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Influence of biocides on corrosion inhibition efficiencies of mono sodium glutamate - Zn^{2+} system

The inhibition efficiencies and biocidal efficiencies of the biocides in the presence and absence of the mono sodium glutamate(MSG)-Zn^{2+} system in river(namely, Cauvery in Trichy, Tamilnadu, India) water and have been assessed. The inhibition efficiencies of MSG-Zn^{2+}system in the presence and absence of the biocides namely cetyl pyridinium chloride (CPC), benzyl trimethyl ammonium chloride (BTAC), and dodecyl benzene sulphonate (DBS) and the biocidal studies of biocides in the presence and absence of inhibitor system are studied. Among the three biocides, BTAC is found to be a very good inhibitor, which controls the corrosion of carbon steel in river (Cauvery) water. On comparing the biocidal efficiency of the biocides CPC is found to be the best among the three biocides which controls the growth of microbes in river water as well as a very good inhibitor which works in concurrence with the MSG-Zn^{2+} system in controlling the corrosion in river water.

Key words: *Corrosion inhibition, carbon steel, river water, synergistic effect., biocide*

INTRODUCTION

Microbial life affects everything including many industrial processes. The nature and activity of microorganisms determine whether their presence is beneficial or destructive. In cooling towers, the destructive capability of these organisms is manifested. The microorganisms that inhabit industrial cooling water systems can adversely affect the efficiency of the operation by their sheer number and diversity, metabolic wastes or deposits and associated corrosion. Microbiologically influenced corrosion is emerging as a serious problem in cooling systems. Microorganisms such as bacteria, fungi and algae can combine with organic compounds to form biofilms. The microbes in these films produce products of metabolism that are corrosive in nature. The result is pitting and corrosion of metal components. To eliminate the threat of such potential problems and achieve optimum system efficiency, microbiological activity within a system must be properly controlled by the addition of suitable biocides. Most industries are adding inhibitors and biocides at the same point in cooling water systems. The interference between biocides and inhibitors were studied in detail and many researchers evaluated the role of biocides in corrosion in the presence of inhibitors [1]. Many studies are in progress with the development of new biodispersing antifouling compositions for recirculating cooling water system [2].

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The inhibition efficiency of mono sodium glutamate (MSG)-Zn^{2+} system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by Leema rose et al [3].The influence of sodium dodecyl benzene sulfonate (SDBS) on the corrosion behaviour of an elaborated annealed Fe-1Ti-20C alloy presenting a cementite phase (Fe_3C), has been investigated in 0.5 M H_2SO_4 solution using electrochemical techniques by Kellou-Kerkouche et al [4]. The inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoxazole (2-MBO) on corrosion of copper in sulphuric acid solution have been studied using electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements by Tavakoli et al[5]. Atul Kumar[6] studied the inhibiting effect of Cetyl Pyridinium Chloride (CPC) on mild steel in 1M Hydrochloric acid by using three techniques namely: weight loss, electrochemical polarization and metallurgical research microscopic techniques.

Rajendran et al [7,8] have studied the influence of CTAB on the corrosion inhibition of mild steel by ATMP-Zn^{2+} system, and also the biocidal efficiency of CTAB in the presence of various phosphonic- Zn^{2+} system and reported that CTAB acts as an excellent biocide as monomer and also as micelle. Manimegalai et al [9] have examined the inhibitive property as well as the biocidal properties of the leaf extracts of Azadiracta Indica and reported that the inhibitor has very effective biocidal property as well as inhibitive property for mild steel in fresh water environment. Stefanova[10] has studied the biocidal efficiency of cetyl pyridinium bromide (CPB), potassium permanganate and sodium benzoate. He has reported that the CPB has a wide range of effect for micro-organisms typical for water media. Lin et al [11] have reported that CPC, a quaternary ammonium salt and a cationic surfactant has been used as a biocide in personal hygiene products. It is reported that CPC acts as an antifungal agent [12], and as a biocide [13] for cosmetics, toiletries and pharmaceuticals activity.

The purpose of the present investigation is to i) study the inhibition efficiency of the biocides in the presence and absence of the MSG-Zn^{2+} system in river water ii) assess the biocidal efficiency of the biocides in the presence and the absence of the inhibitor system.

