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Capsaicinoids as Green Corrosion Inhibitors: Quantum Chemical and Monte Carlo Simulation Studies

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The corrosion inhibition test of capsaicinoids extract from peppers has been previously reported using gravimetric and electrochemical analysis. Results showed that capsaicinoids have good potential as corrosion inhibitors because of their high corrosion inhibition efficiency. However, it should be noted that several types of capsaicinoids are present in the capsaicinoids extract. This variation causes previous study to be unable to identify the compounds with the most potential as corrosion inhibition. In present study, the density functional theory (DFT), *ab initio* and Monte Carlo simulation studies explain the problem. The quantum parameters of the four major compounds in capsaicinoids such as capsaicin, dihydrocapsaicin, nordihydrocapsaicin and homocapsaicin were compared to predict the compound with the highest corrosion inhibition. The Monte Carlo simulation study was applied to study the interaction mechanism between capsaicinoids and metal surfaces. The quantum parameter has linearity with the adsorption energy of capsaicinoids on the metal surface. The most significant role in inhibiting corrosion was shown by homocapsaicin, followed by capsaicin, dihydrocapsaicin and norcapsaicin. The theoretical study is expected to bridge the gap in an experimental study in designing an effective corrosion inhibitor.

Keywords: Capsaicinoids, DFT, Monte Carlo simulation, Quantum chemical, Corrosion inhibition.

INTRODUCTION

Capsaicinoids are active constituents responsible for the pungent and spicy flavour in chilli peppers. The major compounds in capsaicinoids are mainly capsaicin, dihydrocapsaicin, nordihydrocapsaicin and homocapsaicin [1-3]. There are 20 other types of capsaicinoids in chilies, but the amount is not significant [4,5]. Structurally, capsaicinoids have heteroatomic groups (oxygen and nitrogen) and aromatic rings as π-electron donors. This structure allows capsaicinoids to be potential corrosion inhibitors of metals because they qualify as good inhibitors. The heteroatom and benzene rings in the capsaicinoid structures allow them to adhere firmly to metal surfaces and protect the metal from corrosion.

The capsaicinoids extract from peppers have been applied as corrosion inhibition. Those extracts are reported to have high efficiency in inhibiting corrosion [6-9]. Prakash [6] tested the corrosion inhibition efficiency of capsaicinoids extract on carbon steel in hydrochloric acid medium and reported that the corrosion inhibition efficiency of capsaicinoids extract was 85.76%. Other researchers [7] reported that the capsaicinoids have a corrosion inhibition efficiency against carbon steel in sodium chloride medium of 96%. Sun & Yu [8] reported that polyacrylamide containing capsaicin as a new corrosion inhibitor for mild steel in HCl medium and reported the inhibition efficiency was 96.70%. Oguzie *et al.* [9] reported the utilization of *Capsicum frutescens* biomass extracts for corrosion inhibition against carbon steels. The extract was able to inhibit corrosion by up to 93%. However, previous studies have not been able to conclude specifically, which constituents of capsaicinoids have the most effective on corrosion inhibition.

Theoretical studies provided solutions to problems, which have not been explained in experimental studies, especially on corrosion inhibition [10-17]. This study focuses the significant capsaicinoids compounds which are the most effective at inhibiting the corrosion of metals. This theoretical study uses approach density functional theory, *ab initio* MP2 and Monte Carlo simulation studies. The structural and quantum parameters were used to explain capsaicinoids' chemical properties related to their corrosion inhibition ability. Monte Carlo simulation is used to study in detail the interactions between capsaicinoids and metal surfaces and the energy changes experienced by the system.

EXPERIMENTAL

Quantum chemical calculation: All quantum chemical calculations were performed using the Gaussian 09 [18]. The theoretical study of the corrosion inhibition ability of capsaicin and its derivatives used density functional theory and MP2 with a level of 6-311++G(d,p). The dielectric constant for the water solvent was taken as 78.4 and other solvents were used as in the Gaussian code [19,20]. In employing polarized continuum models, the single-point calculations on gas-phase geometries are sufficient for energetics. The re-optimization structure in presence of solvents was found to have a minor influence on energetic. Therefore, the single point approach has been employed in this study, minimizing computational costs without sacrificing much accuracy in solvation energies.

Theoretically, quantum chemical parameters such as ionization potential (I) and electron affinity (A) were calculated using the theorem of Koopmen [21]. This theorem can explain the relationship between ionization potential (I), electron affinity (A) and energy level (HOMO and LUMO) with eqns. 1 and 2:

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

The electronegativity (χ) is calculated by eqn. 3 [22]:

$$\chi = \frac{E_{HOMO} + E_{LUMO}}{2} \quad (3)$$

Hardness (η) can be calculated based on eqn. 4 [23]:

$$\eta = \frac{E_{HOMO} + E_{LUMO}}{2} \quad (4)$$

The interaction between the capsaicinoids and the ferrous metal surface, electrons flow from the lower electronegativity inhibitor to the iron surface with higher electronegativities [24]. The number of electron transfers (ΔN) can be calculated based on eqn. 5 [25]:

$$\Delta N = \frac{\chi Fe - \chi Inh}{2(\eta Fe + \eta Inh)} \quad (5)$$

where χFe and χInh can contribute to the absolute electronegativity of ferrous metal and organic inhibitor molecules, while ηFe and ηInh can contribute absolute hardness of iron and organic inhibitor molecules. Therefore, for the theoretical values $\chi Fe = 7.0$ eV and $\eta Fe = 0$ eV to calculate the number of electrons transferred [26].

