J. Mater. Environ. Sci. 6 (1) (2015) 201-206
ISSN : 2028-2508
CODEN: JMESCN

Nigella Sativa and Natural Honey as Corrosion Inhibitors for Copper in Cooling Water Systems

M. Emad* and M. AL-Rasheedi
Chemistry Department , Taibah University, Saudi Arabia

Received 4 Apr 2013, Revised 11 Sept 2014, Accepted 12 Sept 2014
* Corresponding author. E mail: mhmd_1428@hotmail.com; Tel +966508124193

Abstract
The inhibition effect of natural honey (NH) and the water extract of natural compound, namely nigella sativa (NS) on the corrosion of copper in cooling water systems has been investigated. The investigation was carried out using the weight loss method and potentiodynamic technique. The chemical composition of the make-up water used in the cooling system has been determined. The data obtained showed that this water has low hardness and corrosive behavior. The inhibition efficiency and surface coverage were calculated for various inhibitor concentrations. The obtained results showed that the inhibition efficiencies of these inhibitors enhance with increasing inhibitor concentrations. It was found that the inhibition efficiency reached up to 98% for (NH) and 90.3 % for (NS), which leaded to efficient corrosion inhibition of copper in cooling water systems .The mechanism of inhibition was proposed on the basis of the adsorption of the inhibitor molecules on the copper surface.

Keywords: Nigella sativa, natural honey, corrosion, inhibitors, copper

1. Introduction
Copper is considered to be one of the most important metals which is frequently used in various cooling water systems, because of its excellent electrical and thermal conductivity [1,2]. Corrosion of copper in cooling water systems is a serious problem and the injection of corrosion inhibitors through water systems is very important to reduce the rate of copper corrosion.

Many inhibitors have been used to minimize the corrosion of copper in different media. Particularly, organic compounds containing nitrogen [3,4] and sulfur [5] atoms are often used to protect copper from corrosion. Unfortunately, most of these compounds are synthetic chemicals which may be very expensive and hazardous to living creatures and environment. Therefore, the development of non-toxic, ecologically harmless, natural corrosion inhibitors is regarded as a crucial alternative. Several investigations have been reported using such naturally occurring substances as corrosion inhibitors for several metals in different media [6-14].

The influence of natural honey with black radish juice, on the corrosion of tin in aqueous and sodium chloride solutions was studied by Radojcic et.al [15]. It was found that the addition of black radish juice increased the inhibition efficiency of honey. Recently, many plant extracts as Nigella Sativa as well natural honey [16-20] have been investigated as green inhibitors for the corrosion of metals.

The aim of the present research work is to find a naturally occurring, cheap, and environmentally safe substance that could be used for inhibiting the corrosion of copper in cooling water systems. The use of such substances will fulfill, simultaneously, the economic and environmental goals.

The present work is devoted to study the inhibitive properties of Natural honey (NH) and the aqueous extracts of natural compound, namely Nigella sativa (NS) as a safe and environmentally friendly corrosion inhibitors for copper in cooling water systems.

2. Materials and methods
The chemical analyses of the make-up water used in the cooling system were carried out using standard methods [21]. Copper sheets with exposed surface of 1.7 cm^2 were used for the weight loss measurement. Before immersion, copper sheets were polished using different grades of emery paper, washed with distilled water and finally degreased with acetone. Weight loss experiments were carried out for a period of seven days at 25 ºC. Experiments were repeated four times, each with fresh specimen and fresh solution. The results were quite reproducible and the mean values are reported.

The potentiodynamic current-potential curves were measured using a cell assembly consisting of three electrodes. The working electrode was a copper cylindrical rod with an exposed surface area of 1 cm^2, a platinum sheet was used as counter electrode and a saturated calomel electrode as a reference electrode. Polarization experiments were carried out using a potentiostat /galvanostat (Solarton model SI 1287).

