon, D stands for density and T is the exposure time.

2.1. Linear Polarization Resistance (LPR)

The optimized concentrations of surfactant and BTAH were further tested by using electrochemical LPR technique. This technique was employed to determine the corrosion rate through

electrochemical means. The relation between the corrosion rate (CR) and polarization resistance (R_p) can be expressed as:

$$CR = \frac{\beta_a \beta_c M}{2.3 [\beta_a + \beta_c (R_p F Z D)]} \quad (5)$$

Where β_c and β_a are the cathodic and anodic, respectively, F is the Faraday constant, M is molecular weight, Z is the metal's valence and D is density of the metal [19].

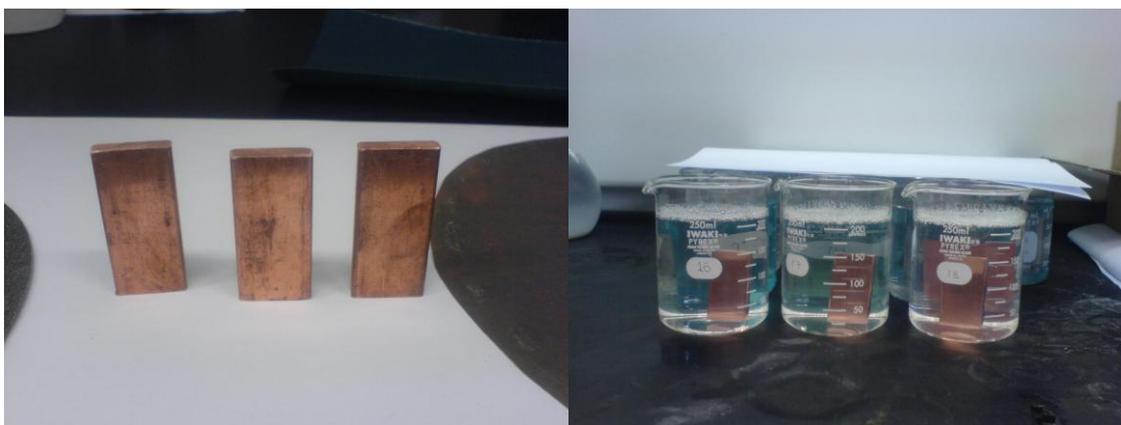


Figure 1. Photographic view of the copper coupons immersed in the solutions.

3. RESULTS AND DISCUSSION

There is a variety of synthetic surfactants which can accumulate on the metal surfaces to form well-defined protective layer to prevent the corrosion. The role of the surfactants for corrosion inhibition of stainless steel, carbons, mild-steel, aluminum, nickel and copper, etc. is well known [10-14]. They can overcome the anodic or the cathodic reactions involved in the corrosion process through adsorption mechanism. Overall the efficiency of corrosion inhibition has direct relationship with the surface coverage or amount of the inhibitor adsorbed.

3.1. Morphological analysis

Fig. 2(a) shows the SEM morphological aspect of copper specimen immersed in 1.5 M H_2SO_4 . It was included as a reference for elaboration of the surface morphology of the treated coupons. Copper was exposed to an uncontaminated 1.5 M H_2SO_4 atmosphere for 21 days. Corrosion started in the deepest polished line, where water droplets were more easily retained. The corrosion layer was non-uniform; the corrosion products developed at certain local surface areas due to droplets of H_2SO_4 adsorbed on the surface. The acid molecules entered patina reactions by their incorporation in droplets, which subsequently interacted with the copper to originate local attack. In these areas, crystalline

copper hydroxide was developed. It was seen that the copper surface completely concealed with corrosion products. The corrosion layer thickness was varying across the surface. It was also observed that corrosion products exhibited precipitation inside a ring due to the deposition of the droplets. In Fig. 2(b), the corrosion products were spread on the copper surface in non-uniformed manners. The coupon structures were more easy to compare without surfactant where SDS post micellar concentration (PMC) reduced the corrosion rate on account of the negative electrostatic interfaces prevailing between sulfuric acid and anionic surfactant [9].

