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**Original Research Article** 

# Investigating the performance of a recently synthesized covalent organic framework as an adsorbent for methylene blue: A DFT Study

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# ABSTRACT

Methylene blue (MB) is an organic dye that is widely used in various industries and have different adverse effects on the environment. Therefore, its removal is of great importance. In this respect, the performance of a recently synthesized schiff base network<sub>1</sub> (SNW<sub>1</sub>) as an adsorbent for the removal of MB was scrutinized by DFT computations. For this purpose, the structures of MB, SNW<sub>1</sub> and their complexes were optimized geometrically and the underwent infra-red (IR) calculations. All of the computations were done by density functional theory approach in the B3LYP/6-31G (d) level of theory. The obtained negative adsorption energies showed MB interaction with SNW<sub>1</sub> is experimentally possible. The achieved negative values of Gibbs free energy changes and adsorption enthalpy changes revealed the MB adsorption process is exothermic and spontaneous. The positive values of entropy alterations and thermodynamic equilibrium constants demonstrated that the adsorption process.

Keywords: Methylene blue, Covalent organic framework (COF), Density Functional Theory, Adsorption

# Introduction

Covalent organic frameworks (COFs) are a novel class of nanostructures from porous coordination polymers group that have been introduced recently [1]. COFs are porous crystalline compounds that are created from the formation of covalent bonds between boron, carbon, nitrogen, oxygen and silicon atoms [2]. COFs are structurally similar to metal organic frameworks (MOFs) and their main difference that discriminates COFs is the lack of metal atoms in their chemical structure [3]. COFs have attractive properties that make them a promising advanced material in analytical chemistry including high specific surface area, the opportunity to choose different building groups in their synthesis process, tunable porosity, predictable and stable structure, low density, admissible biocompatibility, economic price, great photoelectric properties, low toxicity and the ability to being functionalized with several groups [4]. In the recent decade, many studies have been focused on the application of COFs in the fields of gas storage [5], separation [6], nanofiltration [7], adsorption [8], fluorimetry analysis [9] and supercapacitors [10].

However, only a few studies have focused on the applicability of COFs as the electrode modifier in electroanalytical chemistry. Mullen et al. synthesized a series of COFs based on melamine reaction with different structural isomers of phthalaldehyde and because the resulting COFs was full of imine functional groups, Mullen named them Schiff base networks (SNW) and the name Schiff base network<sub>1</sub> (SNW<sub>1</sub>) was selected for the COF produced from the reaction of melamine with terephthaldehyde [11]. The structure of SNW<sub>1</sub> is presented in Figure 1. As can be seen, SNW<sub>1</sub> has several aromatic rings in its chemical structure and consequently is expected to form  $\pi$ - $\pi$  interactions with organic compounds [12]. On the other hand, methylene blue (MB, Figure 2) is a toxic organic dye that has adverse effects on the environment and its removal is of great importance. Therefore, in this research the adsorption of MB on the surface of SNW<sub>1</sub> was investigated by DFT computations.



Figure 1. The optimized structure of SNW<sub>1</sub> (nitrogen: blue, carbon: gray, hydrogen: white)



Figure 2. The optimized structure of MB (sulfur: yellow, 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 SNW<sub>1</sub>, MB, and their complexes [13, 14]. Each of the structures that were designed first underwent geometric optimization. After that, computations for IR, 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 [15]. This level was selected since the findings obtained from earlier studies were acceptable and were consistent with experimental results. All computations were performed in both vacuum and aqueous phases between 298 and 398 K at intervals of 10°.

The following processes were investigated [16]:

$$MB + Adsorbent \rightarrow MB - Adsorbent \tag{1}$$

Adsorption energy values ( $E_{ad}$ ) and thermodynamic parameters, such as thermodynamic equilibrium constant ( $K_{th}$ ), Gibbs free energy changes ( $\Delta G_{ad}$ ), entropy changes ( $\Delta S_{ad}$ ), and adsorption enthalpy changes ( $\Delta H_{ad}$ ), were calculated using equations 2–6 [17-19].

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

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

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

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

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

In the equations above, E stands for the total electronic energy for every structure,  $E_{BSSE}$  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 [20]. R represents the constant of the ideal gas, S is the thermal correction entropy for the studied structures, and T stands for temperature [21-23].