EXPERIMENTAL

Preparation of the carbon steel specimens

Carbon steel specimens (compositions 0.1 per cent C, 0.026 percent S, 0.06 percent P, 0.4 percent Mn and balance Fe) of dimensions 1.0 X 4.0 X 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass-loss studies.

Mass- loss method

The weighed specimens in duplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions. After 3days of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimens, corrosion rates and I.E. were calculated.

$$IE = 100 [1 - (W_2 / W_1)] \%.$$

Where w_1=corrosion rate(mdd) in absence of inhibitor, w_2=corrosion rate (mdd) in presence of inhibitor.

Preparation of inhibitor and biocide solutions

Stock solutions of monosodium glutamate (MSG) and biocides were prepared by dissolving 1 g of the respective compounds in double distilled water and made up to 100 ml. Zinc sulphate solution is prepared by dissolving 1.1 g in double distilled water and made up to 250 ml in a 250 ml standard measuring flask.

Zobell medium

Zobell medium was prepared by dissolving 5 g of peptone, 1 g of yeast extract, 0.1 g of potassium dihydrogen phosphate and 15 g of agar-agar in 1 liter of double distilled water. The medium was sterilized by applying 15 pounds per square inch for 15 minutes in an autoclave.

Determination of biocidal efficiency of the system

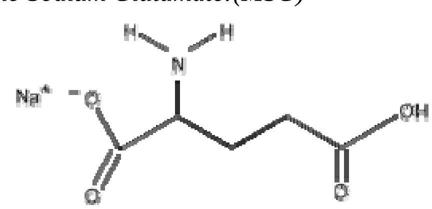
The biocidal efficiency of MSG – Zn^{2+} formulation that offered the best corrosion inhibition efficiency was selected. The biocidal efficiencies of benzyl trimethyl ammonium chloride (BTAC), dodecyl benzene sulphonate (DBS] and cetyl pyridinium chloride (CPC) in the presence and absence of the inhibitor formulation and also the effect of the biocides on the corrosion inhibition efficiency of MSG – Zn^{2+} were determined. The biocidal efficiencies (BE) of the biocides at various concentrations in the presence and absence of the inhibitor system MSG – Zn^{2+} were determined after immersing the specimens for 3 days in test solutions. Inhibitor system that offered the best corrosion inhibition efficiency was selected. After 3 days, one ml each of test solutions from environments was pipetted out into sterile petri dishes each containing about 20 ml of the sterilized zobell medium. The petri dishes were then kept in a sterilized environment inside the laminar flow system fabricated and supplied by CEERI- Pilani, for 48 hrs. The total viable heterotropic bacterial colonies were counted using a bacterial colony counter.

Table 1 - Results of the analysis of the sample of river(cauvery) water

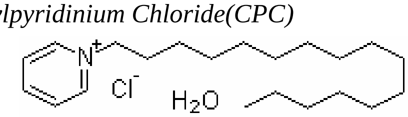
S.No	Chemical Examination	Acceptable limit	Test results
1	pH	7.0-8.5	7.1
4	Total Hardness (ppm)	200-600	106
5	Ca(ppm)	150-200	21
6	Mg(ppm)	50-150	23
7	Fe(ppm)	20	0.62
8	Mn(ppm)	0.5	0.03
10	Nitrite as NO_2 (ppm)	-	0.01
11	Nitrate as NO_3(ppm)	20	0.05
12	Chloride as Cl(ppm)	200-600	254
13	Fluoride as F^-(ppm)	1	0.2
14	Sulphate as SO_4(ppm)	42-45	.08
15	P (ppm)	5	0.1
16	Total dissolved solids (mg/l)	500-1500	153

Structure of inhibitors and biocides

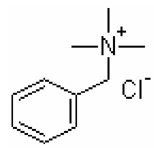
1. Mono Sodium Glutamate:(MSG)



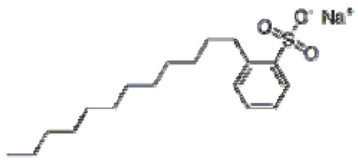
2. Cetylpyridinium Chloride(CPC)