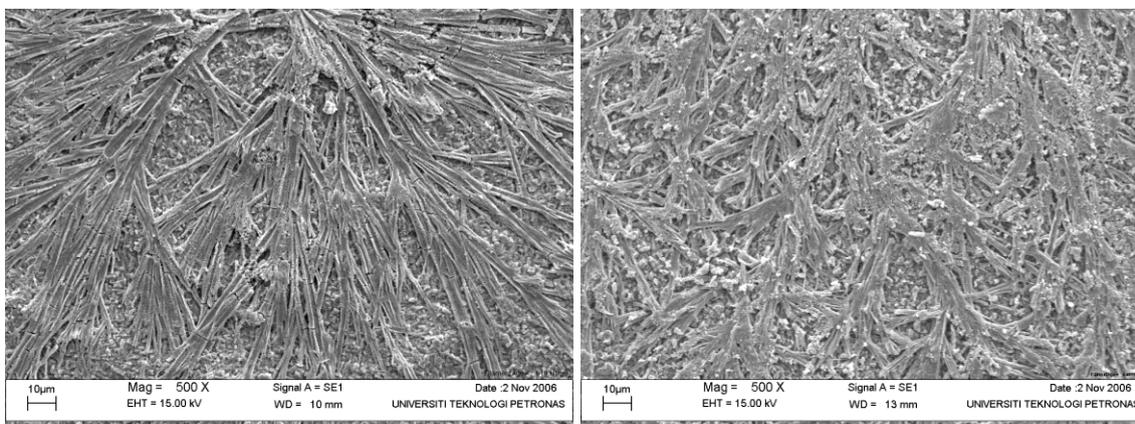


Figure 2. (a) SEM micrograph of coupon in 1.5 M H_2SO_4 (b) Micrograph of coupon in 1.5 M H_2SO_4 with post micellar concentration SDS

Fig. 3(a) shows SEM micrograph of a copper specimen exposed to 1.5 M H_2SO_4 with CTAB post micellar concentration for 21 days. It can be observed that the patina process follows the orientation on the surface. The non-homogeneous grain boundaries were seen due to the cationic surfactant and sulfuric acid solution treatment. Fig. 3(b) shows SEM micrograph of a copper specimen exposed to 1.5 M H_2SO_4 with Triton-100 post micellar concentration for 21 days. The micrograph showed good results for nonionic surfactant compared with other two types of surfactants (cationic and anionic).

Fig. 4(a) shows SEM micrograph of copper specimen exposed to 1.5M H_2SO_4 with 0.75ppm benzotriazole for 21 days. This morphology was consistent with a suspension precipitation mechanism for the formation reaction of copper with organic acid. It was possible to observe plate-like copper acetate crystals over the lower copper oxide phase. It should be pointed out that in this figure, the cementation process of small oxide particles to the lower layer was yielded by the high concentrations of benzotriazole. These results in line with the mechanisms proposed by López-Delgado in relation with copper patina formation processes in atmospheres contaminated with organic compounds [20]. Benzotriazole is of the significant interest as ligand that offers a prospective binding position for many metal ions. It is considered as ligand in solution nearby neutrality by the unshared pair of electron on nitrogen atom. In basic environment, the conjugated base BTA^- is formed which might work as a ligand too. It shows the tendency and development of an inward complex of stoichiometry $\text{M}^+(\text{BTA}^-)$

or M^{++} (BAT)₂, using depositive ions. This complex is generally insoluble in organic solvents and is mostly reflected to be polymeric in nature.

