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COMPUTATIONAL EXPLORATION OF COPPER CORROSION INHIBITION BY MODIFIED CARBON NANOTUBES IN AQUEOUS HCl: AN *AB INITIO* APPROACH*

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In order to develop novel unexplored potential corrosion inhibitors, covalently modified single-walled carbon nanotubes (SWCNT) via benzoic (–PhCOOH) and aniline (–$PhNH_2$) groups are being investigated as corrosion inhibitors for the first time. Utilizing a comprehensive approach, this study employed density functional theory (DFT), Monte Carlo (MC), and molecular dynamics simulations (MD) to assess the adsorption behavior of modified nanotubes as corrosion inhibitors on the Cu(111) surface within a simulated aqueous HCl corrosion medium. The results provided molecular information on the adsorption capability, geometry adsorption centers, and adsorption energies (E_{ads}) of carbon nanotubes on the surface of Cu(111). The adsorption energy values unveiled robust interactions between SWCNT–PhCOOH and SWCNT–$PhNH_2$ inhibitors and the Cu(111) surface, suggesting a highly effective corrosion protection mechanism. The calculated E_{ads} values exhibited notable ranges, spanning from –260.82 to –308.18 kcal/mol for SWCNT–PhCOOH and –220.92 to –261.01 kcal/mol for SWCNT–$PhNH_2$ with the maximum probability values, representing the most favorable adsorption scenarios, determined to be –292.96 and –229.39 kcal/mol, respectively. A key insight from Monte Carlo simulations underscored the inherent spontaneity of the adsorption process, corroborated by the consistently negative E_{ads} values. These findings collectively underscore the substantial affinity of the inhibitors to the copper surface, contributing to a deeper comprehension of their corrosion inhibition capabilities.

Keywords: SWCNT; grafting; diazonium salts; corrosion inhibition; copper; DFT; MC; MD

ПРЕСМЕТКОВНО ИСТРАЖУВАЊЕ НА ИНХИБИЦИЈА НА КОРОЗИЈА НА БАКАР СО МОДИФИЦИРАНИ ЈАГЛЕРОДНИ НАНОЦЕВКИ ВО ВОДЕН HCl: *AB INITIO* ПРИСТАП

Со цел да се развијат нови неистражени потенцијални инхибитори на корозија, како инхибитори на корозија за прв пат беа истражени ковалентно модифицирани јаглеродни наноцевки со еден ѕид (SWCNT) преку бензоеви (–PhCOOH) и анилински (–$PhNH_2$) групи. Користејќи сеопфатен пристап, оваа студија ја примени теоријата за густината на потенцијалот (DFT), како и симулациите Монте Карло (MC) и на молекуларна динамика (MD) за да го процени однесувањето на атсорпцијата на модифицираните наноцевки како инхибитори на корозија на површината на Cu(111) во симулиран корозиски медиум на воден HCl. Резултатите обезбедија молекуларни информации за способноста за атсорпција, за геометриските центри на атсорпција и за енергиите на атсорпција (E_{ads}) на јаглеродните наноцевки на површината на Cu(111). Енергетските вредности на атсорпција откриja силни интеракции помеѓу инхибиторите SWCNT-PhCOOH и SWCNT-$PhNH_2$ и површината на Cu(111), што укажува на високоефективен механизам за заштита од корозија. Пресметаните вредности на E_{ads} покажаа забележителен опсег, кој се протега со максимални вредности на веројатност од –260,82 до –308,18 kcal/mol за SWCNT–PhCOOH и од –220,92 до –261,01 kcal/mol за SWCNT–$PhNH_2$, што претставува најповолна вредност соодветно да биде –292,96 и –229,39 kcal/mol. Клучното согледување од симулациите

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Монте Карло е нагласената природна спонтаност на процесот на атсорпција, потврдена со постојано негативните вредности на E_{ads}. Сите овие наоди го нагласуваат значителниот афинитет на инхибиторите кон бакарната површина, придонесувајќи така за подлабоко разбирање на нивната способност за спречување на корозија.