Monte Carlo calculation: The Monte Carlo simulation is very popular for studying the interactions between organic inhibitor molecules and metal surfaces. This Monte Carlo simulation uses software from Accelrys, Inc., namely Material Studio 7.0 [27,28]. Monte Carlo simulation was used to calculate the low energy adsorption configuration of the interactions between the organic inhibitor molecules and the iron surface in water. The COMPASS force field is used to optimize all mole-cular structure systems. It has the advantage of the COMPASS force field, the *ab initio* force field, which allows accurate prediction of the gas phase and condensation properties. These properties, including structural, conformational, interaction energies for various organic metal molecules, metal oxides and metal halides using various solid properties such as unit cell structure, lattice energy and even polymers. The simulation steps that have been carried out previously [29,30] with the crystal surface of Fe (110) in the simulation box (2.48 × 2.48 × 3.81 nm) with periodic boundary conditions to be able to simulate the atomic target part of the interface without arbitrary boundary effects. The Fe (110) field is then enlarged to become a supercell (8 × 8). After that a vacuum plate with a thickness of 8.0 nm was constructed over the Fe plane (110). Organic inhibitors used, namely capsaicin, homocapsaicin, dihydrocapsaicin and norcapsaicin as corrosion inhibitors along with 100 mL of water were used for the simulation in each case. Water is essential in simulation because it plays an essential role in the natural environment's corrosion.

RESULTS AND DISCUSSION

A suitable corrosion inhibitor's criterion is a compound that can accept electrons from metals and can donate electrons in empty orbitals on the metal. The corrosion inhibitors used in this study were capsaicin, dihydrocapsaicin, nordihydrocapsaicin and homocapsaicin. These four capsaicinoids are predicted to inhibit corrosion because they contain heteroatoms (N, O) groups and π-bonds in their structures. The structure of the capsaicinoids compound is depicted in Fig. 1.

As a consequence of applying electronic structure methods (DFT and MP2) in this theoretical study, method validation is necessary first. Infrared spectroscopic comparison is used to compare the accuracy of theoretical methods with experimental results. The infrared spectrum (Fig. 2) shows an agreement between theoretical and experimental studies so that this method can be applied to the system being studied. The absorption band in the area of 3310.56 cm^{-1} (theoretical: 3361.8 cm^{-1}) provides an indication of the presence of an -OH stretching group with medium absorption intensity and a widened form of absorption band (Table-1). This is reinforced by the presence of uptake in the area of 1072.53 cm^{-1} (theoretical: 1128.5 cm^{-1}), which is the stretch of $-OCH_3$ group. The NH (scissoring) bends are supported by the presence of bending vibrations in the area of 610.82 cm^{-1} (theoretical: 621.6 cm^{-1}), the emergence of a sharp absorption band in the 1599.62 area (theoretical: 1542.0 cm^{-1}) indicates the presence of C=C aromatic. The absorption band that appears in the area of 2931.11 cm^{-1} (theoretical: 2895.6 cm^{-1}) is a -CH stretching group. The presence of this group is strengthened by the appearance of absorption bands in the area of 2835 cm^{-1} (theoretical: 2830.2 cm^{-1}), which indicates the presence of $-CH_2$ group (Table-1). The C=O carbonyl strain appeared at 1519.45 cm^{-1} (theoretical: 1519.45 cm^{-1}) [31].

The quantum chemical parameters of neutral and protonated inhibitors are shown in Tables 2-5. The presence of heteroatoms and π-bonds increases corrosion resistance in mild steel, which means that the inhibitor shows good inhibitory efficiency