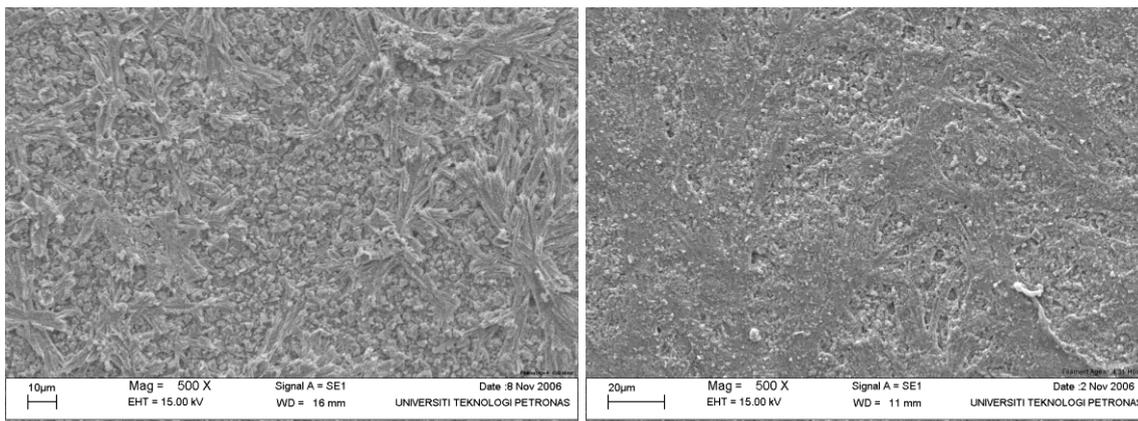


Figure 3. (a) Corrosion of Copper in 1.5 M H₂SO₄ with CTAB Post micellar concentration, (b) Copper in 1.5 M H₂SO₄ with Triton X-100 (post micellar concentration)

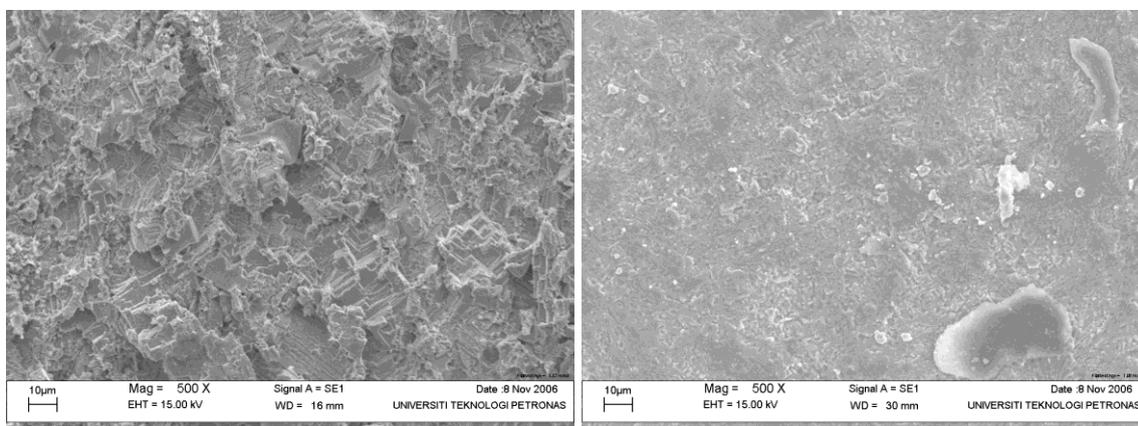


Figure 4. (a) Copper alloy in 1.5 M H₂SO₄ with 0.75 ppm BTAH, (b) Corrosion of copper in 1.5 M H₂SO₄ Triton X-100 (post micellar concentration) with 0.75 ppm BTAH.

3.2. Copper Alloy in 1.5 M H₂SO₄ and SDS (Pre, CMC, Post)

In connection to utilization of the surfactants as corrosion inhibitors to copper alloys, the given work defines the efficiency of organic corrosion inhibitors. Herein, the corrosion rates were determined by weight loss method for different concentrations of surfactants (cationic, anionic and nonionic) and benzotriazole at different time's intervals. The results on corrosion rate are reported in Figs. 5-10.

Adsorption at surfaces is one of the typical properties of surfactants. Surfactants found multifarious industrial applications ranging from mundane (washing cloth) to very sophisticated (preparation of microchips). Corrosion rate of copper in 0.5 M, 1 M and 1.5 M H₂SO₄ is presented in Fig. 5. The corrosion rates for 0.5 M, 1 M and 1.5 M H₂SO₄ were remained in the range of 76.63-

51.33, 92.27-52.25, 137.02-111.11 mpy, respectively. The 1.5 M was taken as optimized concentration as it showed the highest corrosion rate among all the tested concentrations. Three different concentrations were prepared at pre-micellar, critical micelle and post-micellar concentrations of SDS in 1.5 M H₂SO₄ acid solution; the results are presented in Fig. 6.