Клучни зборови: SWCNT; калемење; диазониумски соли; спречување на корозија; бакар; DFT; MC; MD

1. INTRODUCTION

When iron, copper, aluminum, and various other materials interact with environmental elements containing corrosive agents, such as chloride ions and oxygen, they undergo a process of corrosion. Corrosion causes major damage in many major industries (automotive, construction, aerospace, oil and gas, etc.).[1–9] For example, various inhibitors are used to reduce copper corrosion[10] including molecules and compounds such as benzotriazole,[11,12] imidazole derivatives,[13–15] Schiff bases,[16,17] green corrosion inhibitors,[18–20] ionic liquids,[21,22] smart coatings,[23] drugs,[24–26] nanomaterials,[27–29] etc. To our knowledge, there are limited studies on the use of carbon nanotubes containing aryl radicals of the same diazonium salt[30] and there are no studies on the fermentation of carbon nanotubes with aryl resins from diazonium salts, even though such layers have been shown to reduce the corrosion of metals[31–35] and are easy to apply as a surface treatment.[36] Corrosion is usually assessed using a variety of methods including potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), gravimetric measurement, scanning electron microscopy (SEM), atomic force microscopy (AFM), and scanning electrochemical microscopy (SECM).[6,37–42] These methods provide information on the electrical behavior and kinetics of degradation processes and evaluates the performance and degradation levels of inhibitors.[43] However, most molecular studies can be done through sophisticated computer simulations based on Density Functional Theory (DFT), Molecular Dynamic (MD), and Monte Carlo (MC) simulations.[44–47] DFT-derived parameters such as electron donating properties, energy difference between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) levels, fraction of transferred electrons (ΔN), molecular dipole moment, and energy transfer from inhibitor to metal ΔE back-donation have already been demonstrated to be critical parameters for understanding how and why inhibitors interact with metal surfaces to exert their corrosion protection ability.[48,49] In addition, the Monte Carlo method can be combined with molecular models to determine the geometric and mechanical properties of objects.[40–42,50,51] In recent years, there has been a clear indication of a growing interest in the application of carbon nanotubes (CNTs) in the field of corrosion research. Even with the significant progress that modern coatings have made, corrosion prevention is still a topic of significant research and development interest. The use of CNT-based nanocomposite layers to protect metals is still in its infancy.[52,53] Therefore, it is necessary to conduct in-depth research into methodologies that are both straightforward and efficient and that deal with the modification of CNTs regarding the increase of their adsorptive capabilities.[36]

This paper therefore investigates covalently modified single-walled carbon nanotubes (through –PhCOOH and –$PhNH_2$ groups) as corrosion inhibitors for the first time using DFT, MC, and MD simulations to evaluate the adsorption of the modified nanotubes onto the Cu(111) surface. The results provided molecular information on the adsorption capability, geometry adsorption centers, and adsorption energies (E_{ads}) of carbon nanotubes on the surface of Cu(111).

2. CALCULATION DETAILS

2.1. *SWCNT and Cu(111) molecular modeling*

The single-walled carbon nanotube (SWCNT; $n = 6$, $m = 8$) with a diameter of 8.14 Å, length of 19.68 Å and grafted by eleven –PhCOOH or –$PhNH_2$ moieties (as monolayer or multilayer entities) were evaluated using *ab initio* methods as a corrosion inhibitor towards copper. The MC and MD calculations with the modified Cu(111) surface and improved SWCNT model are shown in Figure 1. The simulation was done using Cu(111) with a cell size of 43.451 Å × 43.451 Å × 18.782 Å with the inclusion of a 50 Å vacuum layer on the C axis containing 1800 water molecules / 1 SWCNT–PhCOOH or SWCNT–$PhNH_2$ / 10 hydronium + 10 chloride ions. Well-known for its outstanding stability among all copper facets, the Cu(111) face plays an important role in surface reactivity.[54] Extensively studied, this facet underscores its crucial role in comprehending surface phenomena, making it a common choice in corrosion modeling studies.[55,56]

