Anti-corrosive properties of quercetin and its derivatives on Fe(111) surface: a quantum chemical approach

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Abstract

Quercetin, and its derivatives are potential anti-corrosive agents for mild steel in HCl as evaluated by recent weight-loss techniques as well as electrochemical studies. But the actual mechanism of anticorrosion and mode of adsorption of these inhibitors have not yet been explored. In the present work corrosion inhibition activity of quercetin, and its derivatives, are explored by density functional theory (DFT) in order to obtain inhibition efficiencies and reactive sites of corresponding compounds as possible corrosion inhibitors on Fe(111) surface. Quantum chemical parameters such as frontier molecular orbital (HOMO, LUMO) energies, charge distribution, electron affinity, ionization potential, dipole moment, hardness, softness, electronegativity, electrophilicity and charge transfer between quercetin and Fe(111) surface have been evaluated. Adsorption energies of quercetin derivatives on iron surface revealed that the binding is mostly chemisorptive in nature. There is close agreement between theoretical and experimental values of corrosion inhibition efficiency. Thus, suitably designed quercetin derivatives can act as good anti-corrosive agents on iron surface.

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Graphic abstract

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1 Introduction

Corrosion is the biggest problem in industries which causes container leakage, structural failure etc. often leading to industrial plant shutdown. Corrosion leads to increase of maintenance expenditure, economic loss, product contamination, and plant or structure breakdown [1–5]. Generally, most of the metal surfaces are reactive to air, moisture etc. due to their electropositive nature and high reduction potential, leading to corrosion. The use of corrosion inhibitors is very important to protect metal surfaces from corrosion [6, 7]. There are several ways to prevent corrosion. Anti-corrosion paints, galvanization, cathodic or anodic protection are some of the methods used. Use of organic inhibitors which dissolve in the corrosive solution is an effective alternative to reduce the aggressiveness of acidic media on metal surfaces [8]. Various organic compounds have been reported till now as corrosion inhibitors [2, 6, 9–14]. The interaction between these organic moieties (ligands) and the metal surface may be through (1) ligand π electron interaction with metal, (2) electrostatic forces of attraction between charged

molecules and metal, and (3) interaction between lone pairs of electrons in the ligand with metal [15]. Corrosion inhibition efficiency largely depends upon nature of the functional groups, their electronic structure, presence of heteroatoms like oxygen, nitrogen, sulfur etc., presence of ring and planar structures, medium (environment) [16–19]. Chemically synthesized corrosion inhibitors are generally hazardous to humans and not environment-friendly by themselves or by their method of preparation. Therefore it is important to find environment-friendly corrosion inhibitors, which can be extracted from plants or other green sources. Metal surfaces generally adsorb corrosion inhibitors either by physisorption or by chemisorption mechanism. Corrosion inhibition efficiency of an organic dye increases when the adsorption energy is high, i.e. when adsorption occurs via chemisorption [6].

Generally in acidic medium, nitrogen and sulphur containing materials like amine, imine, thiol, thioaldehyde etc., and compounds with an aromatic ring, can act as corrosion inhibitors. Hence these types of naturally occurring dyes are more important as protecting agents against corrosion than chemically synthesized compounds [20–22].

Quercetin is a naturally occurring molecule which is found in many fruits, leaves, vegetables and grains [8, 23, 24]. It is a bioactive compound which has potential medicinal use and also has some anti-inflammatory [23], anti-oxidant as well as anticancer properties [25] and also can be used as a naturally obtained stabilizing agent for polymeric materials [26]. It may be used as corrosion inhibitor on iron surfaces [8] due to its planar structure and presence of heteroatom e.g. oxygen in keto and alcohol groups. A planar molecule is more easily adsorbed on a flat metal surface than a bent structure. But theoretical studies of quercetin and its derivatives in literature is scarce.

Theoretical investigations of corrosion inhibition efficiency of compounds on metal surfaces are important to select potential and efficient inhibitors. To gain a broad idea about the protecting efficiency of these candidate molecules, theoretical calculations are important. This will not only enhance the overall knowledge of corrosion mechanisms under an organic coating but also become a prerequisite for finding out a highly efficient anti-corrosive dye. To the best of our knowledge, this is the first theoretical investigation of anti-corrosion properties of quercetin and its derivatives.

