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Analysis and comparison of metal-doped on graphene-genistein using QM/MM calculations

Análisis y comparación de metal dopado con metal con grafeno-genisteína mediante cálculos QM / MM

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ABSTRACT: Genistein (5,7,4'-trihydroxyisoflavone) is an isoflavone abundantly found in soy and other legumes and acts as a selective estrogen receptor modulator (SERM). When testing for similar abilities among other flavonoids, it has been found to be a strong topoisomerase inhibitor. Similar to some high-dose chemotherapy drugs, it was strongly toxic to normal cells. In this study, the adsorption of genistein on the surface of exclusive graphene and Ni, Ti, Cr, and Se-doped graphene was theoretically evaluated by means of density functional theory calculation. Initially, we varied the position of genistein from the surface of pristine and decorated graphene by changing the distances between (1-5 Å) and gained the E_{ad} and E_{gap} for each situation. Our calculation indicated that adsorption energies (E_{ad}) of pristine genistein to graphene with Ni decorated graphene, Ti-decorated graphene, and Cr-decorated graphene and Se-decorated graphene are: 954.984, 318.168, 797.480, 946.725, 958.154 kcal/mole, respectively, and the calculated values of adsorption energy in the equilibrium distance (de=3.918^{0}A.) of genistein to Ni-decorated graphene reveal that apparently genistein- Ni-decorated graphene as the most energetically favorable position was correctly selected in comparison with other atom-decorated graphene. In consequence, we explain the density of states (Dos_s) and frontier molecular orbitals HOMO and LUMO for Ni-decorated graphene and complexes with genistein; therefore, data confirmed that a positive charge of Ni-decorated graphene for nucleophile molecules could be achieved.

RESUMEN: La Genisteína (5,7,4'-trihidroxiisoflavona) es una isoflavona abundante en la soya y otras legumbres y actúa como modulador selectivo del receptor de estrógenos. Al probar capacidades similares entre otros flavonoides, se encontró que es un fuerte inhibidor de la topoisomerasa. Al igual que algunos medicamentos de quimioterapia, es muy tóxico para células sanas. Se evaluó la adsorción de genisteína en la superficie de grafeno exclusivo y grafeno dopado con Ni, Ti, Cr y Se mediante la teoría funcional de la densidad. Inicialmente, variamos la posición de genisteína de la superficie del grafeno prístino y decorado cambiando las distancias entre (1-5 Å) y obtuvimos el E_{ad} y E_{gap}. El cálculo indicó que las energías de adsorción (E_{ad}) de genisteína prístina a grafeno con grafeno decorado con Ni, grafeno decorado con Ti y grafeno decorado con Cr y grafeno decorado con Se son: 954.984, 318.168, 797.480, 946.725, 958.154 kcal / mole, y los valores calculados de la energía de adsorción en la distancia de equilibrio (de=3.918^{0}A.) Los datos revelan que el grafeno decorado con genisteína-Ni es la posición más favorable energéticamente. Adicionalmente, explicamos la densidad de estados (Dos_s) y los orbitales moleculares de frontera HOMO y LUMO para el grafeno decorado con Ni y los complejos con genisteína; se confirmó que podría lograrse una carga positiva de grafeno decorado con Ni para moléculas de nucleófilos.

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1. Introduction

Genistein is a flavone compound. The highest amount of flavonoids has been found in soybean; for example,

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soy cheese or soy drinks [1–4], and it is obtained by fermentation or digestion of soybean [5]. It can be used for injunction multiplication of cancer cells. It is also applied to prevent heart diseases [6–8]. There are many analytical methods such as US-visible spectroscopy, mass spectroscopy, liquid chromatography, and biocompatible superparamagnetic drug delivery system, nano-formulation system, and nanoparticles for the determination of genistein [9–11]. Drug delivery systems prosper the pharmacokinetic and pharmacodynamics properties of different types of drug molecules [12]. Moreover, nanoparticles can develop the therapeutic potential of some established anticancer drugs. It is noteworthy that the benefit of using nano techniques in anticancer therapy is the objective delivery of anticancer drugs with few side effects [13–15].

Notably, nano techniques can be employed to receive genistein to the specific cancer cell [16, 17] and, graphene has unique physical, mechanical, electrical and chemical properties [18–21] Accordingly, the use of graphene as an adsorbent for biological molecules has been studied. For example, Ning Ding *et al.* deliberated the adsorption of nitrated tyrosine on the exclusive graphene and Nanometal- decorated graphene using two configurations of phenolic ring and gnitro group coordination on the graphene and found that when Au-Cr and Ni-doped graphene chemisorption occurred, the phenolic ring tended to the physisorption on the pristine graphene [22]. In another study, Zhang and *et al.* investigated the adsorption of H_2 on the Ti-Zn-Al and N-doped graphene sheet, and they concluded that Ti had the largest amount of interaction energy (near -0.299 eV) and Zn-doped graphene sheet (approximately -0.294 eV) and Al-doped graphene sheet (about -0.13 eV). N-doped graphene did not have an effect on adsorption energy to improve adsorption H_2 molecule on graphene sheet [23]. Shadmani *et al.* scrutinized the adsorption of MCM-41 on the graphene sheet by B3LYP/6-31G* and M05-2X/6-31G* basis set at different distances and studied the HOMO and LUMO energies, properties structure, ChelpG have been performed by DFT methods [24], and Shokuhi Rad examined the adsorption of Methanol and ethanol on the surface of t-decorated graphene by (DFT) calculation and discovered higher adsorption energies, low connecting distances, and high orbital hybridizing over adsorption of MeOH and EtOH molecules on PtG surface, the significant shift created in the location of the HOMO and LUMO [25], Shokuhi Rad also mulled over the (DFT) calculation to absorb some boron compounds ($B(OH_3))_3$, BF_3 and (BCL_3) on the surface of pristine and N-doped graphene , and found that N-doped graphene has higher adsorption energy and net charge transfer amount than pristine graphene. In another study, Shokuhi Rad and *et al.* dissected the adsorption of (NO_2) and (N_2O) molecules on the exclusive graphene and Al-decorated graphene by using (DFT) calculations.

