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Theoretical study of 2,3,7,8-tetrachlorodibenzo-para-dioxine removal by boron nitride-nanotube (BNNT): QSAR, IR-DFT

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ABSTRACT

The study examined corrosion inhibition of corrosion inhibition of 5-methyl-2H-imidazol-4-carboxaldehyde and 1H-Indole-3-carboxaldehyde on mild steel in acidic medium using weight loss and Density Functional Theory (DFT) methods. DFT calculations were carried out at B3LYP/6-31+G** level of theory in aqueous medium on the molecular structures to describe electronic parameters. The values of thermodynamic parameters such as free energy of adsorption (ΔG^{o}_{ads}), adsorption equilibrium constant (K_{ads}), adsorption entropy (ΔS^{o}_{ads}), adsorption enthalpy (ΔH^{o}_{ads}) and activation energy (E_a) were calculated, analyzed and discussed. The adsorption process on mild steel surface showed that 4-methylimidazol-5-carboxaldehyde and Indole-3-carboxaldehyde obeyed Freundlich and Temkin adsorption isotherms respectively. Also, the molecular parameters associated with inhibition efficiency such as E_{HOMO}, E_{LUMO}, band gap energy (E_{LUMO}- E_{HOMO}), softness (S), electron affinity (EA) and number of electrons transfer were calculated. The higher inhibitory property of 5-methyl-2H-imidazol-4-carboxaldehyde was attributed to the presence of higher number of protonation sites as a result of higher number of nitrogen atoms, increase in number of plane protonated species and higher net charges on the ring atoms.

Keywords: Boron nitride nanotube (12, 0) (BNNT); 2, 3, 7, 8-tetrachlorodibenzo-p-dioxine (TCDD); Thermodynamics parameters; QSAR; HOMO-LUMO energy

INTRODUCTION

The 2,3,7,8-etrachlorodibenzo-p-dioxin (TCDD) is concluded a human carcinogen by the International Agency for Research on Cancer (Lyon, France) [1]. The TCDD is produced in thermal processes such as incineration, in metal-processing, and in the bleaching of paper pulp with free chlorine [2, 3]. Remove and reduction of them from environment is a requirement, nowadays nano-materials are used for elimination of persistent pollutants (chlorinated aromatic compounds) such as; Pd/nFe nanoparticles [4], TiO_2 nanoparticles [5], silver doped zeolite [6], nano-C60 [7] and so on. Nano-materials have a large surface to volume ratio and porous surface; therefore have high sensitivity and fast response time for pollutants [8]. One of the nano-adsorbents that can be used for the removal of organic compounds is boron nitride (B_nN_m) nano-adsorbents [9-12].

Recently, due to the geometry and stability of nano-structures, boron nitride nanotubes (BNNTs) were examined and

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the results showed. Their structure has the most stable form of energy among different types of boron nitride nano-structure [13]. The B–N bond in it is polar (dipole moment of BNNT (12, 0) is 9.21D in table 1), semiconductor, a slight positive charge of boron atom (B) and slight negative charge of nitrogen atom (N) increases the polarity on the BNNTs in contrast to the non-polar CNTs. BNNTs can adsorb polar species better than CNTs [12]. The important factor in adsorption is the nanotube diameter [14], in this study is used BNNT (12, 0) that its diameter is 9.421 Å because it has more stabilities against thermal and chemical fluctuations, is resistance to oxidation [15]. The wider band gap and polarization of BNNT suitable for applications such as in composite materials, force sensors, absorb polar and non-polar species, the use of luminescence devices of blue and purple and working in nano-devices that work in high temperatures and dangerous environments. Therefore, TCDD is a non-polar material and it is formed in high temperature one can expect that BNNT is a better adsorbent. In this study, passing TCDD from the central axis of BNNT (12, 0) is calculated, results show that middle the length nanotube is a suitable place for the trapping of pollutants and electrical changes produced in BNNT is suitable nanotubes as nano-sensor.

