



EIS and DFT Investigations on Corrosion Inhibition of Imines containing Mono- and Diisatin Moieties

Aliyin Abdul Ghani^{1*}, Hadariah Bahron¹, Mohamad Kamal Harun¹,
Karimah Kassim³ and El Hassane Anouar²

¹Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

²Department of Chemistry, College of Science and Humanities Studies, Prince Sattam bin Abdulaziz University, P.O.Box 83, Al-Kharj 11942, Saudi Arabia

³Institute of Science, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

ABSTRACT

Two imines of different molecular sizes namely 3-(phenylimino) indolin-2-one (PII) and 3,3-(1,4-phenylenebis (azan-1-yl-1-ylidene) diindolin-2-one (PDI) were investigated for their corrosion inhibition on mild steel in 1 M HCl solution using electrochemical impedance spectroscopy (EIS). The bigger molecule PDI containing double the amount of isatin moiety exhibited higher inhibition efficiency of 87.3% while PII that contained monoisatin moiety showed a lower inhibition efficiency of 74.8%. Both compounds had an increase in inhibition efficiencies percentage as concentrations increased. Density functional theory (DFT) was used to determine the correlation between the corrosion inhibition efficiency and electronic parameters. The DFT calculations indicated that the corrosion inhibition efficiency was mainly dependant on the frontier orbital energy gap and the chemical softness/hardness of the imines.

Keywords: Corrosion inhibition, DFT, Isatin, mild steel, Schiff base

ARTICLE INFO

Article history:

Received: 28 September 2016

Accepted: 03 February 2017

E-mail addresses:

aliyinabdulghani@gmail.com (Aliyin Abdul Ghani),

hadariah@salam.uitm.edu.my (Hadariah Bahron),

mkharun@gmail.com (Mohamad Kamal Harun),

karimah@salam.uitm.edu.my (Karimah Kassim),

anouarelhassane@yahoo.fr (El Hassane Anouar)

*Corresponding Author

INTRODUCTION

Imines or Schiff bases are organic compounds synthesised from the condensation of amines and aldehydes/ketones, with characteristic C=N functional group (Shakir et al., 2009). They are prevalent due to ease of synthesis, facile fine tuning of electronic structure; the presence of lone pair of electrons on the imine nitrogen that make them ideal chelating agents with metal centres, producing compounds that have interesting properties

and activities (Bahron et al., 1994). Imines are known for their various fields of application, including biological, physical and analytical chemistry (Vicini et al., 2003; Anouar et al., 2013). Furthermore, they are widely used as effective organic corrosion inhibitors, especially in acidic environments, for various types of metal (Ghani et al., 2012; Daoud et al., 2014). Hydrochloric acid solutions are commonly used for the removal of rust and undesired scales on mild steel in many industrial purposes. To resolve the issue of the corrosion of mild steel in hydrochloric acid solutions many fundamental scientific studies and industrial studies have been conducted (Hegazy et al., 2009).

Density functional theory (DFT) calculations have been extensively used to show the interaction between the corrosion inhibitor and mild steel surface (Ju et al., 2008; Ghailane et al., 2013). The corrosion inhibition efficiency mainly depends on the physicochemical, electronic properties of inhibitors, as well as the binding interaction between the inhibitor and the metal surface. For instance, frontier molecular orbitals (HOMO and LUMO) and the Mulliken atomic charge distributions are used in locating the active sites in the organic inhibitors (Daoud et al., 2014; Ghailane et al., 2013).

The present study is aims to show the relationships between the inhibition efficiencies of two Schiff bases, 3-(phenylimino) indolin-2-one (PII) and 3,3-(1,4-phenylenebis(azan-1-yl-1-ylidene) diindolin-2-one (PDI) on mild steel in 1 M HCl with physicochemical and electronic properties of the studied compounds. The DFT calculations were carried out using the hybrid functional B3LYP combined with 6-311+G (d,p) basis set.

METHOD

The synthesis, characterisation, preparation of working electrode and test solution of PII (4) and PDI (5) were based on Ghani et al. (2014).

