

Effect of MnO_4^- Anion Inhibition on Corrosion of (70%Cu-30%Zn) Brass in Salt and Basic Solutions

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Abstract

This research involves study effect of MnO_4^- anion addition as inhibitor on the polarization behavior of (70%Cu-30%Zn) alloy in salt and basic medium (0.6 M NaCl & 0.6 M NaOH) by potentiostatic method where Tafel slopes and corrosion rate (R_{mp}) and inhibition efficiency (EI%) for each salt and basic environments were measured .

Result of the tests shows that the values of Tafel slopes and corrosion rate decreases with adding the MnO_4^- anion in two solutions, the Inhibition efficiency of 70%Cu-Zn30% alloy in NaOH solution more than that observed in NaCl solution. which means that the basic media is more corrosive Cu-Zn alloy even after the addition of inhibitor.

Keywords: inhibition ,brass corrosion, MnO_4^- anion , $KMnO_4$.

تأثير ايون البرمنكنات المثبطة على تآكل البراس (70%نحاس-30%زنك) في محلول ملحي وقاعدي

الخلاصة

يتضمن هذا البحث دراسة تأثير إضافة ايون البرمنكنات كمادة مثبطة على السلوك الاستقطابي لسبيكة (70%النحاس-30%الزنك) في محلول ملحي (NaCl) بتركيز 0.6 مول ومحلول هيدروكسيد الصوديوم (NaOH) بتركيز 0.6 مول بطريقة المجهود الساكن حيث تم حساب قيم ميول تافل ومعدل التآكل (R_{mp}) وقيم كفاءة التنشيط (EI%) لكل من الوسط الملحي والقاعدي . وقد أظهرت نتائج البحث ان قيم ميول تافل ومعدل التآكل تقل بزيادة إضافة ايون البرمنكنات في كلا المحلولين وان كفاءة التنشيط لسبيكة (70%النحاس-30%الزنك) في المحلول القاعدي أكثر مما ملاحظ في المحلول الملحي مما يعني ان المحلول القاعدي أكثر تآكل لسبيكة نحاس -زنك حتى بعد إضافة المثبط.

Introduction

Copper and copper alloys are materials largely used in drinking distribution systems where sodium hypochlorite is

frequently used to reduce the bacterial content[1,2].The electrochemical behavior of Cu-Zn alloys (brass) has been studied extensively over a wide

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range of experimental conditions in relation to passivation and inhibition corrosion [2,3]. In neutral and alkaline solutions the passivation of brass involves the electroformation of a complex $\text{ZnO} \cdot x\text{H}_2\text{O}$ and Cu_2O layer, as concluded from electrochemical [4]. In general, passivity breakdown depends strongly on the composition of the alloy. In chloride solutions, the first step of the anodic dissolution of Cu is the formation of complex CuCl_2^- . In addition, it was found that during anodic polarization, there is always equilibrium between a thin layer of CuCl and a dense layer of dissolved CuCl_2^- [5].

Corrosion inhibitors are widely used to prevent the dissolution of copper. In this application, the inhibitors should be innocuous for human consumption; Inhibitors that prevent the corrosion process depend upon the nature of the metal and environment. Numerous oxyanions [CrO_4^{2-} , MoO_4^{2-} , TcO_4^- , MnO_4^- , NO_2^- , *etc.*] are known to act as inhibitors of metal corrosion in neutral and alkaline media. Their inhibiting action is often associated with the formation of insoluble compounds, "healing" the passive film on the metal [6,7].

Potassium permanganate is selected as a corrosion inhibitor for copper alloys due to its easy availability, non-toxic nature, cost effectiveness, algacide property, and remarkable corrosion inhibition efficiency [8]. Several reports have pointed out that the permanganate ion is not effective in preventing corrosion on the surface of Cu alloys at low pH values [9,10] but at high pH values, Mn

is capable of inhibiting the corrosion of Cu-based alloys, which is probably due to the fact that the reduction of Mn(VII) in neutral and alkaline media typically leads to the formation of MnO_2 , a less soluble species. KMnO_4 is widely used in passivation baths, in acid pickling, and in chemical descaling. KMnO_4 was studied as an effective inhibitor for aluminium copper, and brass [11,12].

