Original Research Article

Carbon Nanocone as a Potential Adsorbent and Sensor for the Removal and Detection of Ciprofloxacin: DFT Studies

Saeid Abrahi Vahed[1] and Fatemeh Hemmati Tirabadi[2,3,*]

[1]Young Researchers and Elite Club, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

[2]Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre-rey Branch, Islamic Azad University, Tehran, Iran.

[3]Research Center for New Technologies in Chemistry and Related Sciences, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran

ABSTRACT

The removal and detection of ciprofloxacin (CPX) as an emerging environmental contaminant and a medicine are of great importance. In this respect, the performance of carbon nanocone (CNC) as a sensing material and an adsorbent for CPX was investigated by infrared-red (IR), frontier molecular orbital (FMO), and natural bond orbital (NBO) computations. The calculated adsorption energies, Gibbs free energy changes, enthalpy changes, and thermodynamic constants showed that CPX interaction with CNC was experimentally feasible, exothermic, and spontaneous. The NBO results indicated that CPX interaction with CNC was physisorption and no bond was created among the adsorbent and adsorbate. Moreover, findings on the effect of the temperature indicated that the adsorption process was more favorable at lower temperatures. The computed bandgap values showed that when CPX was adsorbed on the surface of CNC, the bandgap of CNC experienced a sharp decline (-26%) from 6.880 to 5.040 (eV). Hence, this nanostructure is a suitable sensing material for the development of novel electrochemical sensors for the determination of CPX.

Keywords: Ciprofloxacin, Carbon nanocone, Density Functional Theory, Adsorption, Sensor

Introduction

Antibiotics as the most widely prescribed medicinal compounds are considered now as a main emerging environmental contaminant all over the world because their existence in environmental matrices not only endanger the health of humans and other living organisms (by creating antibiotic resistance dilemma and inducing their adverse side effects) but also can cause serious