Electrochemical Measurement

A conventional three-electrode system was employed for the electrochemical studies consisting of a mild steel working electrode, a platinum rod and Ag/AgCl electrode with a Luggin capillary as both counter and reference electrode. The mild steel working electrode was immersed for 15 minutes in test solutions to achieve a steady state open circuit potential or OCP. Electrochemical impedance spectroscopy (EIS) measurements were done at open circuit potential over frequency ranging from 0.05 Hz to 100 kHz and sinusoidal potential perturbation was 10 mV in amplitude with data density of 10 points per decade.

Theoretical Details

The optimisation and frequency calculations of the ground states of the two Schiff bases and its precursor compounds as in Figure 1 were carried out using the DFT hybrid functional B3LYP combined with a triple-Pople-type basis set 6-311+G (d,p) as implemented in Gaussian software (Frisch et al., 2009).

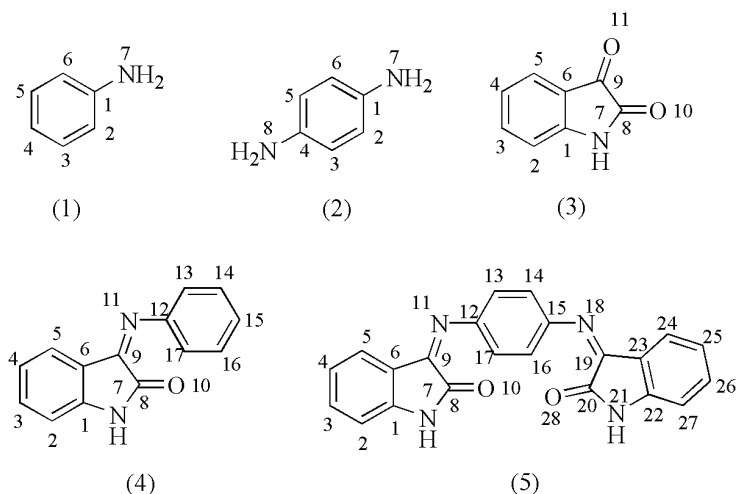


Figure 1. Molecular structures of the precursor compounds: (1) Aniline; (2) p-phenyldiamine; (3) Isatin; and its Schiff bases; (4) PII; (5) PDI

To correlate the corrosion inhibition efficiencies of the compounds on mild steel, a set of electronic properties such as HOMO and LUMO energies, ionisation potential (IP), electronic affinity (EA), energy gap between the HOMO and LUMO, electronegativity (χ), chemical hardness/softness (η), electrophilicity (ω) and dipole moment (μ) were calculated. Mulliken atomic charges were calculated to determine the active sites for the titled inhibitors binding to the mild steel surface. The polarisable continuum model (PCM) were used to take the solvent effects into account when the compound is embedded into a cavity surrounded by solvent described by its dielectric constant ϵ (e.g., for water $\epsilon = 78.3553$) (Tomasi et al., 2005). The frontier molecular orbitals were visualised with Molden software.

RESULTS AND DISCUSSION

Electrochemical Impedance Spectroscopy (EIS)

The corrosion behaviour of mild steel in 1 M HCl in absence of PII and PDI (blank solution) and in the presence of the PII and PDI at different concentrations are shown in Nyquists plots in Figure 2. The capacitive loops have the appearance of slightly depressed semicircles due to a phenomenon called “dispersing effect” where there is heterogeneity, roughness and porosity on the mild steel surface (Tang et al., 2013). The impedance values were significantly enhanced after the addition of both the inhibitors in the acidic solution. The diameter of the semicircles increased with the concentrations of both compounds, but more so in PDI, resulting from the effective surface coverage of the Schiff base inhibitors on mild steel substrate.

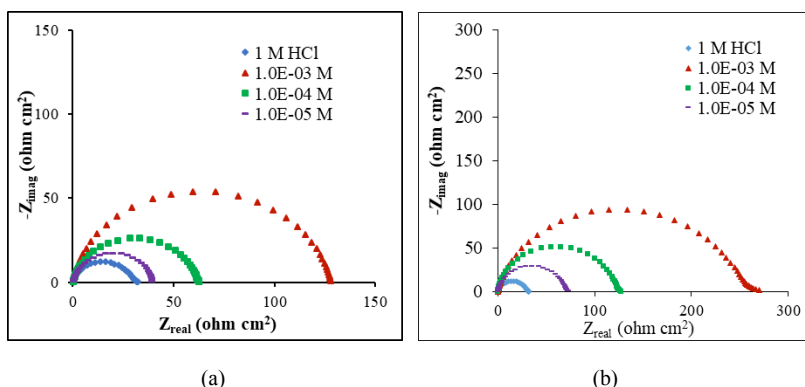


Figure 2. Nyquist plots for mild steel in 1 M HCl with and without the presence of: (a) PII; and (b) PDI in different concentrations

