Corrosion Behavior of Nickel Electrode in NaOH Solution and Its Inhibition by Some Natural Oils

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The corrosion behavior of the nickel electrode in NaOH solution was investigated using open circuit potential measurements, galvanostatic, and potentiostatic polarization techniques. The effect of open circuit potential, current densities, NaOH concentration, Cl^- anions, and some natural oils e.g. sesame oil, water cress oil, wheat germ oil and almond oil as an inhibitors for corrosion of the nickel in1 $x10^{-2}$ M NaOH solution was studied. The percentage inhibition efficiency was found to increase with increasing concentration of these oils. The inhibitive action of these oils was explained due to the adsorption on the Ni surface, making barrier to mass and charge transfer, The adsorption process follows Freundlish isotherm. The inhibition efficiency decreases in the order: sesame oil> water cress oil > wheat germ oil > almond oil.

1. INTRODUCTION

Nickel is one of the most important metals and is similar to iron in most of its properties. The corrosion and anodic behavior of nickel were studied in acidic, neutral and alkaline solutions in order to improve the processes of chemical machining nickel and its alloys [1]. Common uses of nickel include production of stainless steel and other corrosion resistance metals containing nickel [2, 3]. Nickel is also used in electroplating [4] electroforming [5] , and sintered metal coatings [6]. The corrosion resistance of nickel is due to the corrosion media [7]. Nevertheless, nickel could be attacked by alkaline media in considerable rate. Thus, its corrosion rate must be controlled. One of the useful

methods of controlling the corrosion process is the addition of corrosion inhibitor. However, most of the available inhibitors are toxic compounds [8] that should be replaced with new environmentally friendly inhibitors, research is focused on the use of natural products. Several investigations have been reported using economical and naturally occurring substances as corrosion inhibitors [9-15]. Previous work examined extract of henna (lawsonia) as corrosion inhibitor of C- steel, nickel and zinc in acidic, neutral and alkaline solutions [16]. The inhibition effect of this extract was explained as adsorption of the phytoconstituent of lawsonia or henna molecules on the metal surface. Also, natural honey [17] and guar gum [18] was used to inhibit the dissolution of C-steel in acidic solutions. The eugenol derivatives, the main constituent of clove oil, were used to inhibit the metal corrosion [19,20]. The natural clove oil was used as corrosion inhibitor for dissolution of nickel, Inconel 600, and Inconel 690 in 1×10^{-2} M HCl solution using potentiostatic polarization technique [21].

The aim of this work is to study the effect of open circuit potential, current densities, NaOH concentrations, Cl^- anions, and some natural oils e.g. sesame oil, water cress oil, wheat germ oil, and almond oil as corrosion inhibitors on oxide film growth on nickel electrode in 1×10^{-2} M NaOH solution using open circuit potential measurements, galvanostatic, and potentiostatic techniques.

2. EXPERIMENTAL

Pure nickel electrode (99.99%) was used in the present work. For chemical and electrochemical experiments, a cylindrical rod was embedded in araldite leaving an exposed bottom area of (0.196cm²), and used as working electrode. This working electrode was polished with different grades of emery papers, degreased with acetone and washed with running distilled water, before its immersion in the test solution. A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. In galvanostatic polarization technique, before anodic polarization, the nickel electrode was subjected to a cathodic pretreatment process for 10 min. in the test solution with the same polarizing current density (i= 100 to 160μA/cm² until a constant potential was reached). This process was done to reduce any oxides film that formed spontaneously on the metal surface before the experiment. The polarized current was then reversed, and the potential was recorded as function of time (anodic polarization). In potentiostatic polarization technique, the inhibition efficiency (IE) and the surface coverage (θ) were calculated using the following equations:

$$\% \ IE = [(I - Ii) \ / \ I] \ x \ 100 \qquad (1)$$
$$\theta = \ [(I - Ii) \ / \ I] \qquad (2)$$

where I and Ii are the corrosion rates in free and inhibited alkaline solutions respectively. All chemicals used for preparing the test solution were of analytical grade and the experiments were carried out at room temperature 25º±1 º C.

The main constituents of oils are:

- Sesame oil has vitamin A formula + H.
- Water cress oil is γ linolinic acid.
- Wheat germ oil is mixture of (31% oleic acid- 12% palmitic acid - 1% linolinic acid).
- Almond oil is a mixture of (68 % oleic acid- 25% linolenic acid-4% palmitic acid).

3. RESULTS AND DISCUSSION

3.1.1. Variation of the potential of the nickel electrode with time in sodium hydroxide solution

Figure (1) represents the variation of the open circuit potential of nickel electrode in different concentrations of NaOH solution with time till the steady-state potential, E_{st} is attained. It is observed that the electrode potential of the Ni electrode is shifted to more noble values reveals that the pre-immersion air-formed NiO film, found initially on the surface of the metal, is not sufficient to impart passivity and that healing and thickening of the film. Inspection of figure 1, the potential of Ni electrode is shifted directly into noble direction with time in different concentrations of the NaOH solution till the steady-state potentials, E_{st}, is attained. The obtained results illustrate that, as the concentration of NaOH solution increased the steady-state potentials, E_{st}, are shifted from the negative values and tend towards less negative values.
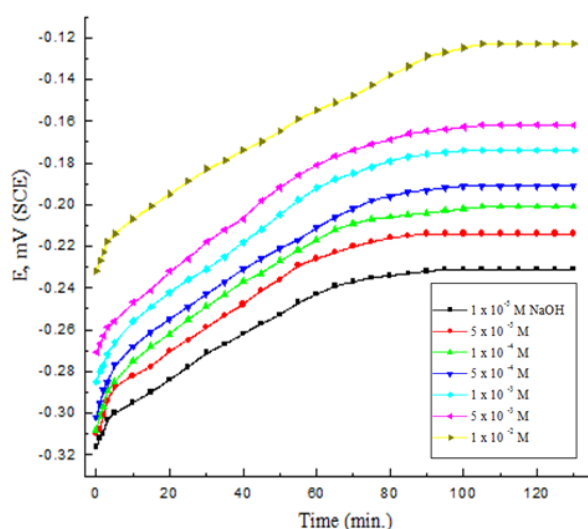

Figure1. Variation of potential of nickel electrode with time in different concentrations of NaOH solution.

