

# New corrosion inhibitor derived from coumarin

Ahmed A. Al-Amiery

Energy and Renewable Energies Technology Centre, University of Technology, Baghdad, Iraq;

\* Correspondence dr.ahmed1975@gmail.com.

**Abstract:** New corrosion inhibitor derived from coumarin-3-amine namely 3-((2-chlorobenzylidene)amino)coumarin was synthesized and characterized by CHN elemental analysis in addition to Fourier transform infrared and nuclear magnetic resonance techniques. The anti-corrosion ability of 3-((2-chlorobenzylidene)amino)coumarin to inhibit the impacts of corrosion has been demonstrated and damage reduction of the mild steel also. 3-((2-chlorobenzylidene)amino)coumarin, has been employed as a good corrosion inhibitor for mild steel in HCL solution. The efficiency of the inhibition was figured according to weight loss method and it was 74.6%.

**Keywords:** 3-((2-chlorobenzylidene)amino)coumarin; corrosion inhibitor; damage reduction

## 1. Introduction

Coumarins become one of the most significant compounds having considerable, medicinal activities [1–3]. Many of these coumarins were proven to be efficient as anti-bacterial [4–6], anti-fungal [7], anti-inflammatory [8], anti-coagulant [9], anti-HIV [10] and anti-cancer [11]. Coumarins are quite, utilized in foods and/or cosmetics as additives [12], in addition to optics [13] and dyes [14]. Some coumarin derivatives were proven to be a superior antioxidant agent [15]. Structure modification of coumarin moiety exhibit inhibition of unit enzyme both in vitro and in vivo [16–20]. Corrosion inhibitors increase the impedance of mild steel toward corrosive solutions and inhibit or retard the corrosion through adsorbing the molecules of inhibitor on the surface of mild steel [21–27] in order to generate a barrier on the surface that block dynamic sites for mild steel [28–30]. Natural or synthesized organic corrosion inhibitors may have adsorbed on metal surface. This issue influenced by various factors. These factors are the nature of the metal surface, second the kinds of electrolyte and the final factor was the composition of the of inhibitor [31,32]. The inhibitors could be bond with mild steel surface to prepare a stable complex which act as barrier to protect the mild steel surface in basic or acidic solutions [33]. To broaden my prior studies on preparation of novel applicable organic chemical compounds [34–39], a new one synthesized as coumarin derivative namely 3-((2-chlorobenzylidene)amino)coumarin which was identified by CHN elemental analysis technique in addition to infrared IR and Nuclear magnetic resonance NMR spectroscopies. The inhibitor in acidic solution has the ability to inhibits the corrosions of mild steel based on weight loss method.

## 2. Materials and Methods

*Materials:* Polar solvents that required for this investigation and other chemical compounds have been bought and employed with no additional purifications. Infra-red spectrum was complete through instrument namely Shimadzu FTIR-8300 spectrometer. Micro-elemental analyses were performed through instrument namely Carlo Erba 5500. NMR spectra were gotten by Bruker instrument at 300MHz Ultra/Shield magnets with two solvents that were dimethylsulfoxied-d6 and TMS as solvent and internal standard, respectively.

*Synthesis of corrosion Inhibitor:* 3-Aminecoumarin in ethanol and 2-chlorobenzaldehyde with molar ratio (1:1) have been refluxed for eight hours. Reaction mixture was cooled, filtration and used ethanol for recrystallization. <sup>1</sup>H NMR: 7.05-7.95 (m, 1H, Ar-H), 8.74 (d, 1H, H-C=N). Elemental analysis (CHN): C 68.07% (67.74%), H 3.51% (3.55%), N 5.26 (4.94).

**Corrosion technique:** Samples of mild steel that were using for this study as an electrode which supplied from metal samples company. Portion of the iron was 99.21%, portion of carbon was 0.21%, portion of silicon was 0.38%, portion of phosphorous was 0.09%, portion of sulfur was 0.05%, portion of manganese was 0.05% and portion of aluminum was 0.01%. The efficient investigations of the studied mild steel surface were 4.5 cm<sup>2</sup> in area and cleaned based on reference [40]. Duplicate suspension specimens of mild steel regarding to typical methodology and in 0.2 L of corrosive solution namely hydrochloric acid at 1M concentration without of 3-((2-chlorobenzylidene)amino)coumarin as inhibitor and also in presence of 3-((2-chlorobenzylidene)amino)coumarin at investigated concentrations 0.001, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.50 g/L for (1, 3, 5, 10, 24 and 72 h). The inhibition activities have been figured based on equation 1:

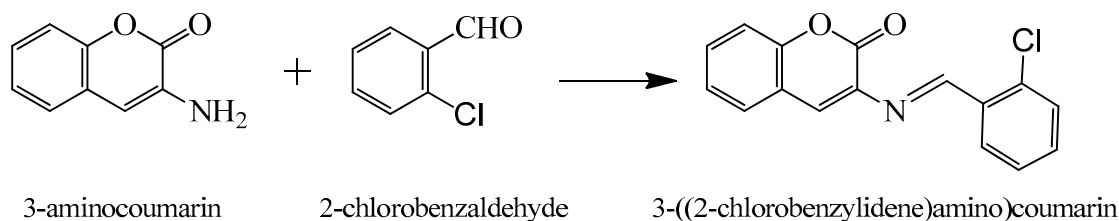
$$IE(\%) = \left(1 - \frac{W_2}{W_1}\right) \times 100 \quad 1$$

where W<sub>1</sub> and W<sub>2</sub> pointing to weight samples of mild steel with and without of 3-((2-chlorobenzylidene)amino)coumarin respectively.

### 3. Results and discussion

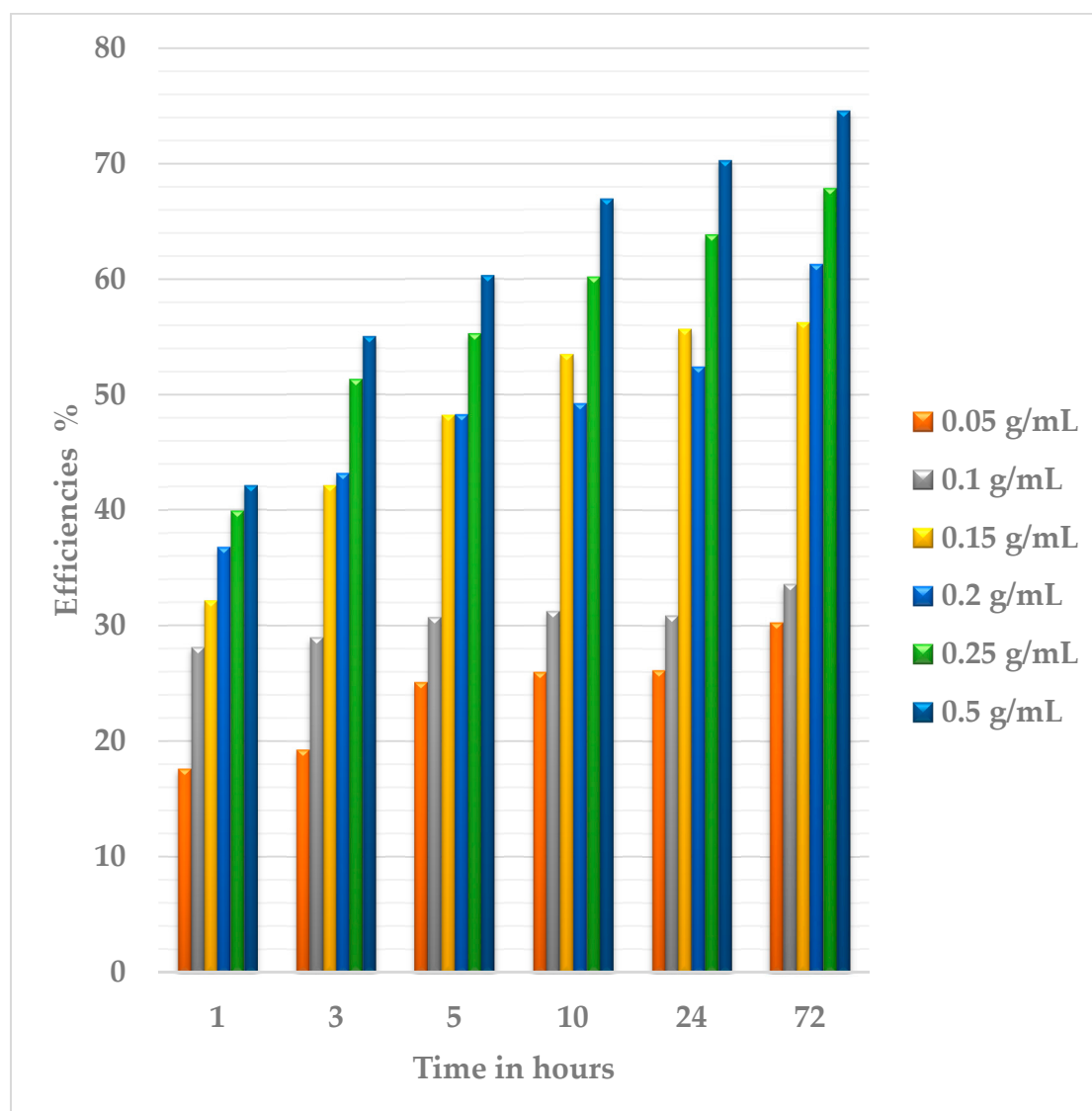
**Synthesis:** The inhibitor 3-((2-chlorobenzylidene)amino)coumarin was prepared in excellent in good yield by reflection reaction of same molar ratio of 4-nitrobenzaldehyde and coumarin-3-amine. The molecular formula of 3-((2-chlorobenzylidene)amino)coumarin was figured based on chemical formula (C<sub>16</sub>H<sub>10</sub>N<sub>1</sub>O<sub>2</sub>) that confirmed regarding to elemental analysis. In infrared spectrum of 3-((2-chlorobenzylidene)amino)coumarin no amino absorption bands were appeared for 3-((2-chlorobenzylidene)amino)coumarin. The Nuclear magnetic resonance spectrum demonstrated doublet at δ 8.74 ppm, due to the proton of C=N). 3-((2-chlorobenzylidene)amino)coumarin was prepared from coumarin-3-amine as in Scheme 1.