Table 1 shows the parameters obtained from EIS fitting of both inhibitors using the equivalent circuit in Figure 3. R_s and R_p represent the solution resistance and the polarisation resistance respectively. Meanwhile, Constant phase element (CPE) is used in the equivalent circuit to replace a double layer capacitance (C_{dl}) for an accurate impedance spectra fit.

Table 1
Impedance parameters for mild steel electrode in 1 M HCl in the presence of different concentrations of PII and PDI.

	C (M)	R_s (Ω cm ²)	R_p (Ω cm ²)	Y_o (S.sec ⁿ /cm ²)	n	IE (%)
Blank	1 M HCl	0.13	31.9	197.2×10^{-6}	0.89	-
PII	1×10^{-5} M	0.16	38.9	153.0×10^{-6}	0.90	17.9
	1×10^{-4} M	0.15	61.9	124.1×10^{-6}	0.89	48.4
	1×10^{-3} M	0.18	126.9	78.1×10^{-6}	0.91	74.8
PDI	1×10^{-5} M	0.19	72.6	97.3×10^{-6}	0.88	56.1
	1×10^{-4} M	0.17	125.7	78.3×10^{-6}	0.91	74.6
	1×10^{-3} M	0.24	250.9	36.9×10^{-6}	0.86	87.3

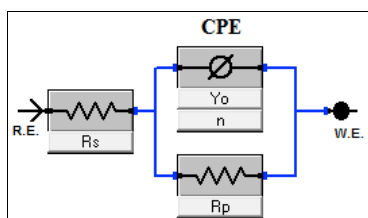


Figure 3. Equivalent circuit used to fit the Nyquist plots

The impedance of constant phase element consists of Y_0 (proportional factor) and n (exponential parameter). n represents the degree of surface roughness where small deviations from 1 indicate a homogenous surface. R_p values represent the degree of difficulty for corrosion reaction to occur, where increasing R_p values indicate decreasing corrosion rate. It can be observed from Table 1 that the R_p values increased with inhibitor's concentrations upon which corrosion reactions were retarded, thus showing improved inhibition efficiency. This effect was more pronounced with PDI, which exhibited higher inhibition efficiency than PII.

The Bode plots for mild steel in the presence and absence of PII and PDI are presented in Figure 4. The Bode phase plots for both inhibitors show a onetime constant feature with only one peak detected per plot as shown in Figure 4(b) and 4(d). This can be correlated with the single semicircle acquired from the Nyquist plot. This one-time constant feature indicates that the inhibitors form intact homogenous layer of protection on the mild steel surface. These plots can also determine the capacitive and resistive behaviour of the system. Both inhibitors show a capacitive behaviour based on Bode phase plot with the phase angle in the range of 69-78° which is approaching 90°, denoting an ideal capacitive response.

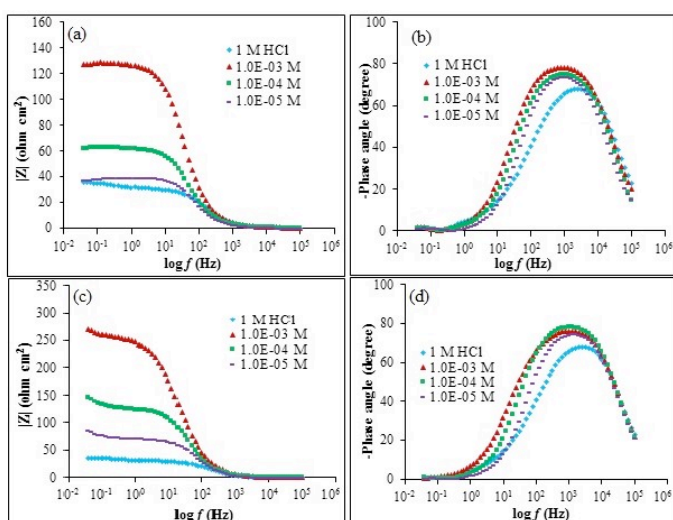


Figure 4. Bode plots of mild steel in 1 M HCl: (a) bode modulus of PII; (b) bode phase of PII; (c) bode modulus of PDI; and (d) bode phase of PDI