The variation of the steady-state potential, E_{st}, with the logarithm of the molar concentration of NaOH is plotted in Fig (2) .Straight line relationship is obtained and satisfying the following equation:

$$E_{st} = \alpha_1 - \beta_1 \log C_{agg} \qquad (3)$$

where, α_1 and β_1 are constants. Similar behavior was also reported for Fe[22], Zn[23,24], Cd[25], Pb[26], and with these last metals, active corrosion was operative, the intensity of which increased with the increase of the anion content of the solution [22],
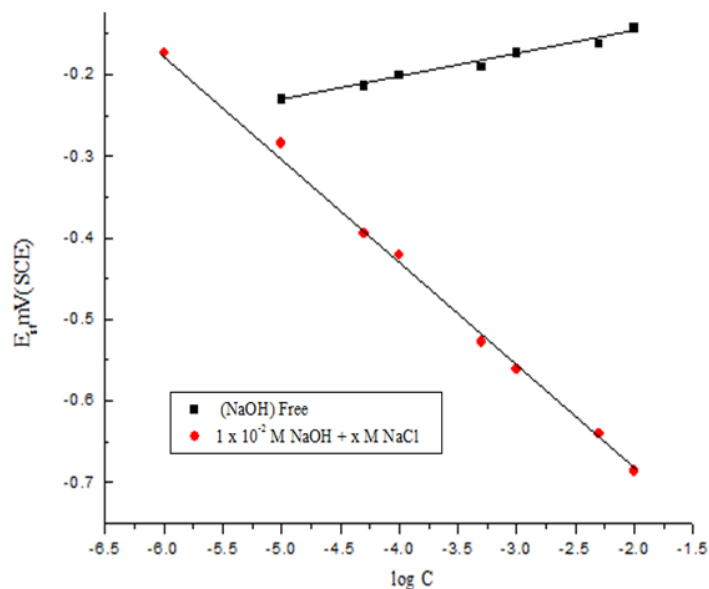
Figure2. Relation between steady state potential of nickel electrode with logarithm of concentration of NaOH and NaCl solutions.

3.1.2. Variation of the open circuit electrode potential of nickel in NaOH solution in the presence of the corrosive anions (Cl⁻):

Figure (3) represents the variation of open circuit potential of nickel electrode in 1×10^{-3} M NaOH with different concentrations of NaCl.
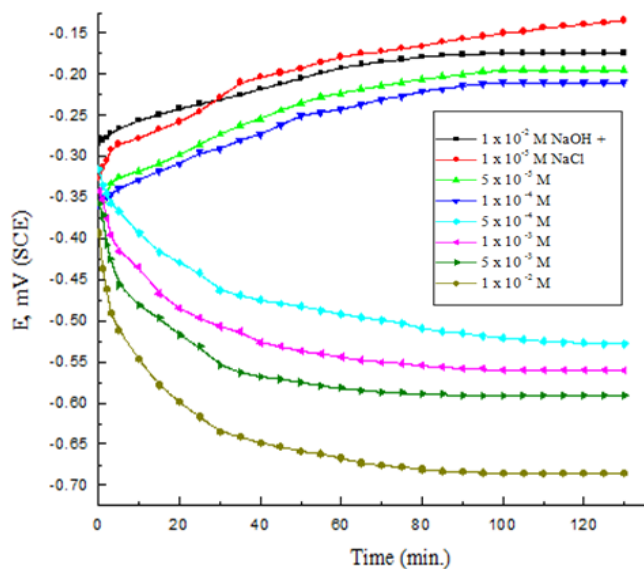

Figure 3. Variation of potential of nickel electrode in 1×10^{-2} M NaOH solution with time in absence and presence of different concentrations of NaCl solution.

Inspection of the curves of this figure, the following conclusions could be drawn:

1.   The presence of small concentrations of NaCl has practically no effect on the stability of the passivating oxide film, but they enhance the process of film-repair and the potential of Ni electrode shifts in the more positive direction. This attributed to the precipitation of Ni^{2+} salts or one of its basic salts on the active sites existing on the nickel surface.

2.   In presence of higher concentrations of the NaCl, the Ni electrode acquires new steady-state potentials which become more negative the higher the corrosive ion content.

The variation of the final steady-state potential of the Ni electrode with the logarithm of the molar concentration of NaCl could be seen in Fig (2). After a definite corrosive ions concentration, which depends on its type, invariably straight lines were obtained which fulfill Brasher's equation (3) [22]. It is clear from the curve that the Cl⁻ anion promotes the corrosion of nickel and the extent of corrosion promotion increases with the salt concentration.

