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Corrosion inhibition of copper by new triazole phosphonate derivatives

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Abstract

New corrosion inhibitors, namely 3-vanilidene amino 1,2,4-triazole phosphonate (VATP) and 3-anisalidene amino 1,2,4-triazole phosphonate (AATP) were synthesised and their action along with biocide on corrosion control of copper in neutral aqueous environment has been studied. Potentiodynamic polarisation measurement and electrochemical impedance spectroscopy (EIS) has been employed to analyse of their inhibition behaviour. VATP showed better protection over the other inhibitors used. The dissolution of copper in presence of VATP and AATP with biocide mixture is negligible compared to blank. A combination of electrochemical methods and surface examination techniques are used to investigate the protective film and explain the mechanistic aspects of corrosion inhibition.

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Keywords: Corrosion; Copper; Inhibitor; Biocide

1. Introduction

Copper is commonly used in heating and cooling systems due to its excellent thermal conductivity and exciting mechanical workability. Copper is one of the most important nonferrous metals used in industry as well as water distribution networks. It is susceptible to different forms of corrosion such as pitting corrosion induced by different corrosive species like chloride, sulphate and nitrate ions [1,2].

Heat exchangers require good thermal conductivity, corrosion, stress-corrosion resistance, and strength at modest cost. These requirements vary in importance for each application. Biological fouling decreases thermal efficiency and inherent to localised corrosion attack; hence, resistance to biofouling is sometimes important. Copper and copper alloys offer good combinations of these properties. Fouling and corrosion are the two important operational problems in heat exchangers and associated cooling water system pipelines. The problems include flow blockage of pipes, pipe punctures and unacceptable general corrosion rates of the system components.

The inhibition of copper corrosion in neutral or slightly alkaline oxygen containing solutions is one of the most hectic tasks for cooling water system operations. A study of mechanistic action of corrosion inhibitors has relevance both from the point of view of a search for new inhibitors and also for their effective usage [3]. Many authors have investigated

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the corrosion control of copper in various media using large numbers of organic and inorganic compounds. Results showed that organic compounds, especially those containing nitrogen [4–6] or sulphur [7] gave a very good inhibition for copper corrosion in different media. It is well known that triazole types of organic compounds are good corrosion inhibitors for many metals and alloys in various aggressive media [8,9]. However, in the presence of an organic inhibitor, the properties of the protective layer can be modified.

Phosphonic acids renowned their hydrolytic stability, scale inhibiting property and ability to form complexes with metal cations, has been a choice as candidate for corrosion inhibitors [10,11]. Hence in the present investigation some triazole derivatives are synthesised that contains phosphonic acid group and their efficiency in the inhibition of copper corrosion in neutral aqueous environment are studied.

Generally, for controlling fouling and corrosion, continuous addition of inhibitors as well as the addition of biocides every week or once in a fortnight is explored. It is not known as to whether interference effect between biocides and inhibitors will lead to any adverse effect. Recently, few researchers have turned their attention to these aspects. However, the knowledge on effect of inhibitors and biocide on corrosion control in cooling water systems are limited.

Hence, it is quite essential to study the interference between inhibitors and biocide for cooling water systems. In the present study synthesised triazole phosphonates was used as inhibitors while the biocide, cetyl trimethyl ammonium bromide (CTAB) is used to study their interference effect on corrosion process of copper.

2. Experimental

2.1. Synthesis of triazole derivatives

Three grams of 3-amino 1,2,4- triazole at a concentration of 0.05 M was dissolved in 20 ml of concentrated HCl and to this solution 2.5 ml of hypophosporus acid was added. The reaction mixture was put inside the fuming cupboard and to this 4.5 ml aldehyde (R) was added [12–14]. The reaction mixture was refluxed for 4 h on an oil bath inside the fuming cupboard. The reaction mixture was evaporated and cooled. Addition of water and methanol to this cooled solution resulted in the formation of solid product. The solid was filtered, washed thoroughly with water and recrystallised from methanol-water mixture. The compounds are characterised by FT-IR and NMR spectra. The structures of the compounds are given in Fig. 1. The schematic representation of synthesis is shown below Scheme 1.

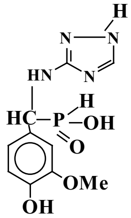
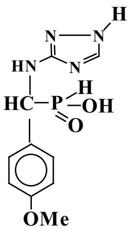
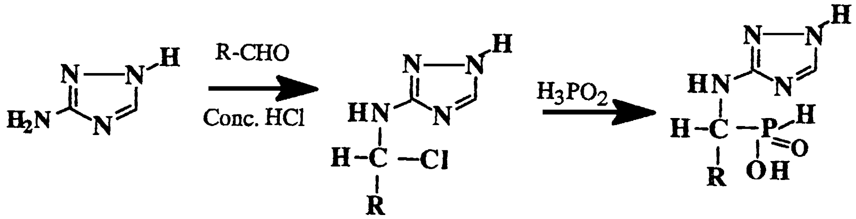
Name	Abbreviation	Structure
3-Vanilidene amino 1,2,4-triazole phosphonate	VATP	
3-Anisalidene amino 1,2,4-triazole phosphonate	AATP	

Fig. 1. Structure and name of the triazole derivatives.