The present work aims

(1) Characterize the effect of permanganate anion as corrosion inhibitors of Cu-Zn alloy in NaCl and NaOH solution using electrochemical methods.

(2) Establish the role of these anions improving the passive film resistance to the corrosion caused by chloride ions in neutral medium.

2- Experimental part

Experiments were carried out in 0.6 M NaCl and 0.6 M NaOH solutions in absence and presence of different concentrations of potassium permanganate. All solutions were prepared from double distilled water, All experiments were carried out at room temperature (25°C).

The brass (70Cu/30Zn) was used in the present work as working electrodes was prepared by metallic cast with rod shape, which put in the holder to insulate all sides except one side with surface area 1cm^2 . The open side polished manually to a mirror finish with abrasive papers used 200, 400, 600, and 1000 mesh grit and finally with cloths and alumina, rinsed in distilled water and stored in desiccators.

Polarization experiments were performed on WINKING M Lab Potentiostat from Bank-lektronik with electrochemical standard cell with provision for working electrode (Brass), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an saturated calomel electrode (SCE) as reference electrode. Electrochemical measurements were performed with a potentiostat at a scan rate 0.5mV.sec-1. Galvanostatic experiments were performed with the range of current density between -80 and +20 mA. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops, The rate (R_{mpy}) of corrosion in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation[13] :

$$R (mpy) = 0.129 * i_{(corr)} * (e / p)$$

Where:

$R_{(mpy)}$: corrosion rate (mil per year or mm per year), $i_{(corr)}$: corrosion current density (microamp/cm² or amp/cm²), e : alloy equivalent weight (gram/equivalent)

p : alloy density (gram/cm³)

Efficiency of Inhibitor were calculated using equation[14]:

$$EI\% = 1 - [(i_{inh.}) / (i_{corr.})] \times 100$$

Where:

$E.I$: Efficiency of Inhibitor

$i_{(corr.)}$: Current density without Inhibitor

$I_{(inh.)}$: Current density with Inhibitor

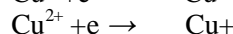
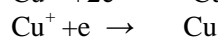
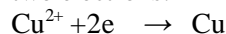
3- Results and Discussion

§ Polarization Behavior

The potentiodynamic polarization curve of brass in 0.6 M NaCl and 0.6 M NaOH solution containing (0.01 and 0.07)M of $KMnO_4$ is shown in Fig. 1. and Fig.2. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}), calculated using the Tafel extrapolation method are given in Table1. this behavior consist of two main regions were cathodic and anodic Tafel regions. At cathodic region, below section, reduction reactions can occur which involves reduction of hydrogen ions in addition to reduction of oxygen:



while at anodic region, upper section; dissolution of brass can occurs which involves oxidation the copper and zinc metals to metal Chlorides and produce two electrons.



The effect of adding increasing amounts of permanganate anions to 0.6 M NaCl and 0.6 M NaOH , The values of corrosion current density, corrosion potential, corrosion rate, cathodic Tafel slop and anodic Tafel slop decreases by the addition of inhibitor in solution. the addition of $KMnO_4$ shifts the E_{corr} towards more negative values and increases the i_{corr} . shows in Figs.1,2; higher the concentration of $KMnO_4$,

higher the shift in E_{corr} and larger the decreases in i_{corr} values. The corrosion rate decreases from 11.727 to 6.752 mils/year when the concentration of KMnO_4 is increased from (0 to 0.07 M) in 0.6 M NaCl and in 0.6 M NaOH decreases from 22.067 to 7.548 mils/year.