3.1.3. *Effect of addition of some natural oils as inhibitors on the corrosion of the nickel electrode in NaOH solution:*

Figure (4) represents the variation of the nickel electrode potential with time in $1x10^{-2}$ M NaOH + $5x10^{-3}$ M NaCl with different concentrations of sesame oil as an example of oils .Similar curves were obtained in case of other oils not shown.
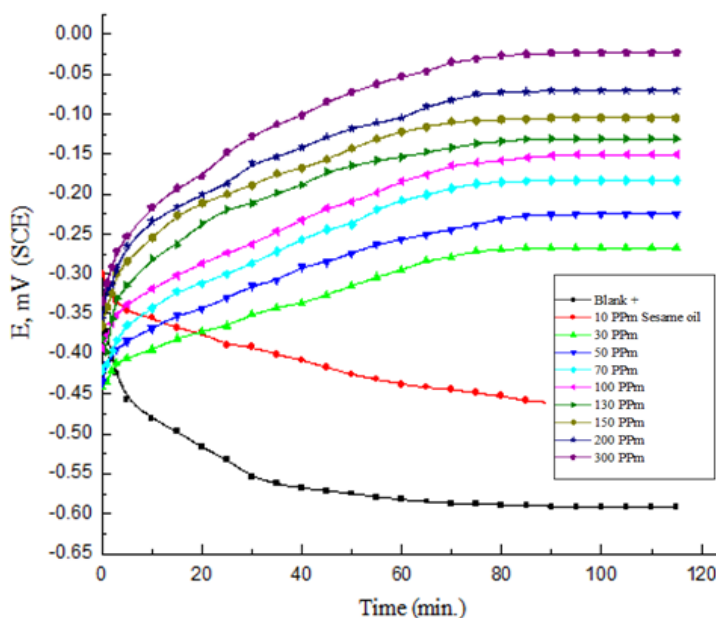

Figure 4. Variation of potential of nickel electrode in $1x10^{-2}$ M NaOH + $5x10^{-3}$ M NaCl solution with time in absence and presence of different concentrations of Sesame oil.

From curves of Fig. (4), the addition of sesame oil there is a shift of electrode potential from negative value to less negative value until reach steady-state potential. Where, the steady-state

potential is reached from negative value and becomes nobler with increasing concentration of sesame oil than the steady-state potential in inhibitor-free solution.
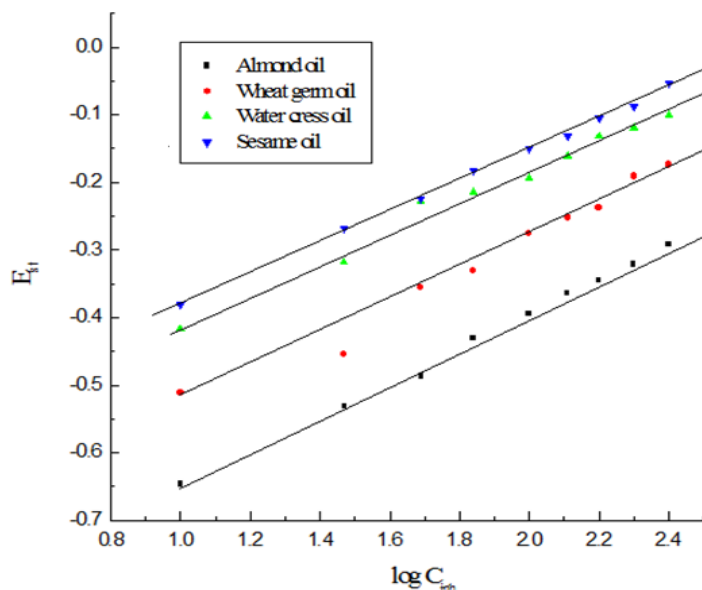

Figure 5. Relation between steady state potential of nickel electrode with logarithm of concentration of inhibitor in 1×10^{-2} M NaOH + 5×10^{-3} M NaCl solution.

The variation of the steady-state potential of nickel, with the logarithm of the molar concentration of these oils is shown in Fig. (5). Straight lines were obtained satisfying the equation:

$$E_{st} = \alpha_2 + \beta_2 \log C_{inh} \qquad (4)$$

where, α_2 and β_2 are constants depending on the nature of the metal and type of anions used. It is clear that, increasing the concentration of one and the same additive causes the shift of the steady-state potential of the nickel into the positive direction. This behavior could be explained on the basis of increasing the inhibiting action of the additive. On the other hand in 1×10^{-2} M NaOH + 5×10^{-3} M NaCl solution and the different inhibitors are depending on the type of the natural oils. Thus, one can arrange the efficiency of these oils as corrosion inhibitors according to their ennobling the steady-state potential of Ni electrode. The sequence of arrangement decreases in the following order: sesame oil > water cress oil > wheat germ oil > almond oil.

3.2. Galvanostatic Polarization Behavior of Nickel in Sodium Hydroxide solution:

3.2.1. The effect of current density

Galvanostatic anodic polarization of nickel electrode in 1×10^{-2} M NaOH solution at 25 ^{o}C using various current densities was studied. Fig. (6) shows the anodic potential -time curve recorded in $1 \times 10^{-}$

[2] M NaOH solution. From the variation of the potential of the nickel anode with time, it can be seen that, there is a rapid and almost linear change of potential (region I) due to both the decay of hydrogen over potential and the subsequent charging of electrical double layer at the metal/ solution interface [25-27], This process occurred over potential range depending upon the magnitude of the polarization current and solution concentration [26]. In (region II), Fig. (6), the anodic potential begins to increase in a linear fashion with time. At this stage, sufficient oxide has accumulated on the electrode surface and therefore, the rate oxide film formation was higher than the rate of oxide dissolution [28]. Finally, the polarization curves of Fig. (6) (region III) deviated from linearity to a reach steady state potential value, E_{st}, which depends upon the concentration of electrolyte and the imposed current density. The potential deviation indicated a decrease in oxide growth efficiency [26, 29-32], since at this stage, both oxygen evolution and transformation of β-Ni(OH)$_2$ can be oxidized to β-NiOOH at higher potentials via a deprotonation reaction [33],