The results presented that Al-doped graphene has substantial adsorption energy in compression of pristine graphene for the sake of existing the orbital hybridization between N_2O as well as N_2O, and Al-doped graphene, the adsorption energy for a most permanent state of NO_2 and N_2O was -62.2 kJ/mole and -33.9 kJ/mole [26–28]. Monajjemi considered liquid-phase –exfoliation (LPE) of graphite towards graphene theoretically and they indicated that sulfonic groups in a surfactant are most effective for any dissipation in the LPE process. They found that aromatic and ionic surfactant interacts with different carbon material, and p-stacking fall within their electron-abundant aromatic cores and conjugated surfaces of the carbon materials [29–31]. graphene material has attractive pure multi-physics, electrical [32], mechanical [33], and adsorption properties [34]. The graphene material is also responsible for modifying the charge carrier density and controlling its carrier mobility [35]. Since adsorption of genistein has not been studied on the surface of Ni-Ti-Cr-Se decorated graphene sheet, the present research aims at investigating and comparing the total adsorption energy and Gap energy for decoration of metallic atoms on the surface of graphene sheet in order to specify which element can be effected on the total and gap energy of adsorption. E_{gap} or Gap energy is an energy range in a solid where no electron states can exist, especially in condensed-matter physics; an energy gap is often known more abstractly as a spectral gap, a term which needs not be specific to electrons or solids. If an energy gap exists in the band structure of a material, it is called a band gap.

The physical properties of semiconductors are determined by their band gaps to a large extent, but also for insulators and metals, and the band structure. Thus, any possible band gaps govern their electronic properties. Graphene, being a gapless semiconductor, cannot be used in pristine form for Nano-electronic applications. Therefore, it is essential to generate a finite gap in the energy dispersion at Dirac point. We present here the metal-binding model considering various interactions for tuning band gap in graphene. Full-field measurements can also be used to retrieve heterogeneous properties by minimizing the equilibrium gap.

2. Computational methods

Genistein (4',5,7-trihydroxy isoflavone) is a molecule with isoflavone groups obtained from soybean extraction (Figure 1). In this study, we used 5 kinds of basis set for calculating total adsorption energy; pristine graphene used PM3MM and MINDO basis set, and for Cr, Se

decorated graphene sheet used PM3 basis set. ZINDO basis set was utilized to measure total adsorption energy for Ti, Ni-decorated graphene sheet. First, we considered a (4×4 graphene supercell) (Figure 2) & (Figure 3) and then placed the genistein molecule in parallel with the graphene sheet by using HYPER CHEM software and converted it to ChemBio3D format to change distances between genistein and graphene decorated sheet. By dint of Equation (2), we obtained the total adsorption energy of genistein on pristine graphene:

$$E_{ad(Ge\ on\ G)} = E_{Ge-G} - (E_G + E_{Ge}) \quad (1)$$

Where:

- E_{Ge-G}: Total electronic energies of interacting graphene with genistein.
- E_{Ge}: Total energy of pristine genistein.
- E_G: Total energy of pristine graphene.

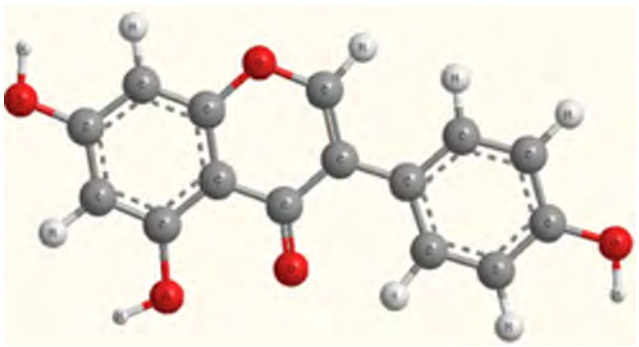


Figure 1 Genistein molecule

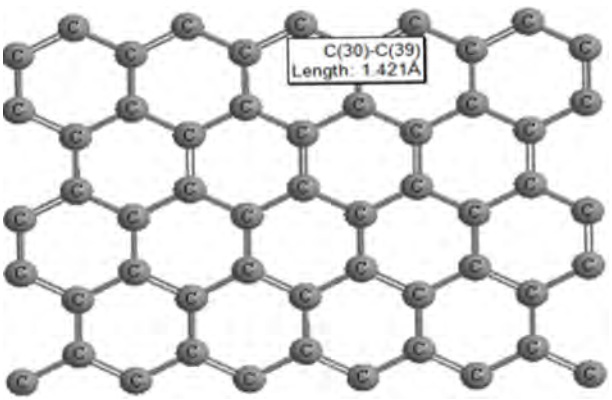


Figure 2 Supercell of pristine graphene

For decorated graphene, we placed 9 atoms of Ni, Ti, Cr, and Se Individually on the graphene sheet (Figure 3) and obtained the total adsorption of genistein on Ni, Ti, Cr, and Se decorated graphene by using Equation 2, 3, 4, 5:

$$E_{ad(\text{ Ge on } Ni-G)} = E_{Ge-Ni-G} - (E_{Ni-G} + E_{Ge}) \quad (2)$$

$$E_{ad(\text{ Geon } Cr-G)} = E_{Ge-Cr-G} - (E_{Cr-G} + E_{Ge}) \quad (3)$$

$$E_{ad(\text{ Ge on } Ti-G)} = E_{Ge-Ti-G} - (E_{Ti-G} + E_{Ge}) \quad (4)$$

$$E_{ad(Ge\text{ on } se-G)} = E_{Ge-se-G} - (E_{Se-G} + E_{Ge}) \quad (5)$$

Where $E_{Ge-Ni-G}$, $E_{Ge-Cr-G}$, $E_{Ge-Ti-G}$ and $E_{Ge-Se-G}$ are the total electronic energies of graphene, and Ni, Cr, Ti and Se decorated graphene interacting with the genistein.

Furthermore, we also obtained EHOMO, ELUMO, and Gap energy for genistein adsorption on Ni, Ti, Cr, and Se decorated graphene. All calculations were performed by the Gaussian09 program.

3. Results and discussion

Primarily, we placed the genistein molecule on the surface of pristine graphene and then changed the distances of genistein from pristine graphene (0.8-5 Å). The calculated values of gap energy, E_{HOMO}, and E_{LUMO}, as well as the equilibrium distance of genistein graphene are listed in Table 1. As can be seen from the values of gap energy given in Table 1, upon adsorption of genistein on pristine graphene energy of E_{HOMO}, E_{LUMO} at distances between (0.8- 2.9 Å) decreased and increased after d=3.18 Å; they declined and became constant in 77 kcal/mole or 0.122 eV. (See Figure 3). Table 1 displays the results of data and illustrates that the amount of minimum E_{gap} for adsorption genistein on pristine graphene is 75.263 Kcal/mole, a favorable distance from genistein – graphene (de=2.2650A.). According to Figure 4, the maximum amount of Egap for adsorption genistein on pristine graphene is (159.148 kcal/mole or 0.25 eV). The calculated values of adsorption energy in the equilibrium distance (de=2.2650A.) of genistein to graphene is 954.984 Kcal/ mol.

3.1 Ni decoration on graphene sheet

We replaced nine atoms of carbon on the graphene sheet with Ni and placed the genistein molecule at different distances from the surface of Ni-decorated graphene d= (0.8-5Å) (see Figure 1). We also measured E_{HOMO}, E_{LUMO} and E_{gap} between distances (0.8-5 Å) genistein from Ni-decorated graphene (see Table 2). The calculation demonstrated that the maximum amount of E_{gap} for Ni-decorated graphene is 85.422 kcal/mole or 0.136 eV in the 1.1780A from genistein distance and Ni-decorated

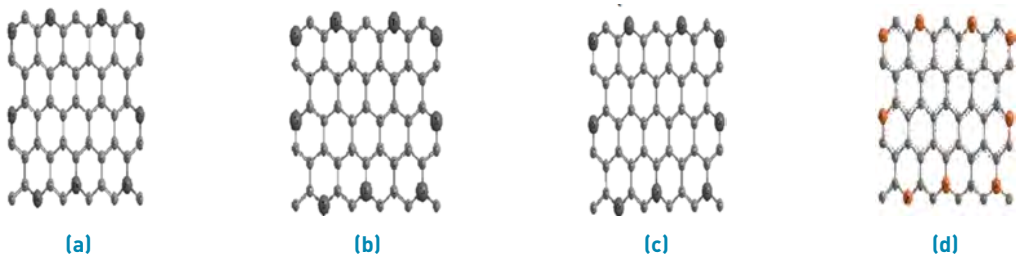


Figure 3 a) Ni-decorated graphene, **b)** Ti-decorated graphene, **c)** Cr-decorated graphene, **d)** Se-decorated graphene

Table 1 The energy of E_{HOMO}, E_{LUMO}, E_{gap} for genistein adsorption on graphene

d(A)	E_{HOMO}	E_{LUMO}	E_{gap} (kcal/mole)	d(A)2	E_{HOMO}	E_{LUMO}	E_{gap} (kcal/mole)
0.839	-0.19694	-0.04748	93.787	2.979	-0.25447	-0.05641	124.284
1.003	-0.1956	-0.06821	79.938	3.018	-0.24391	-0.02935	134.638
1.041	-0.28638	-0.15636	81.588	3.227	-0.27018	-0.14778	76.807
1.109	-0.28703	-0.16577	76.091	3.382	-0.27023	-0.14769	76.894
1.256	-0.20474	-0.06539	87.443	3.44	-0.27024	-0.14769	76.901
1.426	-0.22887	-0.07697	95.318	3.68	-0.23908	-0.11393	78.532
1.55	-0.23178	-0.032217	125.227	3.93	-0.27028	-0.14756	77.007
1.602	-0.22652	-0.08	91.942	4.099	-0.27029	-0.14755	77.020
2.009	-0.25538	-0.04974	129.040	4.172	-0.27031	-0.14754	77.039
2.265	-0.22783	-0.10789	75.263	4.695	-0.27039	-0.14752	77.102
2.325	-0.27568	-0.4838	130.597	4.794	-0.27039	-0.14752	77.102
2.874	-0.28818	-0.03456	159.148	5.112	-0.27045	-0.14752	77.1390