Scheme 1.

2.2. Sample preparation

Copper samples of size 1.0 cm × 1.0 cm × 0.3 cm having the following compositions were used for the experiment. P 0.021%, Fe 0.07%, Ni 0.004%, Zn 1.59%, Cr 0.006%, As 0.003%, S 0.06 % and Cu balance. Before each experiment, the samples were mechanically polished with silicon carbide abrasive papers (from grade 120 to 1000), washed with water, degreased with acetone and dried at room temperature, then placed in a test solution. The lake water was used as the electrolyte and it's analysis report is given as: total dissolved salts 738 ppm, total alkalinity 201 ppm, Cl^- 170 ppm, pH 7.99. Copper specimens in triplicate were immersed in the test solution for a period of 3 days. After immersion period the specimens were removed and the efficiencies assessed in the following systems.

System	Material used	Medium	Parameters of interest
System I	Inhibitors with Mo	Lake water	Inhibition efficiency
System II	CTAB	Lake water	Biocide efficiency
System III	Inhibitors with Molybdate and CTAB (biocide)	Lake water	Interference in the inhibitors and biocide (Inhibitors and biocide are added at same time)
System IV	CTAB (biocide) with Inhibitors and Molybdate	Lake water	Biocide are added first, after 24 h inhibitors were added

2.3. Potentiodynamic polarisation measurement

Potentiodynamic polarisation studies were carried out using Vibrant Potentiostat/Galvanostat Model No.VSM/CS/30 at a scan rate of 1 mV/s under static condition. Platinum electrode and saturated calomel electrode (SCE) were used as auxiliary and reference electrodes respectively. The working electrodes constitute copper specimens of 1 cm^2 area. All the experiments were carried out at constant temperature of 30 ± 2 °C with natural lake water as an electrolyte.

2.4. Electrochemical impedance measurement

The electrochemical impedance studies were carried out in the same setup used for potentiodynamic polarisation studies described above. A Solartron SI 1255 Frequency Response Analyser and a Solartron SI 1287 Potentiostat/Galvanostat electrochemical interface controlled by software programme Zplot, Version 1.2, (C) 1994, Scribner Associates Inc., were used to control the electrode potential potentiostatically at OCP and apply the ac perturbation signal of 10 mV with in the frequency range of 20 KHz to 0.1 Hz. The data was plotted and analysed using software Z-View version 1.5b, (C) 1996, Scribner Associates Inc. The impedance parameters, total impedance, Charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) were calculated using the software Z-View. The electrochemical impedance tests were carried out at open circuit potential condition. All EIS measurements were obtained as soon as the specimen attained the steady state condition.

2.5. Accelerated leaching studies (ICP-AES)

During the anodic polarisation, metal dissolution takes place, releasing considerable amount of metal ion from the material. Hence, the solutions were analysed to determine the leaching characteristic of metal ion. In this study, the concentration of metal ions present in the test solution was determined after ageing for one hour at impressed potentials of OCP. The analysis was carried out using inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES)-Thermo Jarrel Ash-Atom Scan, USA.

2.6. Surface evaluation studies

The copper specimens were immersed in various test solutions for a period of 30 days. After 30 days, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analysed by various surface analytical techniques.

2.6.1. FT-IR spectroscopy

The FT-IR spectra of the films formed on the surfaces of the metal specimens were recorded using Perkin–Elmer 1600 FT-IR spectrophotometer.

2.6.2. Energy dispersive X-ray analysis (EDXA)

The nature of the film formed on the surface of the metal specimens was analysed by energy dispersive X-ray analysis (EDXA) for surface composition. This was carried out with a Philips 501 SEM in conjuction with an energy dispersive spectrometer. The spectra were recorded on samples immersed for a period of 30 days in natural lake water with and without the inhibitors and biocide.

2.6.3. Scanning electron microscopic study

The surface morphological characteristics of inhibited and uninhibited samples were observed under a Philips 501 scanning electron microscopy (SEM). The samples were coated with a thin layer of gold using an Edwards Sputter coater s150B instrument.

2.7. Bacterial killing efficiency

Using a sterile micropipette 1 ml of the sample was added to 9 ml of dilution water to get 10^{-1} dilution. From that dilution 1 ml was added to another 9 ml dilution water to get 10^{-2} dilution. For pour plate method glass petridishes of 65 cm^2 area was used. After thoroughly mixing the diluted sample, 100 μl was placed in a petridish to which a suitable agar media was added.