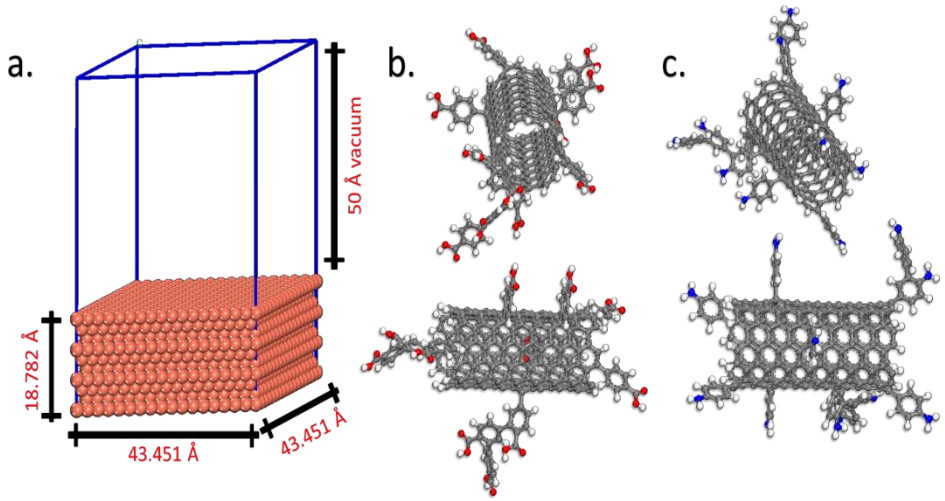

Fig. 1. Molecular models used in the theoretical calculations: a) Cu(111) facet, b) SWCNT–PhCOOH, and c) SWCNT–$PhNH_2$

2.2. *Density-functional tight-binding (DFTB) and density functional theory (DFT) calculations*

DFTB+ integration software is used for all types of digital interfaces[57,58] and is open-source software for fast and efficient testing of quantum cores. This allows for better modeling of large-scale DFT such as density functional based tight-binding (DFTB) method and extended bandwidth, but faster with specialized processes like *ab initio* methods.[58] DFBT, which is an approximation of DFT, is efficient and can be used for organic matter, insulators, solids, clusters, semi-conductors, and metals; it is also relevant to biological systems.

2.3. *MC and MD calculation details*

MC comparisons were made using a model mitigation cycle of 15,000 steps. In each cycle, the temperature was set between 10^5 and 10^2 K. As the temperature gradually decreased, the adsorption rate was corrected.[59–62] MD was conducted using NVT canonical ensemble[56] at 298 K with a simulation time of 0.6 ns (1 fs time step).[38,40,41,63,64] The temperature was controlled by the Berendsen MD thermostat.[5] The previously prominent COMPASS II force field was used for the MC and MD simulations.[38,40,63,65–69] The whole 0.6 ns of the MD trajectory was used for the computation of the radial distribution function (RDF).[63,64,68]

3. RESULTS

3.1. *DFT calculations*

The charge density distribution around the surface of the molecule is shown in the sigma profile, which offers complete information on the molecule as well as information about conjugate solubility or dispersibility in various solvents (in our case water).[70,71] The sigma profile charge density curve is built using calculations based on the COnductor-like Screening MOdel (COSMO). COSMO represents the electrostatic potential utilizing partial atomic charges by exploiting molecularly carved cavities.[62,72] Figure 2 shows how the SWCNT acts as both an acceptor (SWCNT–PhCOOH) and a donor (SWCNT–$PhNH_2$) of H-bonds. As a result, the SWCNT dispersibility is governed by its ability to interact with water molecules via H-bond acceptor/donor interactions (spikes in the region > 0.01 and > –0.01 in Figure 2) with the water molecules.

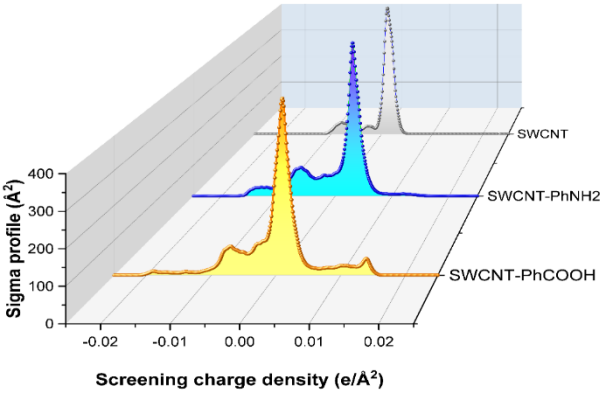

Fig. 2. Sigma profile of the bare and modified SWCNTs

The HOMO and LUMO dispersions and their symmetry are renowned as fundamental parameters for determining the activity of structures and forecasting the development of chemical reac-

tions.[51,59,73] HOMO focuses on the region of the molecule that tends to offer electrons to electrophilic species, while LUMO focuses on the region of the molecule that is more sensitive to accepting electrons from nucleophilic species. The frontier MOs indicate that in the modified SWCNT's HOMO is largely dispersed across the whole middle region of the SWCNT where the degree of the grafting was the highest, the same holds also for the LUMO distributions (Fig. 3).