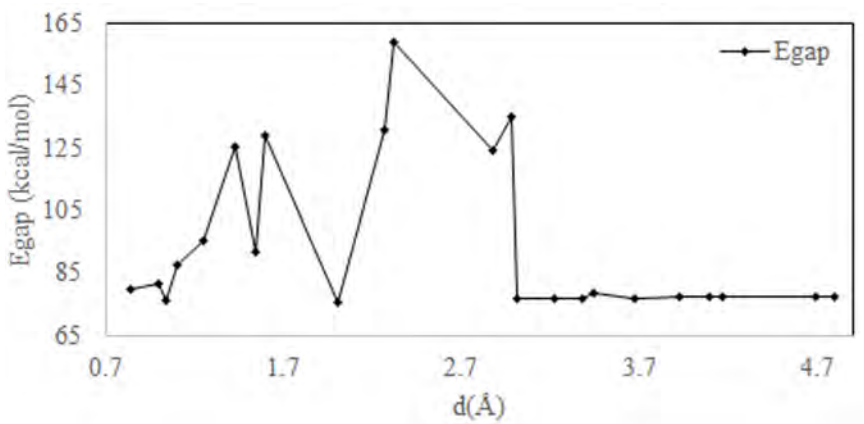


Figure 4 E_{gap} for adsorption genistein on pristine graphene

graphene, the minimum value of E_{gap} at for Ni-decorated is 60.629 kcal/mole or 0.096 eV in the 3.9180A from genistein distance and Ni decorated graphene. Equation 6 is applied to make a connection between conductivity and E_{gap}. As a result, Ni has higher electric conductivity and reactivity in comparison with C.

$$\delta \approx e^{-\frac{E_{gap}}{2KT}} \quad (6)$$

Where δ represents the electric conductivity and K is the Boltzmann constant [36]. The calculated values of the adsorption energy in the equilibrium distance (de=3.9180A.) of genistein to Ni decorated graphene is 318.168 Kcal/mol. Figure 5 shows that increasing distances E_{gap} for adsorption genistein on Ni-decorated graphene in more than five distances reached about 64 kcal/mole, but between d=0.839-1.180Å.

3.2 Ti decoration on graphene sheet

We superseded nine atoms of carbon on the graphene sheet with Ti and placed the genistein molecule at different distances from the surface of Ti-decorated graphene d= (0.8-5Å) (see Figure 1). The calculated values of gap energy, E_{HOMO}, and E_{LUMO}, as well as the equilibrium

Table 2 The energies of EHOMO, ELUMO, Egap-band for Ni-decorated graphene and its complexes with genistein at different distances

d (A°)	E_{HOMO}	E_{LUMO}	E_{gap}(kcal/mole)
0.839	-0.20838	-0.07569	83.264
1.003	-0.20989	-0.07769	82.956
1.081	-0.20822	-0.0725	85.165
1.134	-0.20765	-0.07181	85.240
1.178	-0.21331	-0.07718	85.422
1.180	-0.23339	-0.13001	64.871
2.253	-0.22066	-0.10828	70.519
3.08	-0.22808	-0.12139	66.948
3.121	-0.22807	-0.12157	66.829
3.918	-0.22858	-0.13196	60.629
4.027	-0.23286	-0.12966	64.758
4.064	-0.23289	-0.1297	64.752
4.196	-0.23305	-0.12982	64.777
4.231	-0.2331	-0.12985	64.790
4.251	-0.23308	-0.12984	64.784
4.695	-0.22677	-0.12917	61.244
5.085	-0.23353	-0.13007	64.922
5.112	-0.23363	-0.13014	64.940
5.296	-0.23356	-0.13006	64.947

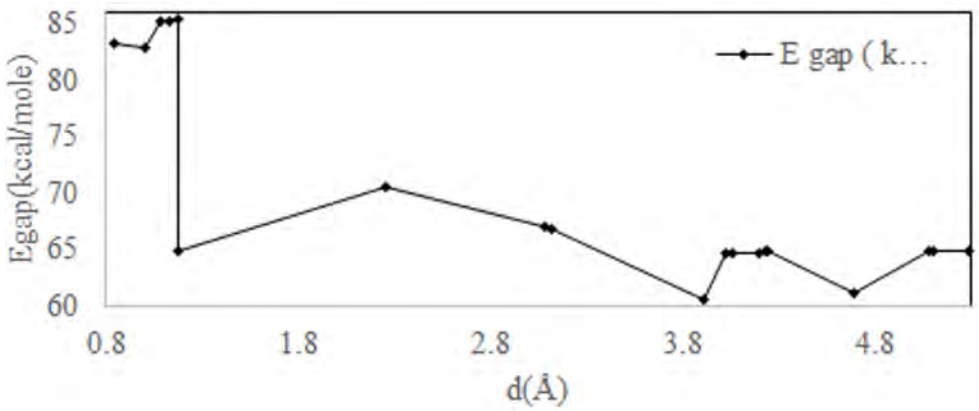


Figure 5 E_{gap} for genistein on Ni-decorated graphene versus distance

Table 3 The energy of E_{HOMO}, E_{LUMO}, and E_{gap} for adsorption × genistein on Ti-decorated graphene