COMPUTATIONAL METHOD

All thermodynamic and electrical properties of the desired reaction were performed by GAMESS-US of the program package on B3LYP/6-31++G(d) method [16]. Pollutant approach to nanotubes, there are many possibilities for interaction between them such as; i) the absorption of TCDD on the end of the BN-nanotube, ii) its absorbing on the wall, iii) cross of TCDD between nanotubes, iv) absorbs pollutants on the inner walls of the nanotube. Due to nanotube diameter is a possibility of pollutant passing from the central axis of nanotubes. In this study is used the BNNT (12, 0) with a diameter of 9.421 Å, the highest probability of pollutant interact with it is the passing of TCDD through its central axis, so is simulated in 5 steps and all steps are optimized by B3LYP/6-31++G(d) method. To evaluate the stability of TCDD passing into a nanotube, the adsorption energy (E_b) has been calculated as follows:

$$E_b = E_{\text{TCDD-nanotube}} - [E_{\text{TCDD}} + E_{\text{nanotube}}] + \delta_{\text{BSSE}} \quad (1)$$

where $E_{\text{TCDD-nanotube}}$ is the passing energies of TCDD intro BN-nanotube, E_{nanotube} and E_{TCDD} is energy of an isolated of the BN nanotube and TCDD molecule and δ_{BSSE} is representing the basis set superposition error.

RESULTS AND DISCUSSION

For investigation the TCDD passing from the central axis of BN-nanotube, initially *is* an optimized geometric structure of TCDD and BN-nanotube separately and thermodynamic and electrical properties of them is calculated, show in Figure 1. The length and diameter of BNNT are 11.154 and 9.421 Å, both ends of the nanotubes have closed by hydrogen atoms. In structure of boron nitride nanotubes, an end of the nanotube is nitrogen atoms and the its other end is boron atoms that bond length of H-N and H-B is 0.979 and 1.205 Å, respectively.

Its optimized structure (Fig.1) shows that the length bond of N-B near to H-N is 1.431Å and the length bond of B-N near to H-B is 1.411Å. Therefore, HOMO/LUMO energy is calculated for TCDD interaction with end of the tube that is H-N, it is indicated in Figure 1. Figure1 shows the

geometrical structure optimized of TCDD and BNNT with calculated theirs HOMO/LUMO energy. The steps of TCDD passing intro BNNT are indicated in Figure 2.

For investigation of this passing, in the first step, TCDD is neared to the central axis from side of H-B-N because this place is more symmetrical and dipole moment is lower than the other end of the nanotube. In the second step, TCDD is coming in BNNT and in the third step, it placed in middle of BNNT then in fourth and fifth step, TCDD is exited in BNNT. All these steps show in Figure 2. The total energy is calculated for all steps, is indicated in Figure 2. The most energy is for 3rd step that TCDD placed in middle of BNNT, is -13116.17kJ.mol^{-1}. The adsorption energy (E_b/kJ.mol^{-1}) of all steps is calculated by Eq (1) and is shown in Figure 3. By TCDD enters to nanotube, E_b increases and after passing through middle of BNNT and it decreases.