The relatively large value of HOMO for SWCNT suggests their potential for electron donation and accepting interactions with the metal surface.[42,50,66,74,75]

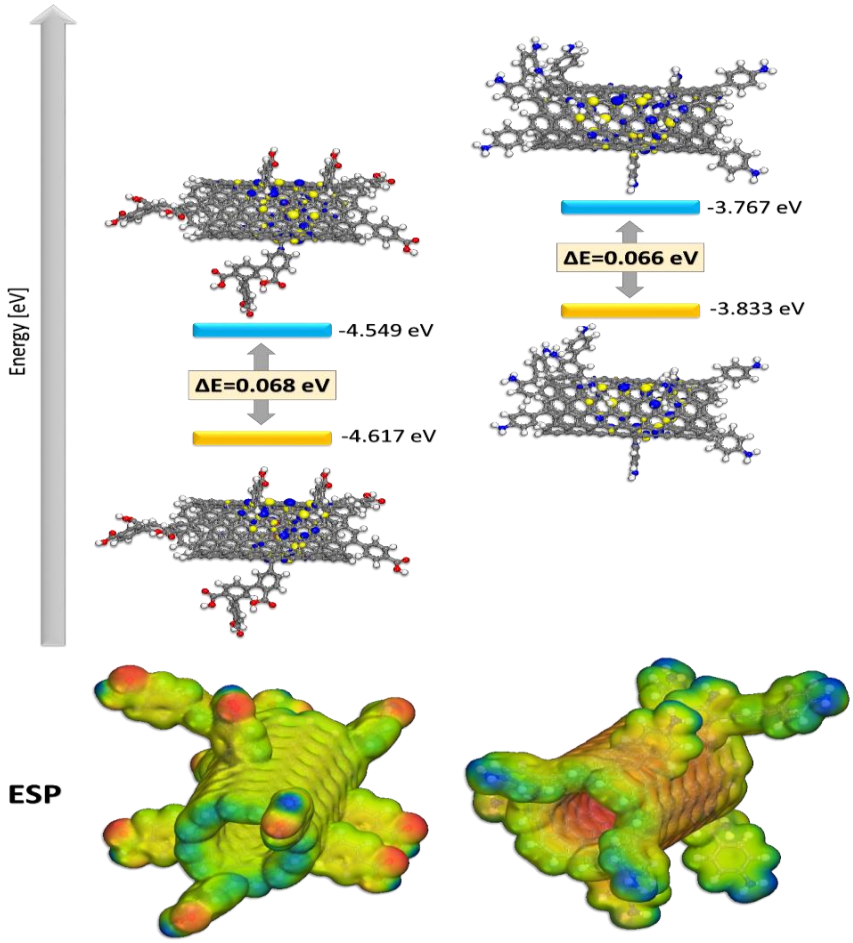

Fig. 3. HOMO, LUMO, Electrostatic potential surfaces (ESP), and energy gap for the modified-SWCNT structures

T a b l e 1

Calculated theoretical descriptors for the SWCNT inhibitors

Descriptor	SWCNT-PhCOOH	SWCNT-PhNH$_2$
HOMO	–4.6170	–3.8330
LUMO	–4.5490	–3.7670
ΔE(HOMO – LUMO)	0.068	0.066
Ionization energy (I)	4.6170	3.8330
Electron affinity (A)	4.5490	3.7670
Electronegativity (X)	4.5830	3.8000
Global hardness (η)	0.0340	0.0330
Chemical potential (π)	–4.5830	–3.8000
Global softness (σ)	29.41	30.30

To demonstrate this reactivity, one may examine their low electron affinity and high ionization potential values, which imply an equal predisposition for electron exchange.[44,47] When these inhibitors are close to the metal surface, their strong reactivity and adsorptive aptitude are supported by their moderately high chemical softness (Table 1) and low hardness.