d(A°)	E_{HOMO}	E_{LUMO}	E_{gap} kcal/mole	d(A°)	E_{HOMO}	E_{LUMO}	E_{gap} kcal/mole
0.888	0.18755	0.09492	58.126	2.714	0.19412	0.10495	55.954
1.229	0.18816	0.09381	59.205	3.067	0.196	0.10065	59.832
1.234	0.18747	0.09413	58.571	3.209	0.19916	0.10458	59.349
1.685	0.20455	0.1029	63.786	3.217	0.18236	0.08733	59.632
1.739	0.13994	0.09844	26.041	3.478	0.20061	0.05324	92.476
1.811	0.14534	0.10327	26.399	3.659	0.20114	0.10451	60.636
1.854	0.14625	0.10511	25.815	3.907	0.20099	0.09916	63.899
1.925	0.16442	0.10549	36.979	4.121	0.20042	0.10092	62.437
2.018	0.18832	0.10232	53.965	4.696	0.18409	0.08912	59.594
2.256	0.19364	0.1072	54.241	4.746	0.20212	0.10496	60.968
2.480	0.19171	0.09923	58.032	5.112	0.20222	0.10505	60.975

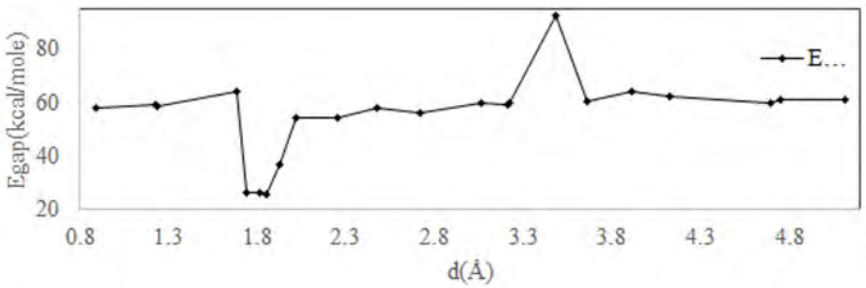


Figure 6 E_{gap} for genistein on Ti-decorated graphene versus distance

Table 4 The energy of E_{HOMO}, E_{LUMO}, E_{gap} for adsorption genistein on Cr-decorated graphene

d(Å)	E_{HOMO}(eV)	E_{LUMO}(eV)	E_{gap}(kcal/mole)	d(Å)	E_{HOMO}(eV)	E_{LUMO}(eV)	E_{gap}(kcal/mole)
0.876	-0.29095	-0.1536	86.188	2.424	-1.11794	-0.9723	91.390
0.886	0.28794	0.15134	85.717	2.671	-1.10343	-0.96546	86.577
0.914	1.15089	0.99781	96.059	2.874	-0.19069	-0.06267	80.333
0.948	1.14844	0.9979	94.465	3.389	-1.06143	-0.95142	69.032
0.98	1.14616	0.99926	92.181	3.594	-1.05226	-0.953	62.286
1.017	-1.14239	-1.00118	88.610	3.669	-1.05014	-0.95142	61.947
1.305	-1.14897	-0.98611	102.196	4.285	-1.04417	-0.92764	73.123
1.666	-1.14875	-0.98557	102.396	4.695	-0.19165	-0.07877	70.833
1.853	-1.12889	-0.99144	86.251	5.085	-1.04243	-0.89968	89.576
2.224	-1.13114	-0.97284	99.334	5.189	-1.04228	-0.89961	89.526

distance of genistein graphene listed in Table 3. The results obtained from the calculations of Table 3, as well as Figure 6, illustrate that Egap was in a minimum amount only at 4 specified distances (d=1.739, d=1.811, d=1.854 Å) and at d=3.478 Å, E_{gap} was in a maximum amount about (92.476 kcal/mole or 0.147 eV) and for the other distances, it was stable, and no significant change was observed. Considering distances about (3.067 – 5.112 Å), the variation of E_{gap} was from 59.832 -63.899 kcal/mole). The maximum amount of E_{gap} for Ti decorated graphene is more than Ni and Cr maximum value of E_{gap} and minimum value of E_{gap} for Ti-decorated graphene about 2.4% fewer than Ni and Cr-decorated graphene exhibiting more conductivity and higher reactivity, in comparison with Ni and Cr decoration graphene. As shown in Figure 5, variations of E_{gap} with changing distances is almost invariable and about 55-60 kcal/mole. Nonetheless, the minimum value of E_{gap} gained just in d=1.854Å, (25.815 kcal/mol) and the maximum E_{gap} gained at d=3.478. Indeed, it is the opposite of Ni-decorated graphene because Ni gained the maximum amount of E_{gap} at d=1.081-1.178Å. The calculated values of adsorption energy in the equilibrium distance (de=1.8540A.) of genistein to Ti-decorated graphene is 797.480 Kcal/mol.