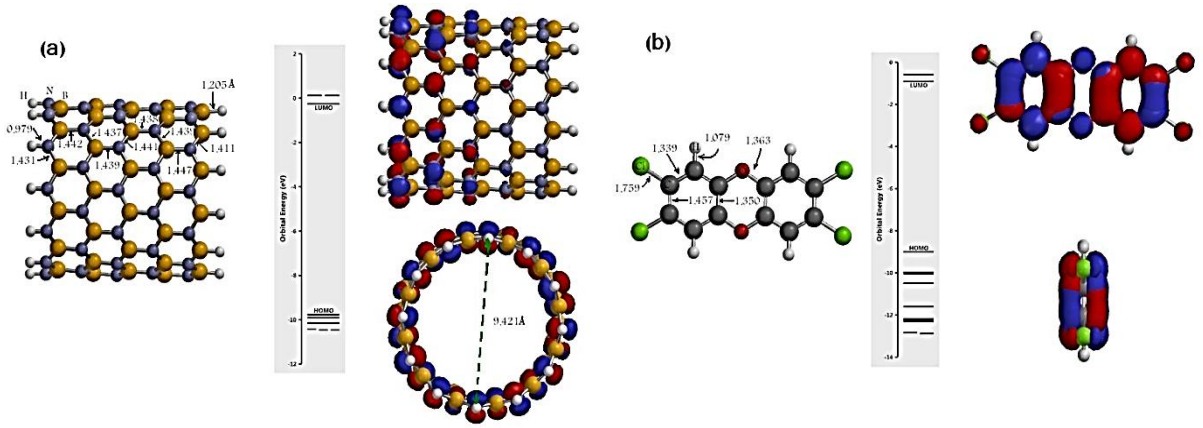

Figure 1. The geometrical structure optimized and HOMO/LUMO energy of a) BNNT (12, 0) and b) TCDD.

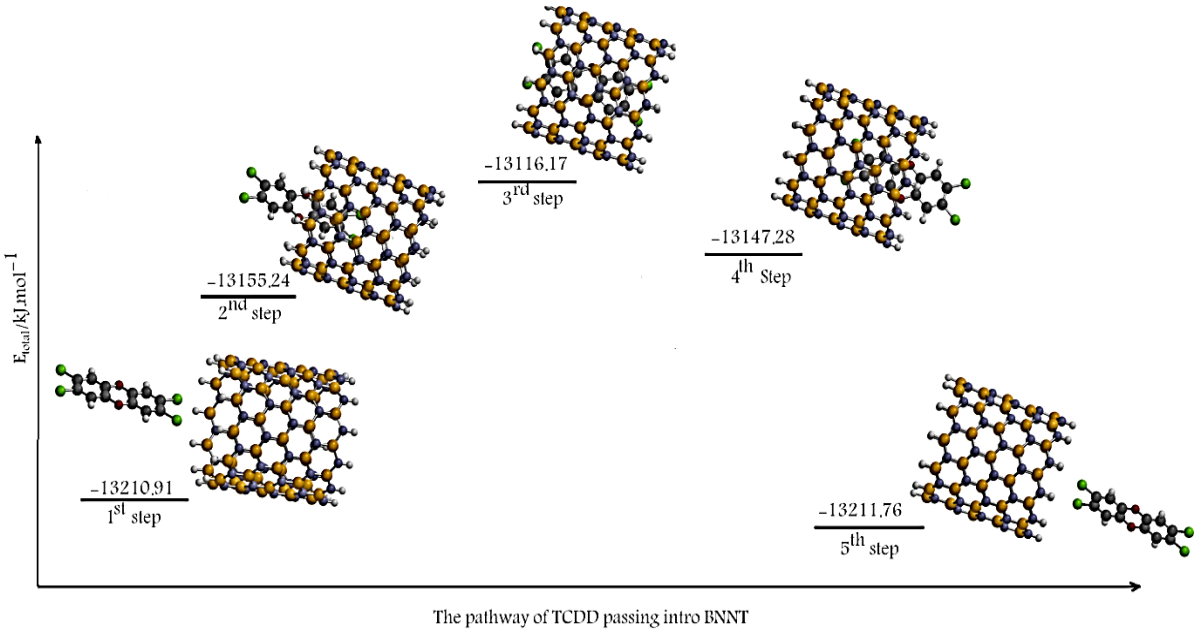

Figure 2. The pathway and total energy of passing of TCDD intro BN-nanotube.

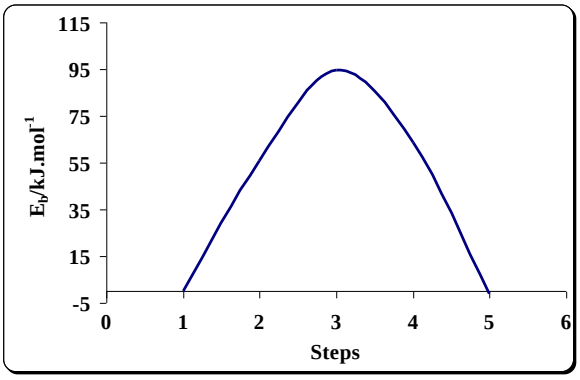

Figure 3. The adsorption energy calculated of TCDD-BNNT complexes for all steps.