The MAC value depends on the identification of the atomic center of the atoms, which is responsible for the absorption of the metal surface. The interaction between copper and SWCNTs is predominantly positive, allowing them to exhibit a high affinity for adsorption in a favorable manner on the copper surface.[38,74,76] Figure 4 shows the Mulliken atomic charges (MAC). The negative results for N and O atoms indicate that the charges have the highest electron density, especially for copper. This is also shown in Figure 3 (area in red).

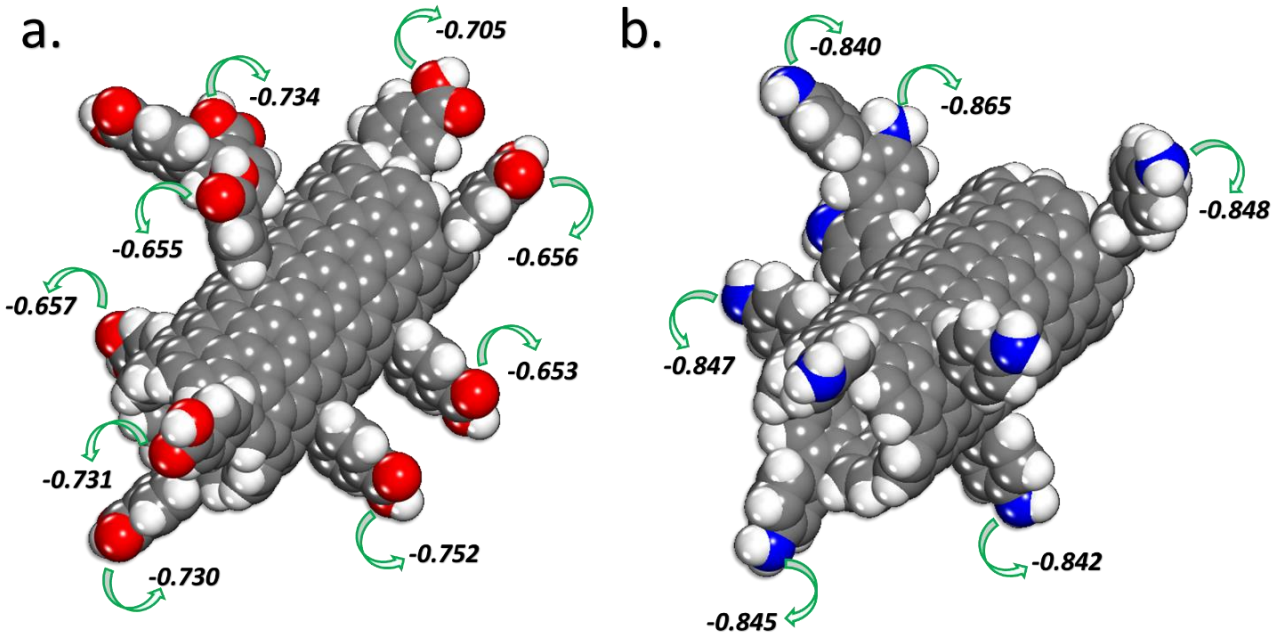

Fig. 4. Optimized structures of the modified SWCNT (a. SWCNT–PhCOOH and b. SWCNT–$PhNH_2$) and their Mulliken atomic charges (MAC)

3.2. *MC and MD simulations*

Figure 5 shows the application of the SWCNT strength on the copper to simulate the corrosion conditions (as selected above). The use of the adsorption geometry (maintained by the Mulliken charge) suggests that nitrogen and oxygen atoms are responsible for this effect. To protect the metal from corrosion, the surface of the metal must be protected.

Equation 1 may be used to calculate the adsorption energies (E_{ads}) of inhibitor molecules (modified SWCNT structures) on the copper surface:

$$E_{ads} = E_{total} - \left[E_{surface+water} + E_{SWCNT\text{–}PhCOOH\ or\ SWCNT\text{–}PhNH2+surface}\right] + E_{water} \quad \text{(eq.1)}$$

where E_{total} represents the total energy of the system, E_{water}, $E_{surface\ +\ water}$ and $E_{(SWCNT\text{–}PhCOOH\ or\ SWCNT\text{–}PhNH2\ +\ surface)}$ are the corresponding energies of the interacting species on the surface of copper.