**Scheme 1:** 3-((2-chlorobenzylidene)amino)coumarin synthesis



**Results of weight loss technique:** In industry, the employment of corrosion inhibitors still the considerable economic style because of the protection of surface of mild steel against acidic solutions [41]. Corrosion inhibitors naturally or synthetic were dominant, tools used in oil and gas industries due to barriers formation to protect the alloys and metals surfaces against corrosive acids or bases solutions. The majority of used inhibitors that have one or more nitrogen, oxygen and/or sulfur atoms, such as pyridines, imidazoles rings [42-44] in addition to polymers with heterocyclic rings [45].

**Concentration effect:** Weight loss studies that were employed to figured the inhibition efficiency of 3-((2-chlorobenzylidene)amino)coumarin at concentrations (0.05, 0.1, 0.15, 0.2, 0.25 and 0.5 g/L) for the time (1, 3, 5, 10, 24 and 72 h) and 303K as temperature degree in solution of hydrochloric acid for mild steel surface. The 3-((2-chlorobenzylidene)amino)coumarin results, which were displayed in Figure 1, point to the capability of 3-((2-chlorobenzylidene)amino)coumarin for reducing corrosion which were done through the acidic solution of mild steel surface with higher inhibition efficiency 74.6% based on highest studied.

**Figure 1.** Function of time at concentrations of 3-((2-chlorobenzylidene)amino)coumarin.

#### 4. Conclusions

3-((2-Chlorobenzylidene)amino)coumarin as new inhibitor for surface of mild steel was prepared coumarin-3amine and the structure of it molecule was identified based on NMR and FT-IR spectroscopy moreover the elemental analyses was also used for characterization. Inhibition activity of 3-((2-chlorobenzylidene)amino)coumarin as inhibitor in corrosive solution of 1M of hydrochloric acid for mild steel has been investigated. 3-((2-chlorobenzylidene)amino)coumarin, displayed an excellent performance as inhibitor and with maximum efficiency 74.6% at the maximum studied concentration of 3-((2-chlorobenzylidene)amino).

#### References

1. El-Agrody A, Abd El-Latif M, El-Hady N, Fakery A, Bedair A. Hetero aromatization with 4-hydroxycoumarin Part II: Synthesis of some new pyrano[2,3-d]pyrimidines, [1,2,4]triazolo[1,5-c]pyrimidines and pyrimido[1,6-b][1,2,4]triazine derivatives. *Molecules*. 2001; 6: 519–527.
2. Rositca DN, Vayssilov, GN, Rodios N, Bojilova A. Regio- and stereoselective [2+2] photodimerization of 3-substituted 2-alkoxy-2-oxo-2H-1,2-benzoxaphosphorines. *Molecules*. 2002; 7: 420–432.
3. Flašík, R.; Stankovičová, H.; Gáplovský, A.; Donovalová, J. Synthesis and study of novel coumarin derivatives potentially utilizable as memory media. *Molecules*. 2009; 14: 4838–4848