The agar media was autoclaved and then maintained at a temperature of 44–46 °C until used. Approximately 10–12 ml of the media was poured into the dish by lifting the cover just high enough to insert the mouth of container. Then the medium was thoroughly mixed with the sample by rotating the dish in one direction and then in the opposite direction. After the medium had solidified, the dishes were inverted and kept for incubation.

Petriplates were incubated at 35 °C for 48 h colonies were counted using Quebec colony counter. Bacterial counts per milliliter were arrived at by multiplying average number of colonies per plate by the reciprocal of the dilution used. Counts were reported as colony forming units (CFU) per ml.

$$\frac{\text{cfu}}{\text{ml}} = \frac{Y}{D} \times V$$

where Y is the number of bacterial colonies in the agar, D dilution plated and V volume plated.

3. Results and discussions

3.1. Electrochemical study

The cathodic and anodic polarisation of copper in lake water in the presence and absence of various concentrations of triazole derivatives for 3 days were carried out. Each inhibitor was studied at different concentration levels e.g. 2, 3, 4, 5, 6, 8 and 10 ppm. The efficiency was found to increase appreciably with the increase in inhibitors concentrations upto 4 ppm after which it decreases. The optimum concentrations of inhibitors were evaluated based on inhibition efficiency.

Various corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) and the inhibition efficiency (IE) were determined by Tafel extrapolation method are given in Table 1. Corrosion rates were calculated from i_{corr} values. The corrosion rate (mpy) and inhibition efficiency of inhibitor was

Table 1
Potentiodynamic polarisation parameters of copper in lake water with and without inhibitor and biocide (System I–IV)

Compounds	System	OCP (mV vs. SCE)	E_{corr} (mV)	I_{corr} (μA/cm^2)	Corrosion rate (mpy)	IE (%)
Blank	–	−200	−165	1.6	0.73	–
VATP	System I	−138	−140	0.37	0.169	76.87
AATP	System I	−170	−178	0.38	0.174	76.25
VATP + Mo	System I	−170	−184	0.33	0.151	79.37
AATP + Mo	System I	−140	−233	0.35	0.160	78.12
CTAB	System II	−127	−127	0.36	0.165	77.50
VATP + Mo + CTAB	System III	−170	−200	0.30	0.137	81.25
AATP + Mo + CTAB	System III	−178	−200	0.32	0.147	80.00
CTAB + VATP + Mo	System IV	−214	−233	0.20	0.091	87.50
CTAB + AATP + Mo	System IV	−201	−226	0.22	0.101	86.25

IE: inhibition efficiency.

calculated by the following equation.

$$\text{Corrosion rate (mpy)} = \frac{0.129 \times I_{corr} \times \text{eq. weight}}{\text{density} \times \text{area}}$$

I_{corr} is the corrosion current density.

Inhibition efficiency of various inhibitors can be calculated from the polarisation data as

$$\text{Inhibition efficiency (IE\%)} = \frac{I_{corr}(\text{blank}) - I_{corr}(\text{inhibitor})}{I_{corr}(\text{blank})} \times 100$$

where $i_{corr(inhib)}$ and $i_{corr(blank)}$ are the corrosion current density values with and without the inhibitor, respectively.

The potentiodynamic polarisation parameters of copper immersed in lake water for all the four systems are given in Table 1 and corresponding polarisation curves are also shown in Figs. 2 and 3. The corrosion current density was decreased considerably in the presence of inhibitor. The value of the corrosion rate of copper in the presence of inhibitor was much smaller than that in the absence of an inhibitor.

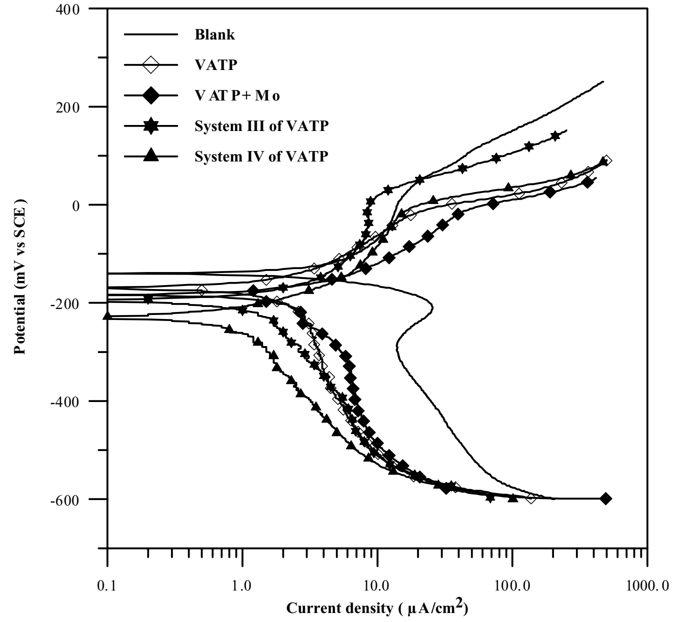


Fig. 2. Potentiodynamic polarisation curves of copper in lake water with and without optimum concentration of VATP and biocide.

