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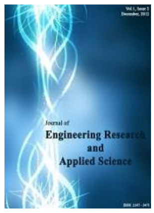

Behavior of Mild Steels by the Action of Corrosion Inhibitors Alone or in Combination in A NaCl Environment

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Abstract

Steel prevention from corrosion is considered one of the essential topics in the industries, of the fatal consequences of this phenomenon. The intention of the research is to look at zinc chloride and potassium molybdate efficiency as mild steel corrosion inhibitors in a harsh environment (NaCl). The results achieved using standard stationary I=f(E) and non-stationary electrochemical techniques (electrochemical impedance) and the mass loss methodology allowed us to evaluate the mixing role of the two inhibitors for better steel protection.

Keywords: *corrosion, steel, inhibitor,* K_2MoO_4, $ZnCl_2$

1. Introduction

Mild steel is the most prevalent type of steel, and it is the market leader in building materials due to its low cost. It has high strength, is rigid, and can be bent and welded into an infinite number of vehicle designs (cars, ships ... etc.) [1, 2]. Due to its unique properties, it has a very good market. The tropical climate (high humidity, significant and constant heat) and the seaside (high chloride level, gaseous emissions linked to the organic decomposition of forest waste, and ultraviolet radiation twice that of temperate zones) promote corrosion. Also, the use of acids the one of causes of deterioration of steel, Hydrochloric acid is a common cleaning agent, acid descaling agent, oil-well acid in oil recovery, petrochemical operations, and steel etching agent [3], which corrodes metals through chemical or electrochemical reactions [4]. This phenomenon considered one of widespread issues in the industry due its worst consequences, On the economic level, the worldwide damage caused by corrosion is estimated to be roughly 2.5 trillion US dollars, or 3.4% of world GDP [5, 6]. In terms of monetary loss, the cost of metallic corrosion in several countries like : Saudi Arabia is around US$900 million, US$26.1 billion in India, US$276 billion in the United States, and US$310 billion in China [7]. Currently, last studies and researchers are interested in mild steel corrosion and its remediation. Indeed, the fight against the corrosion of metals can be envisaged in several approaches, including epoxy polymer coating, have been studied to protect various materials from corrosion[8]. Corrosion inhibitors, on the other hand, are a well-known means of preventing corrosion. and in particular by inhibition of surface reactions. Solution of inhibitor is good to protect material, inhibitor is a stable substance used in small quantities to decrease corrosion rate and preserve metal [9]. Inhibitors often work by adsorbing themselves onto the metal surface by forming a film, nowadays, the most common approach of corrosion prevention is the use of corrosion inhibitors [10]. These inhibitors could be obtained from different sources organic ones or from natural resources , Polyphenol-based extracts may be employed for corrosion inhibition, since these compounds have a great potential for use as eco-friendly metal corrosion inhibitors in a variety of media according to study by Gabsi et al [11]. Schiff bases can be synthesized and

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used for inhibition and showed an excellent performance with various alloys, dehydroacetic acid thiosemicarbazone tested on XC38 carbon steel 1M HCl, with good inhibition efficiency [12]. Extracts derived from natural resources such as herbs, plants, weeds, shrubs, agricultural waste, and other natural sources are frequently used since they are safer and more environmentally friendly than traditional methods [13], several investigations have examined these natural compounds like polysaccharides derived from the prickly pear [13], Rosmarinus officinalis [14]. Citrus aurantifolia [15], Honeysuckle extract [16], and Cinnamomum zeylanicum [17], Cynara cardunculus [18] these compounds were developed and used successfully with various metals in different environments.

However, the look for the application of new types of inhibitors is a crucial step, to improve and increase the efficiency of corrosion inhibition.

This study intends to examine zinc chloride and potassium molybdate as corrosion inhibitors for mild steel in a harsh environment (NaCl), the evaluation of this inhibitor was done by several tests, Stationary and non-stationary including electrochemical methods where polarization curves (Tafel curves) and electrochemical impedance diagrams were used and also mass loss methods.

2. Experimental and numerical methods

2.1. Steel samples preparation

The material for examination is steel, and its constituent composition is as follows: C = 0.10 % wt., S = 0.07 % wt., Mn = 0.07 % wt., Si = 0.15 % wt and balance Fe, in each experiment, The specimens were polished with various classes of abrasive paper and rinsed with distilled water and ethanol.