The natural honey (NH) solutions were prepared with concentrations 100, 300, 500,700 and 900 ppm by dissolving the honey in water. A stock solution of the water extract of nigella sativa (NS) was prepared as follows: 5 gm of (NS) was extracted with 500 ml water under reflex for 2 hours. The resulting extract was found to contain 0.5 gm of (NS). The composition of natural honey is given in Table 1 [22] and the composition of the water extract of nigella sativa (NS) is given in Table 2 [23].

Table 1: The composition of natural honey:

Composition	water	fructose	glucose	sucrose	dextrin	minerals	Acids	unknown
%	17.70	40.50	34.00	21.90	1.15	0.18	0.08	4.90

Table 2: The composition of Nigella sativa:

Composition	Moisture	Crude fat	Crude protein	Crude fibre	Ash	Total carbohydrate
%	2.55	31.95	20.61	10.37	4.51	30.00

3. Results and discussion

Physicochemical characteristics of the make-up water used in this study are given in Table 3.The data indicate that the water has a corrosive behaviour, since Langelier saturation index has negative value (-0.5) and Ryznar stability index is greater than 7 (i.e. 8.2). The corrosivity of the water is due to the presence of the aggressive Cl^- and SO_4^{2-} ions. The Cl^- ions (700 ppm) can strongly adsorbed on the copper surface and destroy any pre-immersion oxide layer on the surface and making it difficult to be passive [24]. On the other hand, SO_4^{2-} ions (400ppm) are less aggressive than Cl^- ions.

Table 3: Typical Make-up Water Analysis:

Sr.No	Test	Unit	Result
1	pH		7.50
2	Total Dissolved Solids (T.D.S)	ppm	2294
3	Total Hardness as $CaCO_3$	ppm	340
4	Chloride [Cl^-]	ppm	700
5	Sulfate [SO_4^{2-}]	ppm	400
6	Sodium [Na^+]	ppm	385
7	Calcium Hardness	ppm	250
8	Magnesium Hardness	ppm	90.0
9	Potassium [K^+]	ppm	40.0
10	Total Iron [Fe]	ppm	0.03
11	Total alkalinity	ppm	400

3.1. Weight loss measurement

The weight loss of copper sheets in the aerated make-up water in the absence and presence of different concentrations of (NH) and (NS) was determined after seven days at 25 ºC. The weight loss values are given in Table 4. Inspection of the data reveals that the weight loss decreases with increasing the concentration of each inhibitor.

The inhibition efficiency P% and the surface coverage θ were calculated from the relation [25]:

$$P\% = \left(1 - \frac{W}{W^o}\right) \times 100 = \theta \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where W^o and W are the weight of copper after immersion in the water without and with the inhibitor, respectively. The values of P% are listed in Table 4.

ISSN : 2028-2508
CODEN: JMESCN

Table 4: Data of the weight loss measurements:

Type of inhibitor	Conc. ppm	Weight Loss (g.cm^{-2}.day^{-1})	θ	P%	C/θ
Blank	---	0.0347	---	---	---
NS	3.0	0.0099	0.715	71.50	4.20
	5.0	0.0097	0.720	72.00	6.90
	13	0.0074	0.787	78.67	16.5
	20	0.0047	0.885	88.50	22.5
	30	0.0044	0.903	90.30	33.2
NH	100	0.00187	0.95	95	105.3
	300	0.00116	0.971	97.1	310.2
	500	0.0014	0.968	96.8	516.5
	700	0.0012	0.9704	97.04	721.3
	900	0.00078	0.98	98	918.4