Some characteristics are helpful in qualitatively interpreting experimental spectroscopic data such as; the width of the valence band, the gap energy in insulators and the number and intensity of the main features. The density of states (DOSs) is calculated by the DFT method (B3LYP/6-31++G (d)). Table 1 shows DOS parameters including E_{LUMO} (Energy of the lowest unoccupied molecular orbital), E_{HOMO} (Energy of the highest occupied molecular orbital), E_g (gap energy), μ (chemical potential or negative of electronegativity), η (chemical hardness), σ (chemical softness), ω (electrophilicity) and ΔN_{MAX} (charge transfer in molecules) [17].

$$\mu = (E_{LUMO}+E_{HOMO})/2 \quad (2)$$
$$\eta = (E_{LUMO}-E_{HOMO})/2 \quad (3)$$
$$\sigma = 1-\eta \quad (4)$$
$$\omega = \mu^2/2\eta \quad (5)$$
$$\Delta N_{MAX} = -\mu/\eta \quad (6)$$

When TCDD is closer to BNNT, has caused a structural change in it. The gap energy (E_g) is a major factor for the determination of the electrical conductivity of nano-sensors. If the calculated amount of E_g for complexes is most, sensitivity and conductivity of between them will be considerable and nanostructure can be used as nano-sensors. In studying interactions, the most amount of gap energy occurred for 1st step because the symmetry structure of BNNT changes and increases BNNT polarity.

Table 1. The DOS calculation for the interactions of TCDD and the intermediate species with BN-nanotube by B3LYP/6-31++G (d)

	E_{LUMO}/eV	E_{HOMO}/eV	E_g/eV	μ/eV	η/eV	σ/eV	ω/eV	ΔN_{MAX}/eV
BNNT(12, 0)	-0.25	-9.76	9.51	-5.01	4.76	-3.76	2.63	1.05
TCDD	-0.91	-9.00	8.09	-4.96	4.05	-3.05	3.03	1.22
1	-0.97	-9.05	8.08	-5.01	4.04	-3.04	3.11	1.24
2	-1.52	-9.54	8.02	-5.53	4.01	-3.01	3.81	1.38
3	-1.70	-9.76	8.06	-5.73	4.03	-3.03	4.07	1.42
4	-1.71	-9.77	8.06	-5.74	4.03	-3.03	4.09	1.42
5	-1.38	-9.44	8.06	-5.41	4.03	-3.03	3.63	1.34

According to table 1, the chemical potential (μ) decreases in 3rd and 4th steps, indicating a transfer of electrons from BNNT to TCDD molecule, because BNNT electronegativity decreases from -5.01 to -5.74 eV. The chemical hardness (η) and chemical softness (σ) are used for evaluation of the hardness and softness of molecules. Hard molecule has a large HOMO-LUMO gap while a soft molecule has a small HOMO-LUMO gap [17, 18]; therefore 3rd and 4th steps are harder than other states and can easily change their electron density. The electrophilicity (ω) is a measure of the electrophilic power of a molecule. The ω value is increasing toward 4th step, which shows higher electrophilicity then other steps. So it is a stronger Lewis acid. The accepted and donor electron charge of molecules can be calculated by a maximum amount of electronic charge (ΔN_{MAX}). The $\Delta N_{MAX}<o$ indicates the molecule acts as an electron donor [18]. All steps, BN nanotube and TCDD are an electron acceptor and have significant power of electron affinity can be capable for identification of TCDD.