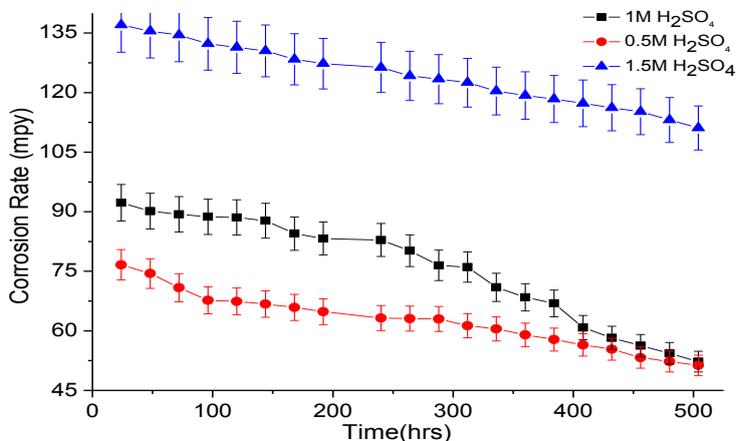


Figure 5. Corrosion rate of Copper alloy in 0.5 M, 1 M and 1.5 M H₂SO₄.

The corrosion rates were remained between 76.12-56.20, 45.67-25.60 and 30.45-12.10 for pre-, critical and post-micellar concentration, respectively. Zhao and Mu [21] studied the effect of three anionic surfactants on the aluminium surface. They revealed that the surfactants inhibit the corrosion on metal surface. They optimized the concentration of the surfactant when it is close to its CMC; aluminum attains its extreme adsorption quantity with minimum weight loss and strongest corrosion repelling property.

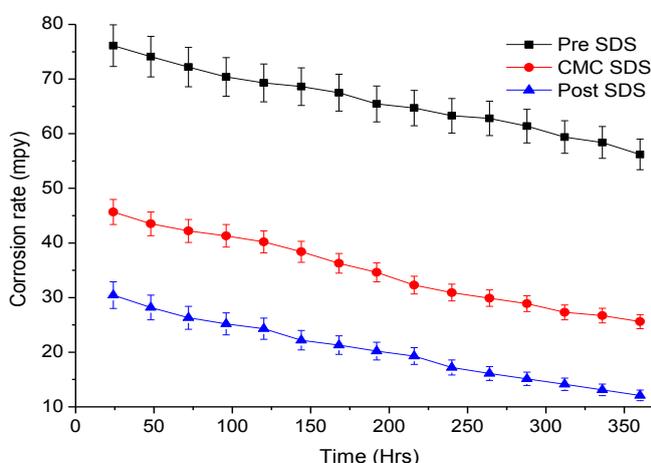


Figure 6. Corrosion rate of copper alloy for SDS (Pre, CMC and post micellar concentration) in 1.5 M H₂SO₄.

3.3. Copper Alloy in 1.5 M H₂SO₄ and CTAB (Pre, CMC, Post)

The long-chain cationic micelles quaternary ammonium bromides were used for corrosion inhibitors for copper. The inhibition efficiency depends on an increase of surfactant alkyl chain above to its CMC concentration [22]. The investigations on CTAB revealed that each film has groups of non-oriented, subjectively linked, spherical and roughly filled elements. Unlike this, rod-shaped elements are generally formed when films are being developed with precipitation from TiCl₄ hydrolyzed solutions [23]. From Fig. 3(a), the formation of rod shaped particles on the copper surface is confirmed due to the creation of thin film by CTAB. CTAB was applied at pre, critical and post-micellar concentration to 1.5 M H₂SO₄ solutions; the results are reported in Fig. 7. The corrosion rates were remained between 60.9-40.20, 45.67-33.89 and 30.45-18.19 for pre, critical and post-micellar concentration, respectively. The results show that the post micellar concentration exhibited low corrosion rates as compared to pre and critical micellar concentrations.

