Computational Chemistry Approach to Interpret the Crystal Violet Adsorption on Golbasi Lignite Activated Carbon

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Abstract. In this paper, adsorption mechanism of Crystal Violet (CV) dye from the aqueous solution on the activated carbon prepared from Gölbasi lignite was explained and interpreted by a computational chemistry approach and experimental studies. Molecular dynamic simulations and Ab initio frontier orbital analysis indicated relatively high energy and electron transfer processes during adsorption, and molecular dynamics simulations showed CV dye molecules moving around on the activated carbon surface after adsorption, facilitating penetration into cracks and pores. The experimental results supported molecular dynamic simulation and showed that the monolayer coverage occurred on the activated carbon surface and each CV dye ion had equal sorption activation energy.

1. Introduction
The rapid increase in the population and the industrial activities increase the water consumption and more than 80 countries accounting for 40% of the world’s population are facing major water crises. According to UN, 2.7 billion people will be affected by water deficiency by 2025. One of the main pollutant sources worldwide is dye-containing wastewater from textile and paper industries. Removal of dyes from wastewater is difficult because they resist breakdown by aerobic digestion, light, heat, and oxidizing agents [1].

Cationic Crystal Violet (CV) dye is extensively used not only in the textile and paper industries, but also in biology, dermatology, and veterinary applications. This dye is toxic and even carcinogenic, and its degree of resistance to breakdown depends on chemical structure and substituted aromatic groups [2]. Activated carbon is the most popular adsorbent, and has been cited by the US Environmental Protection Agency as one of the best available pollution control technologies [3]. In the literature, considerable attention has been given to find low cost and easily available carbon sources to activated carbon for CV dye adsorption. In the present paper, the adsorption mechanism of CV on the activated carbon produced from the lignite was tried to explained and interpreted using computational chemistry approach and experimental studies.

2. Materials and methods
2.1. Adsorption experiments
In the experimental studies, the activated carbon which was produced Golbasi lignite was used. The preparation method and characterization studies were explained in previous work [4]. The activated
carbon has a remarkable surface area (921 m\(^2\)/gr), which is primarily contributed by micropores. Crystal violet (CV) dye employed in the present investigation was supplied from MERCK (101458, CI = 42.555) and used as obtained without any further purification. All the test solutions were prepared using double distilled water. Adsorption tests were conducted in stopper Pyrex glass Erlenmeyer flasks with various dye concentration at 60 min at room temperature. Each test was done with 0.1g activated carbon in 50 ml solution shaken at 300 rpm in a thermo-stated shaking water bed. All the experiments were carried out in duplicate and average values were used for further calculation. The amount of dye adsorbed on activated carbons was calculated by equation (1).

\[ q = \frac{(C_0 - C)V}{W} \]  

where, \( C_0 \) (mg/l) is the initial CV concentration and \( C \) (mg/l) is unabsorbed CV concentration in solution at time \( t \), \( V \) (l) and \( W \) (g) is the volume of the solution and the weight of the dry activated carbons used, respectively.

2.2. Computational chemistry analysis
Computational chemistry analysis (molecular dynamics and ab-initio simulations) was used to further the understanding of CV dye adsorption from aqueous solution by activated carbon. DFT-based frontier orbitals and force field-based molecular dynamics were calculated using Gaussian 09 and other molecular modelling packages: Amber 12, Avogadro and Gabedit. Amber's steered molecular dynamics capability was used to direct crystal violet molecules close to a graphite surface. In this method a simulated rubber band was attached between CV dye molecules and the activated carbon surface, and then removed after close approach. This allowed nano-second simulations to show what happens in real-time minutes--necessary because minutes or hours long simulations are beyond present day computer capabilities. The activated carbon was based on the graphite crystal structure found in the American Mineralogist crystal structure database [5].

3. Results and discussions
DFT-based frontier orbitals and force field-based molecular dynamics were used in characterizing crystal violet adsorption onto activated carbon surfaces. Frontier orbitals were calculated at the relatively accurate DFT 6-31g B3LYP level using Gaussian 09 and other molecular modelling packages. The smallest energy gap (2.25 ev) was between crystal violet's HOMO (-3.02 ev) and graphite's LUMO (-5.27 ev), suggesting that crystal violet was the electron donor and had a comparatively high reactivity. When surface oxygen functionalities [6] such as phenols and carboxylates were present on the graphite (figure 1), this energy gap shrank from 2.25 ev to 1.29 ev, indicating even higher reactivity and chemisorption [7].