4. Kovalenko S, Bylov I, Sytnik K, Chernykh V, Bilokin, Y. A new pathway to 3-hetaryl-2- oxo-2H-chromenes: On the proposed mechanisms for the reaction of 3-carbamoyl-2- iminochromenes with dinucleophiles. *Molecules*. 2000; 5: 1146–1165.
5. El-Saghier A, Khodairy A, Khodiyar A. New synthetic approaches to condensed and spiro coumarins: Coumarin-3-thiocarboxamide as building block for the the synthesis of condense and spiro coumarins. *Phosphorus Sulfur*. 2000; 160: 105–119.
6. Čačić M, Pavić V, Molnar M, Šarkanj B, Has-Schön E. Design and Synthesis of Some New 1,3,4-Thiadiazines with Coumarin Moieties and Their Antioxidative and Antifungal Activity. *Molecules*. 2014; 19: 1163-1177.
7. Azizian J, Mohammadi A, Bidar I, Mirzaei P. KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (alum) a reusable catalyst for the synthesis of some 4-substituted coumarins via Pechmann reaction under solvent-free conditions. *Montash. Chem*. 2008; 139: 805–808.
8. Satyanarayan VS, Sreevani P, Sivakumar A. Synthesis and antimicrobial activity of new Schiff bases containing coumarin moiety and their spectral characterization. *Arkivoc*. 2008; 17: 221–233.
9. Garazd MM, Muzychka OV, Voyk AI, Nagorichna IV, Ogorodniichuk AS. Modified coumarins. 27. Synthesis and antioxidant activity of 3-substituted 5,7-dihydroxy-4- methylcoumarins. *Chem. Nat. Compd*. 2007; 43: 19–23.
10. Smitha G, Sanjeeva R. ZrCl<sub>4</sub>-catalyzed Pechmann reaction: Synthesis of coumarins under solvent-free conditions. *Synth. Commun*. 2004; 34: 3997–4003.
11. Kotali A, Lafazanis I, Harris P. Synthesis of 6,7-diacylcoumarins via the transformation of a hydroxy into a carbonyl group. *Synth. Commun*. 2008; 38: 3996–4006.
12. Nofal ZM, El-Zahar M, Abd El-Karim S. Novel coumarin derivatives with expected biological activity. *Molecules*. 2000; 5: 99–113.
13. Kennedy RO, Thornes RD. *Coumarins: Biology, Applications and Mode of Action*; John Wiley and Sons: Chichester, UK, 1997.
14. Zabradnik M. *The Production and Application of Fluorescent Brightening Agents*; John Wiley and Sons: New York, NY, USA, 1992.
15. Heravi M, Sadjadi S, Oskooie H, Shoar R, Bamoharram F. The synthesis of coumarin-3-carboxylic acids and 3-acetyl-coumarin derivatives using heteropolyacids as heterogeneous and recyclable catalysts. *Catal. Commun*. 2008; 9: 470–474.
16. Kampranis SC, Gormley NA, Tranter R, Orphanides G, Maxwell A. Probing of Coumarins and Cyclothialidines to DNA Gyrase. *Biochemistry*. 1999; 38: 1967–1976.
17. Wang HX, Ng TB. Examination of lectins, polysaccharopeptide, polysaccharide, alkaloid, coumarin and trypsin inhibitors for inhibitory activity against human immunodeficiency virus reverse transcriptase and glycohydrolases. *Planta Med*. 2001; 67: 669–672.
18. Mao PC, Mouscadet JF, Leh H, Auclair CHsu LY. Chemical modification of coumarin dimmer and HIV-1 integrase inhibitory activity. *Chem. Pharm. Bull*. 2002; 50: 1634–1637.
19. Le BG, Radanyi C, Peyrat JF, Brion JD, Alami M, Marsaud V, Stella B, Renoir JM. New novobiocin analogues as antiproliferative agents in breast cancer cells and potential inhibitors of heat shock protein90. *J. Med. Chem*. 2007; 50: 6189–6200.
20. Lin P, Yeh K, Su C, Sheu S, Chen T, Ou K, Lin M, Lee L. Synthesis and Antibacterial Activities of Novel 4-Hydroxy-7-hydroxy- and 3-Carboxycoumarin Derivatives. *Molecules*. 2012; 17: 10846-10863.
21. Al-Amiery AA, Al-Majedy YKA, Kadhun AAH, Mohamad AB. New coumarin derivative as an eco-friendly inhibitor of corrosion of mild steel in acid medium. *Molecules* 2015;20(1):366-383.
22. Al-Amiery AA, Kadhun AAH, Mohamad AB, Musa AY, Li CJ. Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild steel corrosion in hydrochloric acid. *Mater* 2013;6(12):5466-5477.
23. Al-Amiery AA, Kadhun AAH, Mohamad AB, Junaedi S. A novel hydrazinecarbothioamide as a potential corrosion inhibitor for mild steel in HCL. *Mater* 2013;6(4):1420-1431.
24. Junaedi S, Al-Amiery AA, Kadihum A, Kadhun AAH, Mohamad AB. Inhibition effects of a synthesized novel 4-aminoantipyrine derivative on the corrosion of mild steel in hydrochloric acid solution together with quantum chemical studies. *Int J Mol Sci* 2013;14(6):11915-11928.
25. Obayes HR, Al-Amiery AA, Alwan GH, Abdullah TA, Kadhun AAH, Mohamad AB. Sulphonamides as corrosion inhibitor: Experimental and DFT studies. *J Mol Struct* 2017;1138:27-34.