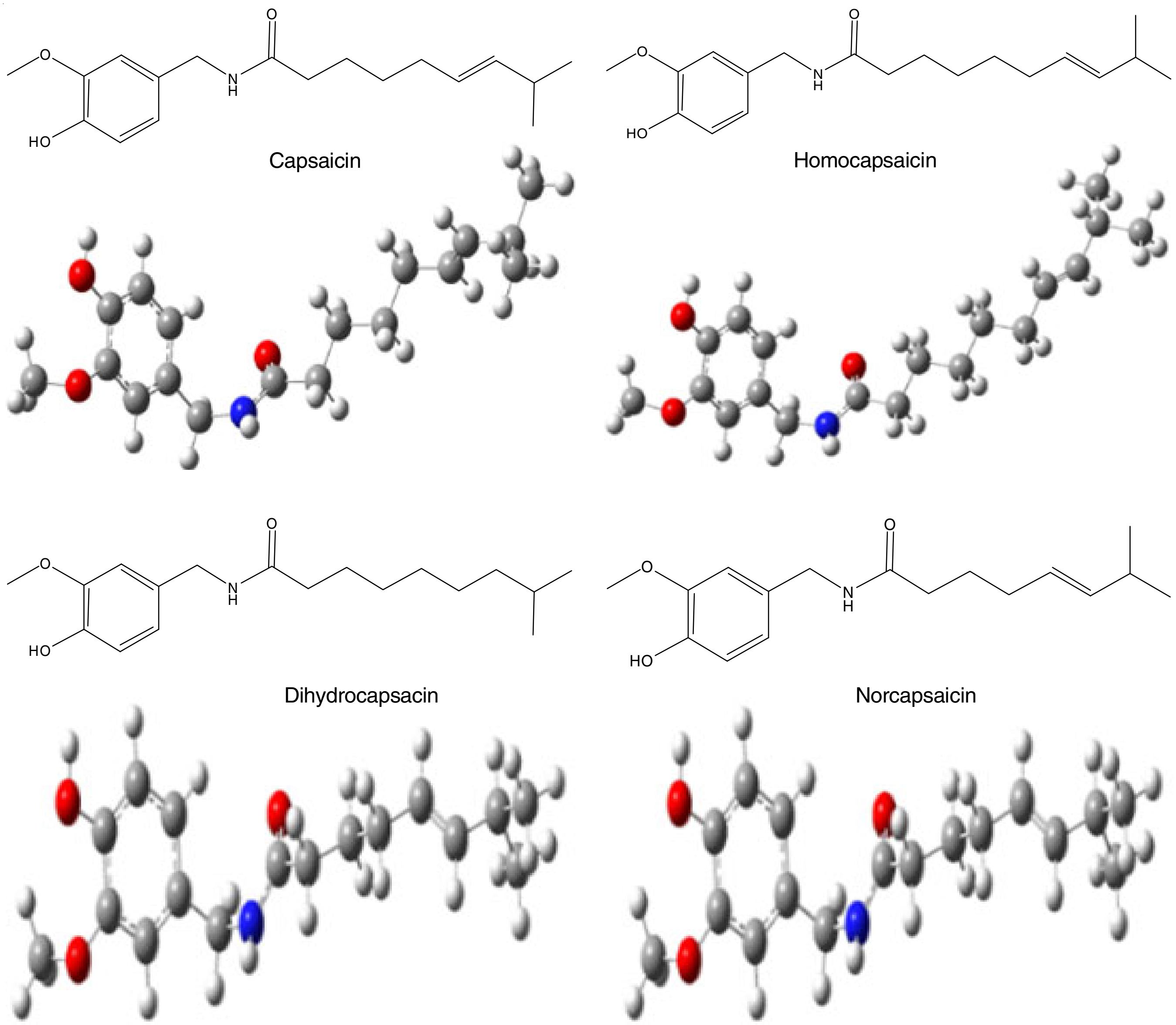


Fig. 1. Molecular structure of capsaicinoids compounds

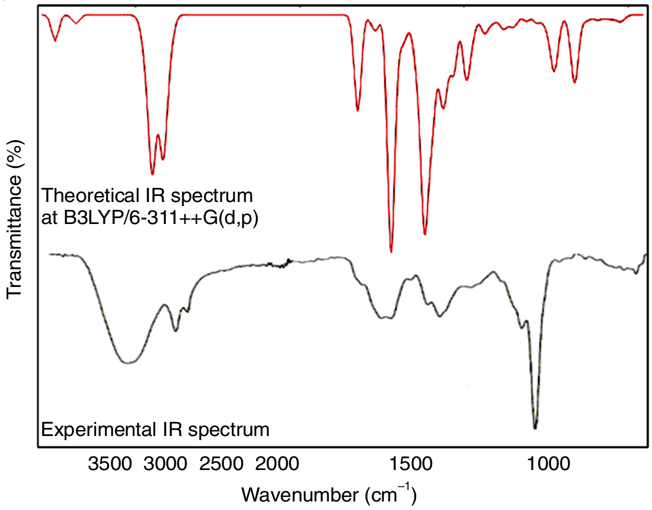


Fig. 2. Comparison of theoretical and experimental of the FT-IR spectrum of capsaicin

TABLE-1
COMPARISON OF THE THEORETICAL AND EXPERIMENTAL FT-IR SPECTRUM FOR CAPSAICIN

	Theory (cm^{-1}) B3LYP/6-311++G (d,p)	Exp. (cm^{-1})
OH	3361.80	3310.56
NH	621.60	610.82
CH_2	2830.20	2835.00
CH_3	2895.60	2931.11
C=C	1542.00	1599.62
C=O	1.644.00	1519.45
OCH_3	1128.50	1072.53

against metal corrosion. HOMO energy indicates the nature of the molecule to donate its electrons; the greater the energy value of HOMO, the stronger the inhibitor adheres to the metal surface so that it has a high corrosion inhibition efficiency [32,33]. Tables 2-5 show the E_{HOMO} values increases in the sequence: homocapsaicin > capsaicin > dihydrocapsaicin >

TABLE-2
QUANTUM CHEMICAL PARAMETERS OF NEUTRAL CAPSAICINOIDS
CALCULATED USING B3LYP AND MP2/6-311++G(d,p) IN THE GAS MEDIUM