3. Benzyl tri methyl ammonium chloride(BTAC)



4. Dodecyl benzene sulphonate(DBS)



RESULTS AND DISCUSSION

Mass-loss method

The corrosion inhibition efficiencies of mono sodium glutamate(MSG)-Zn^{2+} systems, as determined by mass loss method, are given in Table 2. It is found from the table that MSG is a poor inhibitor and 100 ppm of MSG gives a maximum of 36 % IE. Perusal of the table reveals that a combination of Zn^{2+} and MSG shows a better IE. For example, 50 ppm of Zn^{2+} gives an IE of 41 % and 100 ppm of MSG gives 36 %, but their combination offers an IE of 86 %, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn^{2+} and MSG. The synergism may be due to the formation of complex between Zn^{2+} and MSG. Because of the complex formation with Zn^{2+} the inhibitor molecules are readily transported from the bulk to the metal surface.

Table 2 - Inhibition efficiency of MSG-Zn^{2+}system on the corrosion of carbon steel in river (cauvery) water. Immersion period: 3 days

MSG, ppm	Zn^{2+},ppm				
	0	5	10	25	50
0	--	20	33	39	41
10	8	30	61	55	66
25	14	34	58	63	72
50	21	24	55	68	76
75	29	30	47	71	79
100	36	45	47	76	86
125	30	44	51	72	73

On the metal surface, Zn^{2+}-MSG complex is converted into Fe^{2+}- MSG complex on the anodic sites of the metal surface. Zn^{2+} is released. This combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus both the anodic reaction

Fe---------> Fe^{2+} + $2e^-$ and

Cathodic reaction

$O_2 + 4e^- + 2H_2O$---------> $4OH^-$

are controlled effectively. This accounts for a synergistic effect between MSG and Zn^{2+}.

The corrosion rates [CR] and inhibition efficiencies [IE] of carbon steel immersed in river(Cauvery) water containing MSG - Zn^{2+} (100 ppm of monosodium glutamate and 50 ppm of Zn^{2+}) in the presence and absence of the biocides BTAC, DBS and CPC are given in the Table-3.

It is found from the table-3 that on introducing 10 ppm of BTAC to the solution containing 100 ppm of MSG and 50 ppm of Zn^{2+}, a very high increase in the IE is noted, and on increasing the concentration of BTAC the IE of the system is not affected. But on adding 10 ppm of DBS, a slight increase in IE is noticed. But further increase of DBS from 10 to 125 ppm a gradual decrease of IE is noticed. With 125 ppm of DBS, the system offers only 28% of IE. The decrease in IE may be due to micelle formation. And when 10 ppm of CPC is added to the inhibitor combination, which offered maximum IE, it is found that the IE of the system increases from 86% to 99%. On further increase in CPC, IE gradually falls. This may be due to the introduction of chloride ions in to the system because of the ionization of CPC, which corrodes the carbon steel gradually

Table 3 - Inhibition efficiencies offered by the biocides to the inhibitor system in river(cauvery) water

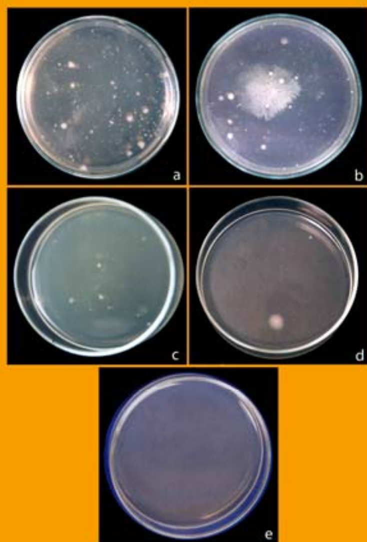
Inhibitor system: 100 ppm of monosodium glutamate and 50 ppm of Zn^{2+}

Biocides, ppm	BTAC		DBS		CPC	
	CR, mdd	IE, %	CR, mdd	IE, %	CR, mdd	IE, %
0	3.66	86	3.66	86	3.66	86
10	1	96	3	88	0.33	99
25	0.66	97	8	68	1	96
50	0.50	98	11.33	55	1.66	94
75	0.50	98	13.33	48	2	90
100	0.33	99	15.66	38	3.33	84
125	0.33	99	18.33	28	5.66	78