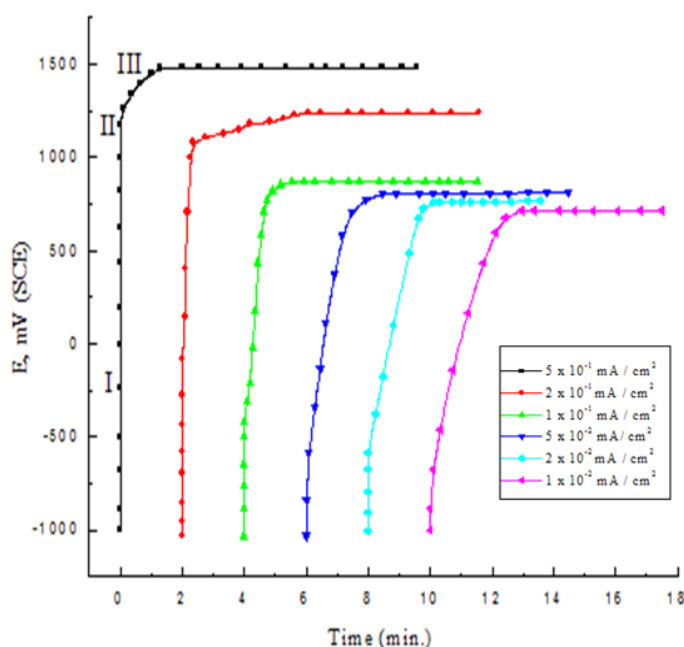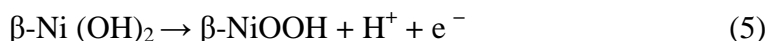$$\beta\text{-Ni (OH)}_2 \rightarrow \beta\text{-NiOOH} + H^+ + e^- \tag{5}$$

Figure 6. Anodic polarization curves of nickel electrode in 1x10^{-2} M NaOH solution at 25 ^{o}C at different current densities.

Figure (7) There is a relation between log (dE/dt)$_i$. vs. log (i) for 1x10^{-2} M NaOH solution, straight line will appear according to this empirical equation:

$$(dE/dt)_i \rightarrow \alpha\,(i)^{\beta} \tag{6}$$

or

$$\log (dE/dt)_i \rightarrow \log \alpha + \beta \log I \tag{7}$$

where α and β are constants characteristics of the metal/solution system [31], where the value of the constant, α, in eq. (7) was found to be concentration dependent while the value of the constant, β, of the parallel line was 54×10^{-2}. It is clear from Fig. (7), that the oxide film formation rate increases with increasing imposed current density, i, at the same sodium hydroxide concentration.
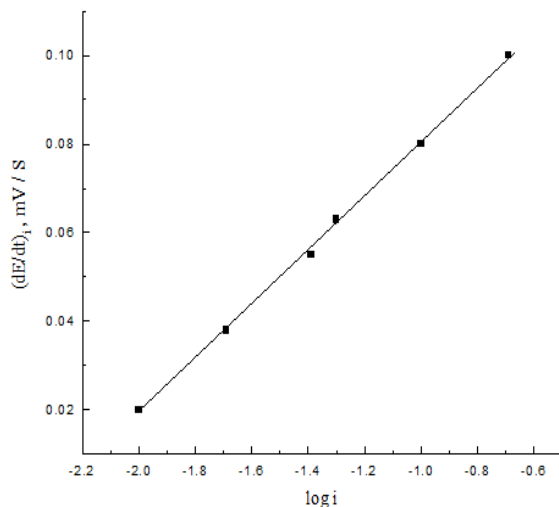

Figure 7. Relation between logarithm of oxide formation rate, log (dE/dt), and logarithm of current density, i, in 1×10^{-2} M NaOH solution.

3.2.2. The effect of concentration of NaOH solution:

The anodic polarization experiments were carried out in concentration range from 1×10^{-4} M to 1×10^{-1} M NaOH solutions at constant current density, i, of 1 mA/cm^2. From Fig. (8), the starting potential of the arrest, E_{ar}, the duration of the passivation time, t, the oxide formation rate $(dE/dt)_i$, and oxygen evolution potential, E_{st}, were affected as the concentration of the solution increased.
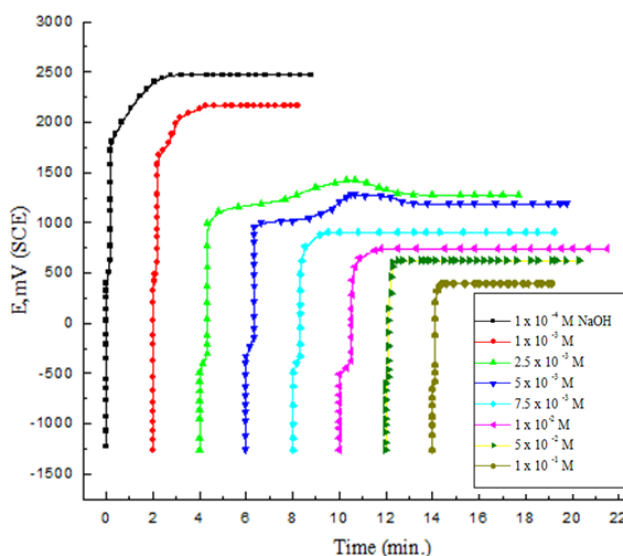

Figure 8. Anodic polarization curves of nickel electrode at a current density of 1 mA/cm^2 in different concentrations of NaOH solution.

Figure (9) shows the relation between potential of the arrest, E_{ar}, and the logarithm of NaOH concentration. It is obvious that the potential of the arrest, E_{ar}, decreases linearly with increasing OH⁻ anions concentration.
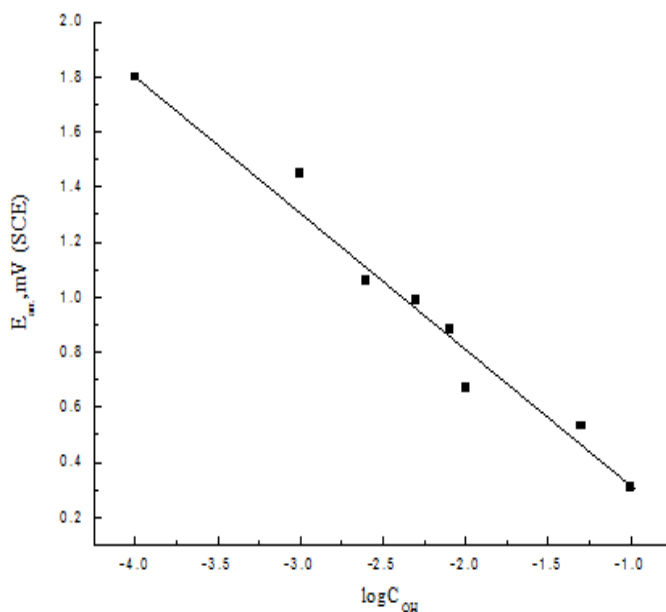

Figure 9. Relation between potential of the arrest, E_{ar}, and logarithm of NaOH concentration.