	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	H	ΔN
Capsaicin								
B3LYP/6-311++G(d,p)	-6.1988	-0.5861	-5.6126	6.1988	0.5861	3.3924	2.8063	0.6428
MP2/6-311++G(d,p)	-8.4315	0.9739	-9.4053	8.4315	-0.9739	3.7288	4.7027	0.3478
Homocapsaicin								
B3LYP/6-311++G(d,p)	-6.1936	-0.5821	-5.6115	6.1936	0.5821	3.3878	2.8058	0.6437
MP2/6-311++G(d,p)	-8.4266	0.9791	-9.4056	8.4266	-0.9791	3.7237	4.7028	0.3483
Dihidrocapsaicin (DHC)	-6.1993	-0.5883	-5.6110	6.1993	0.5883	3.3928		
B3LYP/6-311++G(d,p)	-6.1993	-0.5883	-5.6110	6.1993	0.5883	3.3938	2.8055	0.6427
MP2/6-311++G(d,p)	-8.4344	0.9859	-9.4203	8.4344	-0.9859	3.7243	4.7102	0.3477
Norcapsaicin (NC)								
B3LYP/6-311++G(d,p)	-6.2061	-0.5889	-5.6172	6.2061	0.5889	3.3975	2.8086	0.6413
MP2/6-311++G(d,p)	-8.5827	1.1007	-9.6834	8.5827	-1.1007	3.7410	4.8417	0.3366

TABLE-3
QUANTUM CHEMICAL PARAMETERS OF NEUTRAL CAPSAICINOIDS
CALCULATED USING B3LYP AND MP2/6-311++G(d,p) IN THE AQUEOUS MEDIUM

	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	H	ΔN
Capsaicin								
B3LYP/6-311++G(d,p)	-6.2959	-0.6327	-5.6632	6.2959	0.6327	3.4643	2.8316	0.6243
MP2/6-311++G(d,p)	-8.5789	1.0972	-9.6761	8.5789	-1.0972	3.7409	4.8381	0.3368
Homocapsaicin								
B3LYP/6-311++G(d,p)	-6.2937	-0.6316	-5.6621	6.2937	0.6316	3.4627	2.8311	0.6247
MP2/6-311++G(d,p)	-8.5770	1.1051	-9.6821	8.5770	-1.1051	3.7360	4.8410	0.3371
Dihydrocapsaicin								
B3LYP/6-311++G(d,p)	-6.2984	-0.6362	-5.6621	6.2984	0.6362	3.4673	2.8311	0.6239
MP2/6-311++G(d,p)	-8.5819	1.1135	-9.6954	8.5819	-1.1135	3.7342	4.8477	0.3368
Norcapsaicin								
B3LYP/6-311++G(d,p)	-6.3008	-0.6329	-5.6679	6.3008	0.6329	3.4669	2.8339	0.6234
MP2/6-311++G(d,p)	-8.5827	1.1007	-9.6834	8.5827	-1.1007	3.7410	4.8417	0.3366

TABLE-4
QUANTUM CHEMICAL PARAMETERS OF PROTONATED CAPSAICINOIDS
CALCULATED USING B3LYP AND MP2/6-311++G(d,p) IN THE GAS MEDIUM

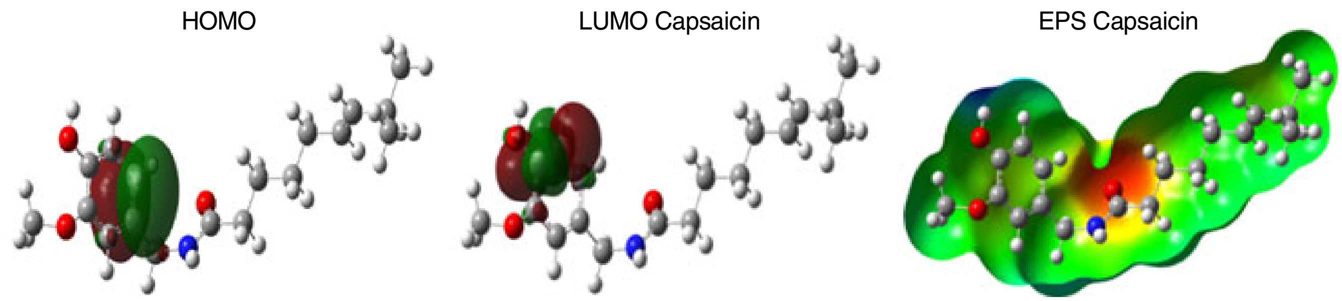
	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	H	ΔN
Capsaicin								
B3LYP/6-311++G(d,p)	-8.7730	-6.1408	-2.6322	8.7730	6.1408	7.4569	1.3161	-0.1736
MP2/6-311++G(d,p)	-11.3161	-2.5761	-8.7400	11.3161	2.5761	6.9461	4.3700	0.0062
Homocapsaicin								
B3LYP/6-311++G(d,p)	-8.4864	-6.1375	-2.3489	8.4864	6.1375	7.312	1.1744	-0.1328
MP2/6-311++G(d,p)	-11.0465	-2.5946	-8.4519	11.0465	2.5946	6.8205	4.2259	0.0212
Dihydrocapsaicin								
B3LYP/6-311++G(d,p)	-9.2856	-5.9974	-3.2882	9.2856	5.9974	7.6415	1.6441	-0.1951
MP2/6-311++G(d,p)	-11.9371	-2.5666	-9.3705	11.9371	2.5666	7.2518	4.6853	-0.0269
Norcapsaicin								
B3LYP/6-311++G(d,p)	-9.1292	-6.1152	-3.0139	9.1292	6.1152	7.6222	1.5070	-0.2064
MP2/6-311++G(d,p)	-11.6933	-2.5829	-9.1104	11.6933	2.5829	7.1381	4.5552	-0.0152

norcapsaicin. Homocapsaicin shows the highest HOMO energy value of -8.5770 eV, in MP2/6-311++G(d,p) calculations, compared to other capsaicinoids. The high HOMO energy value in homocapsaicin indicates that this inhibitor readily donates its lone pair to ferrous metal to interact to form complex compounds with the metal surface. It causes the bonds formed to be strong and have a good effect on the inhibition of corrosion.