Thus, adding increasing the inhibitor anions adding to 0.6 M NaCl and NaOH on the potentiodynamic polarization curves was investigated. Figure 1. indicates that the increasing of MnO_4^- concentration leads to decreasing the corrosion rate. This result is suggesting that these anions are acting as corrosion inhibitors for the brass alloy in NaCl and NaOH solution. The calculated inhibition efficiency (IE%) from the corrosion rate can be indicated in Table 1. and Fig.3 The inhibition efficiency of MnO_4^- ion increases with increasing of their concentrations. The inhibiting effect of that anion can be explained on the basis of the competitive adsorption between these anions and the aggressive Cl^- ions on the passive electrode surface and thus retards their corresponding destructive action [9]. The inhibitive anions may be incorporated into the passive layer on the alloy surface, forming an improved stability against the aggressive ions. The increase of the Mn content (from inhibitor) in the passive layer leads to a significant increase in corrosion resistance [10,11]. The protective properties of permanganate anion is directly dependent on the pH of the solution, an increase in the concentration of KMnO_4

is accompanied by an increase in the pH and consequently an increase in the stability of the passive film obtained. The corrosion rate of Cu-Zn alloys in basic solution is higher than that in presence of MnO_4^- anion from the corrosion rate of alloy in salt solution, Figure (4,5) shows Photographs microscopy of the brass surface after examining the corrosion with and without addition inhibition to the solutions and that shows for corrosion is less when adding permanganate anion as an inhibitor to the basic solution compared with the corrosion occurred to the alloy in salt solution, which was less than with the addition of inhibitor. This is consistent with the results of the inhibition efficiency (IE%) of brass. This can be illustrated through, The protective properties of permanganate anion is directly dependent on the pH of the solution, an increase in the concentration of KMnO_4 is accompanied by an increase in the pH and consequently an increase in the stability of the passive film obtained. Which leads to a decrease in corrosion.

4-2 Conclusions

1. The permanganate act as inhibitors for the corrosion of the brass alloy samples.
2. The values of corrosion current density, corrosion potential, corrosion rate, cathodic Tafel slope and anodic Tafel slope decreases by the addition of inhibitor.

- 3 .The rate of corrosion with permanganate anion for brass in basic medium is more than the rate of corrosion in salt medium .
3. Efficiency of Inhibitor in basic solution is higher than that in presence of MnO_4^- anion from the Efficiency of Inhibitor for alloy in salt solution.

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Table (1) :Effect of varying concentrations of KMnO_4 on the corrosion behavior of brass in 0.6 M NaCl solution and 0.6 NaOH solution evaluated by polarization and EI% studies.

S.	Solution	Con. inhibitor	E_{corr} (mV -)	i_{corr} ($\mu\text{A.cm}^{-2}$)	R (mpy)	$-\beta_c$	$+\beta_a$	IE%
1-	NaCl	0	1327	80.64	11.727	454.5	158.5	0
2-	NaCl + KmnO_4	0.01M	596	365.14	11.249	252.8	114.5	4.0721
3-	NaCl + KmnO_4	0.07M	456.4	219.17	6.752	235.8	187.2	42.465
4-	NaOH	0	1398	716.26	22.067	683.3	365.5	0
5-	NaOH + KmnO_4	0.01M	1270	521.17	16.057	608	343.3	26.749
6-	NaOH + KmnO_4	0.07M	1085	245	7.548	562.4	313.3	65.745