2.2. Corrosive solutions

The Sodium chloride medium (NaCl at 1M) was used to produce the acidic corrosive solution.

2.3. Methods

2.3.1. Gravimetric method

Mass loss measurement for mild steel was calculated using a Sodium chloride medium solution containing varied inhibitors concentrations K_2MoO_4 and $ZnCl_2$. The cleaned and weighed samples were immersed in inhibitor-free and inhibitor-containing solutions. The samples were weighed after immersion times ranging from one day to ten days.

2.3.2. Electrochemical method

Potentiodynamic polarization was done using a METROHM AUTOLAB (potentiostat/galvanostat). A three-electrode electrochemical system has been used, it's primarily made of a steel working electrode, a platinum auxiliary electrode, and a saturated Ag/AgCl reference electrode; polarization curves are generated at a scanning rate of 0.5 mV/s in the -200 mV to +200 mV range.

3. Results and discussions

3.1. Gravimetric measurements

In weight loss studies, corrosion rate in both of inhibitor absence, $ZnCl_2$ and $ZnCl_2$ + K_2MoO_4 inhibitor. The results illustrated in Fig. 1-2.

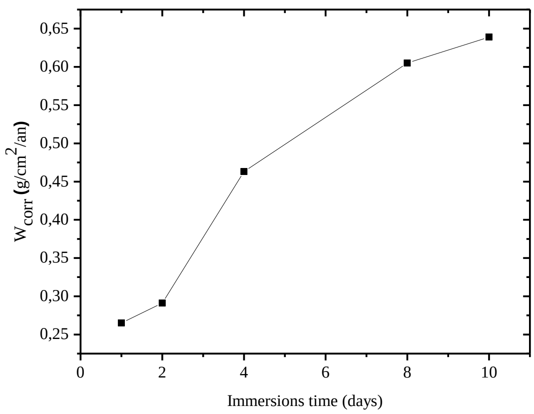


Figure 1. Mild steel amount of corrosion in a 1M NaCl solution without inhibitor within 10 days

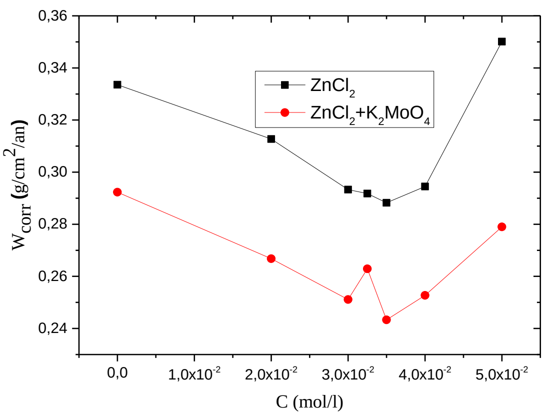


Figure 2. Corrosion rate of mild steel in a 1M NaCl solution, in the presence of $ZnCl_2$ and mixed $ZnCl_2$ + K_2MoO_4 after 10 days of immersion

Figures highlighted the following findings: in the absence of inhibitor, there is an increase in corrosion rate with days, which is reflected in mild steel deterioration; in the presence of only $ZnCl_2$, the addition of increasing doses of it minimizes the corrosion rate until it reaches $3.5.10^{-2}$ mol/l, where the corrosion rate rapidly increases. The inclusion of a mixed inhibitor resulted in a greater drop in corrosion rate and an improvement in corrosion inhibition efficiency [19].

3.2. Electrochemical measurements

3.2.1. Open circuit potential

Fig. 3 depicted the effect of various NaCl concentrations ranging from 0.1M to 1 M in mild steel in the lack of an inhibitor, indicating that increasing the concentration increased the corrosion potential [20].