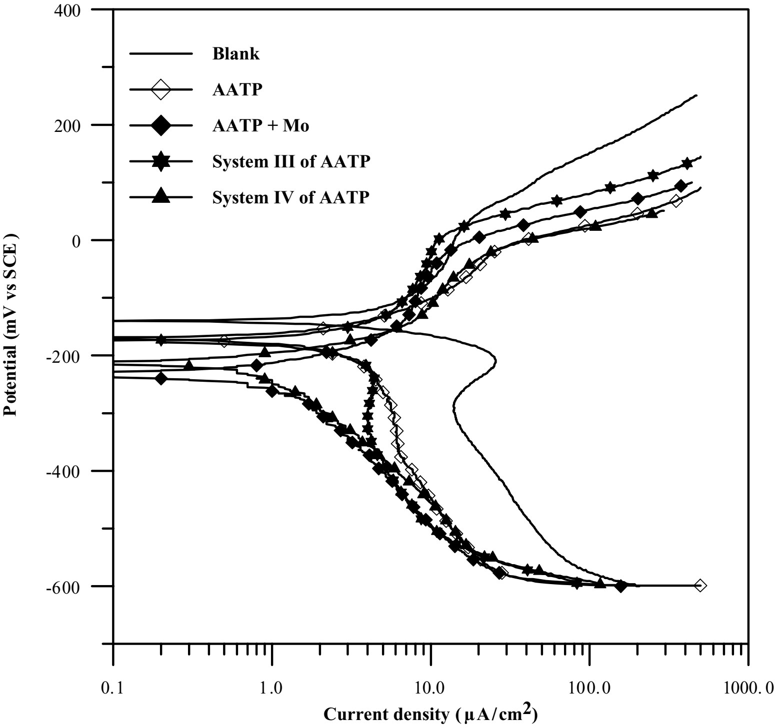


Fig. 3. Potentiodynamic polarization curves of copper in lake water with optimum concentration of AATP and biocide.

In the presence of inhibitors, the corrosion potential slightly shifts towards the active direction in comparison to the result obtained in the absence of the inhibitor. Both the anodic and cathodic current densities were decreased indicating that all the tested inhibitors suppressed both the anodic and cathodic reactions, although mainly the cathodic one.

Optimum concentrations were determined for all investigated compounds by Tafel extrapolation method. For 3-vanilidene amino 1,2,4-triazole phosphonate (VATP) and 3-anisalidene amino 1,2,4-triazole phosphonate (AATP), the corrosion inhibition efficiency of 76.87 and 76.25%, respectively was obtained at 4 ppm concentration. The inhibiting effect decreases at lower and higher concentrations and the compounds act as activators at the highest investigated concentration.

Addition of molybdate controls both cathodic as well as anodic reaction. But along with inhibitor they also predominantly control the cathodic reaction site. In presence of molybdate, the increased efficacy of VATP and AATP are 79.37 and 78.12%, respectively. The synergism is an enhanced inhibition, which may be related either to interaction between the inhibitor compounds or to interaction between the inhibitor compound and one of the ions present in the aqueous media.

In system II, the inhibitive effect of CTAB on copper corrosion in neutral aqueous solution was investigated. By comparing polarisation curves in the absence and presence of CTAB, it is observed that the increase in CTAB concentration shifted the open circuit potential in the positive direction and a lowering of both the anodic and cathodic current densities. The corrosion potential and corrosion current for copper in CTAB were obtained listed in Table 1. The results reveal that the IE increases with the CTAB concentration up to a maximum (77.5%) in a concentration of 15 ppm and then it decreases.

The shift in corrosion potential to the more noble values and increase in the potential (anodic) indicate that CTAB acts as an anodic inhibitor. Corrosion of metal is initiated at reaction sites (defects) [15]. During dissolution, the metal atoms are removed from the reactive (Kink) sites. The adsorption CTAB molecules on the metal surface retard the dissolution of metal atoms from the reactive sites. Under such conditions the removal of copper atoms becomes more difficult and needs high energy. Surfactants get adsorbed on cathodic/anodic site of the metal surface and thus prevent the dissolution of metal from the surface.

In system III the inhibition efficiency was about 81.25 and 80.00%, respectively for VATP and AATP. The higher inhibition efficiency shown by VATP compared to AATP may attributed to the increased electron density leading to electron transfer mechanism from functional group to metal surface, producing greater coordinate bonding with a greater adsorption and inhibitor efficiency. Similar explanation has been sought to explain the discrepancy in the order of inhibition efficiency by triazoline derivative [16]. In system IV, the corrosion inhibition percentage was higher compared to system III. In the presence of VATP the efficiency was about 87.50% and OCP was −214 mV. It was observed from the results that the combination of VATP and AATP with molybdenum acted as good inhibitor.