The data shows that the inhibition efficiencies of these inhibitors are enhanced with increasing inhibitor concentrations. It was found that the inhibition efficiency reached up to 98% for (NH) as shown in Figure 1. This behaviour could be attributed to the increase of the surface coverage θ due to the adsorption of honey on the copper surface as (NH) concentration was increased. The chemical composition of honey was investigated by other authors [24] to identify the probable cnstituents responsible for the inhibation effect of honey. It was found Fructose has the highest inhibition efficiency among the other contituents. These results in agreement with previous studies [22,26] which considered that compounds containing sugars can be used as corrosion inhibitors.The surface coverage θ values for different concentrations of (NH) were evaluated from weight loss data (Table 4). The data were tested graphically to find a suitable adsorption isotherm. A plot of C/θ versus honey concectration C (Figure 3) shows a straight line, indicating that the adsorption of natural honey (NH) on copper surface follows the Langmuir adsorption isotherm [27,28].

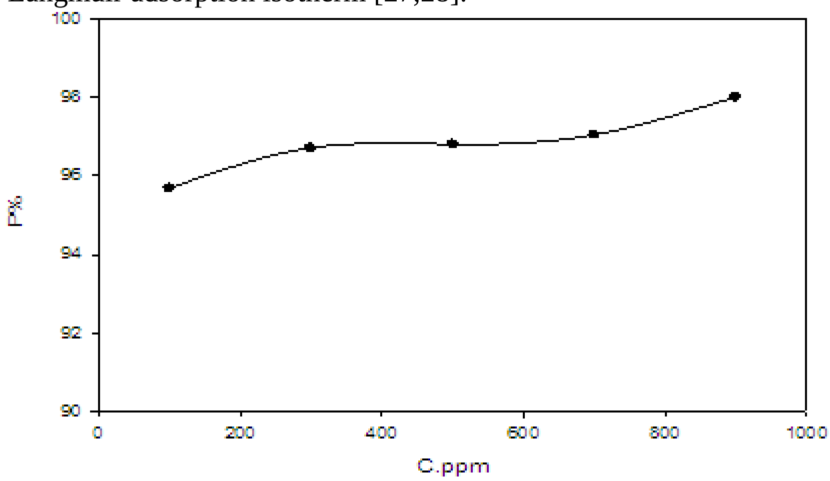

Figure 1: Effect of the concentration of Honey on the protection of copper in cooling water at 25°C.

Inspection of Figure 2 shows that the inhibition efficiency of (NS) also increased with increasing (NS) concentrations and reached up to 90.3% . This behaviour could be explained as (NS) extract contains more than one component. Each component is expected to exert a retarding effect on the dissolution process of copper, since it contains functional groups, which can oprate as adsorption centers. The surface coverage θ values for different concentration of (NS) were also evalated from weight loss data (Table 4). These data were tested graphically to find a suitable adsorption isotherm. A plot of C/θ versus the extract of nigella sativa concectration C (Figure 4) shows a straight line, indicating that the adsorption of nigella sativa (NS) on copper surface follows the Langmuir adsorption isotherm.These results are in agreement with the results obtained by Azzouyaha et al. [29].

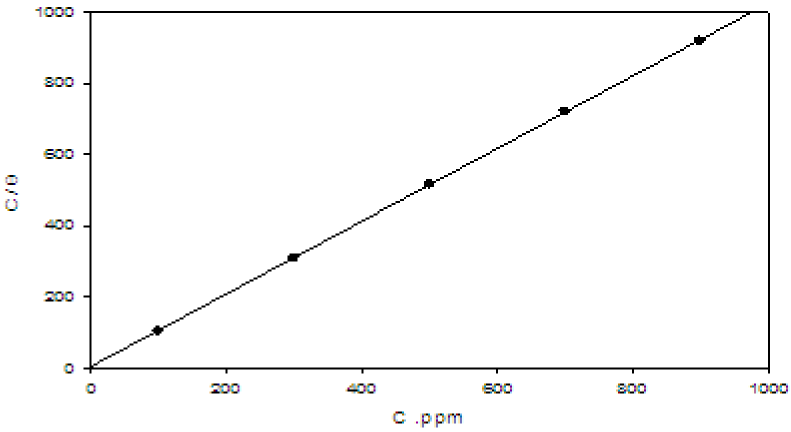

Figure 3: Langmuir adsorption isotherm at 25°C for natural Honey.