For calculated of thermodynamics parameters is used the IR-DFT methods. Figure 4 shows the IR spectrum of TCDD, BNNT and complex of TCDD in middle nanotube. As shown in Fig. 4, the IR characteristic peak of isolated TCDD molecule at 1652cm^{-1}, which corresponds to in-plane scissoring vibration of C-H bonds on benzene rings, is still recognizable in TCDD-BNNT complex. However, it is shifted to 1657cm^{-1} in TCDD-BNNT but the intensity of its peak is very low and shows a characteristic single peak at 3184cm^{-1}, which corresponds to the benzene ring skeleton vibration. BNNT exhibits two distinct peaks at 1493 cm^{-1} and 824 cm^{-1}which can be attributed to the in-plane B–N transverse optical mode of the BNNTs and the B–N–B out-of-plane bending vibration perpendicular to the axis of the nanotube respectively. Another peak is at 3584 cm^{-1} for in-plane H–N that is still in the TCDD-BNNT complex.

The thermodynamics parameters for these interactions are calculated, show in Table 2. The most changes are indicated in middle nanotube, the dipole moment of BNNT decreases in first until third step then increases. ZERO POINT ENERGY (ZPE) has most among in 3rd step, is 2899.48 kJ.mol^{-1}. The heat of reaction formation (H^o) and Gibbs free energy (G^o)/a.u. are negative, show these interactions are exothermic. The heat capacity (C_v) and entropy (S^o) have the most changes in this step.

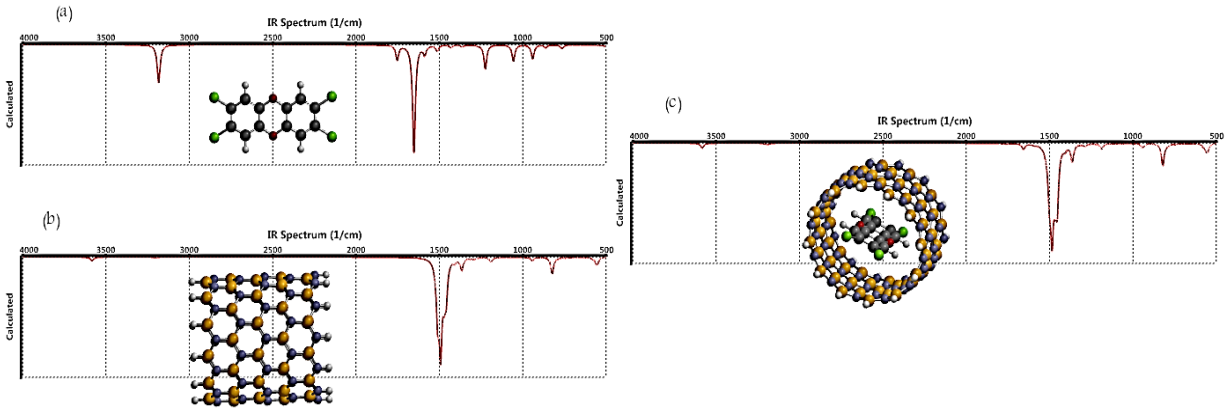

Figure 4. The calculated IR spectra of a) TCDD, b) BNNT and c) complex of TCDD inter middle BNNT.

Broad interpretation is essentially a "sensitivity analysis" of these interactions have presented a method to measure the importance property of the descriptor in quantitative structure-activity relationship (QSAR) model. The parameters of calculated for these interactions by QSAR method are Area/$Å^3$ (Molecular Surface Area), Volume/$Å^3$, PSA/$Å^2$ (Polar surface area), Ovality is described by a ratio of volume to area, Acc.Area/$Å^2$ (Accessible area), P-Area/$Å^2$ (polar area corresponding to absolute values of the electrostatic potential greater than 75), Acc.P-Area(75)/$Å^2$(Accessible polar area corresponding to absolute values of the electrostatic potential greater than 75), Min.Elpot/kJ.mol^{-1} (Minimum energy of ionization potential), Max.Elpot/kJ.mol^{-1} (Maximum energy of ionization potential), Min.LocIonPot/kJ.mol^{-1}(Minmum values of the local ionization potential (as mapped on to an electron density surface) and Polarizability, show in Table 3 [20].