From the observation of results, VATP and AATP found to act as better inhibitor (76%). Besides in system IV, the inhibitor recorded higher efficiencies than system III and elucidates the low interference between biocide and inhibitors system. In system III, the biocide (CTAB) adsorption may disturb the absorption of triazole phosphonate, which may interfere with the inhibitor action. But in system IV the interference between biocide and inhibitor was least. The IE of inhibitors with biocide decreased in the following order VATP > AATP.

The polarisation curve for the blended mixture (system IV) indicates a shift in the corrosion potential toward positive values of potential compared with the control sample without inhibitor. The cathodic region shows a decrease in the limiting current for oxygen reduction as a result of cathodic inhibition. However, according to corrosion potential the inhibitor trended towards cathodic inhibition. This indicates that the blended mixture (system III and IV) inhibit the cathodic reaction more strongly.

3.2. Electrochemical impedance spectroscopy (EIS)

There are two methods to describe the EIS spectra for the inhomogeneous films on the metal surface or rough and porous electrodes. In the inhibited as well as in the uninhibited solution the impedance spectra were characterised by two slightly distorted capacity behaviour, one at higher frequency and the other at lower frequency. Deviations from the ideal semicircles can be attributed to the inhomogenities of the surface as well as due to mass transport process [17]. Impedance measurements were carried out at the open circuit potential for copper in lake water in the presence and absence of optimum concentrations inhibitors and biocide (system IV) under study is shown in Fig. 4.

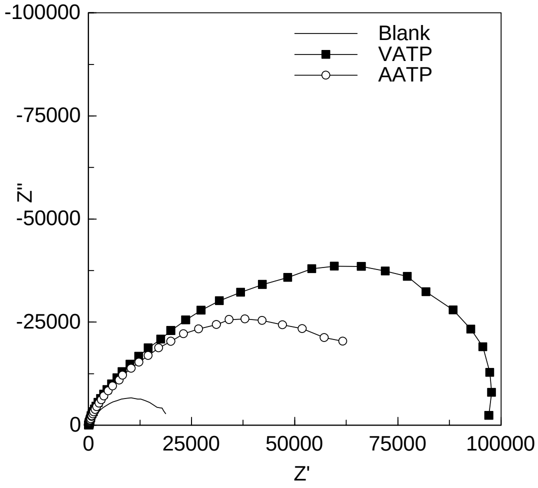


Fig. 4. Nyquist plot of copper in lake water with optimum concentration of VATP and AATP with biocide mixture (system IV).

The admittance plots are not semicircles these plots were not used for calculating the impedance parameters. The electrochemical parameters like solution resistance (R_s) and charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were obtained by using the semicircle fitting method [18]. This can be achieved by selecting the best fitting for the semi circle on the complex plane (Nyquist) plot, by using computer software on the impedance system.

As can be seen from the impedance results shown in Fig. 4 the increase in resistance in the presence of VATP (compared to inhibitor-free solution) is related to the corrosion protection effect of the molecule. The value of C_{dl} decreases in the presence of VATP with biocide mixture, indicating that the surface oxide layer thickness decreases and changes the influence of the oxide layer on the kinetics of the electrode process. It is seen from the Fig. 4 that the charge transfer

Table 2
Impedance measurements for copper in natural aqueous environment containing with and without inhibitor and biocide (System IV)

System	R_{ct} (Ω cm^{-2})	C_{dl} (F cm^{-2})	IE (%)
Blank	20551.1	1.76954×10^{-5}	–
VATP-system IV	128104	6.45608×10^{-6}	83.95
AATP-system I V	79876.4	6.45608×10^{-6}	74.27

resistance (R_{ct}) is maximum (128104 Ω) with an inhibition efficiency of 83.95% after immersion of the sample in VATP with CTAB mixture.

The EIS parameters like charge transfer resistance and capacitance of the inhibitors are presented in Table 2. Copper with CTAB + VATP + Mo mixture exhibited higher resistance and impedance whereas lower capacitance value for as immersed in lake water medium. The inhibition efficiencies calculated from ac measurement show the same trend as those observed from dc polarisation results. Maximum efficiency was noticed for the compounds with the methoxy phenyl substituents, since the basicity of the coordinating atoms are increased by electron donating groups.

3.3. Accelerated leaching studies (ICP-AES)

The results of the accelerated leaching study are presented in Fig. 5, which show the concentration of copper leached from the copper at the open circuit potential. For copper, significant amounts of metal ions were released into the solution even at the OCP region. The effects of chemical additives on the copper dissolution are shown in Fig. 5 among the options studied, the most effective treatment for reducing copper dissolution was the application of 4 ppm of VATP + 5 ppm of molybdate with 15 ppm of CTAB to lake water.

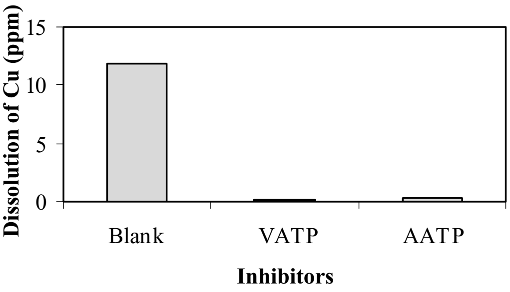


Fig. 5. Concentration of copper present in the solution after leaching of copper at various inhibitor mixtures.