Biocidal efficiencies of biocides in river(cauvery) water

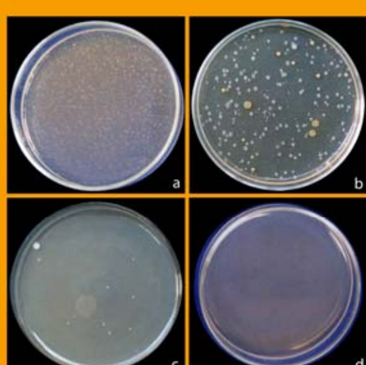
The biocidal efficiencies (BE) of BTAC, DBS & CPC in the presence and absence of the inhibitor formulation (MSG + Zn^{2+}) in river(Cauvery) water after suspending the metal pieces for 72 hours are given in Table – 4,5 & 6. The visuals of the bacterial colonies formed in river water in the presence and absence of the inhibitor system are shown in Figure-1-6.

Figure-1



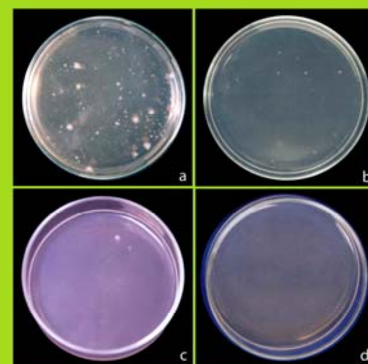
Bacterial colonies formed in river (cauvery) water in the presence of various concentrations of DBS.
a) 0 ppm b) 25 ppm c) 50 ppm d) 100 ppm e) 150 ppm

Figure-2



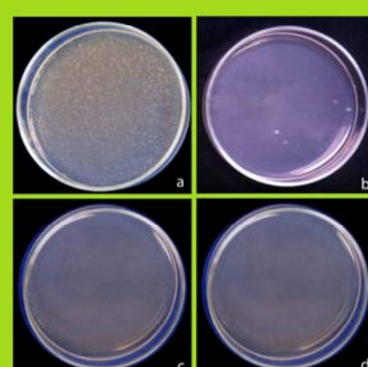
Bacterial colonies formed in river (cauvery) water contaning 50 ppm of zn^{2+} and 100 ppm of MSG in the presence of various concentrations of DBS
a) 0 ppm b) 25 ppm c) 50 ppm d) 100 ppm

Figure-3



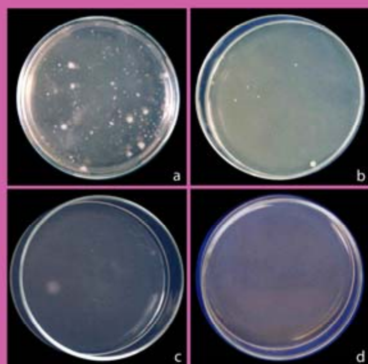
Bacterial colonies formed in river (cauvery) water in the presence of various concentrations of BTAC
a) 0 ppm b) 10 ppm c) 25 ppm d) 50 ppm

Figure-4



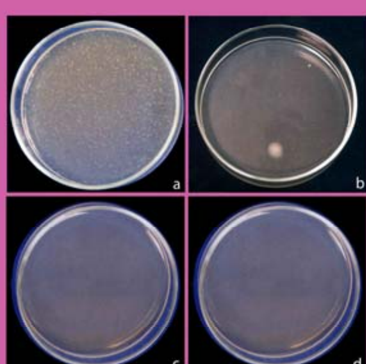
Bacterial colonies formed in river (cauvery) water contaning 50 ppm of zn^{2+} and 100 ppm of MSG in the presence of various concentrations of BTAC
a) 0 ppm b) 10 ppm c) 25 ppm d) 50 ppm

Figure-5



Bacterial colonies formed in river (cauvery) water in the presence of various concentrations of CPC
a) 0 ppm b) 10 ppm c) 25 ppm d) 50 ppm

Figure-6



Bacterial colonies formed in river (cauvery) water containg 50 ppm of zn^{2+} and 100 ppm of MSG in the presence of various concentrations of CPC
a) 0 ppm b) 25 ppm c) 50 ppm d) 100 ppm