The polar surface area/$Å^2$ (PSA) of a molecule is currently defined as the surface sum over all polar atoms, primarily boron and nitrogen, shows the critical role of the charge and polarity of the molecules. Min and Max Elpot of calculating for TCDD, so they are the most toxic. The polarizability of a molecule, an important physical property, is currently attracting our attention, particularly in the area of QSAR for chemical and biological interactions [21]. The all parameters indicate that 3rd step is conducive to activity for adsorption of TCDD to inner BNNT.

Table 2. The calculation of total energy (E_{total}), Dipole moment (DM), ZERO POINT ENERGY (ZPE), heat of reaction formation (H^o), Gibbs free energy (G^o), heat capacity (C_v) and entropy (S^o) for BN-nanotubs, TCDD and passing steps of TCDD in BNNT by the B3LYP/6-31++G (d) method in 298K

Steps	BNNT (12, 0)	TCDD	1	2	3	4	5
E_{total}/kJ.mol^{-1}	-13129.05	-81.80	-13210.91	-13155.24	-13116.17	-13147.28	-13211.76
Dipole moment/D	9.21	0	8.78	8.88	8.06	9.16	10.38
ZERO POINT ENERGY (ZPE)/kJ.mol^{-1}	2537.91	360.47	2898.54	2899.18	2899.48	2898.75	2898.81
H^o/a.u.	-3.97	0.12	-3.85	-3.83	-3.82	-3.83	-3.85
G^o/a.u.	-4.11	0.07	-4.02	-3.99	-3.98	-3.99	-4.02
Cv/J.mol^{-1}	982.86	162.46	1145.40	1145.98	1146.30	1145.98	1145.34
S^o/J.mol^{-1}	1227.74	468.56	1430.70	1423.03	1420.07	1423.11	1429.87

Table 3. The QSAR calculated for BN-nanotubs, TCDD and passing steps of TCDD in BNNT by the B3LYP/6-31++G (d) method in 298K

Steps	BNNT (12, 0)	TCDD	1	2	3	4	5
Area/$Å^2$	995.32	258.60	1253.93	1212.47	1183.19	1211.93	1253.87
Volume/$Å^3$	1277.75	242.36	1520.12	1516.52	1513.96	1516.27	1520.10
PSA/$Å^2$	159.21	14.45	173.69	173.85	173.857	173.94	173.73
Ovality	1.75	1.38	1.96	1.90	1.86	1.90	1.96
Acc.Area/$Å^2$	713.93	355.86	882.22	654.57	534.76	632.73	876.44
P-Area(75)/$Å^2$	902.29	428.20	1127.20	1114.27	1102.81	1115.70	1127.19
Acc.P-Area(75)/$Å^2$	712.93	355.86	882.22	654.57	534.76	632.73	876.44
Min Elpot/kJ.mol^{-1}	40615.23	-635544512.26	29599.27	40374.15	48216.31	43043.42	30463.64
Max Elpot/kJ.mol^{-1}	64799.61	-284738638.91	69712.21	79242.18	84059.09	80625.61	70130.11
Min LocIonpot/kJ.mol^{-1}	155.96	0	105.31	106.31	109.83	109.76	106.23
Polarizability	142.79	59.13	162.78	162.51	162.29	162.48	162.79

CONCLUSION

Dioxins are highly toxic compounds and are considered dangerous. It is noteworthy that the identification and quantitative determination, and ultimately eliminate and reduce it to low-risk products is one of the main goals of this research. In this study, simulate and calculate the thermodynamic parameters for interaction of these pollutants with boron nitride nanotubes (12, 0) is investigated. The complex structure of TCDD passing into BNNT was optimized by the DFT method with basis set B3LYP/6-31++G (d). The results of calculating show, BNNT have tended to enter the pollutants in its central axis and show significant changes in the electrical and thermodynamic properties when TCDD into nanotube and most of these changes have been achieved in the middle of nanotubes. The data are calculated by QSAR method, indicated toxic decreased of TCDD in BNNT.

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