3.3 Cr decoration on graphene sheet

We replaced nine atoms of carbon on graphene sheet with Cr and placed the genistein molecule at different distances from the surface of Cr-decorated graphene d= (0.8-5Å) (see Figure 1). When we used Cr for decoration graphene, it did not have a considerable change in total adsorption energy because the adsorption energy was higher than the other distances at d=0.886Å. Furthermore, we calculated the E_{gap}, E_{HOMO} and E_{LUMO} listed in Table 4. As indicated in Table 4, the amount of E_{HOMO} changed from -0.290 eV or -182.26 kcal/mole to -0.104 eV or -65.40 kcal/mole. Figure 7 presented that the maximal amount of E_{gap} occurred at d=1.666Å, E_{gap}=102.396 kcal/mole, and the minimum value of E_{gap}=61.947 kcal/mole at d=3.669Å. Since they are less than the pristine graphene, the lower of E_{gap} for Cr-decorated graphene corresponds to its higher conductivity and higher reactivity. The total adsorption energy was obtained at 946.725 kcal/mole.

3.4 Se decoration on graphene sheet

We displaced nine atoms of carbon on the graphene sheet with Se and placed the genistein molecule at different distances from the surface of Se-decorated graphene d= (0.8-5Å) (see Figure1). Table 5 features out the energy of E_{HOMO}, E_{LUMO}, and E_{gap} for adsorption genistein on Se-decorated graphene. Figure 7 shows that the maximal amount of E_{gap} occurred at d=2.119Å, E_{gap}=94.691 kcal/mole, and the minimum value of E_{gap}=45.252 kcal/mole at d=1.744Å. As they are less than the pristine graphene, the lower of E_{gap} for Se-decorated graphene corresponds to its higher conductivity and higher reactivity. Moreover, E_{gap} has little reduced at d=4.827

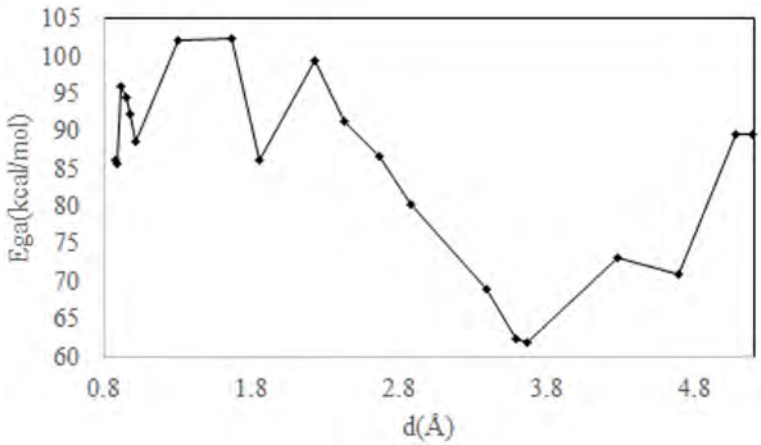


Figure 7 E_{gap} genistein on Cr-decorated graphene versus distance

Table 5 The energy of E_{HOMO}, E_{LUMO}, E_{gap} for adsorption genistein on Se-decorated graphene

d(A°)	E_{HOMO}	E_{LUMO}	E_{gap} kcal/mole	d(A°)	E_{HOMO}	E_{LUMO}	E_{gap} kcal/mole
0.982	0.28181	0.15891	77.120	2.700	0.29845	0.16014	86.790
0.991	0.28068	o.16149	74.790	2.898	0.29926	0.16096	86.784
1.005	0.26668	0.15221	71.830	3.343	0.29986	0.16166	86.721
1.012	0.28114	0.16148	75.090	3.512	0.29993	0.16174	86.715
1.072	0.27921	0.16195	73.581	3.584	0.29995	0.16175	86.721
1.167	0.27522	0.15685	74.278	3.594	0.29994	0.16177	86.702
1.273	0.27377	0.15613	73.820	4.032	0.30001	0.16175	86.759
1.331	0.27276	0.15566	73.481	4.171	0.30002	0.16174	86.771
1.543	0.25508	0.15663	61.778	4.375	0.30004	0.16171	86.803
1.744	0.23987	0.19703	45.252	4.827	0.28104	0.1612	75.200
2.119	0.28713	0.1509	94.691	4.865	0.28105	0.16121	75.200
2.286	0.29233	0.1564	85.297	5.144	0.28108	0.16122	75.213

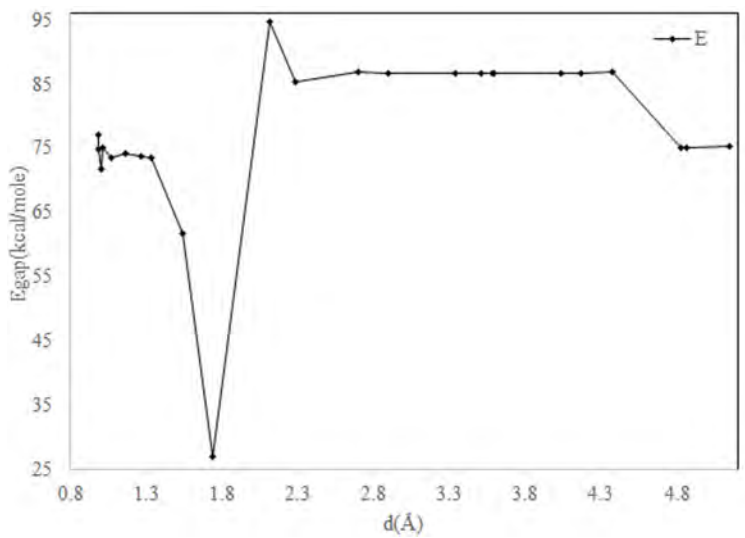


Figure 8 E_{gap} for genistein on Se-decorated graphene versus distance

to 5.144 Å, and also, the maximum value of E_{gap} for Se-decorated graphene is lower than that maximum value of E_{gap} for pristine graphene; therefore, it is the same for a minimum amount of E_{gap}. As a result, this reduction in the E_{gap} implies more conductivity of decorated graphene by Se in compression with pristine graphene (see Figure 8).