environmental issues [1-3]. Since the discovery of penicillin by Alexander Fleming in 1942, more than 250 antimicrobial agents were synthesized and introduced in the pharmaceutical market for the treatment of different bacterial infections in humans and animals [4]. Moreover, antibiotics are also utilized as food additives for promoting the growth of livestock animals [5]. The statistical studies estimate the amount of utilized antibiotics is 1×10^5 to 2×10^5 tons globally each year [6]. Most antibiotics are not metabolized in the body and are excreted in the primitive form through urine and feces to the environment [7, 8]. The inappropriate discharge of pharmaceutical companies' sewages and improper disposal of unused or expired medicines are other sources that contribute to the occurrence of antibiotics in the water sources and soils in the ecosystem [9, 10]. Ciprofloxacin (CPX, Figure 1) is a highly consumed and wide spectrum fluoroquinolone antibiotic that is highly effective for the treatment of both gram-positive and gram-negative microbes infections [11]. CPX adverse effects are depression, nausea, vertigo, headache, hallucinations, tremor, and insomnia [12, 13]. In this respect, developing a simple, rapid, and reproducible technique for its removal and determination is of great importance. Electrochemical sensors are portable devices that have simple and economic instrumentation, high selectivity and sensitivity, time-saving analysis procedure, and applicability in opaque and colored samples [14, 15]. Hence, electrochemical sensors can be an ideal analytical method for the determination of CPX. Besides, adsorption is an ideal technique for the removal of antibiotics because of its simplicity, low cost, versatility in the chemical and physical features of adsorbents, high efficiency, insensitivity towards hazardous materials, rapidness, flexibility, and easy operability [16]. But, in the adsorption method finding a good adsorbent with high reusability, admissible selectivity, and repeatability is still a big challenge. On the other hand, the first and main step in the development of a new electrochemical sensor and an adsorbent for the detection and removal of an analyte is finding an appropriate material that has a good and selective interaction with the desired compound [17]. Therefore, the performance of carbon nanocone (CNC, Figure 1) as a sensor and adsorbent for the electrochemical detection and removal of CPX was investigated by DFT computations for the first time.
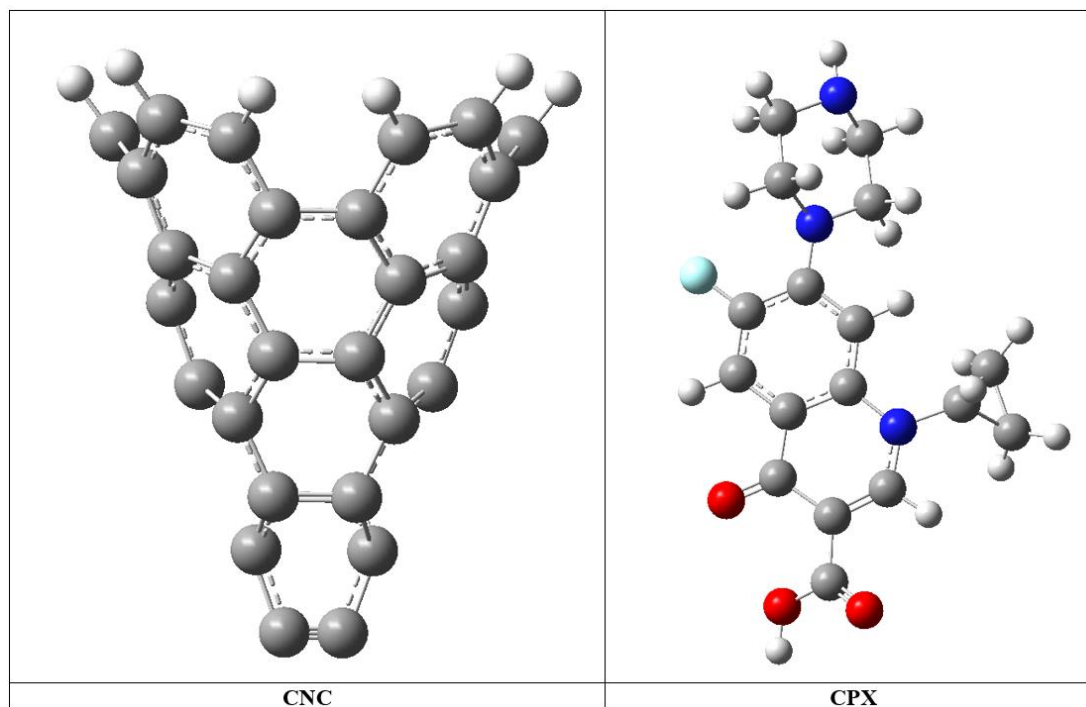
Figure 1. The optimized structures of CNC and CPX (oxygen: red, nitrogen: blue ,carbon: gray

hydrogen: white)

Computational Details

Software versions GuassView 6 and Nanotube modeler 1.3.0.3 were used to design the structures of CNC, CPXA, and their complexes [18-19]. Each of the structures that were designed first underwent geometric optimization. After that, computations for IR, FMO, and NBO were performed on designed structures. The density functional theory method was used throughout the computations by Gaussian 16 software at the B3LYP/6-31G (d) level of theory [20]. This level was selected since the findings obtained from earlier studies were acceptable and were consistent with experimental results. All computations were performed in the vacuum between 298 and 398 K at intervals of 10˚.

The following processes were investigated [22]:

Drug + Adsorbent → Drug-Adsorbent   (1)

Adsorption energy values (Ead) and thermodynamic parameters, such as thermodynamic equilibrium constant (Kth), Gibbs free energy changes (ΔGad), entropy changes (ΔSad), and adsorption enthalpy changes (ΔHad), were calculated using equations 2–6 [23-25].