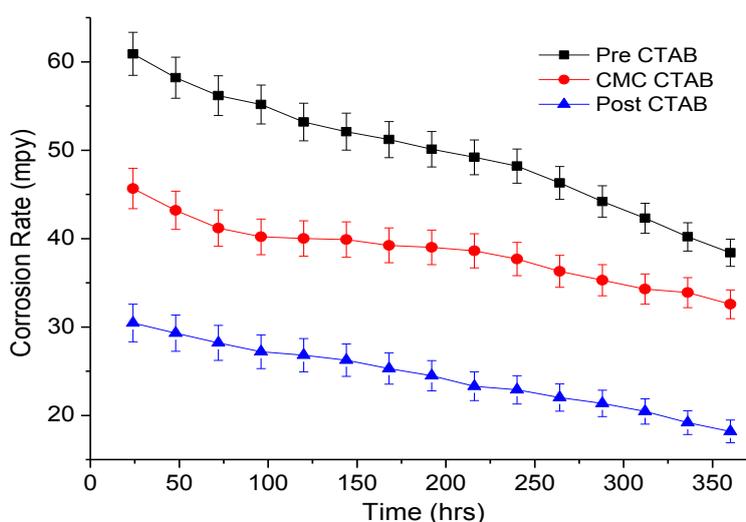


Figure 7. Corrosion rate of Copper Alloy for CTAB in 1.5M H₂SO₄.

3.4. Copper Alloy in 1.5M H₂SO₄ and Triton X-100

Three different micellar concentrations (pre, critical, and post) of Triton X-100 were prepared in 1.5 M H₂SO₄ solutions and the obtained results are reported in Fig. 8. At pre, critical and post-micellar concentrations, the corrosion rates were remained in the range of 91.35-78.03, 60.90-48.18 and 45.67-33.21, respectively. The experimental data showed that corrosion rate was decreased for all tested concentrations of Triton X-100 in the order of post micellar concentration > CMC > Pre, which indicate that corrosion inhibition efficiency has a direct relationship with the surfactant concentration.

3.5. Copper alloys in 1.5 M sulfuric acid and benzotriazole

Benzotriazole is an organic compound containing of triazole and benzene rings and its chemical formula is C₆H₅N₃. Three different concentrations of benzotriazole i.e. 0.25, 0.5 and 0.75

ppm were individually applied to 1.5 M sulfuric acid solution and were found more corrosive towards copper alloys. The results of this investigation are reported in Fig. 9, the corrosion rate was appreciably decreased in the presence of benzotriazole in the solution. This trend was attributed to development of thin shielding layer on the surface of copper in the order of 0.75 > 0.5 > 0.25 ppm.

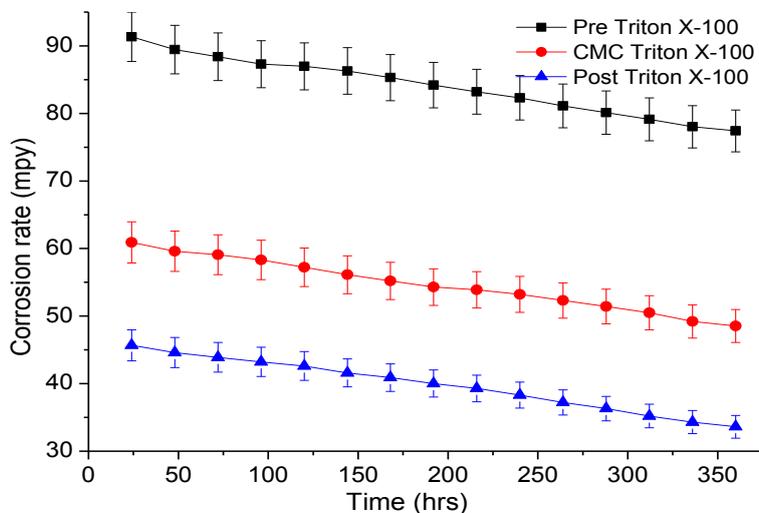


Figure 8. Corrosion rate of Copper for Triton X-100 in 1.5 M H₂SO₄

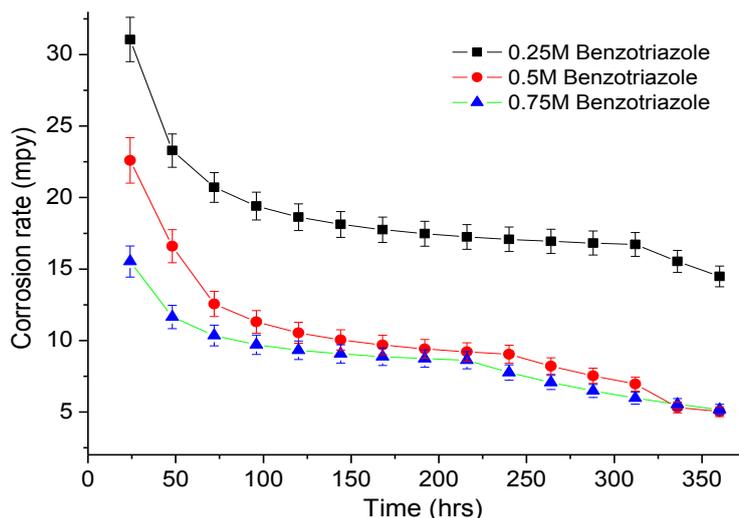


Figure 9. Corrosion rate of copper for benzotriazole in 1.5 M H₂SO₄.