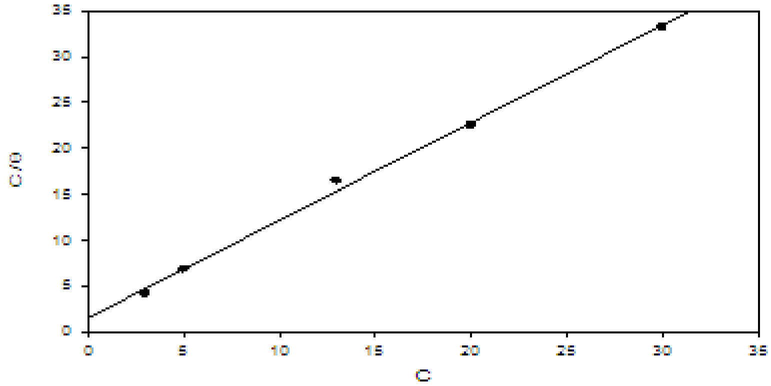

Figure 4: Langmuir adsorption isotherm at 25°C for Nigella sativa.

3.2. Potentiodynamic polarizatiom measurements:

The anodic and cathodic behavior of copper in cooling water containing (NH) and (NS) inhibitors at different concentrations is illustrated in Figure 5 and Figure 6, respectively. The various electrochemical parameters which are obtained from these figures are given in Table 5. It was found that an increase in the concentration of (NH) causes a significant shift in the corrosion potential (E_{corr}) towards more noble region and the magnitude of the displacement of the Tafel plot is proportional to the concentration of (NH) inhibitor. Moreover, the corrosion current (I_{corr}) decreases markedly in the presence of (NH), which is indicative of its pronounced inhibition effect. It was found that the calculated values of inhibition efficencies of (NH) in Table 5, increases with increasing (NH) concentration. Further inspection of Table 5, reveals that the values of anodic and cathodic Tafel constants are markedly changed in the presence of (NH). These results indicate that the natural honey acts as a mixed type inhibitor (i.e. both anodic and cathodic polarization curves are affected by the inhibitor). These results are in agreement with the results obtained by Vrsalovic et al. [30]. Table 5 reveals that, for all concentrations of (NH), the values of (βa) are greater than the values of (βc). This suggests that, although the inhibition is under mixed control, the effect of the inhibition on the anodic polarization is more pronounced than on the cathodic polarization.

Similarly, the various electrochemical parameters which are obtained from Figure 6 for Nigella sativa (NS), are given in Table 5. Inspection of these data, reveals that the addition of (NS) shifts the corrosion potential (E_{corr}) towards more noble direction and decreases the corrosion current (I_{corr}) markedly with increasing (NS) concentrations, which is indicative of the pronounced inhibition effect of this inhibitor. Such results prove that the nigella sativa (NS) acts as a mixed type inhibitor, but the effect of the inhibition on the anodic polarization is more pronounced than on the cathodic polarization, since the values of (βa) are greater than those of (βc).