Bode modulus plots 4(a) and 4(c) indicate the real impedance (Z_{real}) values from high to low frequency region. Z_{real} at low frequency increases with the increase in concentration of the Schiff base inhibitors. This demonstrates that at higher concentrations, the adsorption of inhibitors increases, hence improving the corrosion resistance.

Theoretical Calculations

The corrosion inhibition efficiencies IE (%) and the calculated electronic properties of the compounds 1-5 are shown in Table 2. Simple and multiple linear regression curves between the inhibition efficiencies (IE) and the electronic parameters of the compounds 1-5 are displayed in Figure 5.

Table 2
Electronic properties (eV) of the 1-5 compounds calculated at the B3LYP/6-311+G (d, p) level of theory.

	ϵ_{HOMO}	ϵ_{LUMO}	IP	EA	ϵ_{Gap}	c	h	S	ΔN	μ (D)	IE %
1	-5.69	-0.47	5.69	0.47	5.22	3.08	2.61	0.19	0.75	2.46	20.8
2	-4.81	-0.43	4.81	0.43	4.38	2.62	2.19	0.23	1.00	0.00	35.3
3	-6.84	-3.18	6.84	3.18	3.66	5.01	1.83	0.27	0.54	8.99	46.3
4	-6.37	-2.96	6.37	2.96	3.41	4.66	1.70	0.29	0.69	3.04	74.8
5	-5.92	-3.06	5.92	3.06	2.86	4.49	1.43	0.35	0.88	2.79	87.3

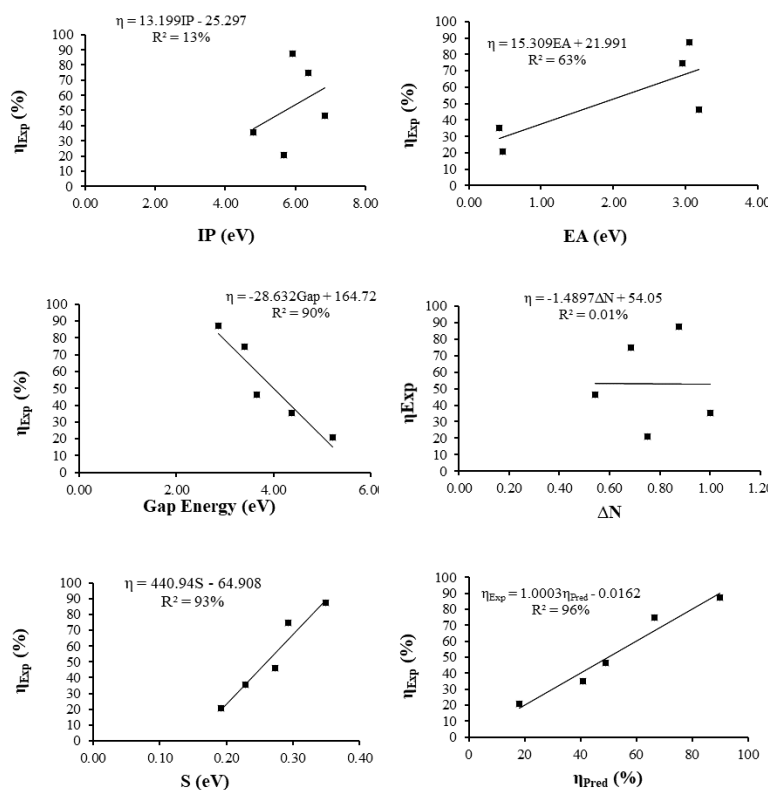


Figure 5. Regression curves between the corrosion inhibition efficiency and electronic properties of the compounds 1-5

There were strong correlations between energy gap, hardness and softness parameters with correlation coefficients (R^2) of 90, 90 and 93%, respectively. Moderate correlations were obtained with the electronic affinity and electrophilicity with R^2 of 63 and 66% respectively. Surprisingly, weak correlations were obtained with the number of transferred electron, dipole moment and ionisation potential with R^2 of 0.01, 0.03 and 13% respectively.