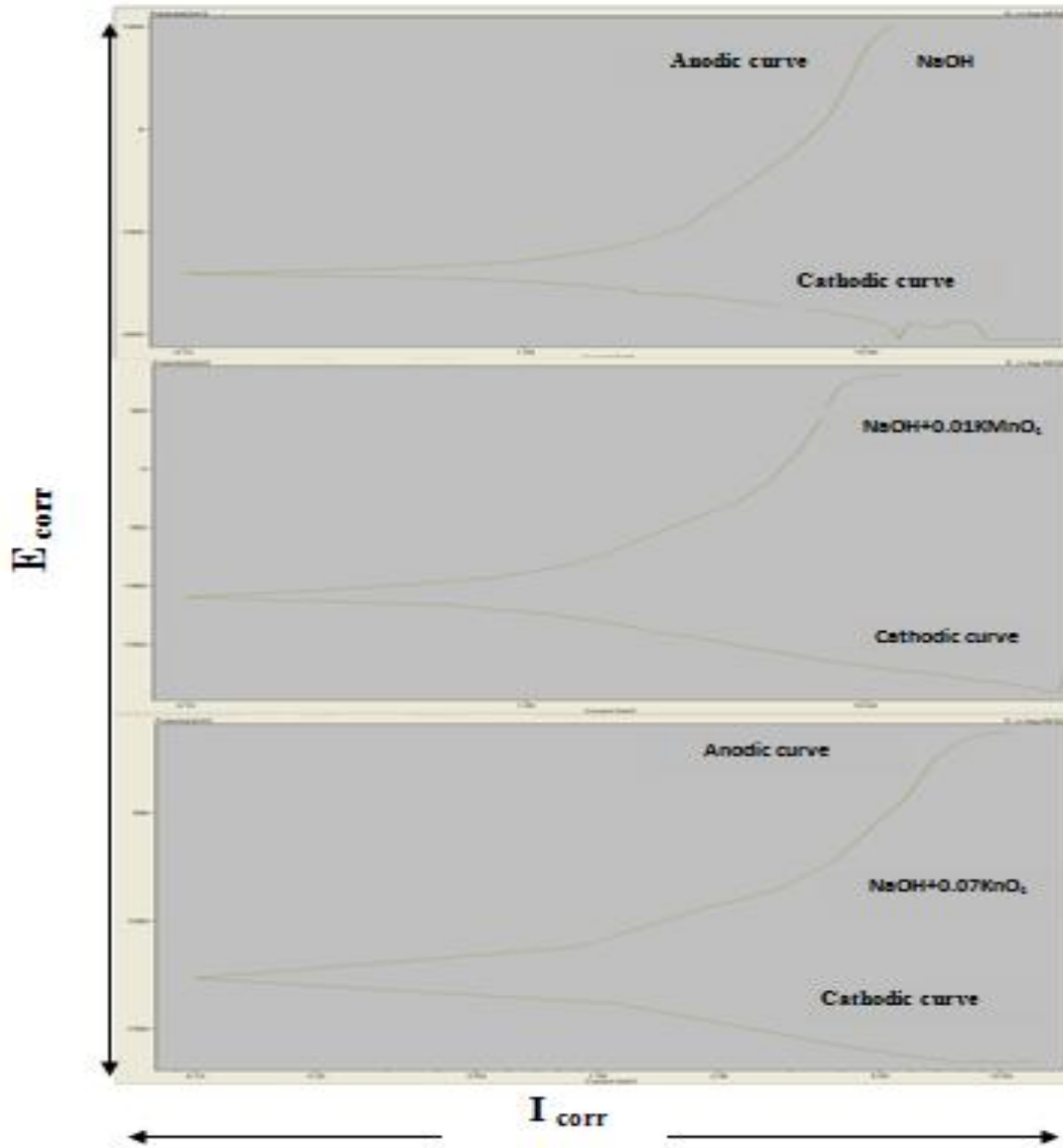


Figure (1) Potentiodynamic polarization curve of brass in (0.6M) NaCl solution containing varying concentrations of (0.01 to 0.07) KMnO_4