Table 4 - Biocidal efficiencies of DBS in the presence and absence of MSG+ Zn^{2+} system in river(Cauvery) water environment

MSG, ppm	$Zn^{2+,}$ ppm	DBS, ppm	Colony Forming Units/ml	Biocidal Efficiency %
0	0	0	1357	--
0	0	25	135	90
0	0	50	10	99.26
0	0	100	2	99.85
0	0	150	0	100
100	50	0	678	50
100	50	25	746	45
100	50	50	12	99.1
100	50	100	0	100

Table 5 - Biocidal efficiencies of BTAC in the presence and absence of MSG + Zn^{2+} system in river (Cauvery) water environment

MSG, ppm	Zn^{2+}, ppm	BTAC, ppm	Colony Forming Units/ml	Biocidal Efficiency %
0	0	0	1357	--
0	0	10	10	99.26
0	0	25	2	99.85
0	0	50	0	100
100	50	0	678	50
100	50	10	4	99.18
100	50	25	0	100
100	50	50	0	100

The table-4 shows that 150 ppm of DBS is required for 100 % prevention of bacterial growth in the absence of the inhibitor formulation in river water. The inhibitor formulation in the absence of DBS, offers 50 % BE. The addition of 50 ppm of DBS reduces the BE of the inhibitor system. This is due to the reaction of DBS with mono sodium glutamate which reduces the concentration of DBS and mono sodium glutamate and hence the reduction in the BE is noted. It is also confirmed in the corrosion studies. Therefore 150 ppm of DBS is required for complete eradication of the microbes in the river water. But the addition of DBS reduces the IE of the system drastically and hence DBS is not recommended as a good additive as biocide for the inhibitor formulation in river water.

From the table-5 it is noted that 50 ppm of BTAC alone in the absence of the inhibitor shows 100 % efficiency in river water. River water containing inhibitor system in the absence of BTAC shows a biocidal efficiency of 50 %. This shows that mono sodium glutamate favours the growth of certain type of microbes. However the addition of 25 ppm of BTAC to the inhibitor system gives 100 % biocidal efficiency. Hence a minimum of 25 ppm of BTAC is required for the control of bacterial growth. However, the Table-5 shows that 100 ppm of BTAC along with the inhibitor system gives a maximum corrosion inhibition efficiency of 99 %. Hence it is suggested that a synergistic combination of 100 ppm of MSG, 50 ppm of Zn^{2+} and 100 ppm of BTAC is required to reach a maximum IE of 99% and 100 % BE.

Table 6 - Biocidal efficiencies of CPC in the presence and absence of MSG + Zn^{2+} system in river (Cauvery) water environment

MSG, ppm	Zn^{2+}, ppm	CPC, ppm	Colony Forming Units/ml	Biocidal Efficiency %
0	0	0	1357	--
0	0	10	5	99.65
0	0	25	2	99.85
0	0	50	0	100
100	50	0	678	50
100	50	25	2	99.85
100	50	50	0	100
100	50	100	0	100

Table-6 shows that 50 ppm of CPC gives 100 % biocidal efficiency for river water in the absence of inhibitor system. The inhibitor formulation shows 50 % BE. The addition of 10 ppm of CPC gives a biocidal efficiency of 100 % in the presence of the inhibitor system. Hence, a combination of 50 ppm of Zn^{2+}, 100 ppm of mono sodium glutamate and 10 ppm of CPC will be ideal for the corrosion inhibition and biocidal activity in river water.

Therefore along with the inhibitor combination, which offers maximum IE, 125 ppm of BTAC offers 99% IE and 100% BE and 125ppm of DBS offers a maximum of 88% of IE and 100% BE whereas 10 ppm of CPC offers 99% IE and 100 % BE.

CONCLUSION

Along with the synergistic combination (MSG + Zn^{2+}), 125 ppm of BTAC offers 99% IE and 100% BE whereas minimum concentration of CPC is required to get 99 % IE and 100 % BE. And DBS offers a maximum of 88% IE and 100% BE. So to get maximum benefit CPC is found to be the best biocide among the three biocides chosen for this inhibitor formulation, which controls corrosion and bacterial growth.

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