26. Kadhum AAH, Mohamad AB, Hammed LA, Al-Amiery AA, San NH, Musa AY. Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin. *Mater* 2014;7(6):4335-4348.
27. Obayes HR, Alwan GH, Alobaidy AHMJ, Al-Amiery AA, Kadhum AAH, Mohamad AB. Quantum chemical assessment of benzimidazole derivatives as corrosion inhibitors. *Chem Cent J* 2014;8(1).
28. Al-Azawi KF, Al-Baghdadi SB, Mohamed AZ, Al-Amiery AA, Abed TK, Mohammed SA, et al. Synthesis, inhibition effects and quantum chemical studies of a novel coumarin derivative on the corrosion of mild steel in a hydrochloric acid solution. *Chem Cent J* 2016;10(1).
29. Issa AY, Rida KS, Salam AQ, Al-Amiery AA. Acetamidocoumarin as a based eco-friendly corrosion inhibitor. *Int J ChemTech Res* 2016;9(11):39-47.
30. Al-Amiery AA, Binti Kassim FA, Kadhum AAH, Mohamad AB. Synthesis and characterization of a novel eco-friendly corrosion inhibition for mild steel in 1 M hydrochloric acid. *Sci Rep* 2016;6.
31. Alobaidy AH, Kadhum A, Al-Baghdadi SB, Al-Amiery AA, Kadhum AAH, Yousif E, et al. Eco-friendly corrosion inhibitor: Experimental studies on the corrosion inhibition performance of creatinine for mild steel in HCl complemented with quantum chemical calculations. *Int J Electrochem Sci* 2014;10(5):3961-3972.
32. Yousif E, Win Y-, Al-Hamadani AH, Al-Amiery AA, Kadhum AAH, Mohamad AB. Furosemide as an environmental-friendly inhibitor of corrosion of zinc metal in acid medium: Experimental and theoretical studies. *Int J Electrochem Sci* 2015;10(2):1708-1715.
33. Rubaye AYI, Abdulwahid AA, Al-Baghdadi SB, Al-Amiery AA, Kadhum AH, Mohamad AB. Cheery sticks plant extract as a green corrosion inhibitor complemented with LC-EIS/MS spectroscopy. *Int J Electrochem Sci* 2015;10(10):8200-8209.
34. Al-Amiery AA, Al-Majedy YK, Kadhum AAH, Mohamad AB. Hydrogen peroxide scavenging activity of novel coumarins synthesized using different approaches. *PLoS ONE* 2015;10(7).
35. Al-Majedy YK, Al-Amiery AA, Kadhum AAH, Mohamad AB. Antioxidant activities of 4-methylumbelliferone derivatives. *PLoS ONE* 2016;11(5).
36. Al-Amiery AA, Al-Temimi AA, Sulaiman GM, Aday HA, Kadhum AAH, Mohamad AB. Synthesis, antimicrobial and antioxidant activities of 5-((2-oxo-2H- chromen-7-yloxy)methyl)-1,3,4-thiadiazol-2(3H)-one derived from umbelliferone. *Chem Nat Compd* 2013;48(6):950-954.
37. Al-Amiery AA, Kadhum AAH, Obayes HR, Mohamad AB. Synthesis and antioxidant activities of novel 5-chlorocurcumin, complemented by semiempirical calculations. *Bioinorg Chem Appl* 2013;2013.
38. Al-Amiery AA, Al-Bayati RIH, Saour KY, Radi MF. Cytotoxicity, antioxidant, and antimicrobial activities of novel 2-quinolone derivatives derived from coumarin. *Res Chem Intermed* 2012;38(2):559-569.
39. Al-Amiery AA, Al-Majedy YK, Kadhum AAH, Mohamad AB. Novel macromolecules derived from coumarin: Synthesis and antioxidant activity. *Sci Rep* 2015;5.
40. Al-Amiery AA, Al-Majedy YK, Kadhum AAH, Mohamad AB. Synthesis of new coumarins complemented by quantum chemical studies. *Res Chem Intermed* 2016;42(4):3905-3918.
41. ) Al-Amiery AA, Musa AY, Kadhum AAH, Mohamad AB. The use of umbelliferone in the synthesis of new heterocyclic compounds. *Molecules* 2011;16(8):6833-6843.
42. Al-Majedy YK, Kadhum AAH, Al-Amiery AA, Mohamad AB. Synthesis and characterization of some new 4-hydroxycoumarin derivatives. *Molecules* 2014;19(8):11791-11799.
43. Al-Amiery AA, Kadhum AAH, Mohamad AB. Antifungal activities of new coumarins. *Molecules* 2012;17(5):5713-5723.
44. Al-Amiery AA, Al-Majedy YK, Al-Duhaidahawi D, Kadhum AAH, Mohamad AB. Green Antioxidants: Synthesis and Scavenging Activity of Coumarin-Thiadiazoles as Potential Antioxidants Complemented by Molecular Modeling Studies. *Free Radicals and Antioxidants* 2016;6(2):173-177.
45. Naama JH, Alwan GH, Obayes HR, Al-Amiery AA, Al-Temimi AA, Kadhum AAH, et al. Curcuminoids as antioxidants and theoretical study of stability of curcumin isomers in gaseous state. *Res Chem Intermed* 2013;39(9):4047-4059.
46. Al-Amiery AA, Al-Majedy YK, Ibrahim HH, Al-Tamimi AA. Antioxidant, antimicrobial, and theoretical studies of the thiosemicarbazone derivative Schiff base 2-(2-imino-1-methylimidazolidin-4-ylidene)hydrazinecarbothioamide (IMHC). *Org.Med.Chem.Lett.* 2012;2(4):1-7.