![Crystal violet molecule adsorbed onto the bottom side of a partially oxidized graphite surface.](image)

(Carbon, light blue; oxygen, red; hydrogen, light gray; nitrogen, dark blue.)
Furthermore, a somewhat large energy transfer (1.47 ev) as well as electron transfer (2.26 ev) also indicated that chemisorption occurred (Table 1). Mutual attraction was also to be expected from overall positively charged crystal violet being attracted to negative oxides on the graphite surface. The energy and electron transfer between crystal violet and graphite was calculated from the equalization of chemical potentials, as shown below [8]. Here the electro-negativity (C) and hardness (D) of crystal violet and graphite were denoted C(cv), C(g), and D(cv), D(g), respectively. The calculations were done using electron affinity \( A = - \text{HOMO} \), ionization potential \( B = - \text{LUMO} \), electro-negativity \( C = (A + B)/2 \), hardness \( D = (A – B)/2 \), electron transfer \( E = 0.5*[C(g) – C(cv)] / [D(g) – D(cv)] \), energy transfer \( F = 0.25*[C(cv) – C(g)]^2 / [D(cv) – D(g)] \).

|                | Electron affinity | Ionization potential | Electro-negativity | Hardness | Electron transfer | Energy transfer |
|----------------|-------------------|----------------------|-------------------|----------|------------------|-----------------|
| Crystal Violet | 3.02              | -0.32                | 1.35              | 1.67     | -1.47            | 2.26            |
| Graphite       | 5.78              | 5.27                 | 5.52              | 0.26     |                  |                 |

Crystal violet had a lower electron affinity, ionization potential, and electro-negativity as expected from an electron donor. However, crystal violet had a somewhat higher hardness that perhaps adds a footnote to the generally accepted concept that 'hard likes hard'. Bonding occurred despite this difference in hardness. Even though crystal violet was a positive cation coming from a chloride salt that was dissolved in water, quantum-based Mulliken charges showed the complexity of charge. Crystal violet's nitrogen atoms had a negative Mulliken charge, as expected, and were connected to both positive and negative carbon atoms (figure 2). These alternating Mulliken charges were also mirrored in graphite where connected carbon atoms changed between positive and negative.

**Figure 2.** Mullikan charges in one arm of the three-armed crystal violet cation (Nitrogen, blue; carbon, dark gray; hydrogen light gray)

In GAFF force field-based molecular dynamic simulations using the above charges, Amber's steered molecular dynamics capability was used to direct crystal violet molecules close to a graphite surface (snapshot from a molecular dynamics simulation, figure 3). There, once adsorbed, they did not remain stationary, but scooted around on the surface and over edges. This would facilitate penetration into cracks and pores, as was observed experimentally. Furthermore, while they were mostly flattened on
the surface, crystal violet molecules would also fold or flap up and down. In addition, other crystal violet molecules would close in and expel intervening water. This occurred both during approach and while on the surface through mutual hydrophobicity, though the crystal violet molecules seemed to crawl over each other and were clearly not bonded. In summary, frontier orbital calculations and molecular dynamics simulations showed mixed chemisorption and physisorption behaviour.

Figure 3. Snapshot from a steered molecular dynamics simulation of crystal violet adsorbing onto graphite (Water, lines; graphite and crystal violet, van der Waal radii)

The experimental parts evaluated using Langmuir isotherm model, since our preliminary investigation indicated that it was the best fitting model (other not given in the text). This model has been employed extensively by many researchers to explain the adsorption mechanism of adsorbate due to their simplicity and applicability. Langmuir model isotherm equation is given below:

\[
q_e = \frac{Q_0 b C_e}{1 + b C_e}
\]  

\( C_e \) is the equilibrium CV ions concentrations in the liquid phase (mg/L), \( q_e \) is the adsorption capacity (mg/g), \( b \) (L/mg) and \( Q_0 \) (mg/g) are Langmuir isotherm constants, where \( Q_0 \) signifies the theoretical monolayer capacity. The fitted values of the Langmuir isotherm is given in figure 4, inferring that the monolayer coverage occurred on the activated carbon surface and each CV dye ion had equal sorption activation energy.

4. Conclusions
Frontier orbital analysis suggested that the interaction between CV dye and activated carbon was relatively strong, but molecular dynamics simulations revealed mobile CV dye molecules moving freely over the activated carbon surface making possible easy penetration of cracks and pores. The simulations showed mixed chemisorption and physisorption behaviour and especially monolayer adsorption mechanism. The experimental results showed the monolayer adsorption within a pore and supported the finding from molecular dynamic simulation. In addition, Gölbasi lignite activated carbon was a promising adsorbent for the adsorption of basic dyes.
Figure 4. The plot of linear Langmuir model for the removal of CV at different temperature and pH of the solutions

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