Table 6 Values of gap energy, and Adsorption energy, as well as the equilibrium distance of genistein to any atom: (Ni, Cr, Ti, and Se) decorated graphene

System	de(^{0}A)	E_{ad}(kcal/mole)	E_{gap}(kcal/mole)
genistein- PG	2.265	954.984	75.263
genistein- NiG	3.918	318.168	60.629
genistein- TiG	1.854	797.480	25.815
genistein- CrG	3.669	946.725	61.947
genistein- SeG	1.744	958.154	45.252

Consequently, the lower E_{gap} for Se-decorated graphene corresponds to its higher conductivity and higher reactivity. Its adsorption energy was obtained at 958.154 kcal/mole.

We can see that the maximum amount of E_{gap} for Ni-decorated graphene is 85.42 kcal/mole or 0.136 eV. Thus, this amount is lower than E_{gap} of Cr-decorated graphene and also E_{gap} of pristine graphene. This trend proved that Ni has higher conductivity and reactivity in compression with C, the minimum value of E_{gap} for Ni-decorated is 60.629 kcal/mole or 0.096 eV that is near the lowest amount of E_{gap} for Cr-decorated graphene and also less than the minimum amount of E_{gap} for pristine graphene. The calculated values of gap energy and adsorption energy, as well as the equilibrium distance of genistein to any atom (Ni, Cr, Ti, and Se) decorated graphene as listed in Table 6. This table displays that the arrangement of adsorption and gap energy for different atoms is achieved as: E_{ad} genistein to Ni-decorated graphene < E_{ad} genistein to Ti-decorated graphene < E_{ad} genistein to Cr-decorated graphene < E_{ad} genistein -PG < E_{ad} genistein to Se- decorated graphene. This order in the value of adsorption energy is in good agreement with the equilibrium of their distance of genistein surface.

Based on our calculations, the amounts of gap energies and also adsorption energies are listed in Table 6. Apparently, genistein- Ni-G complex, energetically, has a favorable position compared with other decorated graphenes. Therefore, the density of states (DOS) as well as frontier molecular orbitals HOMO and LUMO have been explained (Figure 9a to Figure 9f) to perfectly understand these structures such as Ni-decorated graphene - genistein, complex. The NBO analysis contributed to confirm the positive charges of Ni decorated graphene metal stability results. HOMO and LUMO energies of decorated Ni on graphene are listed in Table 6. As can be seen, HOMO and LUMO energies are increased to -0.23 and -0.13 at d=5.112 Å. and the gap band (E_{HOMO}-E_{LUMO}) decreased from 83.26 to 64.94 (kcal/mole).

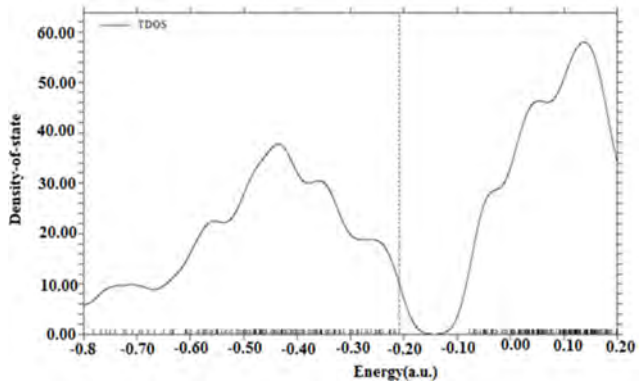
As observed in Figure 9a to Figure 9f, the HOMO and LOMO gap energies of the system are obtained in Table 2 with swelling distance between genistein from Ni-decorated graphene. In comparison with other atoms, the electrical conductivity of the system becomes higher for Ni-decorated graphene by increasing E_{gap}.

4. Conclusion

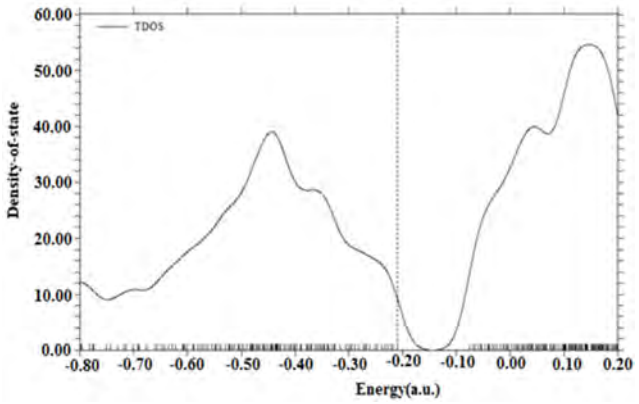
Using drug delivery methods in biotechnology, the adsorption of genistein on the surface of exclusive graphene and Ni, Ti, Cr, and Se doped graphene can bring about some significant information. Our calculations have been accomplished theoretically using density functional theory. We investigated the adsorption energy of the genistein molecule on the surface of pristine graphene and Ni, Cr, Ti and Se decorated graphene. The calculated values of gap energy and Adsorption energy, as well as the equilibrium distance of genistein to any atom (Ni, Cr, Ti, Se) decorated graphene, demonstrate that the order of adsorption and energy gap for different atoms is achieved as: E_{ad} genistein to Ni-decorated graphene < E_{ad} genistein to Ti-decorated graphene < E_{ad} genistein to Cr-decorated graphene < E_{ad} genistein -PG < E_{ad} genistein to Se decorated graphene. This order in the value of adsorption energy is in good agreement with the equilibrium of their distance of genistein surface. Subsequently, our results presented that the pristine graphene is the weakest adsorbent for genistein. Henceforth, we measured the maximum and minimum of Egap for genistein adsorption of Ni-Cr-Ti-Se decorated graphene sheet and the order of reactivity from higher to less is achieved as Ni > Ti > Se > Cr > pristine graphene. Apparently, the Ni atoms are more effective on reactivity and conductivity and can be a good choice for genistein adsorption on the graphene sheet towards the Cr-Ti and Se atoms.