$$E_{ad} = \left(E_{(Complex)} - \left(E_{(Drug)} + E_{(Adsorbent)} + E_{(BSSE)} \right) \right) \tag{2}$$

$$\Delta H_{ad} = \left(H_{(Complex)} - \left(H_{(Drug)} + H_{(Adsorbent)} \right) \right) \tag{3}$$

$$\Delta G_{ad} = \left(G_{(Complex)} - \left(G_{(Drug)} + G_{(Adsorebnt)} \right) \right) \tag{4}$$

$$\Delta S_{ad} = \left(S_{(Complex)} - \left(H_{(Drug)} + H_{(Adsorbent)} \right) \right) \tag{5}$$

$$K_{th} = \exp\left(-\frac{\Delta G_{ad}}{RT} \right) \tag{6}$$

In the equations above, E stands for the total electronic energy for every structure, EBSSE stands for the basis set superposition correction, and H represents the total energy of the evaluated materials plus the thermal correction of enthalpy. For each structure under study, the G denotes the total energy plus the thermal correction of the Gibbs free energy [22]. R represents the constant of the ideal gas, S is the thermal correction entropy for the studied structures, and T stands for temperature [26-28].

Equations 7–12 were used to calculate the bandgap (Eg), chemical hardness (η), chemical potential (μ), maximum charge capacity (ΔNmax), and the electrophilicity (ω) of frontier molecular orbitals [29-31].

$$E_g = E_{LUMO} - E_{HOMO} \tag{7}$$

$$\%\Delta E_g = \frac{E_{g2} - E_{g1}}{E_{g1}} \times 100 \tag{8}$$

$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2} \tag{9}$$

$$\mu = \frac{(E_{LUMO} + E_{HOMO})}{2} \tag{10}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{11}$$

$$\Delta N_{max} = -\frac{\mu}{\eta} \tag{12}$$

ELUMO, in the equations above, is the energy of the lowest unoccupied molecular orbital, and EHOMO is the energy of the highest occupied molecular orbital. The bandgaps of the Nano-adsorbent and NA-Adsorbent complexes are shown as Eg1 and Eg2, respectively [29].

Results and Discussion

CPX interaction with CNC was scrutinized at two various configurations to achieve the conformer with the highest stability. The initial structures and the optimized versions of those are presented in Figure 2. It demonstrates that the CPX molecule was inserted near the CNC towards its outside wall at A-Conformer. In B-Conformer, the adsorbate was located in a parallel form towards the cavity of CNC. As seen from the provided optimized structures in Figure 2, after geometrical optimizations, the CPX molecule only come closer to CNC, and no tangible structural deformations occurred in the adsorbate and adsorbent molecules. Both findings indicate that CPX interaction with CNC is relatively weak. Table 1 displays the determined adsorption and total electronic energies. As shown, all of the scrutinized conformers have negative adsorption energy values, which shows experimentally possibility of the adsorption of CPX on the CNC surface at all of the studied configurations. Also, according to this table, CNC is an effective adsorbent for CPX removal [25-30]. The next matter that can be perceived form the table is that the total electronic and adsorption energies of B-Conformer are more negative than the ones for A-Conformer indicating interaction in this situation is more favorable and formation of B-Conformer is more preferable than A-Conformer.

The optimized structures were also subjected to IR computations, and Table 1 provides the highest and lowest obtained IR frequencies. According to this table, all the structures that were investigated are true local minimums since there is obviously no negative vibrational frequency. Dipole moment values were also computed. These values revealed that with CPX adsorption on the surface of CNC, the dipole moment increases remarkably, indicating that with the formation of CPX-CNC complexes, their reactivity becomes higher than pure CPX. The optimized structures were also subjected to NBO computations to learn more about the adsorption mechanism. The outcomes demonstrated that the formation of a chemical bond between CPX and nanostructure was prevented in all the examined conformers [26-34].

The thermodynamic parameters calculated for the process of CPX adsorption are shown in Figure 3 as a function of temperature, including ΔH_{ad}, ΔG_{ad}, ΔS_{ad}, and the logarithm of K_{th}. Clearly, all the conformers under investigation have negative ΔH_{ad} values. These values show the exothermic nature of the adsorption process. The CPX adsorption process is spontaneous, two-sided and equilibrium as shown by the low quantities of thermodynamic constants and the negative amounts for ΔG_{ad}. The drop-in chaos is shown by the negative values of ΔS_{ad} in the CPX adsorption process. Also, these negative values exhibit that the entropy of the CPX interaction with CNC is unsuitable. According to the results of the investigation into how temperature affects all of the thermodynamic parameters, the temperature fluctuations did not