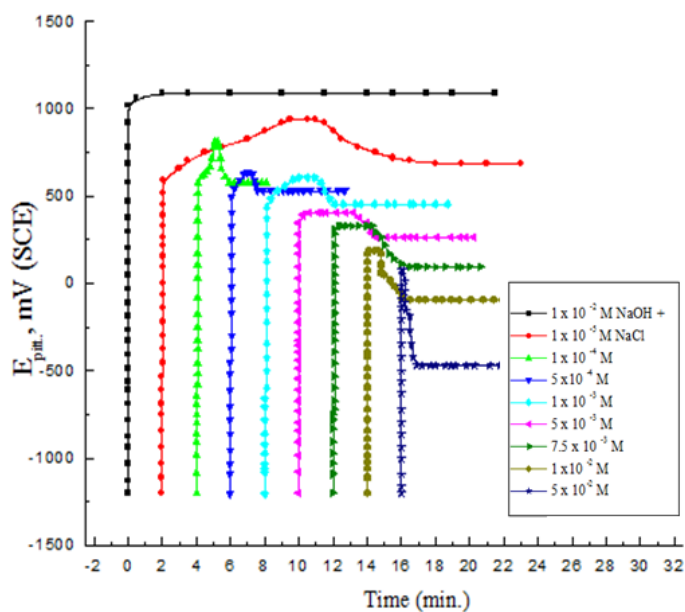### 3.2.3. *The effect of aggressive anions:*

Figure 10. Anodic polarization curves of nickel electrode in 1×10^{-2} M NaOH solution at a current density of 1 mA/cm^2 in absence and presence of different concentrations of NaCl solution.

Figure (10) shows the galvanostatic anodic polarization experiments on Ni electrode in 1×10^{-2} M NaOH solutions in absence and presence of NaCl as pitting corrosion agent, at current density 1 mA/cm^2. Where at low concentration, there is no change on the shape of the polarization curve recorded in halide free solution. By increasing of concentrations of Cl$^-$ anions cause a drastic change in the anodic behavior of nickel and there is a destruction of passivity film and initiation of pits [25,27,34]. Where the breakdown potential shifts towards more negative values as concentration of the Cl$^-$ anion increases in the solution.

The dependence of the breakdown potential on the concentration of the halide anions can be seen in Fig.(11). This figure represents the plot of the breakdown potential $E_{pitt.}$, vs. the logarithm of the Cl$^-$ anions, C_{Cl}^-, this fulfills the following equation:

$$E_p = \alpha_3 - \beta_3 \log C_{agg} \tag{8}$$

where α_3 and β_3 are constants. The value of the constant, α_3 and β_3, in Eq.(8) is observed to depend on the type of halide anion and S shape reflects its tendency towards the aggressive action.
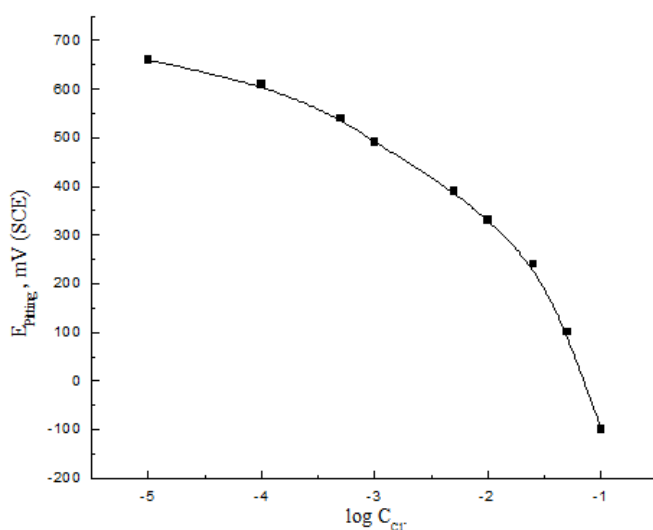

Figure 11. Relation between logarithm of chloride ion concentration and breakdown potential.

3.2.4. Effect of addition of some natural oils as an inhibitors on the corrosion of the nickel electrode in NaOH solution