5. Declaration of competing interest

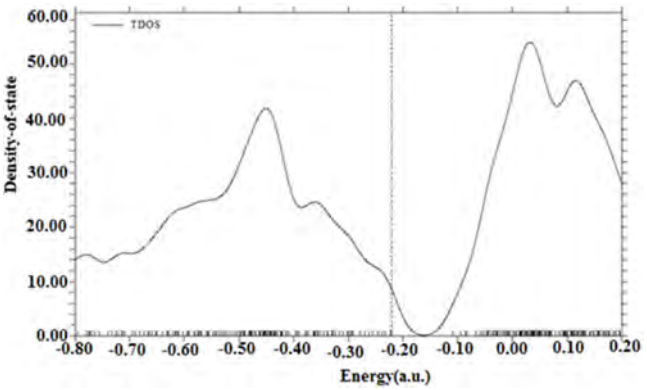
We declare that we have no significant competing interests including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.



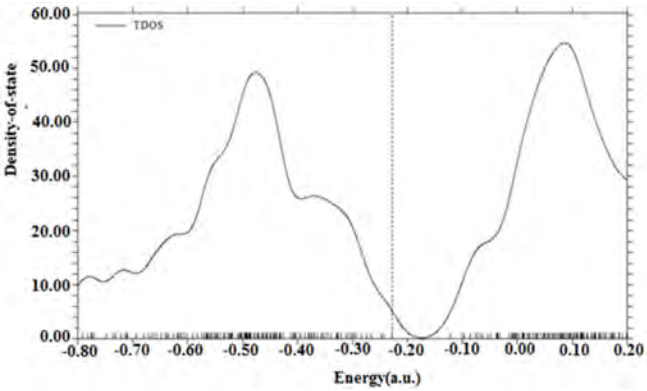
(a) Dos of Ni-decorated graphene for genistein adsorption at d=0.839 Å



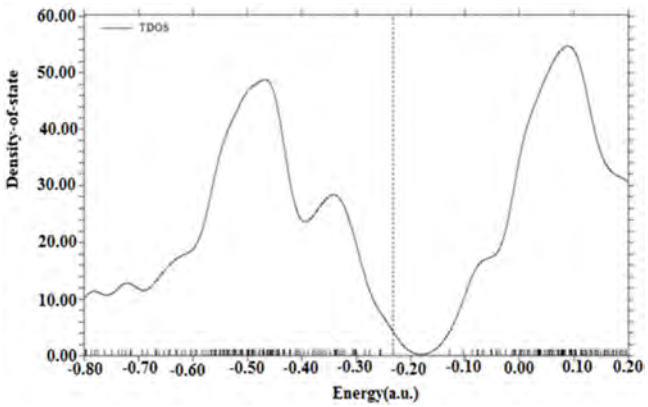
(b) Dos of Ni-decorated graphene for genistein adsorption at d=1.003 Å



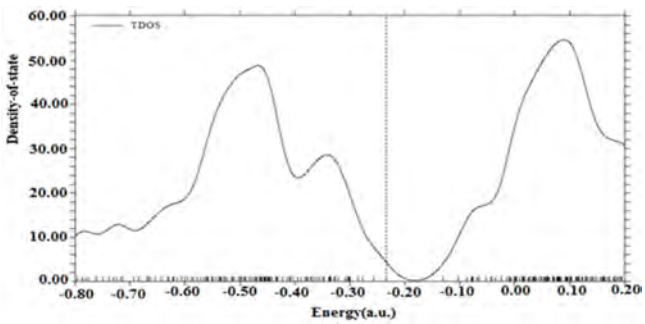
(c) Dos of Ni-decorated graphene for genistein adsorption at d=2.253 Å



(d) Dos of Ni-decorated graphene for genistein adsorption at d=3.121 Å



(e) Dos of Ni-decorated graphene for genistein adsorption at d=4.027 Å



(f) Dos of Ni-decorated graphene for genistein adsorption at d=5.112 Å

Figure 9 Dos of Ni-decorated graphene for genistein adsorption

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7. Funding

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8. Author contributions

- **Afshar Alihosseini:** Revising the manuscript, supervision.
- **Marziyeh Choupani:** Writing, draw the tables, and figures, calculation, checking the grammar and dictation.
- **Majid Monajjemi:** Idea, and revision and super vision.
- **Hossein Sakhaeinia:** Control the instruction of manuscript and refrences.

9. Data availability statement

Devices and software used in the study was prepared of the Islamic Azad University Tehran Branch, Iran.

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