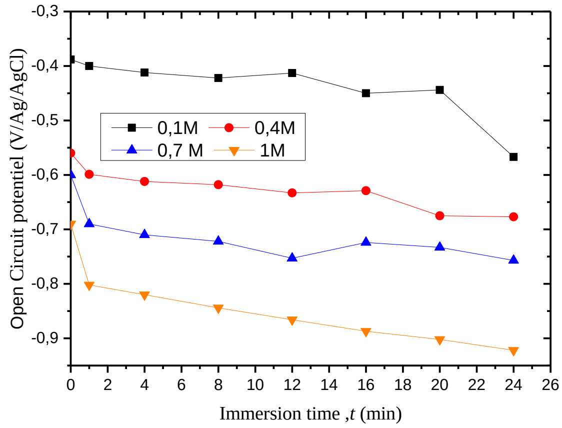


Figure 3. Variation of corrosion potential with time of steel mild immersed in various concentration of blank solution ranging from 0.1M to 1 M.

3.2.2. Polarization curves (Tafel curves)

Fig. 4 present Tafel curves in both of presence of $ZnCl_2$, K_2MoO_4 and mixed inhibitor $ZnCl_2$ + K_2MoO_4 in different concentrations.

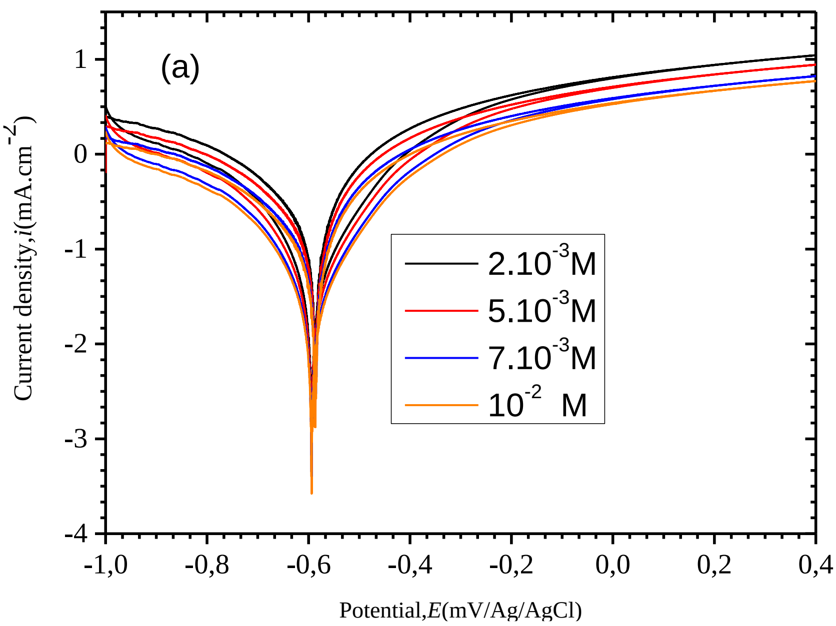
As the inhibitor concentration increases, the current density "I_{corr}" decreases and, as a result, the polarization resistance "Rp" increases. Which led to more protection against corrosion. The addition of mixte inhibitor provides more corrosion efficiency with the concentration increasing.

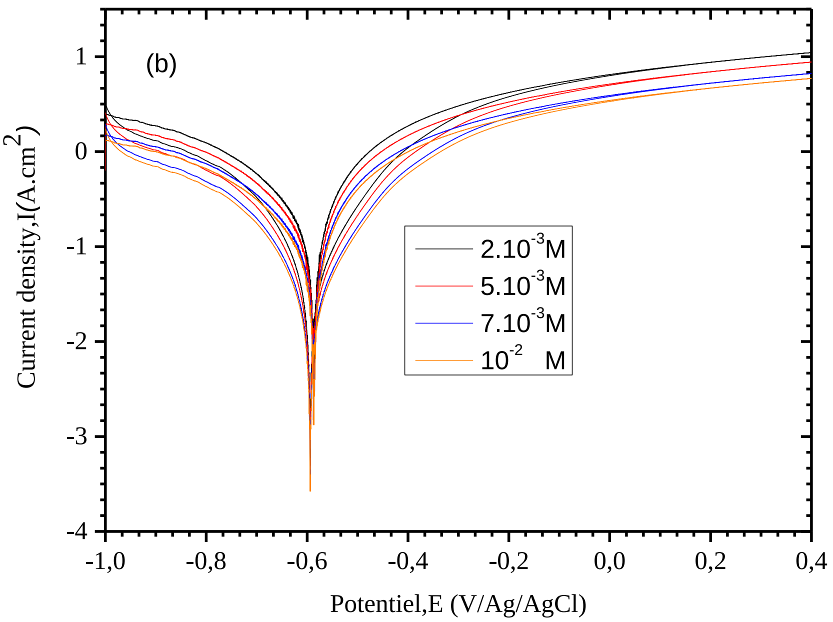
In case of $ZnCl_2$ the best results obtained in concentration of 7.10^{-3} M with Rp = 2886 Ω cm² and inhibition efficiency = 82%, in K_2MoO_4 inhibitor case, best results also got in concentration of 7.10^{-3} M with Rp= 1480 Ω cm² and inhibition efficiency = 72%.