Figure (12) represents the effect of addition of increasing concentrations of sesame oil as an example of the studied oils as pitting corrosion inhibitors on galvanostatic polarization curves of Ni electrode in 1×10^{-2} M NaOH + 1×10^{-2} M NaCl at 1 mA/cm^2 at 25 ^{o}C. Similar curves were obtained for other oils. From curves of figure (12), small concentrations of sesame oil, there is a shift of pitting potential towards more positive values. Apparently, the additives compete with the aggressive Cl$^-$ anions for adsorption sites on the metal surface reducing, thus their surface concentration. As the concentration of the additives is further increased, the extent of the potential oscillation is markedly decreased and finally reaches a stable potential whose value depends on the type of the added inhibitors
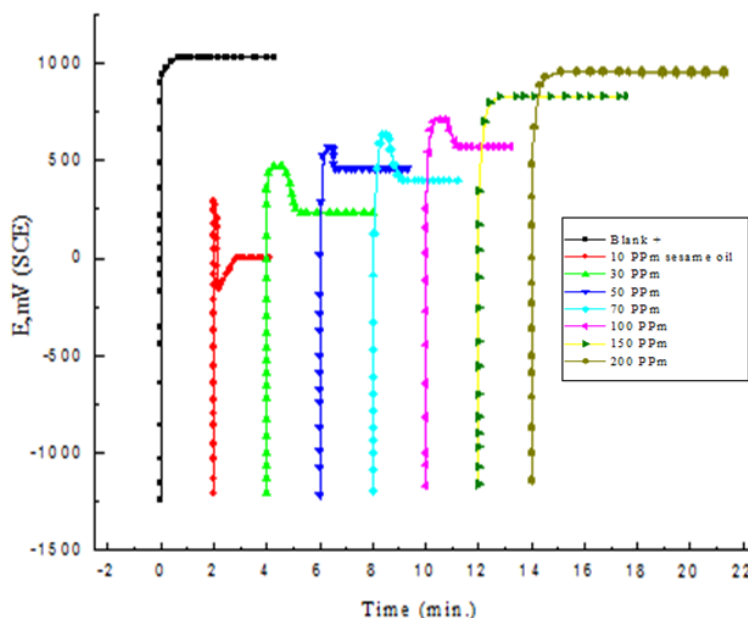
Figure 12. Anodic polarization curves of nickel electrode in 1×10^{-2} M NaOH + 1×10^{-2} M NaCl solution at a current density of 1 mA/cm^2 in absence and presence of different concentrations of Sesame oil.

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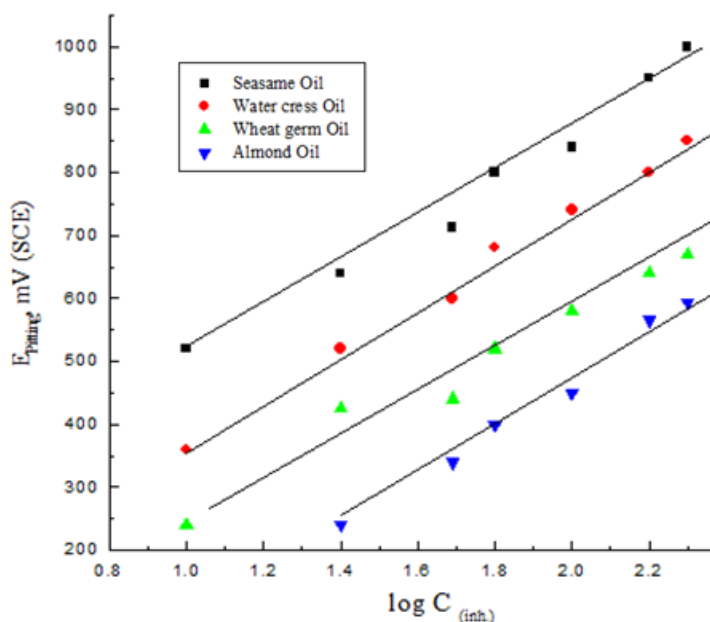
Figure 13. Variation of breakdown potential, E$_{pitt}$, with logarithm concentration of inhibitors.

The dependence of the pitting potential of Ni electrode, E$_{pitt}$, on the concentration of the added these natural product oils can be seen by the curves of Fig. (13). This figure represents the variation between E$_{pitt.}$ and log C$_{inh.}$ according to the following relation:

$$E_{pitt.} = \alpha_4 + \beta_4 \log C_{inh} \qquad (9)$$

where α_4 and β_4 are constant, which depend on both type of additive and the nature of the electrode. Inhibition affords by these compounds decreases in the following order: (sesame oil > water cress oil > wheat germ oil > almond oil).

3.3. Effect of Natural Oils on the Potentiostatic Polarization Behavior of Nickel in Sodium Hydroxide Solution

The effect of addition of some natural product oils (sesame oil, water cress oil, wheat germ oil, almond oil) on the anodic and cathodic polarization curves for Ni in 1×10^{-2} M NaOH solution at 25° C was studied. The effect of increased concentration of sesame oil is represented in Fig. (14) as an example. However, similar curves were obtained for other three oils (not shown). From Fig. (14) one can observe at first a transition region in which the potential increases (anodic polarization) or decreases (cathodic polarization) slowly with current density, followed by a rapid linear build up of the potential with current density (Tafel region). The transition region starts from the corrosion potential and extends to the beginning of the tafel region starts from the corrosion potential and extends to the beginning of the tafel region and characterized by simultaneous occurrence of cathodic hydrogen evolution and anodic dissolution of the electrode sample [35]. The inspection of curves of figure (14) show that the polarization curves are shifted toward less negative potential and less current density upon addition of sesame oil. This result confirms the inhibitive action of sesame oil toward the corrosion of Ni electrode.
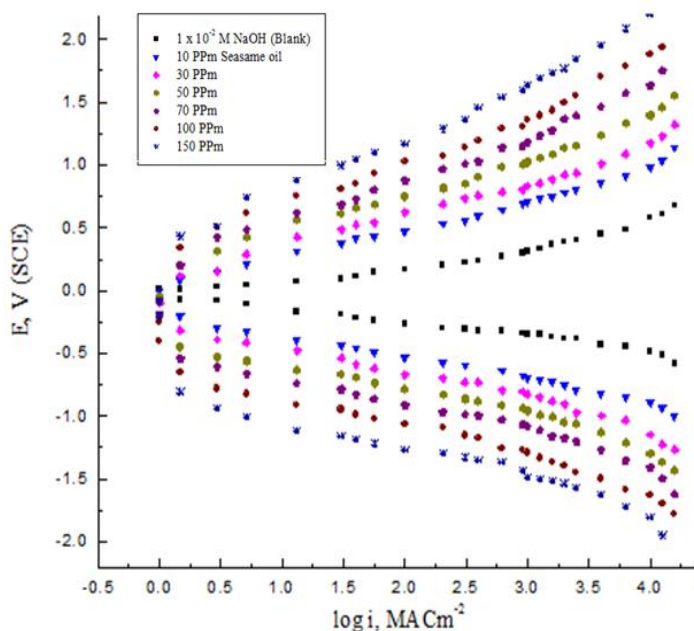

Figure 14. Galvanostatic polarization curves for nickel in 1×10^{-2} M NaOH solution in absence and presence of different concentrations of Sesame oil.