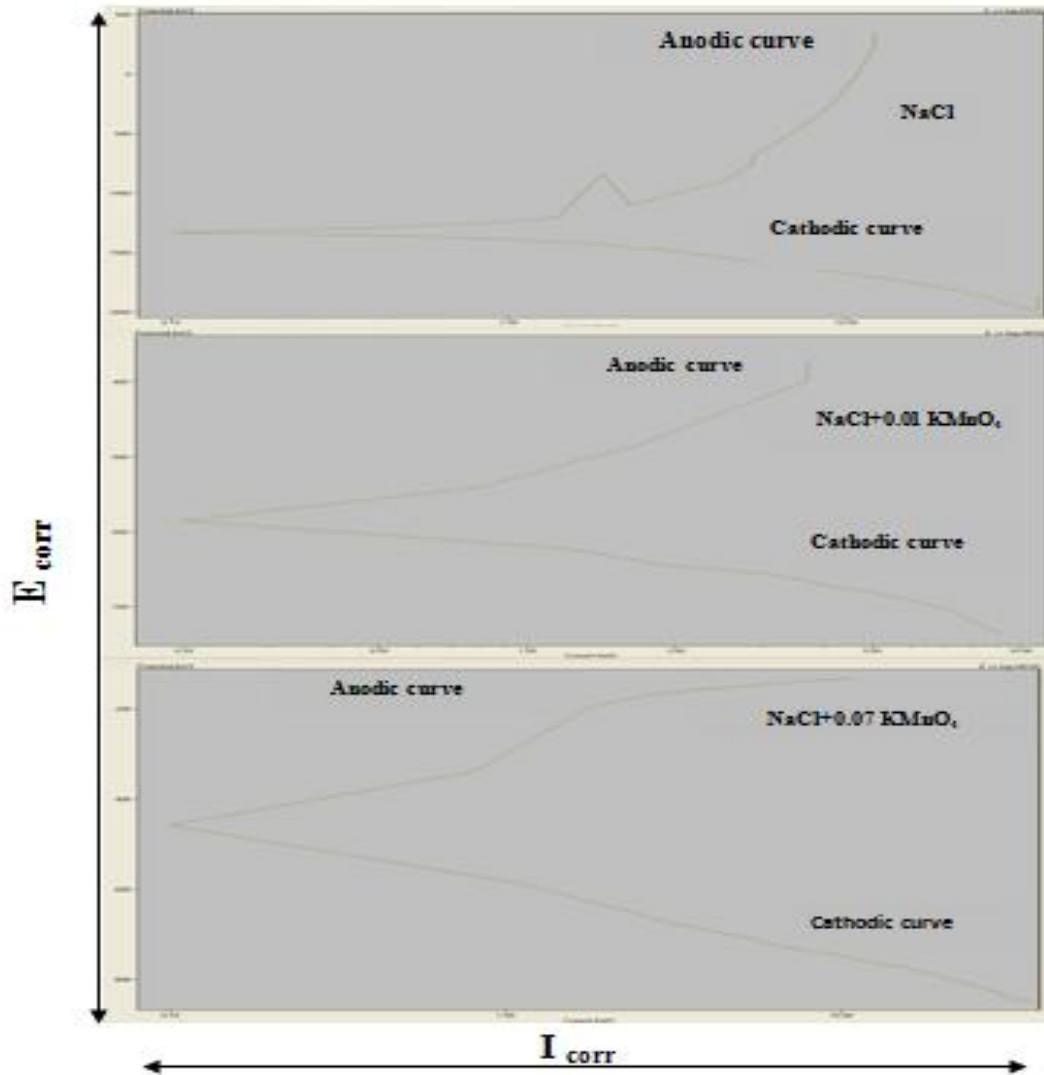


Figure 2. Potentiodynamic polarization curve of brass in (0.6M)