Meanwhile, the best results and maximum results obtained with mixing $ZnCl_2$+ K_2MoO4 inhibitors with concentration 7.10^{-3} M with an efficiency = 99%, and must mentioned that all inhibition efficiency results of mix inhibitors are more than 85%.

3.2.3. Electrochemical impedance diagrams

Fig. 5 illustrates the results of Nyquist diagrams for steel specimen in 1M NaCl In without and with of different inhibitor doses.





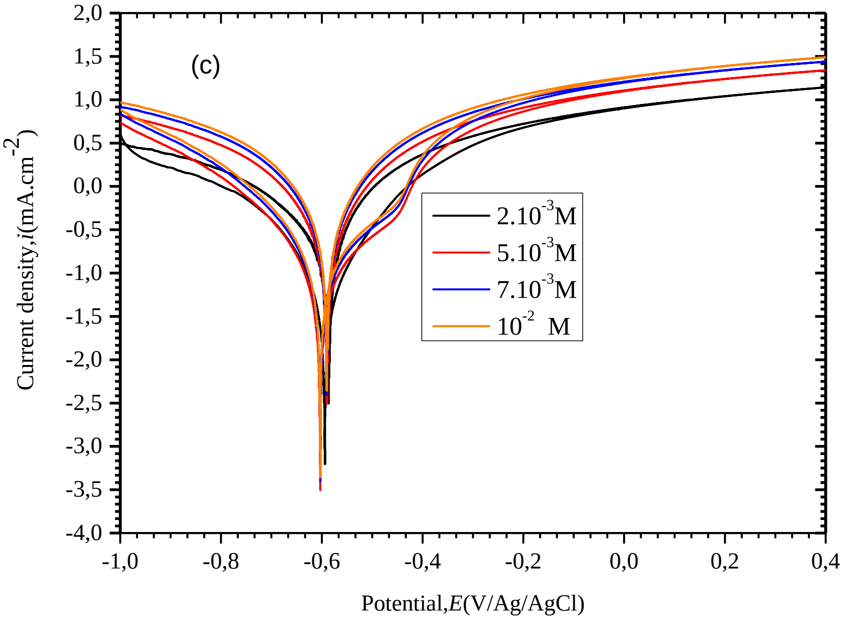
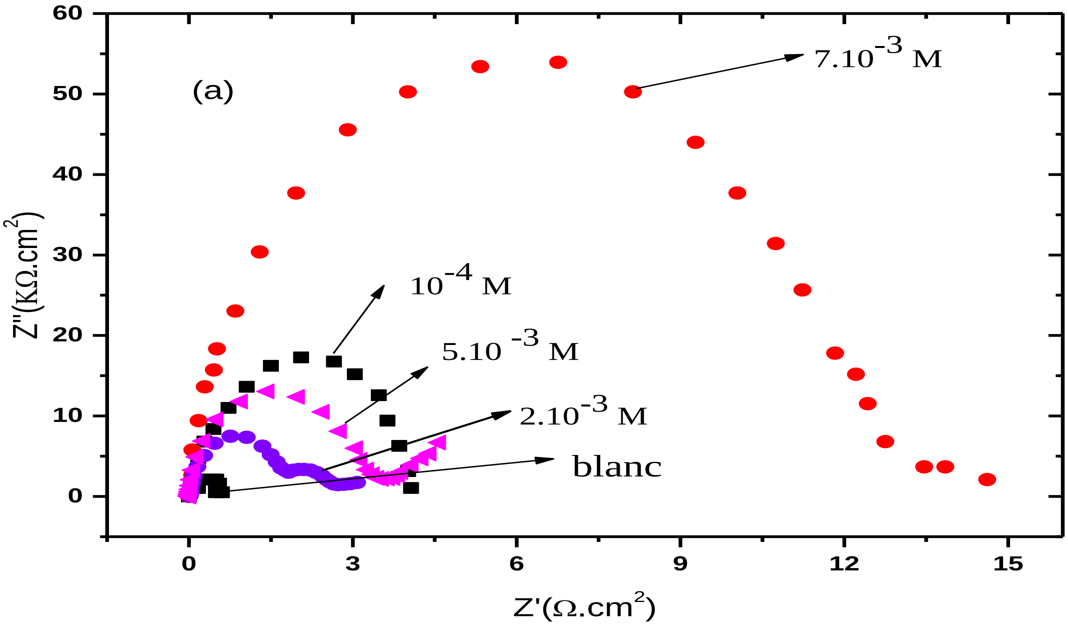
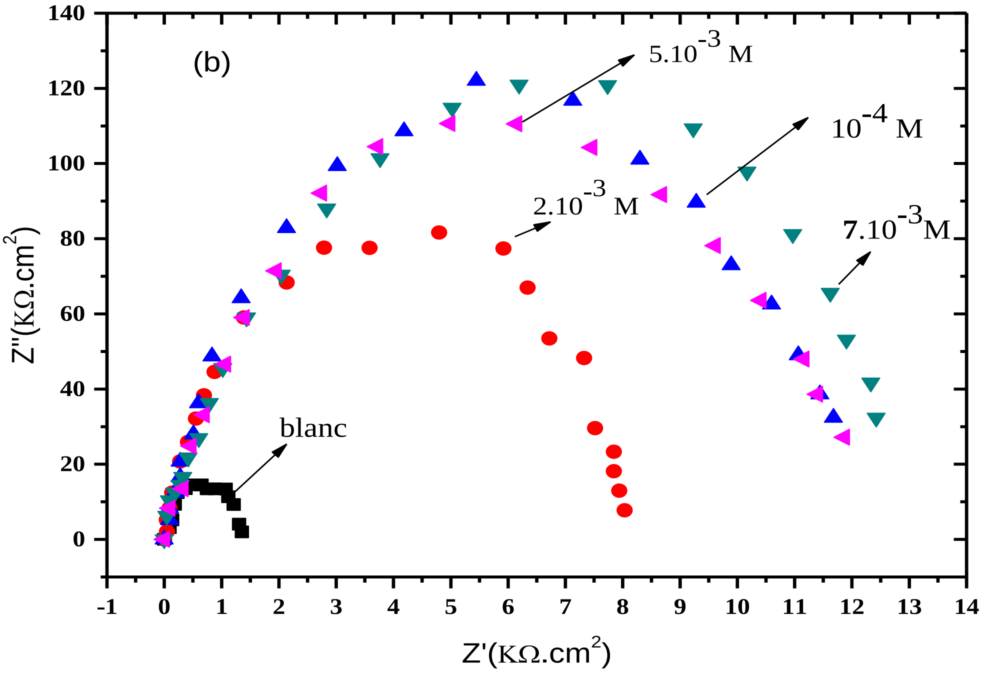


Figure 4. Tafel curves of mild steel in 1 M NaCl in presence of (a) $ZnCl_2$, (b) K_2MoO_4 and (c) mixed inhibitor $ZnCl_2$ + K_2MoO_4 in different concentrations


(a)
7.10-3 M
10-4 M
5.10 -3 M
2.10-3 M
blanc
Z''(KΩ.cm2)
Z'(Ω.cm2)
60
50
40
30
20
10
0
0
3
6
9
12
15