Table 1. Corrosion parameters for nickel electrode in free NaOH and inhibited NaOH solution at 25 ^{o}C.

Conc. ppm	E_{corr} mV(SCE)	I_{corr} mA.cm^{-2}	$-\beta_C$ mV.dec^{-1}	β_a mV. dec^{-1}	θ	% IE
1×10^{-2} M NaOH + x ppm Sesame Oil						
0	250	355	68	10	-	-
10	190	168	19	28	0.52	52
30	165	153	18	24	0.56	56
50	90	134	17	24	0.62	62
70	80	122	15	22	0.65	65
100	60	110	14	20	0.69	69
150	50	100	14	18	0.72	72
1×10^{-2} M NaOH + x ppm Water cress Oil						
0	250	355	68	10	-	-
10	200	190	32	26	0.46	46
30	197	169	22	25	0.52	52
50	185	158	21	24	0.55	55
70	170	140	19	23	0.60	60
100	130	125	18	22	0.65	65
150	90	120	17	21	0.66	66
1×10^{-2} M NaOH + x ppm Wheat germ Oil						
0	250	355	68	10	-	-
10	222	200	32	31	0.43	43
30	214	177	30	27	0.50	50
50	203	165	29	25	0.54	54
70	190	150	27	23	0.58	58
100	150	134	25	23	0.60	60
150	120	127	24	21	0.62	62
1×10^{-2} M NaOH + x ppm Almond Oil						
0	250	355	68	10	-	-
10	242	220	35	33	0.38	38
30	226	210	33	30	0.40	40
50	215	190	29	28	0.46	46
70	204	180	29	26	0.49	49
100	198	170	28	24	0.52	52
150	174	154	26	24	0.56	56

The corrosion parameters e.g. corrosion potential(E_{corr}), corrosion   current density (I_{corr}), cathodic Tafel slope (β_C), anodic Tafel slope (β_a), surface coverage (θ) and percentage inhibition efficiency (%IE) of Ni in 1×10^{-2} M NaOH containing different concentrations of natural product oils were calculated and presented in Table (1).

Table (1) reveals that, the increasing in the concentration of natural oils show the following:

a.   The Tafel lines are shifted to more positive and negative potential for anodic and cathodic processes, respectively, relative to the blank curve. The values of β_C and β_a are nearly constants. This means that these compounds influence both cathodic and anodic processes. However, the data suggested that these compounds act as mainly as mixed type inhibitors. They are assumed to block both the anodic and cathodic sites of the metal surface.

b. E_{corr} changed slightly and the values of I_{corr} decrease indicating the inhibiting effect of these natural product oils.

c.   The inhibition efficiencies of these tested compounds by the galvanostatic polarization method decreases in the following order: sesame oil > water cress oil > wheat germ oil > almond oil. This order is consistent with previous techniques.

3.3.1. Adsorption isotherm

The experimental data for the test compounds have been applied to different adsorption isotherm equations. The best correlation fits the Freundlish adsorption isotherm [22], which is given as:

$\theta = K\,C^{\,n}$ (10) or alternatively, by

$\log \theta = \log K + n \log C$ (11)

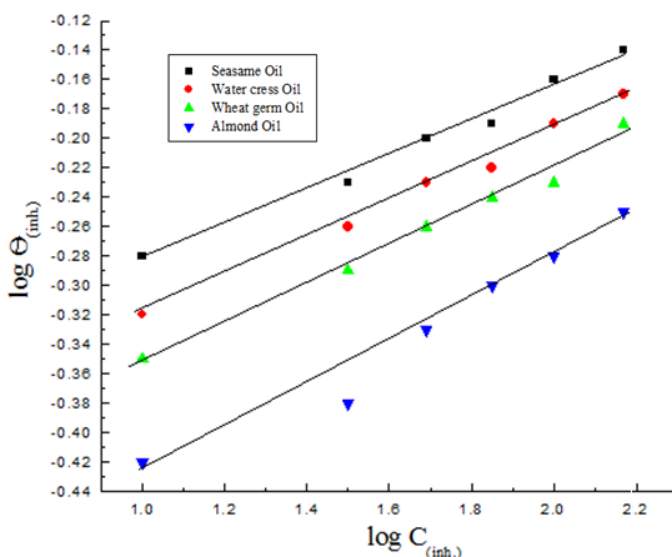where K and C represent the equilibrium constant of adsorption process and additive concentration respectively.

Figure 15. Freundlish adsorption isotherm

Figure (15) represents Freundlish adsorption plots for the natural product oils studied (log θ vs. log C). The data gave straight lines with intercept of   log K. The calculated values for the equilibrium constant of adsorption was found to be 1.44, 1.32, 1.23, and 1.04 for a sesame oil, water cress, wheat germ, and almond oils, respectively.

The equilibrium constant value K is related to the standard free energy of adsorption Δ G^o_{ads} by the following equation [37]:

K = 1/55.5 exp [-Δ G^o_{ads}/ RT]   (12)

Where 55.5 is the concentration of water in solution in mol /l, R is the universal gas constant, T is the absolute temperature. The values of Δ G^o_{ads} for a sesame oil, water cress, wheat germ, and almond oils, amount to -2.43, -2.39, -2.36, and -2.29 k J mol $^{-1}$, respectively. The negative values of Δ G^o_{ads} indicate the spontaneous adsorption of the inhibitor on the metal surface and is usually characteristic of strong interaction with the metal surface.