NaOH solution containing varying concentrations of (0.01 to 0.07) $KMnO_4$

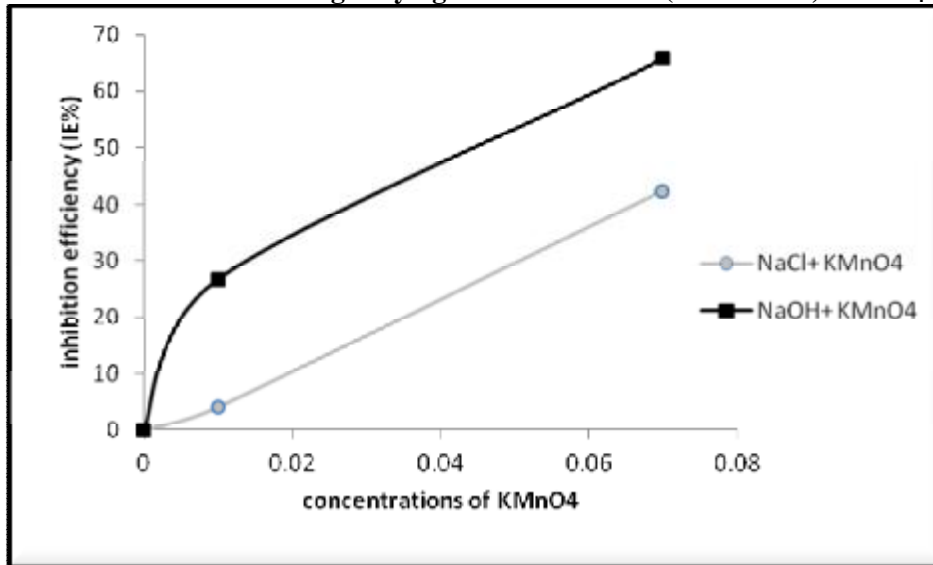
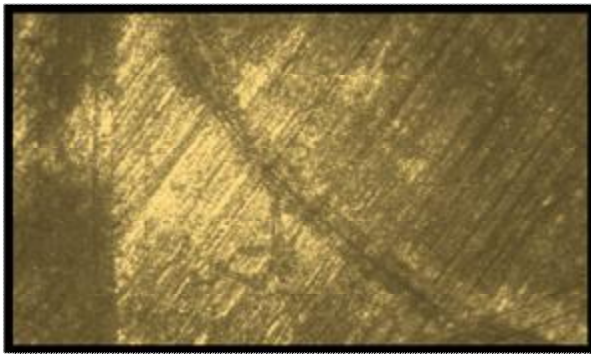
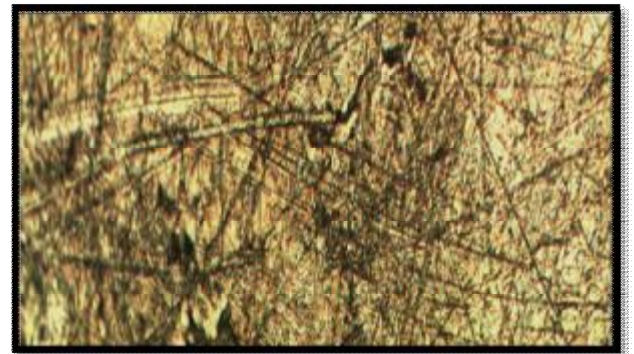


Figure 3. inhibition efficiency (IE%) with concentration of $KMnO_4$

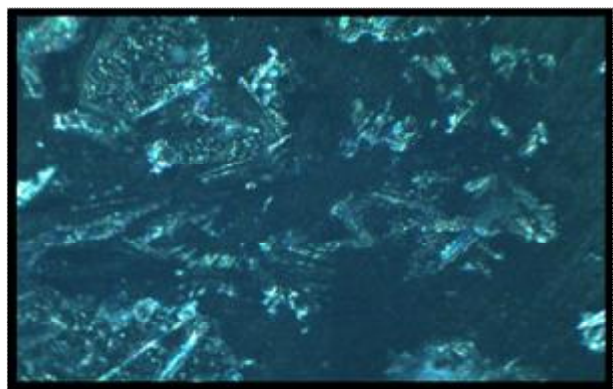


a

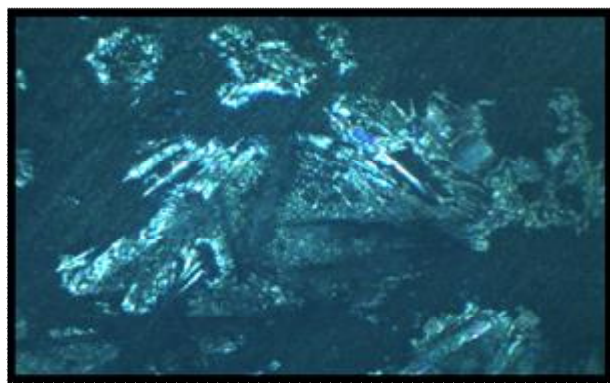


b

Figure.4 Photographs of Sample after corrosion by salt solution NaCl (a) without inhibitor (b) with inhibitor at concentration (0.07M) $KMnO_4$



a



b

Figure. 5 Photographs of Sample after corrosion by basic solution NaOH
(a) Without inhibitor (b) with inhibitor at concentration (0.07M) KMnO_4