Figure 6 depicts the distribution of the E_{ads} for the large number of adsorptive configurations developed and computed by the Monte Carlo method for the SWCNT inhibitor molecules.

These high adsorption energies indicate that the inhibitors have a strong interaction with the copper surface, resulting in excellent corrosion protection. According to both the MC and MD computations, SWCNT has been adsorbed onto the Cu surface. Monte Carlo simulations (Figs. 5 and 7) have revealed that the resulting negative values of E_{ads} are indicative of the spontaneity with which the adsorption process takes place (Fig. 7).[38,63,67,74]

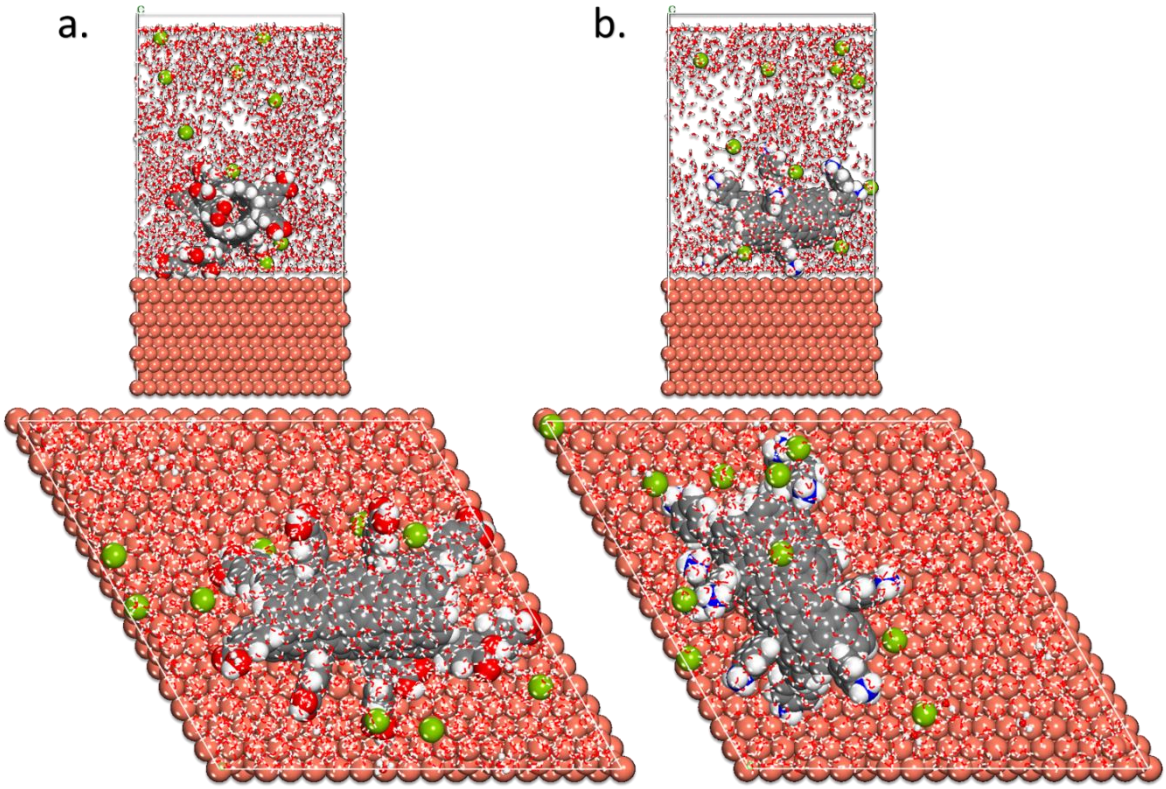

Fig. 5. MC positions of the lowest adsorption configurations for the SWCNT (a. SWCNT–PhCOOH and b. SWCNT–$PhNH_2$) in the simulated corrosion media on the copper surface periodic boundary condition (PBC) model