In order to improve the correlation, different parameters were combined using multiple linear regressions. The combination of the gap energy, softness and hardness parameters give the best correlation with R^2 of 96%. The band gap energy plays an important role in determining the inhibitors capability to donate/accept electrons to/from the mild steel surface. The energy gap of PDI and PII are 2.86 and 3.41 eV respectively. The low gap energy value for PDI is an indication that it is easier for the electrons to be transferred due to the low energy barrier between the HOMO and LUMO. Thus, explaining the higher inhibition efficiency value of PDI compared with PII.

The HOMO and LUMO molecular orbitals of compounds 1-5 are shown in Figure 6. The HOMO orbitals are well delocalised over the whole compounds, except for the PDI where the delocalisation is mainly in the central part. Similar observation has been obtained with the LUMO orbitals. HOMO and LUMO orbitals are useful to predict the adsorption centres of interaction between the inhibitor and metal surface (Fang et al., 2002; Bereket et al., 2002).

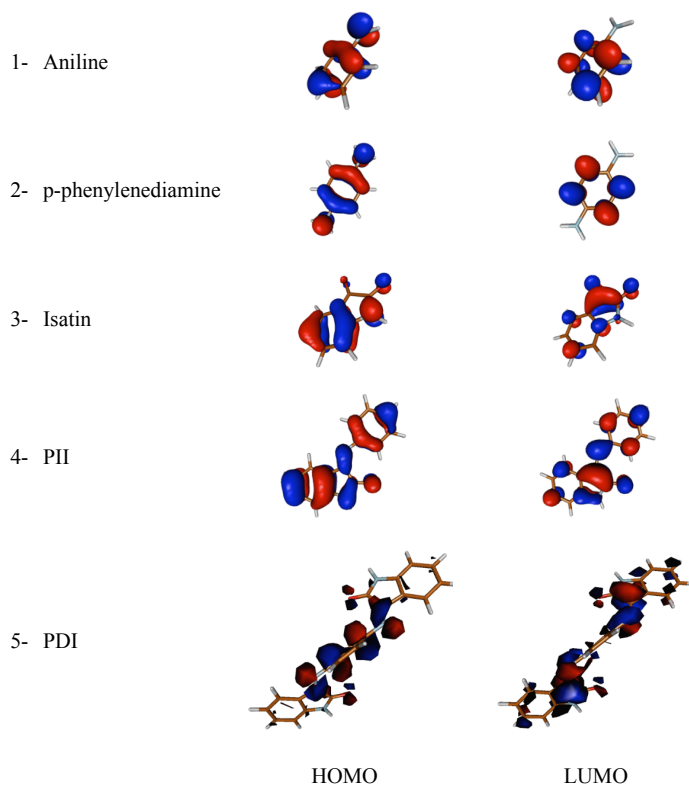


Figure 6. Frontier molecular orbitals of the Schiff base inhibitors (Isovalue 0.03)

The efficient inhibitors are those donating electrons to *d*-orbital of the metal, and accepting electrons from the metal surface (Ju et al., 2008). The electronic density delocalisation of HOMO and LUMO orbitals clearly showed that the compounds have donor/acceptor electron to/from the metal surface.

The number of transferred electrons from the inhibitor to the metal (ΔN) was calculated. The higher inhibition efficiency of PDI compared with PII is in good agreement with the increased ΔN values (0.69 and 0.88 for PII and PDI respectively). This is consistent with previous studies, which reported that the inhibition efficiency increased with electron-donating ability of the metal surface (ΔN) (Torres et al., 2013).