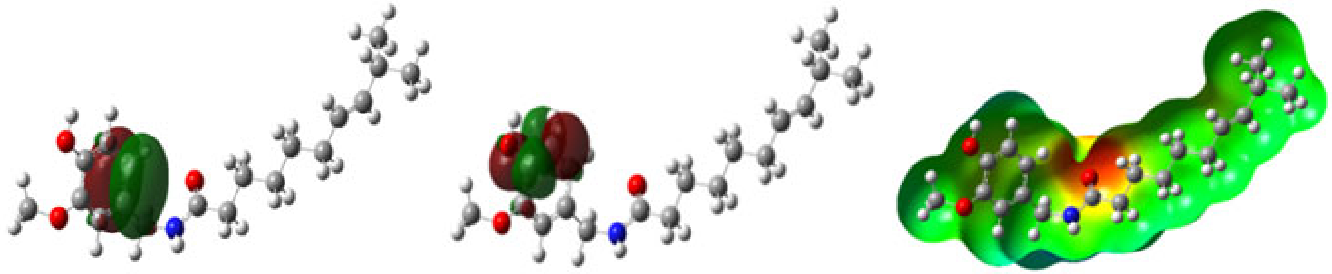
The low ionization potential indicates that it is easy for an atom to release its outer electrons to donate electrons from the metal surface's molecule more quickly. This condition can increase the value of the inhibitory efficiency of an inhibitor. The high ionization potential indicates the difficulty of removing electrons from the outer shell, which implies the difficulty of transferring electrons to the iron surface. It lowers the corrosion inhibition efficiency value. Table-2 shows that the highest ionization potential value is norcapsaicin, namely 8.5827 eV, while the lowest ionization potential value is homocapsaicin, namely 8.5770 eV. Homocapsaicin is reactive to iron, which causes a strong inhibitor interaction with the metal surface, resulting in high efficiency of corrosion inhibition.

TABLE-5
QUANTUM CHEMICAL PARAMETERS OF PROTONATED CAPSAICINOIDS
CALCULATED USING B3LYP AND MP2/6-311++G(d,p) IN THE AQUEOUS MEDIUM

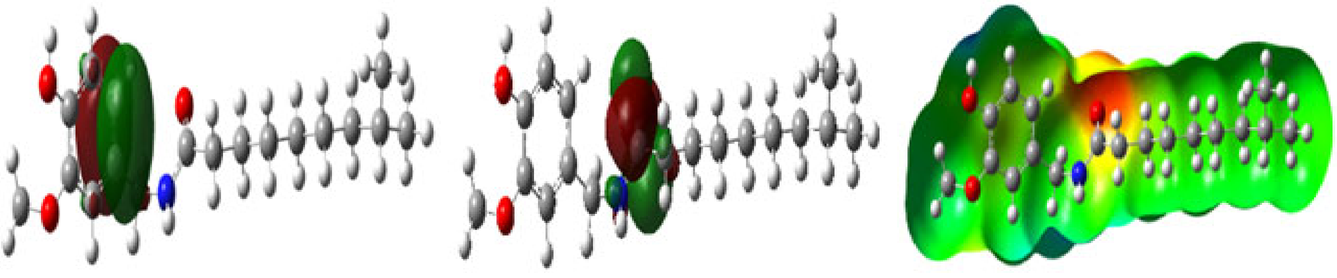
	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	H	ΔN
Capsaicin								
B3LYP/6-311++G(d,p)	-6.7378	-2.4751	-4.2627	6.7378	2.4751	4.6065	2.1313	0.5615
MP2/6-311++G(d,p)	-9.0764	1.0041	-10.0805	9.0764	-1.0041	4.0361	5.0402	0.2940
Homocapsaicin								
B3LYP/6-311++G(d,p)	-6.7354	-2.4757	-4.2597	6.7354	2.4757	4.6055	2.1298	0.5621
MP2/6-311++G(d,p)	-9.0747	1.0106	-10.0854	9.0747	-1.0106	4.0320	5.0427	0.2943
Dihydrocapsaicin								
B3LYP/6-311++G(d,p)	-6.7411	-2.4648	-4.2763	6.7411	2.4648	4.6029	2.1381	0.5605
MP2/6-311++G(d,p)	-9.0802	1.0204	-10.1006	9.0802	-1.0204	4.0299	5.0503	0.2941
Norcapsaicin								
B3LYP/6-311++G(d,p)	-6.7403	-2.4754	-4.2648	6.7403	2.4754	4.6078	2.1324	0.5609
MP2/6-311++G(d,p)	-9.0788	1.0063	-10.0851	9.0788	-1.0063	4.0363	5.0425	0.2939