Density Functional Theory (DFT) allows one to calculate quantum chemical parameters such as energy of the highest occupied molecular orbital (ϵ_{HOMO}) and of the lowest unoccupied molecular orbital (ϵ_{LUMO}), electronegativity (χ), ionization potential (IP), electron affinity (EA) and hardness (η) among others, and analyze their correlation with the corrosion inhibition effect [27–29]. There is much experimental evidence on electrochemical behavior of quercetin [30, 31], especially via cyclic voltammetry [32]. Hence these properties may be correlated with corrosion inhibition by multivariate methods.

The objective of the present work is to derive a simple charge transfer model for metal–ligand (M–L) electron donation and back-donation, using a density functional approach, to try to explain the corrosion inhibition capacity of quercetin and its derivatives. In order to evaluate corrosion inhibition efficiency, electronic properties named above were used. As quercetin can be synthesized or extracted easily, several derivatives were designed, and calculations carried out with them. In particular, all anti-corrosion property of the molecules was tested on Fe(111) surface which is more prone to corrosion and has high corrosion index [33]. Optimized geometries of the molecules were planar, and presence of phenolic OH, NH_2 and ketone groups make the molecules good corrosion inhibitors. The amount of charge transferred between ligand and iron surface give an idea of corrosion efficiency of the molecules.

2 Methodology

All geometry optimization of the model quercetin dyes both in gas and solvent phase were carried out in Density Functional Theoretic (DFT) formalism, with 6-311G++(d,p) basis set [34, 35] and B3LYP functional [36, 37] by Gaussian 09 W program suite [38] using Onsager's self-consistent reacting field (SCRf) method [39, 40]. With each optimized geometry, different quantum chemical reactivity parameters such as ionization potential (IP), electron affinity (EA), electronegativity (χ), hardness (η), softness (S) and electrophilicity index (ω) were computed. Koopmans' approximation gives ionisation potential as $\text{IP} = -\epsilon_{\text{HOMO}}$ and electron affinity as $\text{EA} = -\epsilon_{\text{LUMO}}$ [39, 40]. Here, ϵ_{HOMO} and ϵ_{LUMO} are the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals (MOs) respectively. Electronegativity (χ), hardness (η), softness (S) can all be calculated from the orbital energies as follows [28]:

$$\chi = -0.5(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) \quad (1)$$

$$\eta = 1/S = 0.5(\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}) \quad (2)$$

The fraction of electron which is transferred between the metal surface and the corrosion inhibitor is given by the following relation [29].

$$\Delta N = \frac{\chi_{\text{metal}} - \chi_{\text{molecule}}}{2(\eta_{\text{metal}} + \eta_{\text{molecule}})} \quad (3)$$

where χ represents electronegativity and η represents global hardness of the entity (metal or inhibitor). The theoretical values of χ_{metal} and η_{metal} for Fe are +7 eV and 0 eV^{-1} respectively [29]. The value of ΔN indicates the amount of electron transferred from molecule to metal ($\Delta N > 0$) or metal to molecule ($\Delta N < 0$) [41].

Now to find out total interaction energy (E_{ads}) between the Fe (111) surface and the molecule the following equation is used [41].

$$E_{\text{ads}} = E_{(\text{Fe-Inhibitor})} - (E_{\text{inhibitor}} + E_{\text{Fe}}) \quad (4)$$

The Fukui functions [26] f_k^+ and f_k^- , for electrophilic and nucleophilic attack on the k th atom of a molecule, can be written as

$$f_k^+ = \rho_{k(N+1)}(r) - \rho_N(r) \quad (5)$$

$$f_k^- = \rho_N(r) - \rho_{k(N-1)}(r) \quad (6)$$

Here $\rho_{k(N+1)}$, ρ_N and $\rho_{k(N-1)}$ are the electron densities of $(N+1)$, N and $(N-1)$ electron systems respectively. Probability of such attacks are more where the values of f_k^+ and f_k^- are large.