In order to determine the main active sites for the compounds, Mulliken atomic charges were calculated at the B3LYP level of theory as in Table 3 where some of the atomic centres possess negative charges, while others positive ones. As for aniline and PPD there are excess of negative charge on nitrogen heteroatoms (N7 and N8 with atomic charges of -0.49 and -0.53 Cb in aniline and PPD respectively). These heteroatoms play the role of electron donors to the vacant *d*-orbitals of metal surface atoms. Meanwhile, the carbon atoms C1, C2, C4, C5, C22, C24 and C27 in aromatic rings of isatin, PII and PDI are the most active sites compared with nitrogen heteroatoms. Therefore, the adsorption/interaction between isatin, PII and PDI with the metal surface atoms are mainly related to the electrostatic interactions between aromatic rings in the compounds with the metal substrate. The N atoms are weaker adsorption centres due to the steric hindrance of benzyl rings.

Table 3
Mulliken atomic charges for the 1-5 compounds calculated at the B3LYP/6-311+G (d, p) level of theory

Inhibitor	1	2	3	4	5
C1	-0.024	-0.023	-0.988	-0.705	-0.57991
C2	-0.075	-0.127	-0.923	-0.564	-0.57067
C3	-0.195	-0.126	-0.233	-0.234	-0.25756
C4	-0.189	-0.023	-0.064	-0.430	-0.24313
C5	-0.195	-0.127	-0.405	-0.509	-0.67136
C6	-0.075	-0.126	2.545	1.350	1.253635
N7	-0.490	-0.530	-0.170	-0.256	-0.21951
N8	-	-0.530	-	-	-
C8	-	-	0.382	0.398	0.102577
C9	-	-	-0.388	0.213	0.308284
O10	-	-	-0.407	-0.395	-0.35462
O11	-	-	-0.343	-	-
N11	-	-	-	0.034	0.193489
C12	-	-	-	0.274	-0.42945
C13	-	-	-	0.027	0.229582
C14	-	-	-	-0.426	0.229758
C15	-	-	-	-0.093	-0.42937
C16	-	-	-	-0.577	-0.0293

Table 3 (continue)

C17	-	-	-	0.112	-0.02919
N18	-	-	-	-	0.193549
C19	-	-	-	-	0.308038
C20	-	-	-	-	0.102552
N21	-	-	-	-	-0.2195
C22	-	-	-	-	-0.57975
C23	-	-	-	-	1.253771
C24	-	-	-	-	-0.67141
C25	-	-	-	-	-0.24314
C26	-	-	-	-	-0.25753
C27	-	-	-	-	-0.57079
O28	-	-	-	-	-0.35461

CONCLUSION

The corrosion inhibition investigation through EIS showed that both Schiff base compounds displayed inhibitor properties where the inhibition efficiencies increased with concentration of inhibitors. The higher inhibition efficiency of PDI compared with PII was confirmed by DFT calculations. Simple and multiple linear regressions showed that the corrosion inhibition efficiency mainly depends on energy gap, chemical hardness and softness of the studied compounds. Frontier orbital delocalisation and Mulliken atomic charge clearly showed that the PDI compound have different active sites as donor or acceptor of electrons to/from mild steel, which promotes the protection of mild steel against corrosion in acidic solution.

ACKNOWLEDGEMENTS

The authors express their gratitude to the Research Management Institute for its Research Acculturation Grant Scheme (600-RMI/RAGS 5/3 (139/2014)), the Faculty of Applied Sciences and Institute of Science of Universiti Teknologi MARA for providing research facilities. Authors would also like to thank Mr. Mohamad Safwan bin Jusof from Universiti Malaya for his help to access the supercomputer (PTMLXSMP).

REFERENCES

- Anouar, E., Raweh, S., Bayach, I., Taha, M., Baharudin, M. S., Di Meo, F., Hasan, M. H., Adam, A., Ismail, N. H., Weber, J. -F. F., & Trouillas, P. (2013). Antioxidant properties of phenolic Schiff bases: structure–activity relationship and mechanism of action. *Journal of Computer Aided Molecular Design*, 27, 951-964.
- Bahron, H., Larkworthy, L. F., Marecaux, A., Povey, D. C., & Smith, G. W. (1994). Structures of bis (Nn-butylsalicylideneiminato) cobalt (II) and bis (N-tert-butylsalicylideneiminato) cobalt(II) complexes and reactivity towards oxygen and nitric oxide. *Journal of Chemical Crystallography*, 24(2), 145-150.