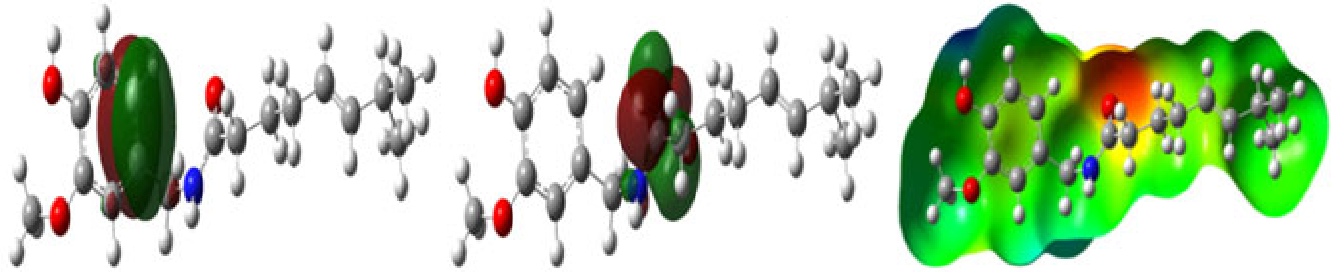
Capsaicin



Homo capsaicin (HC)



Dihidrocapsaicin (DHC)



Norcapsaicin (NC)

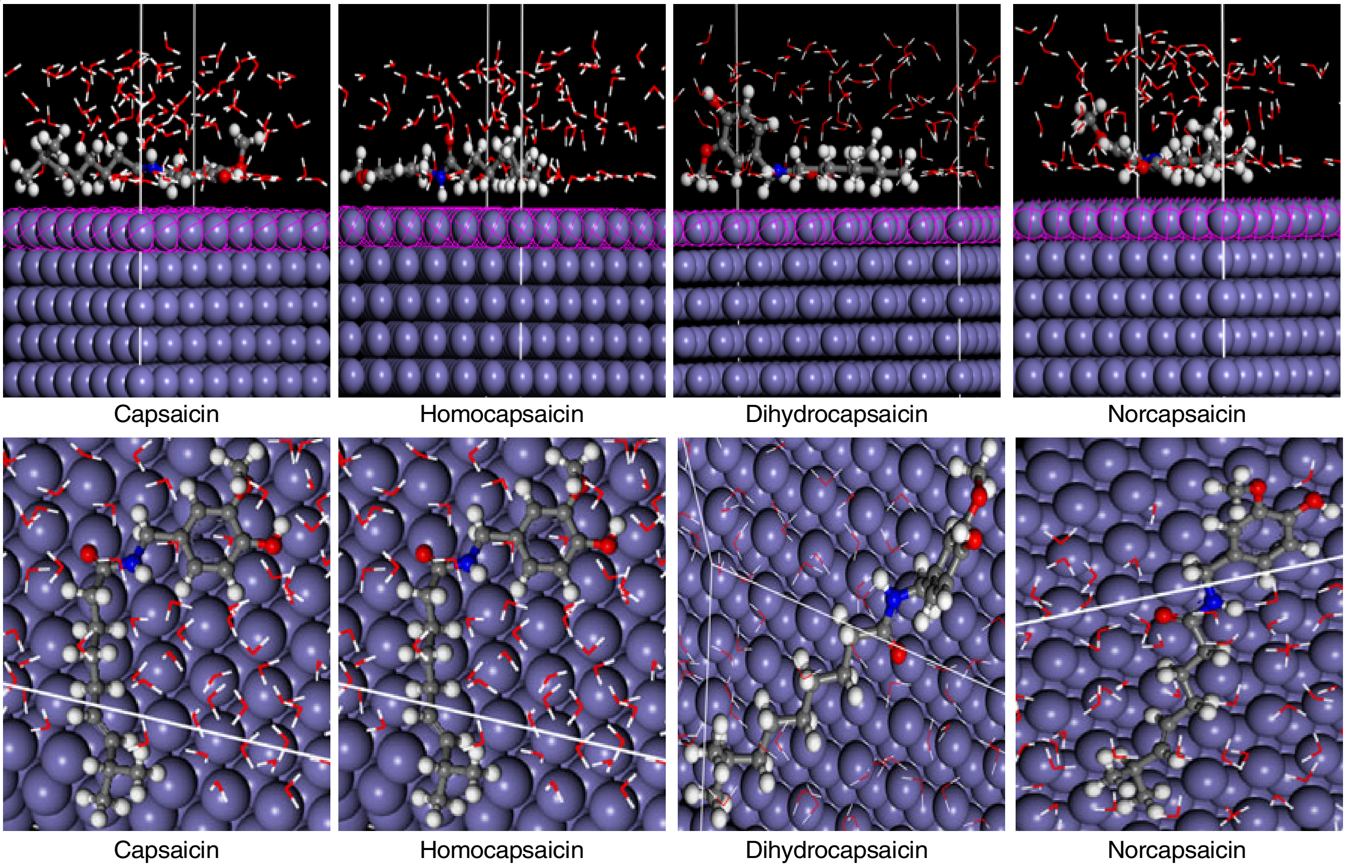
Fig. 3. Visualization of HOMO, LUMO, ESP of capsaicinoids

The interaction between the inhibitor and the metal causes electrons to move from molecules with low electronegativity to high electronegativity molecules. The small electronegativity of a molecule makes it easy to donate electrons to become more reactive. Conversely, a large electronegativity shows the molecule to be unreactive [34]. The iron electronegativity, 7 eV, is higher than the homocapsaicin's electronegativity, 3.7360 eV, hence iron is more likely to release its electrons. Thus, on electronegativity, homocapsaicin has a high inhibitory efficiency compared to the other three capsaicinoids.