In the present investigation, VATP and AATP mixture exhibited a very low tendency to leach metal ions compared to blank. This can be attributed mainly to the stable complex film that inhibits metal dissolution by forming a barrier layer between the metal and the environment, thus preventing the bare metal contacting solution. The amount of copper leached out from metal with all inhibitors show the following order, AATP > VATP. The dissolution of copper in presence of VATP and AATP is negligible compared to blank.

3.4. Surface evaluation study

Copper specimens were immersed in various test solutions for a period of 30 days. After 30 days, the specimens were taken out and dried. The nature of the film formed on the surface on the metal specimens was analysed by the various surface analytical techniques. Topographic examinations of the corroded surfaces were made by SEM and compositional analysis of the corrosion products films were performed, where possible using FT-IR and Energy dispersive X-ray analysis.

3.4.1. Analysis of FT-IR spectra

FT-IR of inhibitor VATP is presented in Fig. 6a. The stretching mode of P=O bond gives rise to a strong band in the region 1320–1140 cm^{-1} as expected [19]. The two prominent bands at 1080 and 930 cm^{-1} are attributed to the PO_3H_2 group of the molecule. The band at 1080 cm^{-1} is assigned to the P–O stretch of the ionic species and the other at 930 cm^{-1} is assigned to the P–OH stretch [20,21]. The reflectance absorption spectra of the film formed on copper immersed in inhibitor and mixture of inhibitor with biocide (system IV) are presented in Fig. 6c and d. The band at 930 cm^{-1} almost disappeared in Fig. 6c and d compared to a. This can be attributed to a P–O–M bond in which a free P^+–O^- interact with metallic species. The fact that the band at 930cm^{-1} due to P–OH stretching is weak further indicates the possibility of a P–O–M (P–O–Cu) bond [22]. This suggests that phosphonates are coordinated with Cu^{2+}, resulting in

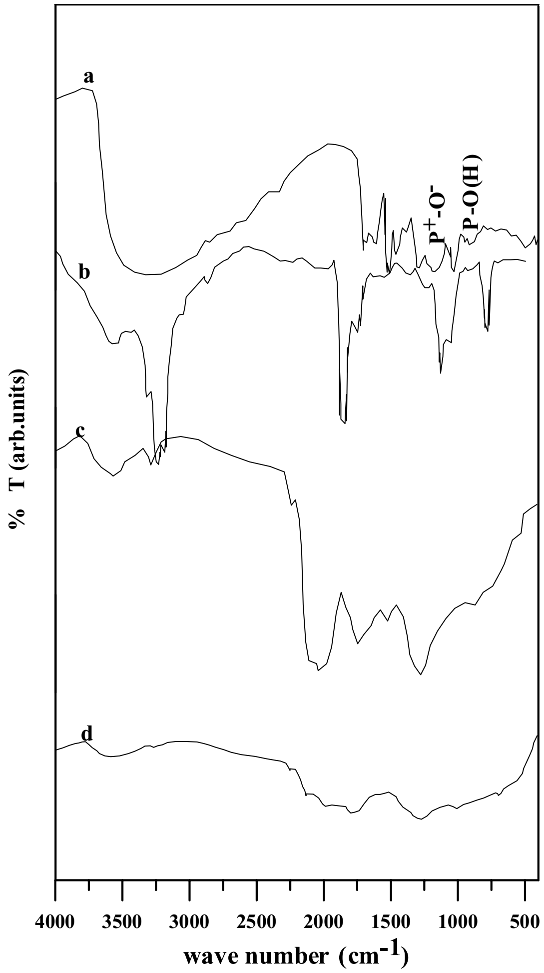


Fig. 6. Infrared transmission spectra of (a) VATP; (b) CTAB Infrared reflection absorption spectrum of the film formed on the copper substrate after immersion in the solution containing; (c) VATP; (d) mixture of VATP + Mo + CTAB.

the formation of Cu–phosphonate complex on the metal surface.

The FT-IR spectrum of pure CTAB is given in Fig. 6b. The absorption band due to 2854 cm^{-1} represents CH_2 stretching frequency. The aliphatic C–H stretches cause absorption at 2923 and 2854 cm^{-1}. The band at 1126 cm^{-1} corresponds to C–N stretching. The absorption bands at 2923 cm^{-1} and 2854 cm^{-1} suggest the adsorption of CTAB on the anodic sites of the metal surface.

In addition to the metal-inhibitor complex, the CTAB-Cu^{2+} complex also deposit as a layer on the metal and as a part of the protective film. From the inhibition characteristics it supplements the corrosion inhibiting capability of the Cu-inhibitor complex, probably through the formation of more impervious films.