significantly impact the adsorption process, and CPX interaction with CNC is somewhat more favorable at lower temperatures [25-28].
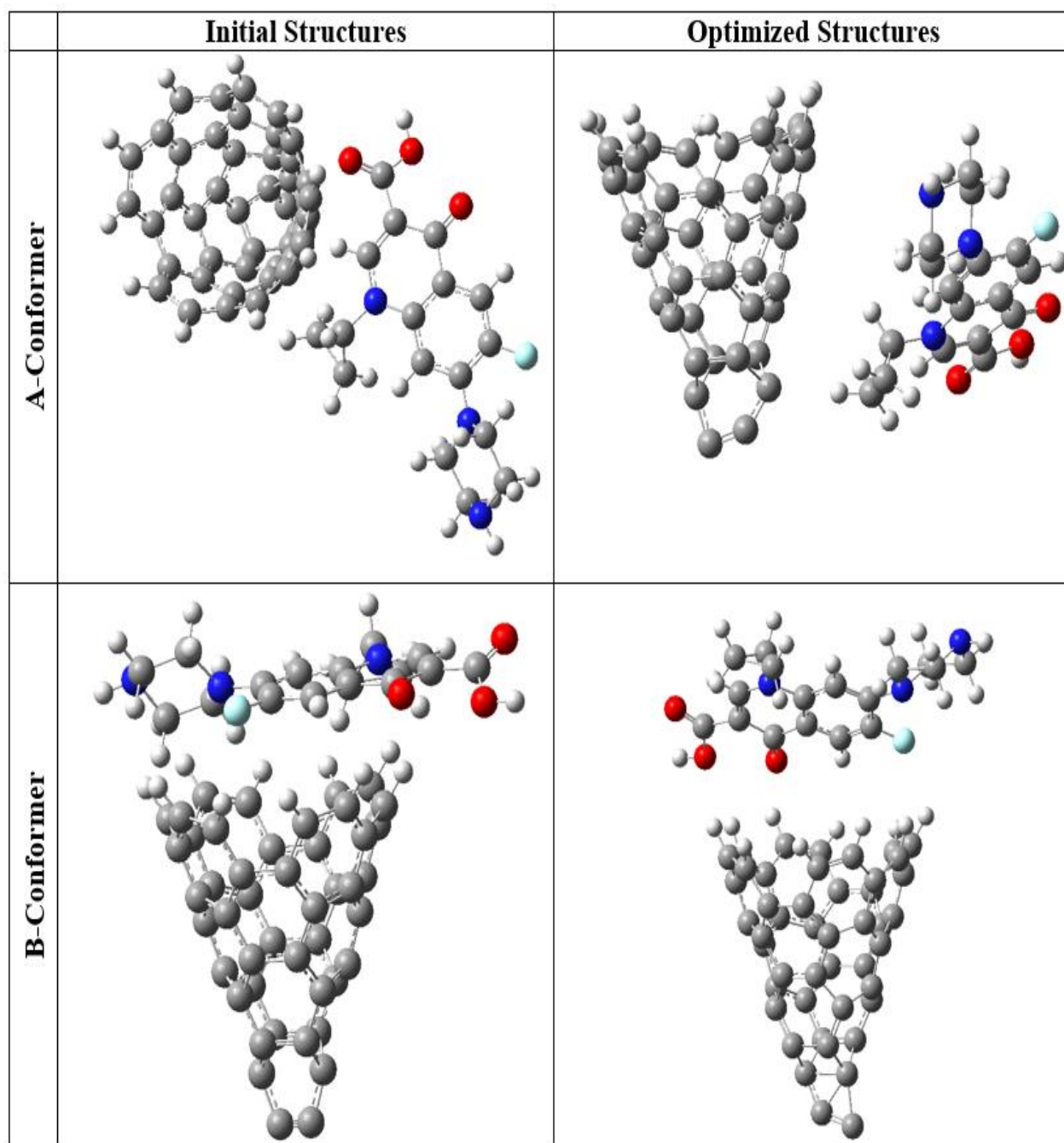