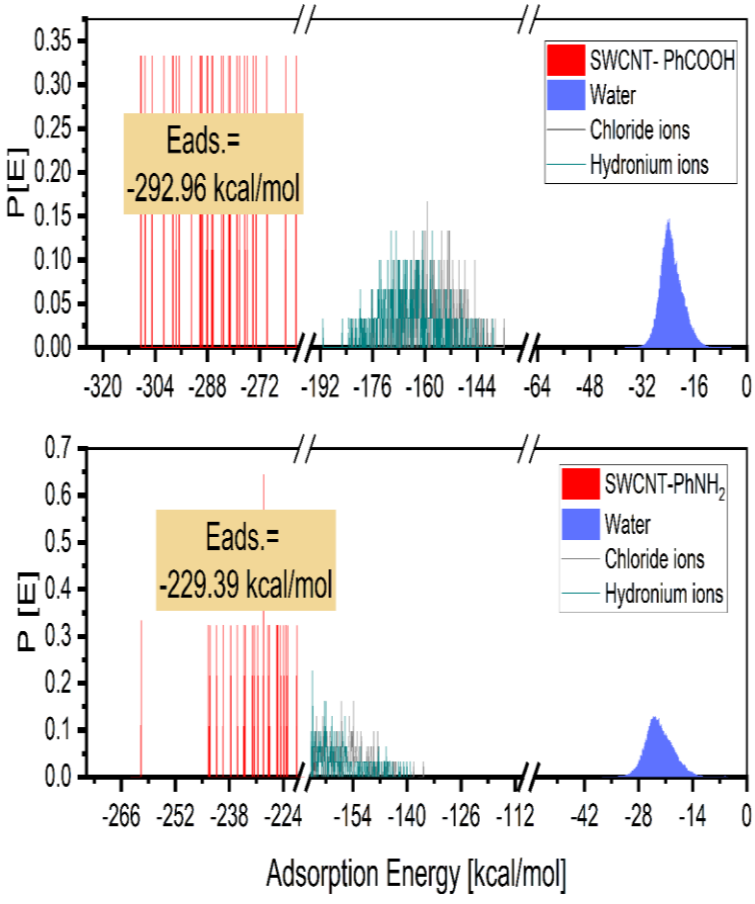

Fig. 6. Adsorption energies distribution for SWCNTs (SWCNT–PhCOOH and SWCNT–$PhNH_2$) on the Cu(111) surface

T a b l e 2

The E_{ads} values on the Cu(111) surface in HCl media for the studied molecules

Inhibitor	Min. (kcal/mol)	Max. (kcal/mol)	Max. Probability (kcal/mol)
SWCNT-PhCOOH	–260.82	–308.18	–292.56
SWCNT-$PhNH_2$	–220.92	–261.01	–229.39