The value of the electron transfer indicates that there is an inhibitory effect resulting from the electron donation. If the value of $\Delta N < 3.6$, the value of corrosion inhibition efficiency increases electron donors' ability to the metal surface [35]. The presence of heteroatom groups increases corrosion inhibition efficiency because it can increase the transfer of electrons to the metal surface. The highest electron transfer (ΔN) results in the best inhibitor efficiency [36]. Table-2 shows the high electron transfer value, namely the homocapsaicin inhibitor of 0.3371 eV, increasing the efficiency of corrosion inhibition and the number of electron transfers to the metal surface. Electron transfer values were sequentially homocapsaicin > capsaicin > dihydrocapsaicin > norcapsaicin. It indicates that homocapsaicin plays the most dominant role in inhibiting corrosion.

The HOMO orbital electrons can be evenly distributed in the molecule, whereas the LUMO orbital has an anti-bonding character [37]. Electron density indicates a negative charge in red which is easily localized to the N atom, because it can be caused by an electron cloud of the lone pair [38-40]. Electrostatic surface potential (ESP) is the opportunity to find the charge distribution of an electron in coordinates (x, y and z) in a molecule. ESP deals with electron density regions, where electrons can be found to explain molecular properties, predict molecular structure, bond strength, reactivity and stability. EPS shows the active site of homocapsaicin in aromatic and heteroatomic regions. Fig. 3 shows that there are red and yellow areas in homocapsaicin, which indicate the distribution of the electron charge is more than the green and blue areas, thus indicating a small electron density.

Monte Carlo simulations are carried out to predict the position of the interaction between the inhibitor and the iron surface in aqueous solutions. Fig. 4 shows the lowest energy value of the most stable energy adsorption configuration of the inhibitor in the Fe(110)/capsaicinoids/100H_2O system using a Monte Carlo simulation. The analysis results on the shortest length of the inhibitor active site bond with iron measuring less than 3.50 Å, which indicates the formation of a strong adherent layer between the inhibitor and the iron surface [41,42]. This inhibitory layer coats the metal surface and prevents the iron from being attacked by aggressive solutions. This strongly bonded layer also indicates a transfer of electrons from the inhibitor's active site to the *d*-orbital in the iron. This electron transfer causes a strong interaction between the inhibitor and



Capsaicin Homocapsaicin Dihydrocapsaicin Norcapsaicin

Capsaicin Homocapsaicin Dihydrocapsaicin Norcapsaicin

Fig. 4. Adsorption of capsaicin, homocapsaicin, dihydrocapsaicin, norcapsaicin and metal surfaces in the Metropolis Monte Carlo Simulation system of Fe(110)/capsaicinoids/100H_2O