Figure 2. Initial and optimized structures of CNC-CPX complexes (oxygen: red, nitrogen: blue, carbon: gray, hydrogen: white)

Table1. The values of total electronic energy, adsorption energy, zero-point energy (ZPE), the maximum and minimum IR frequencies and dipole moment for CPX, CNC and their complexes

	Total electronic energy (a.u)	Adsorption energy (kJ/mol)	ZPE (kJ/mol)	v_{min} (cm^{-1})	v_{max} (cm^{-1})	Dipole Moment (Debye)
CPX	-1127.139	---	1030.243	28.470	4242.294	1.210
CNC	-1725.750	---	1160.7803	97.058	3735.568	5.090
A-Conformer	-2852.923	-89.845	2199.917	4.326	4244.115	10.580
B-Conformer	-2852.946	-149.932	2196.181	3.248	4241.284	8.450

The difference between the HOMO and LUMO orbital energies is the band gap, which is inversely related to the electrical conductivity of materials. The electrical conductivity of materials with a narrow band gap is higher than the materials with a wide one [29]. Therefore, to assess the efficiency of CNC as an electrochemical sensor for measuring CPX, this parameter was computed for the each of individual structures. According to the data presented in Table 2, the E_g of CNC is 6.880 (eV). When CPX is adsorbed on its surface, this parameter tangibly decreases to 5.040, and 5.080, respectively, for A, and B conformers. It appears CNC can be used as an appropriate material for developing electrochemical sensors for CPX detection, as this nanostructure bandgap variation is only about -26% for all investigated configurations [30].
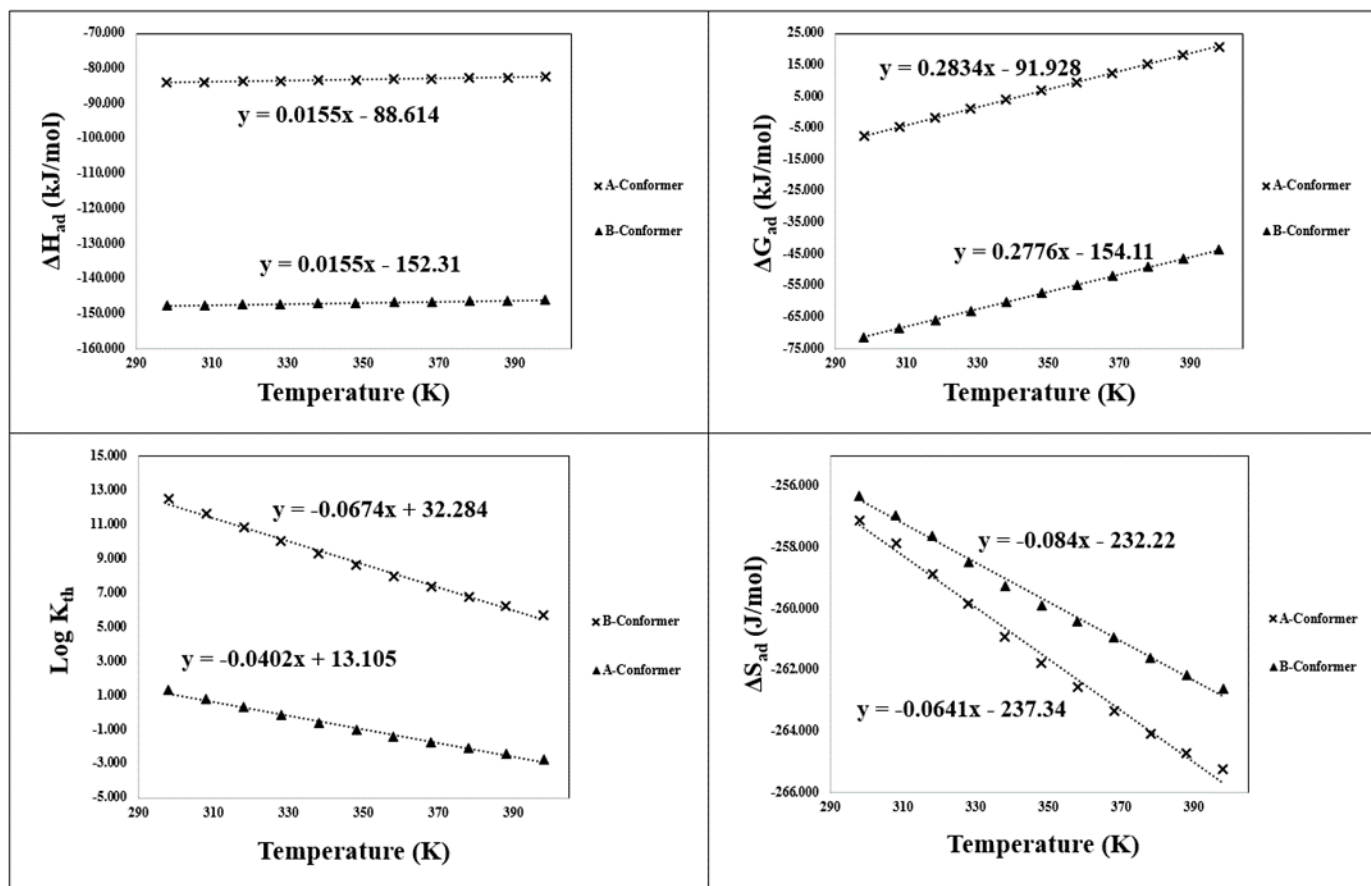
Figure 3. Thermodynamic parameters of CPX adsorption process including ΔH_{ad}, ΔG_{ad}, ΔS_{ad}, and the logarithm of K_{th} in the temperature 298-398 K at 10° intervals