To study the adsorption behaviour of quercetin and its derivatives onto Fe(111) surface, the PW-SCF code was used, as implemented in the Quantum Espresso

[42] package, which allows execution of periodic density functional theory (DFT) calculations using projector augmented wave (PAW) method [43]. The convergence threshold on total energy is 10^{-6} and the one on forces is 10^{-3} (both in a.u.). Kinetic energy cutoff of 50 Ry was used for wavefunctions, and that for charge density was 200 Ry [44]. The calculations were performed with norm-conserving pseudopotentials and the Marzari–Vanderbilt [45] smearing method using a smearing parameter of 0.02 and a $2 \times 2 \times 1$ k-point mesh [46] within the Perdew–Zunger exchange–correlation parametrization. A (6×6) lateral cell of the Fe(111) surface was modeled as periodically repeated slabs with six layers. The bottom three atomic layers were kept frozen and set to the estimated bulk parameters, whereas the remaining layers were fully relaxed during the calculations. The lateral cell has dimensions were $a = b = 16.2148 \text{ \AA}$ and $c = 49.1345 \text{ \AA}$, which

includes a vacuum region of thickness greater than $30 \text{ \AA}$ to ensure no interaction between the slabs has been optimized and then 6×6 surface with six layer is used for dye adsorption calculations. From this, adsorption energies were calculated using the following equation.

$$E_{\text{ads}} = E_{\text{Fe(111)mol}} - E_{\text{mol}} - E_{\text{Fe(111)}} \quad (7)$$

Inhibition efficiency (IE) was calculated following previous work [47, 48]. Reactivity parameters as given above were calculated for two molecules, 2-aminopyrazine and 2-amino-5-bromopyrazine, with SBKJC basis [49] and B3LYP functional in DFT formalism. Regression analysis was carried out between experimental IE values and ΔE , η and ΔN . The regression parameters were used in predicting IE values of Q2, Q3, Q4 and Q7.

3 Results and discussion

Figure 1 shows the model chemical structure of quercetin derivatives considered in the present work. Quercetin is indicated by Q2. Recent experimental studies showed that quercetin can be used as a potential corrosion inhibitor against C38 steel [21] due to the presence of heteroatoms. Fe(111) surface was chosen for this study, as it is more reactive and has a very open surface structure [50, 51]. Due to the planar structure of quercetin backbone, a parallel interaction between the metal surface and the molecule was expected to occur which would enable facile adsorption of the molecule.

Fig. 1 Chemical structure descriptors of quercetin derivatives

Fig. 2 Electronegativity (χ), ionization potential (IP), electron affinity (EA) and chemical hardness (η) of different derivatives of quercetin in aqueous phase (Table S1)

The reactivity parameters of the molecules viz. ϵ_{HOMO} , ϵ_{LUMO} , ΔE , χ , η , IP, EA etc. in both gas and solvent phase are presented in Table S1.

HOMO (LUMO) energies and charge densities are important parameters which control the electron donation (acceptance) ability of a molecule. Here we find Q2, Q3, Q4 and Q7 have higher HOMO energy value among the seven derivatives i.e. they are more likely to donate electrons. Another important index is the HOMO and LUMO energy gap (ΔE), which measures the reactivity of a molecule. A lower ΔE value (Fig. 3) indicates higher reactivity and hence higher inhibition efficiency. Due to the stabilization in the solvent phase, band gap of the model systems are lower in solvent phase than in gas phase as indicated in Table S1.

Among the series, the lowest HOMO–LUMO gap of 3.17 is found for Q7 derivative. Electronegativity (χ) plays an important role for determining reactivity analysis. The tendency of a molecule to donate electrons towards another species varies inversely to its electronegativity. Hence the molecule with lower electronegativity value is more prone to donate electrons. Among the series Q1–Q7, very low electronegativity is found for Q2, Q3, Q4, Q7 and which follow the order $Q7 < Q3 < Q2 < Q4$ as indicated by the Fig. 2. Ionisation potential is an index which is also a descriptor of reactivity of a species. A low ionization potential indicates

that the molecule will ionise easily i.e. it can easily donate an electron. From Fig. 2, it is clear that among the seven derivatives Q2, Q3, Q4 and Q7 have low ionisation potential which follow the increasing order $Q7 < Q3 < Q2 < Q4$ indicating that Q7 possesses the lowest ionization potential. One can also describe the reactivity of a species by its electron affinity (EA). Lower EA indicates higher reactivity. Figure 2 shows Q2, Q3, Q4, Q7 have lower electron affinity, indicating that they are good electron donors as explained from their corresponding ϵ_{HOMO} level. The global hardness (η) is also an important reactivity descriptor. All the derivatives of quercetin possess very low hardness value indicating their higher softness, which means they are more reactive. This reactivity order of first four derivatives is $Q4 < Q2 < Q3 < Q7$. So from the above Fig. 3 it is clear that Q2, Q3, Q4 and Q7 have lower HOMO energy, lower ΔE , lower electronegativity, lower IP and EA and also lower hardness, which imply that these four derivatives are likely to be more reactive among all seven derivatives. Therefore these four molecules were selected as model corrosion inhibitors on iron surface.