Fig. 9 reveals that the corrosion rates of BTAH were in the range of 31.06-14.49, 22.60-5.02 and 15.53-5.17 mpy for 0.25, 0.5 and 0.75 ppm, respectively. BTAH can work as a weak acid by discharging a proton, or a base by accepting a proton for one of the nitrogen lone pairs of electrons. In this mode, a bridging complex can be made on the surface of copper which can behave as an inhibitor beside the rust. This property of benzotriazole makes it an effective inhibitor for corrosion of copper in

aqueous environment [24]. These results showed less corrosion rate compared to surfactants reported above.

3.5. Corrosion rate of Copper for 0.75 ppm BTAH and SDS, CTAB Triton X-100 in 1.5 M H₂SO₄

To study the synergetic effect, the optimized concentrations of anionic SDS, cationic CTAB and nonionic Triton X-100 with organic inhibitor BTAH 0.75 ppm were used in 1.5 M H₂SO₄. The results are shown in Fig. 10. The corrosion rates were remained in the range of 31.50-10.12 for post micellar concentration of CTAB with 0.75 ppm BTAH. The corrosion rates for post micellar concentrations of SDS with 0.75 ppm BTAH were persisted in the range of 22.77-5.41. Triton X-100 was used at post micellar concentration with 0.75 ppm BTAH for which the corrosion rates remained in the range of 15.24-5.44 mpy. Corrosion inhibition increased in case of CTAB, SDS and Triton X-100 with 0.75 ppm BTAH in 1.5 M H₂SO₄ showing a synergistic effect between surfactants and BTAH. Therefore, it can be concluded that corrosion inhibition was further enhanced as a result of this treatment. The highest corrosion inhibition was noted in post-micellar concentrations of Triton X-100 and CTAB with 0.75 ppm BTAH, 5.41 and 5.44 mpy, respectively.

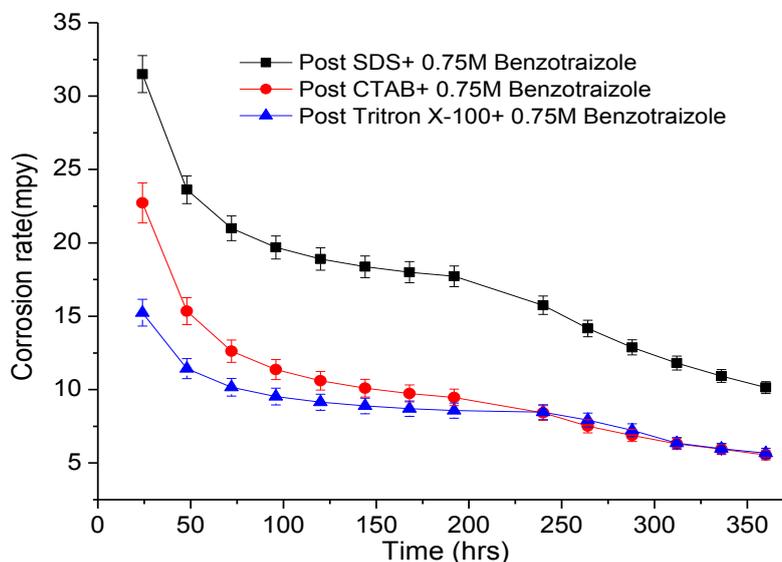


Figure 10. Corrosion rate of copper for 0.75 ppm BTAH and SDS, CTAB Triton X-100 in 1.5 M H₂SO₄.