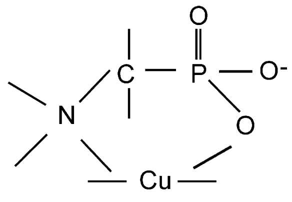
Nitrogen containing organic heterocyclic compounds is considered to be excellent complex or chelate forming substances with metals of transition series [23]. Such complexes of substance or their salts with transition metals are strongly adsorbed forming a thin, adherent film providing a barrier between the metal surface and the corrosive medium, there by bringing down the corrosion rate.

The formation of complex is the result of the reaction between the triazole on the metal surface [24] through the NH group and the metal cation formed during the corrosion of metal. It is known that aromatic triazoles are effective inhibitors for copper and its alloys. The protective action of the triazole is based on the formation of a semi-permeable, insoluble, polymeric copper-triazole complex film on the copper surface. The polymeric complex was formed by covalent and coordinate covalent bonds.

The adsorption (chemisorption) may be viewed as a result of Lewis acid–base electron exchange, resulting in the formation of 5- and 6-membered metal inhibitor ring complexes (except O–PO_4, which forms a 4-membered ring), as shown in the following figure Scheme 2. These metal inhibitor complexes will successfully inhibit corrosion if they have a large surface activity and a low level of aqueous solubility [25].

3.4.2. Energy dispersive X-ray analysis (EDXA)

Energy dispersive X-ray analysis (EDXA) technique was employed in order to get additional information on the inhibition mechanisms. The results obtained from these techniques showed that the corrosion inhibition process was related to the development of inhibitor film over the metal surface.



Scheme 2.

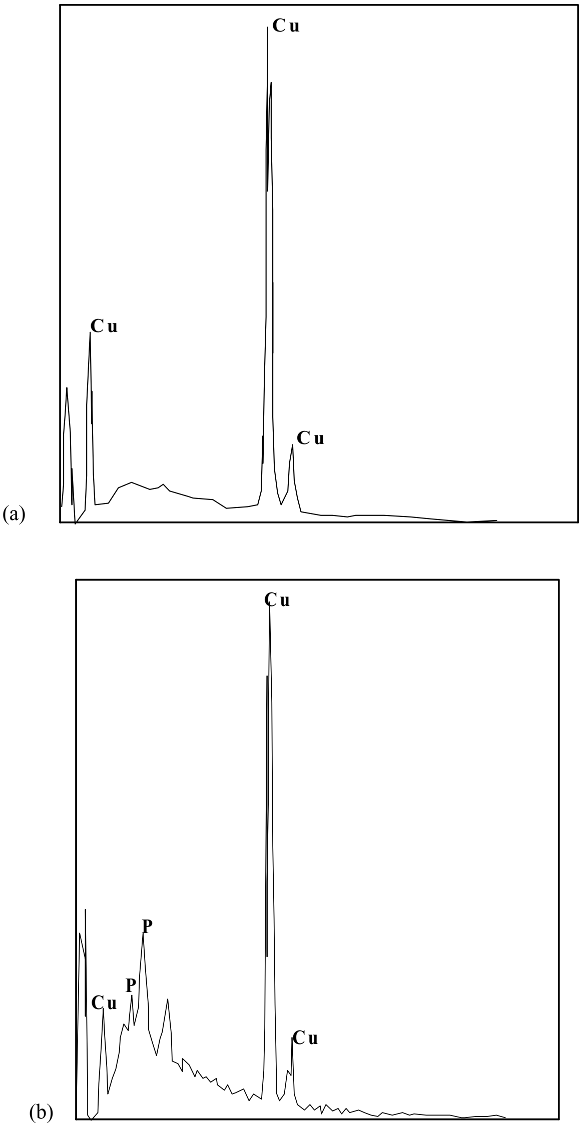


Fig. 7. EDXA spectrum of copper in natural lake water: (a) blank and (b) VATP with biocide mixture.

Attempts to identify the surface films using X-ray diffraction were not successful, possibly because of the poor crystalinity of the material, but more probably due to the fact that the films were very thin. The cross section analyses of the corrosion layers were performed by EDXA. Mapping of C, O, P and Cu was carried out to investigate the distribution of these elements in the surface layers.

EDXA analysis (Fig. 7) conformed that the phosphorus layer was formed on metal exposure to natural lake water. Furthermore the outer layer was poorly adherent. A similar behaviour was reported by Gomex de Saravia et al. [26] for 70/30 and 90/10 Cu–Ni alloys in an environment containing bacteria. The instrument used is not capable of detecting oxygen and sodium.

The EDXA analysis of the microcrystalline produced a spectrum in which P and Cu were prominent. The phosphorus peak is due to the fact that the lake water was treated with a phosphonate-based inhibitor. It was found that an adsorbed layer is formed on copper, which inhibits corrosion. This observation clearly proves that the inhibition is due to the formation of an insoluble stable film through the process of complexation of the organic molecules on the metal surface. Studies also reveals the formation of a thin and very adherent organic film on the metal surface in all the cases; which is actually responsible for the inhibition of corrosion of the metal in lake water.