Optimized geometries and HOMO–LUMO plots of the seven dyes in aqueous medium are shown in Fig. 3 which provides information about the potential of charge transfer of the studied molecules. From Fig. 3 it is clear that HOMO charge density on the heteroatoms follows the order $Q7 > Q3 > Q2 > Q4$ for first molecules. Again from gas phase to solvent phase, both the HOMO and LUMO have nearly same charge density but in acidic medium the charge density is slightly increased on heteroatoms on HOMO which imply that these derivatives are more efficient corrosion inhibitors in acidic medium.

Based on the above results, one can now calculate the corrosion inhibition efficiency of Q2, Q3, Q4 and Q7 on Fe(111) surface in gas phase. In order to do that, the total negative charge (TNC) on the adsorbate is needed. This is also a good descriptor of charge transfer from inhibitor to metal surfaces. With higher negative charge a molecule has better tendency to be adsorbed on the metal surfaces [15]. In the present work, Mulliken atomic charges [28] have been used to calculate atomic charges. It is found that all the heteroatoms present in these compounds (adsorbates) have negative Mulliken atomic charges (Table 1), which indicates transfer of negative charge can be possible to the metal surface. Mulliken atomic charge

Fig. 3 HOMO-LUMO gap of quercetin derivatives in aqueous phase

Table 1 Mulliken atomic charges on heteroatoms of molecules Q2, Q3, Q4 and Q7

Molecule	Mulliken atomic charges on heteroatoms (atom numbers are in parentheses)					
Q2	−0.275 (O11)	−0.207 (O12)	−0.329 (O13)	−0.240 (O14)	−0.296 (O21)	−0.232 (O22)
Q3	−0.277 (O11)	−0.207 (O12)	−0.330 (O13)	−0.239 (O14)	−0.272 (O21)	−0.342 (O22)
Q4	−0.275 (O11)	−0.206 (O12)	−0.329 (O13)	−0.236 (O14)	−0.244 (O21)	−0.156 (O22)
Q7	−0.277 (O11)	−0.209 (O12)	−0.366 (O13)	−0.134 (O14)	−0.276 (O22)	−0.346 (N23)

Fig. 4 Fukui indices for electrophilic (f_k^+) and nucleophilic (f_k^-) sites in gas phase of Q2, Q3, Q4 and Q7 (isosurface value 0.08)

density also follow the order $Q7 > Q3 > Q2 > Q4$ which is reflected from Table 1.

Fukui Functions, f_k^+ and f_k^- which are important descriptors of transfer of electrons from one species to another, indicate the atomic sites where the possibility of electrophilic and nucleophilic attack would be more. The f_k^+ and f_k^- surfaces are shown in Fig. 4 which indicates that the electron densities are mainly populated on the heteroatoms.

Hence for a given species, nucleophilic attack is more facile on heteroatoms than electrophilic attack. A clear look at Table 2 indicates that the value of ΔN (calculated by using Eq. 3), the fraction of electrons transferred from molecule to Fe(111) surface, for these systems increases in the order $Q4 < Q2 < Q3 < Q7$ which indicates Q7 is more prone to donate electrons to metal surface than the other molecules.

Now to measure the inhibition efficiency towards Fe (111) surface of Q2, Q3, Q4 and Q7, the adsorption energy (E_{ads}) of these molecules have been calculated. Adsorption energy, E_{ads} is calculated by using Eq. 4 on these systems. It increases in the same order as ΔN . Higher negative value of interaction energy indicates higher stability of the adsorbed form.

Figure 5 presents the side and top views of the most stable (lowest energy) adsorption of these species upon Fe(111) surface. Adsorption energy indicates how strongly the dye binds to the metal surface. Inhibitor energy (E_{inh}), energy of Fe surface (E_{Fe}), energy of metal-inhibitor composite (E_{Fe-Inh}) and the adsorption energy (E_{int}) are presented in Table 3. From Table 3, it is seen that all the dyes are chemisorbed on the metal surface and the adsorption energy increases in the order $Q7 < Q3 < Q2 < Q4$ which is in good agreement with other parameters like E_{HOMO} , ΔE , electronegativity, ionisation potential, hardness or softness, Fukui indices and ΔN which can also be correlated with inhibition efficiency.