3.6. Linear Polarization Resistance (LPR) of Corrosion rate of Copper

The optimized concentrations of CTAB and Triton-100 with 0.75 ppm BTAH were further tested by using LPR technique. LPR for the copper in 1.5 M H₂SO₄ was measured at PMC of CTAB, Triton X-100 with 0.75 ppm BTAH. The respective plots were obtained in the potential range of -30 to +30 mV with a scan rate of 1 mV/min and I Range (A) of 5 A. The kinetic parameters were recorded as given in Table 1.

Table 1. Summary of the electrochemical parameters extracted from LPR test.

PMC with 0.75 ppm BTAH	R _p [ohm]	b _a [V/div]	b _c [V/div]	CR [mmPY]
Triton X-100	891.426	0.120	0.120	0.89123
CTAB	785.688	0.120	0.120	0.78739

Fig. 11 shows that the cationic surfactant gives high corrosion rates as compared to non-ionic surfactant (Triton X-100). R_p of the copper treated with Triton X-100 and CTAB was measured 891.426 ohm and 785.688 ohm, respectively. A decrease in R_p of CTAB treated copper generally suggests a decline in the corrosion resistance in the presence of surfactant in acidic environment. This trend reveals that the metal would suffer with high corrosion rates. The observed trend of polarization resistance can be clarified in terms of stability of the externally formed corrosion product layer. The R_p rate remains more or less constant, if product layer is stable and is not separable from the metal surface. The R_p value will fluctuate if the product layer is not stable. In this case, the layer forms and detaches again from the metal surface.

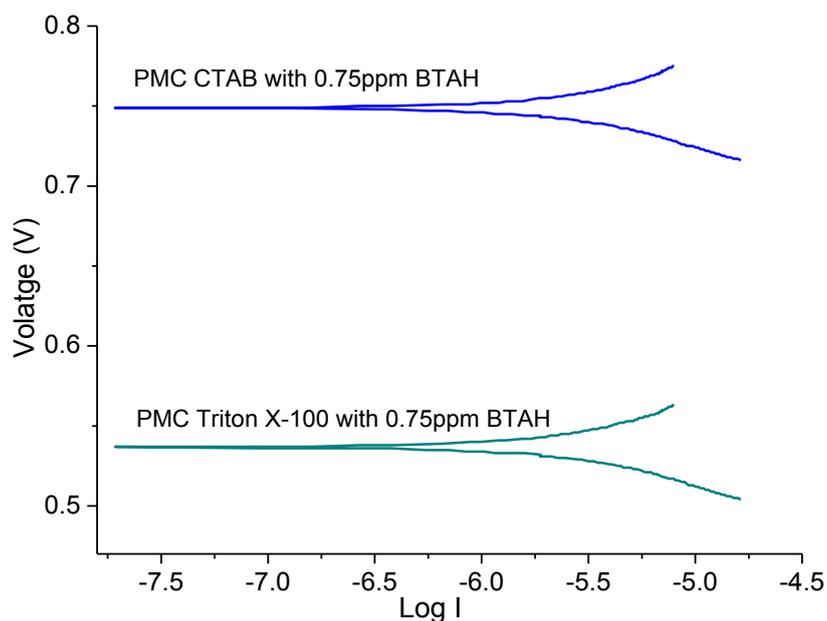


Figure 11. LPR of corrosion rate of copper for CTAB and Triton X-100 in 1.5 M H₂SO₄.

4. CONCLUSIONS

In this detailed note, corrosion inhibition of copper alloys in H₂SO₄, in the existence of surfactants (SDS, CTAB and Triton X-100), were studied using weight loss method. From the results, it was confirmed that with an increase in acidic concentration, the corrosion rates will also increase. The post-micellar concentrations of SDS, Triton X-100 and CTAB have enhanced the process of

corrosion inhibition w.r.t their pre-micellar and critical micellar concentrations in 1.5 M H₂SO₄ solution. It was observed that the corrosion rate considerably decreased in the presence of BTAH due to formation of a thin layer on copper surface. Corrosion rates were further reduced using BTAH 0.75 ppm with post micellar concentrations of SDS, CTAB and Triton X-100 in 1.5 M H₂SO₄ signifying the presence of synergistic effect between BTAH and surfactants. The highest corrosion inhibition was noted in post-micellar concentrations of Triton X-100 and CTAB with 0.75 ppm BTAH, 5.41 and 5.44 mpy, respectively. The results were also validated by using the LPR technique which showed that Triton X-100 has significant corrosion inhibition performance as compared to CTAB.

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