Equations 9–12 were used to calculate the electrophilicity, chemical hardness, maximum transferred charge capacity, and chemical potential. Table 2 shows the results. It reveals that the CPX chemical hardness for the A, and B conformers decreases from 3.440 (eV) to 2.520, and 2.540 (eV), respectively, when CPX is adsorbed on the surface of CNC. As a result, CPX-CNC complexes are softer and more reactive than pristine CPX that does not contain a nano adsorbent [28]. All investigated structures have a negative measured chemical potential, suggesting that they all have thermodynamic stability [29]. Following its interaction with CNC, CPX becomes more electrophilic and has a higher maximum transferred charge capacity, indicating that CPX-CNC complexes have higher electrophilicity and, compared to pristine CPX, and are more likely to absorb electrons [24-31].

Table 2. The calculated FMO parameters for CPX, CNC and their complexes

NO	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg (eV)	%ΔEg	η (eV)	μ (eV)	ω (eV)	ΔNmax (eV)
CPX	-5.780	4.800	10.580	---	5.290	-0.490	0.023	0.093
CNC	-4.230	2.650	6.880	---	3.440	-0.790	0.091	0.230
A-Conformer	-3.340	1.700	5.040	-26.744	2.520	-0.820	0.133	0.325
B-Conformer	-3.750	1.330	5.080	-26.163	2.540	-1.210	0.288	0.476

Conclusion

This study used density functional theory computations to examine CPX adsorption on the surface of CNC. The negative values for E_{ad}, ΔG_{ad}, and ΔH_{ad}, as well as little values for K_{th}, showed that the CPX interaction with CNC was experimentally possible, exothermic, spontaneous, and reversible. The NBO results showed that CPX and CNC did not form any chemical bond; hence, according to a physisorption adsorption process. The computed FMO parameters revealed that whereas CNC bandgap increased by -26% during the adsorption process. Because of the sharp variation of electrical conductivity during the adsorption process, it is clear that CNC makes a great sensing material for the development of cutting-edge electrochemical sensors for CPX measurement. In this respect, the performance of the CNC as an adsorbent and sensing material for the removal and detection of CPX is recommended to be evaluated by analytical chemist.

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