Finally, the results of calculations of inhibition efficiency (IE) of anti-corrosion agents are presented. First, some functional relation between IE and common reactivity descriptors involving electron transfer (viz., ϵ_{HOMO} , ϵ_{LUMO} , χ) is needed. IE of 2-Aminobenzimidazole (ABI), Benzo-triazole (BTA) and 1,3-Benzothiazole (BTH) are known [9]. Similar calculations were carried out on these molecules in aqueous phase, and following the reported procedures, pairwise linear regression analysis was carried out between IE and the reactivity descriptors named above. The detailed procedure is described in Supporting Information. The following linear equations were obtained as a result.

$$IE = 5.481 \times \epsilon_{HOMO} + 125.9 \quad (8)$$

Table 2 Interaction between inhibitor and metal surface

Molecule	ΔN	TNC	E_{Fe-Inh} (eV)	E_{inh} (eV)	E_{Fe} (eV)	E_{ads} (eV)
Q2	0.72	-4.8	-119,573.36	-5382.15	-114,189.04	-2.17
Q3	0.75	-4.8	-119,436.23	-5244.36	-114,189.04	-2.85
Q4	0.71	-4.8	-119,756.73	-5566.53	-114,189.04	-1.16
Q7	0.80	-5.2	-119,622.16	-5429.35	-114,189.04	-3.78

ΔN =charge transferred from Qi to Fe(111) (vide Eq. (3)), TNC=total negative charge on Qi, E_{Fe-Inh} =energy of Fe-Qi complex, E_{inh} =energy of Qi, E_{Fe} =energy of Fe surface, E_{ads} =adsorption energy (vide Eq. (7)), Qi=quercetin derivatives

Fig. 5 Side and top views after adsorption of four Quercetin derivatives on Fe(111) surface

Table 3 Corrosion inhibition efficiency (IE) of quercetin derivatives

Inhibitor	Prediction of IE using equation			Average IE (%)	Experimental IE ^a (%)
	8	9	10		
Q2	92.14	84.43	88.27	88.28	92.10
Q3	93.39	84.70	89.03	89.04	–
Q4	91.97	84.43	88.19	88.19	–
Q7	93.78	84.37	89.06	89.07	–

^aRef [52]

$$IE = 5.423 \times \epsilon_{LUMO} + 96.36 \quad (9)$$

$$IE = -5.462 \times \chi + 111.1 \quad (10)$$

These relations are used, with data presented in Table S2, for the quercetin derivatives Q2, Q3, Q4 and Q7, to estimate corrosion inhibition efficiency (IE) of the latter. The results are shown in Table 3 below.

We find reasonable agreement between theoretical and experimental values for quercetin. It is to be noted that while IE values of Q2 and Q4 are comparable, IE value of Q3 value is a little higher and that of Q7 is significantly higher than the others. The only difference between Q2 and Q4 on one hand and Q3 and Q7 on the other is the presence of NH₂ group on the phenyl group on right (see Fig. 1). The electron donating ability of the group must be aiding in the corrosion inhibition of the molecules. The methoxy group on Q7 must have an additional (synergistic) effect.

4 Conclusion

In this study, quantum chemical parameters like HOMO and LUMO energies (ϵ_{HOMO} , ϵ_{LUMO}), energy gap between them (ΔE), electronegativity (χ), hardness (η), ionisation potential (IP), electron affinity (EA), Mulliken atomic charges and Fukui indices for a series of quercetin derivatives were calculated. The fraction of electrons transferred or the electron donating ability is also measured for the same species, which follows the order Q7 > Q3 > Q2 > Q4. Based on these parameters, adsorption of these four dyes on iron(111) surface has been simulated quantum mechanically. Highly negative adsorption energies clearly indicate that the adsorption is most likely to be purely chemisorptive in nature. Adsorption energy of these dyes increases in the order of Q4 < Q2 < Q3 < Q7. We argue that presence of amine nitrogen increases the electron donating power and is primarily responsible for strong adsorption of the molecules on iron surface. Predicted corrosion inhibition efficiency value of quercetin is close to the experimentally observed value. Therefore, suitably designed quercetin derivatives can act as good corrosion inhibitors on iron(111) surface.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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