- Behpour, M., Ghoreishi, S., Mohammadi, N., Soltani, N., & Salavati-Niasari, M. (2010). Investigation of some Schiff base compounds containing disulfide bond as HCl corrosion inhibitors for mild steel. *Corrosion Science*, *52*, 4046-4057.
- Bereket, G., Hür, E., & Öğretir, C. (2002). Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium. *Journal of Molecular Structure – THEOCHEM*, *578*, 79-88.
- Daoud, D., Douadi, T., Issaadi, S., & Chafaa, S. (2014). Adsorption and corrosion inhibition of new synthesized thiophene Schiff base on mild steel X52 in HCl and H₂SO₄ solutions. *Corrosion Science*, *79*, 50-58.
- Emregül, K. C., Düzgün, E., & Atakol, O. (2006). The application of some polydentate Schiff base compounds containing aminic nitrogens as corrosion inhibitors for mild steel in acidic media. *Corrosion Science*, *48*, 3243-3260.
- Fang, J., & Li, J. (2002). Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides. *Journal of Molecular Structures-THEOCHEM*, *593*, 179-185.
- Frisch, M. J. (2009). *Gaussian 09*, Revision A.02.
- Ghailane, T., Balkhmima, R., Ghailane, R., Souizi, A., Touir, R., Ebn Touhami, M., Marakchi, K., & Komiha, N. (2013). Experimental and theoretical studies for mild steel corrosion inhibition in 1M HCl by two new benzothiazine derivatives. *Corrosion Science*, *76*, 317-324.
- Ghani, A. A., Bahron, H., Harun, M. K., & Kassim, K. (2012). Corrosion inhibition study of a heterocyclic Schiff base derived from isatin. *Advanced Materials Research*, *554-556*, 425-429.
- Ghani, A. A., Bahron, H., Harun, M. K., & Kassim, K. (2014). Schiff bases derived from isatin as mild steel corrosion inhibitors in 1 M HCl. *The Malaysian Journal of Analytical Sciences*, *18*, 507-513.
- Hegazy, M. (2009). A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution. *Corrosion Science*, *51*, 2610-2618.
- Ju, H., Kai, Z.P., & Li, Y. (2008). Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: a quantum chemical calculation. *Corrosion Science*, *50*, 865-871.
- Keleş, H. (2011). Electrochemical and thermodynamic studies to evaluate inhibition effect of 2-[(4-phenoxy-phenylimino) methyl]-phenol in 1M HCl on mild steel. *Materials Chemistry and Physics*, *130*, 1317-1324.
- Li, J., & Zhang, M. (2014). Atomic insights into adsorption of thiophenol derivatives as corrosion inhibitors for mild steel in hydrochloric acid solution. *Materials Research Innovations*, *18*, 38-42.
- Pearson, R. G. (1988). Absolute electronegativity and hardness: application to inorganic chemistry. *Inorganic Chemistry*, *27*, 734-740.
- Shakir, M., Azam, M., Parveen, S., Khan, A. U., & Firdaus, F. (2009). Synthesis and spectroscopic studies on complexes of N, N'-bis-(2-pyridinecarboxaldehyde)-1, 8-diaminonaphthalene (L); DNA binding studies on Cu (II) complex. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *71*, 1851-1856.

- Tomasi, J., Mennucci, B., & Cammi, R. (2005). Quantum Mechanical Continuum Solvation Models. *Chemical Reviews*, *105*, 2999-3093.
- Touir, R., Dkhireche, N., Ebn Touhami, M., Lakhrici, M., Lakhrici, B., & Sfaira, M. (2009). Corrosion and scale processes and their inhibition in simulated cooling water systems by monosaccharides derivatives: Part I: EIS study. *Desalination*, *249*, 922-928.
- Torres, V., Rayol, V., Magalhães, M., Viana, G., Aguiar, L., Machado, S., Orofino, H., & D'Elia, E. (2013). Study of thioureas derivatives synthesized from a green route as corrosion inhibitors for mild steel in HCl solution. *Corrosion Science*.
- Vicini, P., Geronikaki, A., Incerti, M., Busonera, B., Poni, G., Cabras, C. A., & La Colla, P. (2003). Synthesis and biological evaluation of benzo [d] isothiazole, benzothiazole and thiazole Schiff bases. *Bioorganic and Medicinal Chemistry*, *11*, 4785-4789.