## **Results and Discussion**

MB interaction with SNW<sub>1</sub> 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 3. It demonstrates that the MB molecule was inserted near the central triazine ring SNW<sub>1</sub> towards its outside amine group at A-Conformer. In B-Conformer, the benzene ring of adsorbate was located in a parallel form towards the aromatic rings of SNW<sub>1</sub>. As seen from the provided optimized structures in Figure 3, after geometrical optimizations, the MB molecule only come closer to SNW<sub>1</sub>, and no tangible structural deformations occurred in the adsorbate and adsorbent molecules.



Figure 3. Initial and optimized structures of SNW1-MB complexes (sulfur: yellow, nitrogen: blue, carbon: gray, hydrogen: white)

Both findings indicate that MB interaction with  $SNW_1$  is a physisorption. 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 MB on the SNW<sub>1</sub> surface at all of the studied configurations. Also, according to this table, SNW<sub>1</sub> is an effective adsorbent for MB removal [24]. The next matter that can be perceived form the table is that the presence of water as the solvent cannot affect the interaction meaningfully because the obtained adsorption energies in the aqueous phase are also negative [25]. 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 [26]. Dipole moment values were also computed. These values revealed that with MB adsorption on the surface of SNW<sub>1</sub>, the dipole moment decreases remarkably, indicating that with the formation of MB- SNW<sub>1</sub> complexes, their reactivity becomes lower than pure MB [27]. 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 MB and nanostructure was prevented in all the examined conformers [28].

**Table1.** The values of total electronic energy, adsorption energy, zero-point energy (ZPE), the maximum and minimum IR frequencies and dipole moment for SNW<sub>1</sub>, MB and their complexes

NO	Total electronic	Adsorption	ZPE	<b>v</b> <sub>min</sub>	v <sub>max</sub>	Dipole
	energy	energy	(kJ/mol)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	Moment
	(a.u)	(kJ/mol)				(Debye)
MB (V)	-1199.293		941.278	31.102	3962.159	7.159
MB (V)	-1199.611		943.871	30.088	3959.931	8.951
COF (V)	-3570.035		3087.434	5.036	4190.810	0.591
COF (W)	-3570.018		3085.429	8.736	4188.692	0.633
A-Conformer (V)	-4769.386	-152.069	4591.126	4.986	4188.209	2.194
B-Conformer (V)	-4769.371	-112.686	4596.519	6.833	4184.982	1.495
A-Conformer (W)	-4769.639	-26.255	4595.395	10.923	4190.046	1.984
B-Conformer (W)	-4769.655	-68.263	4591.194	11.104	41.86.529	1.395

The thermodynamic parameters calculated for the process of MB adsorption are shown in Figure 4 as a function of temperature, including  $\Delta H_{ad}$ ,  $\Delta G_{ad}$ ,  $\Delta S_{ad}$ , and the logarithm of K<sub>th</sub>. Clearly, all the conformers under investigation have negative  $\Delta H_{ad}$  values. These values show the exothermic nature of the adsorption process. The MB adsorption process is spontaneous, twosided and equilibrium as shown by the low quantities of thermodynamic constants and the negative amounts for  $\Delta G_{ad}$ . The increment of chaos is shown by the positive values of  $\Delta S_{ad}$  in the MB adsorption process. Also, these positive values exhibit that the entropy of the MB interaction with SNW<sub>1</sub> is suitable. 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 MB interaction with SNW<sub>1</sub> is somewhat more favorable at lower temperatures. Besides, the presence of water cannot affect the interactions [25-28].



Figure 4. Thermodynamic parameters of MB adsorption process including  $\Delta H_{ad}$ ,  $\Delta G_{ad}$ ,  $\Delta S_{ad}$ , and the logarithm of K<sub>th</sub> in the temperature 298-398 K at 10° intervals

#### Conclusion

This study used density functional theory computations to examine MB adsorption on the surface of SNW<sub>1</sub>. The negative values for  $E_{ad}$ ,  $\Delta G_{ad}$ , and  $\Delta H_{ad}$ , as well as little values for K<sub>th</sub>, showed that the MB interaction with SNW<sub>1</sub> was experimentally possible, exothermic, spontaneous, and reversible. The NBO results showed that MB and SNW<sub>1</sub> did not form any chemical bond; hence, according to a physisorption adsorption process. In this respect, the performance of the SNW<sub>1</sub> as an adsorbent for the removal MB is recommended to be evaluated by experimental chemist.

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