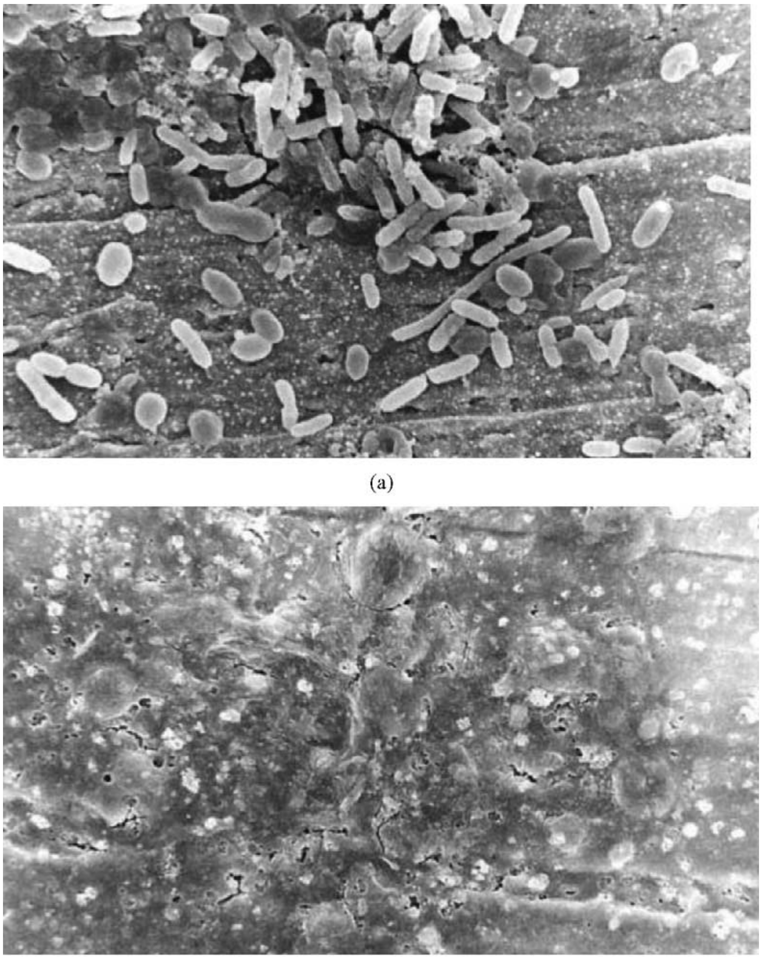
3.4.3. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was employed in order to get additional information on the inhibition mechanisms. The SEM micrographs of copper specimens exposed to natural lake water over a period of 30 days are given in Fig. 8a. It reveals a biofilm with abundant bacteria along with corrosion products on metal surface.

Fig. 8b shows the SEM micrographs of copper in natural lake water containing VATP along with biocide. Absence of any corrosion pit and other form of corrosion products in the micrograph suggest that the specimen is covered with a inhibitor layer. However, in treated solutions no microorganism was found on copper surface.

3.5. Bacterial killing efficiency

The bacterial killing efficiency of inhibitors along with biocide is presented in Table 3. The bacterial densities of about 1.23×10^6 was observed in the presence of VATP. In presence of CTAB the bacterial count was measured as 5.2×10^2 and CTAB acts as a effective biocide by disturbing the arrangements of phospholipid molecules in the bacterial cell. When biocides and inhibitors were simultaneously injected, the bacterial killing efficiency was found to be meager.



(a)

(b)

Fig. 8. Surface morphology of copper in: (a) blank and (b) presence of VATP and biocide mixture.

Probably biocide lost their activity against bacteria. Hence it is suggested that biocide and inhibitors should be added separately for achieving higher efficiency.

Table 3
Bacterial density of lake water in various systems for 24 h

System	Concentration (ppm)	Bacterial count (cfu/ml)
Control	–	1.86×10^6
VATP	4	1.23×10^6
CTAB	15	5.2×10^2
VATP + Mo + CTAB	4 + 5 +15	1.15×10^6

4. Conclusions

The present study leads to the following conclusion in corrosion control of copper in natural aqueous environment.

1. In various inhibitor systems, system IV has higher efficiencies than system III and elucidates the minimal interference between biocide and inhibitors system.
2. The inhibition efficiencies calculated from ac measurement show the same trend as those observed from dc polarisation results.

3. The dissolution of copper in presence of VATP and AATP with biocide mixture is negligible compared to blank.
4. A combination of electrochemical methods and surface examination techniques are used to investigate the protective film and explain the mechanistic aspects of corrosion inhibition.
5. FT-IR and SEM-EDXA clearly proves that the inhibition is due to the formation of an insoluble stable film through the process of complexation of the organic molecules on the metal surface.

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