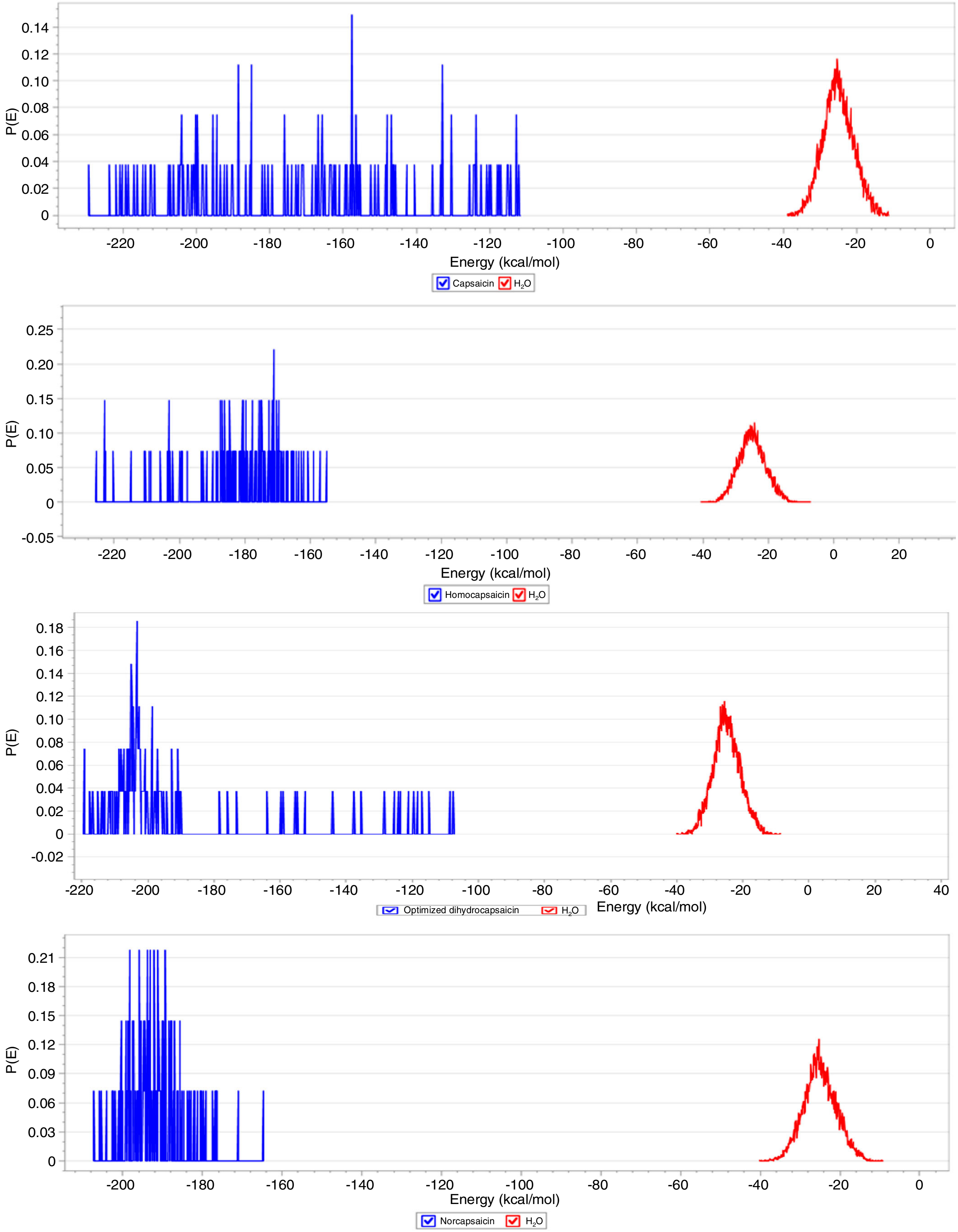


Fig. 5. Energy distribution of adsorption for Fe(110)/capsaicin/100H_2O, Fe(110)/homocapsaicin/100H_2O, Fe(110)/dihidrocapsaicin/100H_2O and Fe (110)/norcapsaicin/100H_2O systems

the iron, thereby inhibiting the corrosion rate. Furthermore, van der Waals interactions are also involved in the adsorption of inhibitor on the iron surface. It is evident from observations with bond distances above 3.50 Å [43]. Table-6 shows the adsorption energy for the most stable configurations for the Fe(110)/capsaicin/100H_2O, Fe(110)/dihydrocapsaicin/100H_2O, Fe(110)/homocapsaicin/100H_2O and Fe(110)/norcapsaicin/100H_2O. Table-6 also shows that the adsorption energy of the inhibitor is much higher than that of water. It suggests the possibility of replacing water molecules by inhibitors on the iron surface, which results in the formation of a stable layer that protects the ferrous metal from corrosion in water. Table-6 shows that the adsorption inhibitor's energy decreases in the order of homocapsaicin > dihidrocapsaicin > capsaicin > norcapsacin. The adsorption energy distribution of the inhibitor and water is depicted in Fig. 5. It shows that homocapsaicin forms a more stable layer on the iron surface compared to other capsaicin derivatives. The energy distribution of homocapsaicin and water adsorption can be separated from one another. On the other hand, at some points, the energy of other capsaicinoids with water is quite far away from forming a weaker layer because at some points of energy, water can compete with the inhibitor.

TABLE-6
ADSORPTION ENERGY OF THE Fe(110)/INHIBITOR/100H_2O SYSTEM WITH MONTE CARLO SIMULATION

Systems	Adsorption energy (inhibitors) kJ.mol^{-1}	Adsorption energy (water) kJ.mol^{-1}
Neutral inhibitor		
Fe(110)/capsaicin/100H_2O	-211.59549241	-17.75074524
Fe(110)/homocapsaicin/100H_2O	-222.91098095	-18.27646547
Fe(110)dihidrocapsaicin/100H_2O	-219.22786266	-16.06893764
Fe(110)/norcapsaicin/100H_2O	-204.05427574	-16.25778101
Protonated inhibitor		
Fe(110)/capsaicin/100H_2O	-143.00492094	-16.35564942
Fe(110)/homocapsaicin/100H_2O	-179.42752846	-17.00653828
Fe(110)dihidrocapsaicin/100H_2O	-176.55174611	-16.50743916
Fe(110)/norcapsaicin/100H_2O	-130.44164937	-15.00983908

Conclusion

The purpose of this study was to identify the main compounds of capsaicinoids which have the most significant role in inhibiting corrosion. The DFT and *ab initio* MP2 methods have been used to calculate the quantum chemical parameters of capsaicinoids. Quantum parameters such as HOMO and LUMO energy levels, ionization potential, electron affinity, electronegativity, hardness and the number of electron transfers show the order of homocapsaicin > capsaicin > dihidrocapsaicin > norcapsaicin. It is predicted that homocapsaicin plays the most crucial role in inhibiting corrosion against mild steel. Monte Carlo simulations described the corrosion inhibition mechanisms of capsaicinoids on metal surfaces. The results obtained showed that homocapsaicin was the most effective at preventing corrosion as compared to other capsaicinoids. This theoretical study can help in the designing of effective corrosion inhibitors.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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