4. CONCLUSIONS

i)   Sesame oil, water cress oil, wheat germ oil and almond oil act as corrosion inhibitors for nickel in 1 x10^{-2} M NaOH solution at 25°C, using open circuit potential, galvanostatic, and potentiostatic polarization techniques, where there is a shift of potential to noble direction by increasing concentration of inhibitors.

ii)   The inhibition efficiency increases with increases in the concentration of these inhibitors.

iii)   The inhibition is due to the adsorption of the inhibitor molecule on   nickel surface.

iv)   The adsorption of these oils on the nickel surface follows Freundlish adsorption isotherm.

v)   Sesame oil, water cress oil, wheat germ oil and almond oil provide protection against pitting corrosion of nickel in presence of chloride anions.

References

1. V.V. Parshutin, N.L. Bogdashkina, and G.P. Chernova: *Prot. of Metals,* 43(1),(2007) 59.
2. P.A. Selembo, M.D. Merrill, B.E. Logan: *J. Power Sources*, 190 (2009) 271.
3. J.C. Grant, Nickel- Cadmium Battery Application Engineering Handbook, third ed., General Electric Company, Gainesville, (1975).
4. K.H. Ahn, K.G. Song, H.Y. Cha, I.T. Yeom, *Desalination,* 122 (1999) 77.
5. J.A. Mc Geough, M.C. Leu, K.P. Rajurkar, A.K.M. De Silva, Q. Liu: Electroforming process and application to micro/macro manufacturing, CIRP *Ann. Manuf. Technol*., 50 (2001) 499.
6. S. Rossi, F. Deflorian, F. Venturini: *J. Mater. Process. Technol*., 148 (2004) 301.
7. G. Gilli, P. Borea, F. Zucchi, G. Trabanelli: *Corros. Sci*., 9 (1969) 673.
8. J. Sinko: *Prog. Org. Coat*., 42 (2001) 267.
9. P.B. Raja, A.K. Qureshi, A.F. Abdul Rahim, H. Osman, K. Awang, *Corros. Sci*., 69 (2013) 292.
10. A.Y. EL-Etre: *J. Colloid Interface. Sci*., 314 (2007) 578.
11. E.E. Oguzie: *Corros. Sci*., 49 (2007) 1527.

12. A. El Bribri, M. Tabyaoui, B. Tabyaoui, H. El Attari, F. Bentiss, *Mater. Chem. and Phys.*, 141 (2013) 240.
13. A. Bouyanzer, B. Hammouti, and L. Majidi: *Mater. Lett.,* 60 (2006) 2480.
14. E. Chebouat, B. Dadamoussa, N. Gherraf, M. Gouamid, M. Allaou, A. Cheriti, A. Khiari*, Int. J. Electrochem. Sci.*, 8 (2013) 12147.
15. M. Belkhaouda, L. Bammou, R. Salghi, A. Zarrouk, Eno. E. Ebenso, H. Zarrok, B. Hammouti. *Int. J. Electrochem. Sci.*, 8 (2013) 10987.
16. A.Y. EL-Etre, M. Abdallah, and Z.E. EL-Tantawy: *Corros. Sci*., 47 (2005) 385
17. A.Y. EL-Etre, and M.Abdallah: *Corros. Sci*., 42 (2000) 731.
18. M.Abdallah: *Port. Electrochim. Acta*, 22 (2004) 161.
19. E.L. EL-Chaieb, A. Bouyanzer, B. Hammouti, and M. Benkaddour: *Appl. Surf. Sci*., 246 (2005) 199.
20. K. Hnini, A, Chtaini, and A. EL-Bouadilil: *Bull. Electrochem*., 20 (2004) 481.
21. M. Abdallah, S.O. AL-Karanee, and A.A. Abd EL-Fattah: *Chem. Eng. Comm*., 196 (2009) 1406
22. D. M. Brasher: *Nature. Lond*., 193 (1962) 868.
23. V.K. Gouda, M.G.A. Khedr, and A.M. Shams El Din*: Corros. Sci*., 7 (1967) 221.
24. D.M. Brasher, J.G. Beynon, A.D. Mereer, and J.E. Rhoades Brown: Proc 2nd Eur. Symp. Corrosion Inhibitors, Ferrara, (1965) 559 (Univ.of Ferrara).
25. F.M. Abd El Wahab , J .M. Abd El Kader , H.A. El Shayed and A.M. Shams El Din: *Corros. Sci*., 18 (1978) 997.
26. E.E. Abd El Aal: *Corrosion. NACE*, 55 (1999) 582.
27. E.E. Abd El Aal: *Corros. Sci*., 42 (2000) 1.
28. E.E. Abd El Aal: *J. Power Sources*, 75 (1998) 36.
29. I.A. Ammar, and A. Saad: *Electroanal.Chem*., 34 (1972) 159.
30. I.A. Ammar, and M.W. Khalil: *Electrochim. Acta,* 16 (1971)1601.
31. I.A. Ammar, S. Darwish, W.W. Khalil, and S.El Taker*: Corrosion, NACE*, 46 (1990) 197.
32. S. Darwish*: Corrosion,. NACE*, 27 (1971) 265.
33. R.E. Hummel, R.J. Smith, and E.D. Verink Jr.: *Corros. Sci.,* 27 (1987) 803.
34. E.E. Abd ELAal: *Corrosion, NACE*, 48 (1992) 482.
35. M. Abdallah, S. Abd El Wanees, and R. Assi: *Port. Electrochim. Acta*, 27 (2009) 77.
36. B.B. Damskin, O.A. Petrii, and V.V. Kov. Batre: Plenum Press, New York, (1971).
37. M. Kliskic, J. Rosevic, and Gndic: *J. Appl.Electrochem*., 27 (1997) 947.