(b)
5.10-3 M
10-4 M
2.10-3 M
7.10-3M
blanc
Z''(KΩ.cm2)
Z'(KΩ.cm2)
140
120
100
80
60
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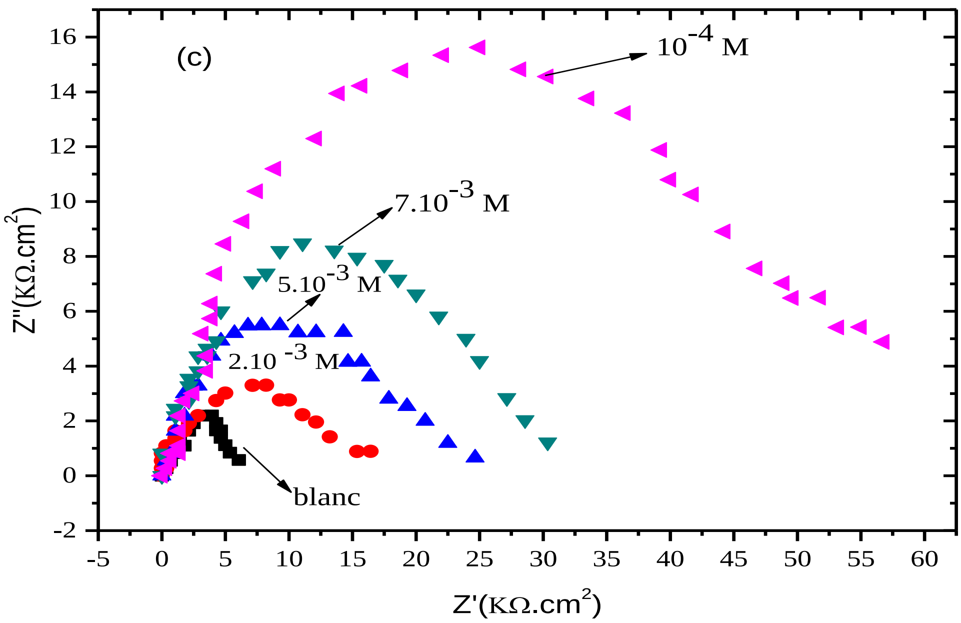

Figure 5. Nyquist diagrams for mild steel in 1M NaCl in the absence and presence of different concentrations of inhibitors (a) $ZnCl_2$, (b) K_2MoO_4 and (c) K_2MoO_4+$ZnCl_2$

Results of Figure 5 confirmed the Tafel curves findings, where in case of $ZnCl_2$, best results got in 7.10^{-3} M in both of $ZnCl_2$ and K_2MoO_4, where the largest half circles obtained in this concentration
In case of the inhibitor of K_2MoO_4+$ZnCl_2$, the largest half circles recorded in concentrations 10^{-2} M and 7.10^{-3}M.

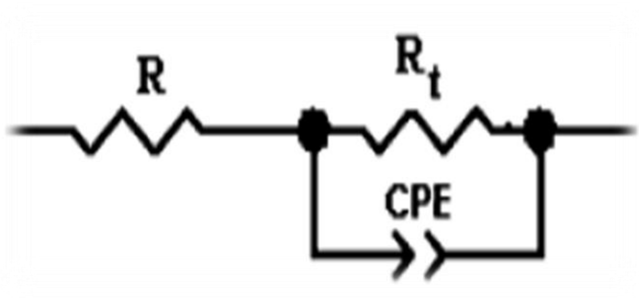

Figure 6. Equivalent circuit diagram for the metal-electrolyte interface

Figure 6 depicted the equivalent circuit, which comprises of a constant phase element (CPE) connected in parallel with a resistor R_{ct}.

4. Conclusion

Nowadays, extensive research has been conducted to better understand the kinetics of the development of protective corrosion products in response to various conditions.

The electrochemical behavior of mild steel in the absence and presence of numerous inhibitors (K_2MoO_4+$ZnCl_2$) in an aggressive solution (1M NaCl) is the objective of this study.

The results obtained using traditional stationary I=f(E) and non-stationary electrochemical techniques (electrochemical impedance) and the mass loss methodology allowed us to evaluate the mixing role of the two inhibitors for improved steel protection, where the best inhibition efficiency = 99% obtained in concentration of 7.10^{-3} M, with an inhibition of corrosion rate much Better than using each inhibitor separately.

Acknowledgements
Some results in this paper were presented at the 6^{th} International Colloquium of corrosion and material's protection CMP'22 Which was held between 12 and 15 December 2022 in Hammamet, Tunisia (https://cmp22.corrosioncolloquium.com/).

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