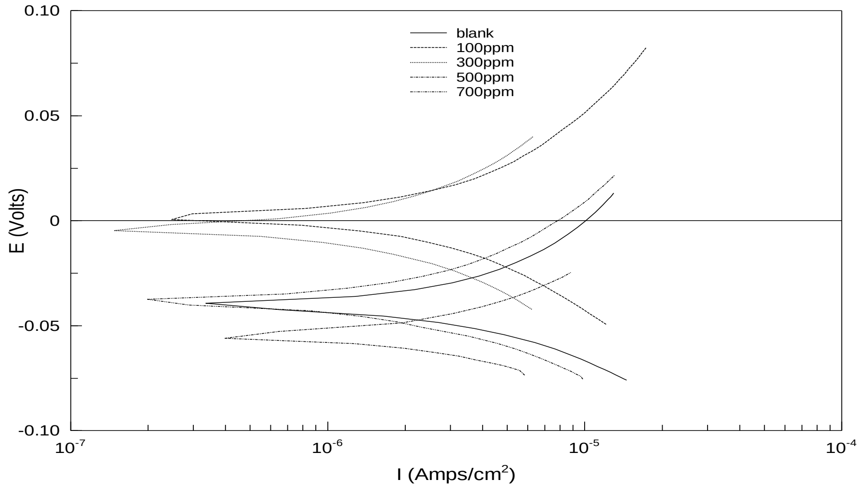

Figure 5: Polarization curves of copper in cooling water in the absence and in the presence of different concentrations of (NH).

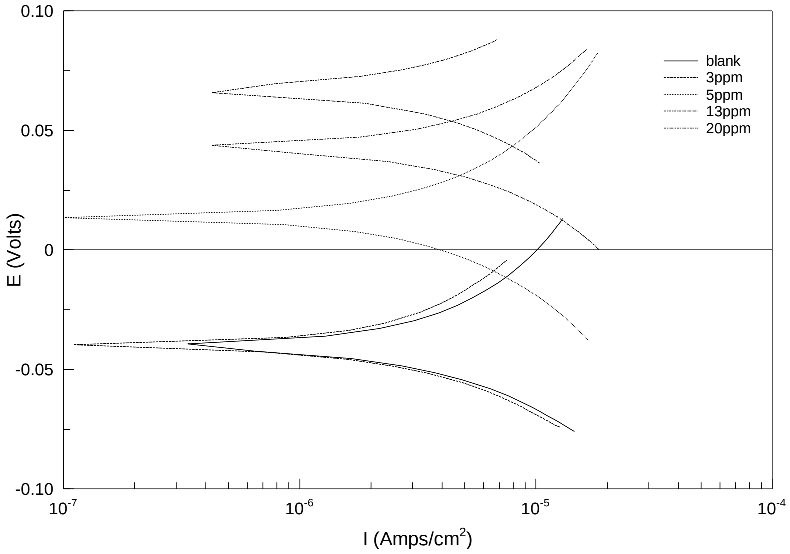

Figure 6: Polarization curves of copper in cooling water in the absence and in the presence of different concentrations of (NS).

Table 5: Electrochemical corrosion parameters for copper in cooling water in presence and absence of inhibitors of Honey and Nigella sativa:

Type of inhibitor	Conc. ppm	I_{corr} A/cm^2	E_{corr} mV	βa mV/dec	βc mV/dec	P%
Blank	---	8.3044E-6	-0.039846	197.13	93.177	---
NS	3	7.3968E-6	-0.039078	151.68	62.773	18.00
	5	6.236E-6	-0.016092	88.884	85.222	25.50
	13	4.5044E-6	-0.044332	96.432	97.204	46.20
	20	4.383E-6	-0.043704	110.22	127.25	51.10
	100	6.6875E-6	-0.001705	187.98	64.75	25.00
NH	300	2.7082E-6	-0.003237	132.70	85.796	69.90
	500	2.1974E-6	-0.055408	122.10	93.177	75.66
	700	1.8349E-6	-0.06682	102.88	101.20	79.60

Conclusions

The results obtained show that both Natural honey (NH) and the extract of Nigella sativa (NS) acts as efficient inhibitors for copper in cooling water systems.The inhibition efficencies for both (NH) and (NS) was found to increase with increasing inhibitor concentrations. The results of polarization measurements have shown that both (NH) and (NS) acts as mixed type inhibitors, but the effect of the inhibition on the anodic polarization is more pronounced than on the cathodic polarization. The adsorption of both (NH) and (NS) on the copper surface was found to obey Langmuir adsorption isotherm.