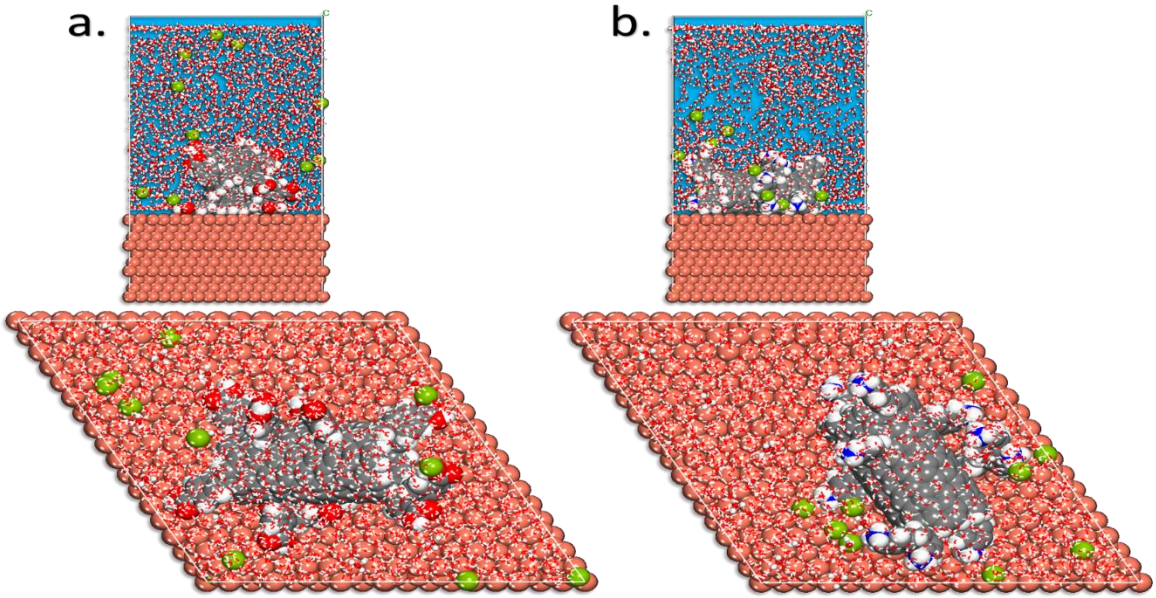

Fig. 7. MD results were observed in the minimally modified-SWCNTs (a. SWCNT–PhCOOH and b. SWCNT–$PhNH_2$) in the simulated corrosion environment on the Cu surface PBC model

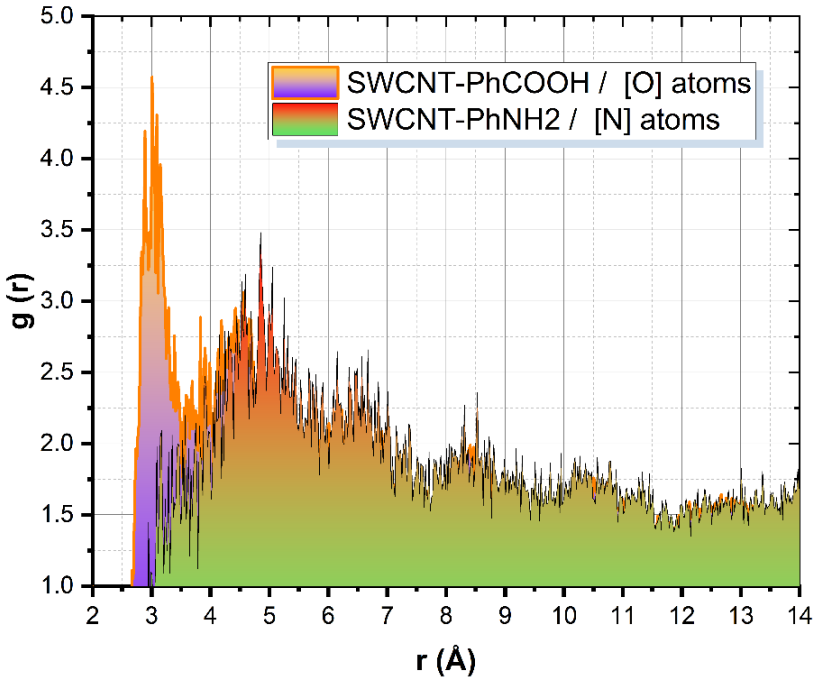

Fig. 8. Radial distribution function of N and O atoms of the SWCNTs on the Cu(111) surface derived from MD simulations

MD tests are important because they provide a direct way to study and record the kinetics of the studied adsorption of the molecule on a Cu surface. Figure 7 shows the final order of the studied molecules on the Cu surface.

The presence of a peak between 1 and 3.5 Å in the plane of the Cu and O atom in the RDF (Fig. 8) is often considered conclusive evidence that the value of RDF (lower than 3.5 Å) confirms chemisorption; at longer distances there is strong evidence that physisorption occurs.[41,56,63,67,75–78]

The oxygen atoms of the RDF in SWCNTs (Fig. 8) are close to 3.5 Å, indicating that these materials affect the metal surface. Studies by MD and RDF confirm the high tendency of these studied inhibitors to inhibit and protect metals because they have different effects on the acceptance/donation of electrons with the Cu(111) surface.[41,42,68]

4. CONCLUSION

This study focuses on several technical methods (DFT, MC, and MD simulations). This approach provides insight into the evolution of SWCNTs that are attached to the copper to prevent corrosion. Determining the DFT data is a good way to assess why these compounds interact with the surface and adhesive sites (N and O atoms) in the adsorption process. The MC and MD simulations show that inhibitor molecules spontaneously lay flat on the copper (111) surface and form a barrier that slows down the migration of corrosive agents toward the copper surface. The high adsorption strength facilitates the interaction between SWCNTs and the copper surface.

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