47. Al-Amiery AA, Al-Bayati RI, Saed FM, Ali WB, Kadhum AAH, Mohamad AB. Novel pyranopyrazoles: Synthesis and theoretical studies. *Molecules* 2012;17(9):10377-10389.
48. Al-Amiery AA, Kadhum AAH, Mohamad AB. Antifungal and antioxidant activities of pyrrolidone thiosemicarbazone complexes. *Bioinorg Chem Appl* 2012;2012.
49. Kadhum AAH, Mohamad AB, Al-Amiery AA, Takriff MS. Antimicrobial and antioxidant activities of new metal complexes derived from 3-aminocoumarin. *Molecules* 2011;16(8):6969-6984.
50. Mohamad AB, Kadhum AAH, Al-Amiery AA, Ying LC, Musa AY. Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0 M H<sub>2</sub>SO<sub>4</sub>. *Met Mater Int* 2014;20(3):459-467.
51. Al-Amiery AA, Kadhum AAH, Kadhum A, Mohamad AB, How CK, Junaedi S. Inhibition of mild steel corrosion in sulfuric acid solution by new schiff base. *Mater* 2014;7(2):787-804.
52. Al-Amiery AA, Kadhum AAH, Alobaidy AHM, Mohamad AB, Hoon PS. Novel corrosion inhibitor for mild steel in HCL. *Mater* 2014;7(2):662-672.
53. Kadhum AAH, Mohamad AB, Jaffar HD, Yan SS, Naama JH, Al-Tamimi AA, et al. Corrosion of Nickel-Aluminum-Bronze alloy in aerated 0.1 M sodium chloride solutions under hydrodynamic condition. *Int J Electrochem Sci* 2013;8(4):4571-4582.
54. Musa AY, Mohamad AB, Al-Amiery AA, Tien LT. Galvanic corrosion of aluminum alloy (Al2024) and copper in 1.0M hydrochloric acid solution. *Korean J Chem Eng* 2012;29(6):818-822.
55. Junaedi S, Kadhum AAH, Al-Amiery AA, Mohamad AB, Takriff MS. Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino 5-Oleyl-1,3,4-Thiadiazol (AOT). *Int J Electrochem Sci* 2012;7(4):3543-3554.