Acknowledgment: The authors thank the Chemistry Department, Taibah University for providing the various facilities utilized in this work.

References

1. Stupnisek E., Loncaric A., Cafuk, I., *Corros.* 54 (1998) 713.
2. Gasparac R., Martin C.R., Stupnisek E. , *J. Electrochem. Soc.* 147 (2000) 548.
3. Singh M.M., Upahyay R.B., Upahyay B., *Electrochem.* 12 (1996) 26.
4. El-Taib H.F., Haruyama S., *Corros. Sci.* 20 (1980) 887.
5. Elmorsi M.A., in Electrochem. Soc., Spring Meeting, Los Angeles, 1 (1996) 167.
6. Arora P., Kumar S., Sharma M.K., Mathur S.P., *E-J Chem.* 4 (2007) 450.
7. Al-Sehaibani H., Materialwissenschaft und Werkstofftechnik 31 (2000) 1060.
8. Chaieb E., Bouyanzer A., Hammouti B., Benkaddour M., *Appl Surf Sci.* 246(2005) 199.
9. Chaieb E., Bouyanzer A., Hammouti B., Benkaddour M., Berrabah M., *Transactions of the SAEST* 39 (2004) 58.
10. Chauhan L.R., Gunasekaran G., *Corr. Sci.* 49 (2007) 1143.
11. El-Etre A.Y., Abdallah M., El-Tantawy Z.E., *Corr. Sci.* 47 (2005) 385.
12. Olusegun K., Abiola N.C., Oforka E.E., Ebenso J., *Corr. Sci. Eng.* 5 (2004) 10.
13. Orubite, O.K., Oforka, N.C., *Mater. Lett.* 58 (2004) 1768.
14. Rehan, H.H., *Materialwissenschaft und Werkstofftechnik* 34 (2003) 232.
15. Radojcic I., Berkovic K., Kavoc S., Vorkapic-Furac J., *Corr. Sci.* 50 (2008) 1498.
16. Abdel-Gaber A.M., Abd-El-Nabey B.A., Sidahmed I.M., El-Zayady A.M., Saadawy M., *Corr. Sci.* 48 (2006) 2765.
17. I.B. Obot, S. A Umoren, A.S. Johnson, *J. Mater. Environ. Sci.* 4 (2013) 1013-1018.
18. Gerengi H., Goksu H., Slepski P., *Mater. Res.* 17 (2014) 255-264.
19. *Rosliza R., Nik W.B.W., Izman S.*, Advanced Materials Research, *1025-1026 (2014) 668-671.*
20. Wan Nik, W.B., Zulkifli, M.F., Rosliza, R., Ghazali, M.J., Khaled, K.F. P., *World Applied Sciences Journal*, 14 (2011) 215-220
21. Lenore S., Arnold E., Andrew D., "Standard methods for examination of water and wastewater" 20th edition, January, (1999).
22. EL-Etre A.Y., *Corr. Sci.* 40 (1998) 1845.
23. Fahad M.J, Mohammed S. J., *the Scientific World Journal*,10 (2012) 5.
24. Husnu G., Haydar G., Pawel S., *Mater. Res.* 17 (2014) 255.
25. Emad M., *J. Am. Sci.* 8 (2012) 266.
26. Rajendran S., Uma V., Krishnaveni A., Jeyasundari J., Shyamaladevi B., Manivannan M. *Arab. J. Sci. Eng.* 34 (2009) 147.
27. Ben Aoun S. *Int. J. Electrochem. Sci.* 8 (2013) 10788.
28. Ben Aoun S., *Der Pharma Chemica* 5 (2013) 294.
29. Azzouyahar E., Bazzi L., Essahli M., Belkhaouda M., Lamiri A. *Chem. Sci. Rev. Lett.* 3 (2014) 80.
30. Vrsalovic L., Gudic S., Kliskic M. *Indian J. Chem. Tech.* 19 (2012) 96.