Investigation of methylene blue adsorption on activated carbon surfaces: A combined approach of experimental study and molecular simulation

Nguyen Thanh Tung*, Nguyen Dinh Chinh, Nguyen Van Linh,
Tran Anh Khoi, Nguyen Thi Thuy, Ngo Van Thanh Huy

Vietnam Institute for Tropical Technology and Environmental Protection, Academy Science and Technology, 57A Truong Quoc Dung, Phu Nhuan, Ho Chi Minh City, Vietnam.
*Corresponding author: thanhtung130192@gmail.com
Received 10 Dec. 2024; Revised 25 Jan. 2025; Accepted 04 Apr. 2025; Published 15 Apr. 2025.
DOI: https://doi.org/10.54939/1859-1043.j.mst.102.2025.84-93

ABSTRACT

Wastewater containing methylene blue, commonly found in dyeing and textile effluents, poses significant environmental risks if left untreated. It can severely pollute water bodies, disrupt ecosystems, and threaten human health due to its toxicity. This study examined the ability of activated carbon to adsorb methylene blue from water. The activated carbon was pre-treated with various KOH ratios, achieving a maximum adsorption capacity of 619.92 mg/g. The adsorption process was analyzed using kinetic and isothermal models. Results showed that the process was best described by the pseudo-second-order kinetic model and the Langmuir isotherm model, both demonstrating high R^2 values. Molecular simulation methods were applied to explore the adsorption mechanism in greater detail. The findings indicated a multilayer adsorption mechanism dominated by electrostatic interactions, which facilitate strong bonding between the activated carbon surface and methylene blue molecules. Overall, the study highlights the potential of activated carbon as an effective solution for removing methylene blue from polluted water sources.

Keywords: Activated carbon; Methylene blue; Molecular simulation.

1. INTRODUCTION

Methylene blue is a cationic dye widely used in the textile industry for coloring products. A significant concern with textile wastewater is that it is often highly colored, concentrated, and resistant to biodegradation [1]. Methylene blue, commonly found in such wastewater, poses potential health risks, including eye damage in humans and animals [2]. Exposure to the toxins of methylene blue can result in acute symptoms such as rapid breathing and shortness of breath. When ingested, it may cause a burning sensation, nausea, excessive sweating, painful urination, and other adverse effects. From an environmental perspective, methylene blue is a non-biodegradable pollutant, harming both human and animal life when released into water sources [3]. The efficient and cost-effective removal of methylene blue from water sources is a pressing issue that has garnered considerable interest and research efforts from scientists.

Conventional methods for treating methylene blue include chemical and physicochemical techniques such as neutralization, pH adjustment, coagulation, and oxidation. However, these approaches are often difficult to implement and involve high investment costs along with the use of expensive chemicals [4]. Consequently, researchers are increasingly exploring the use of low-cost, easily manufactured, and eco-friendly adsorbents made from industrial and agricultural waste materials to treat dye-contaminated wastewater from the textile industry. Activated carbon is one of the most cost-effective materials for adsorption applications. It features a uniform pore size distribution, surface functional groups that readily interact with adsorbates, and a large number of adsorption sites due to its high specific surface area [5]. After the treatment process, activated carbon can be easily desorbed and reused, which is a significant advantage. This makes activated carbon an increasingly popular solution for water pollution treatment technologies [6].

Haitham et al. (2022) explored the adsorption of methylene blue and phenol using activated

carbon produced from lignocellulosic agricultural waste [7]. By applying KOH activation, they developed a material with a specific surface area of 1771.2 m^2/g, achieving a 95% removal efficiency of methylene blue at an initial concentration of 100 ppm. Ali H.J. et al. (2021) studied methylene blue adsorption using activated carbon derived from dragon fruit peel treated with KOH [8]. The surface area analysis revealed a value of 756.3 m^2/g, with complete methylene blue adsorption observed. The kinetic data aligned with a first-order kinetic model, while the adsorption isotherms followed the Langmuir model. These studies underscore the effectiveness of KOH-activated carbon in removing organic compounds. The focus of this study is to evaluate the adsorption capacity of activated carbon for methylene blue dye. Methylene blue was chosen not only because it can be easily adsorbed and captured by mesoporous materials like activated carbon, but also because it is commonly used as a model compound to study the removal of organic pollutants and non-biodegradable dyes from water. Additionally, this study employs molecular simulation tools to investigate the adsorption behavior of methylene blue dye on the surface of activated carbon. This provides deeper insight into the mechanisms involved in the adsorption of organic dyes by activated carbon.

2. MATERIALS AND METHODS

2.1. Materials

Activated carbon AC (0.5-1 mm particle size powder – China), methylene blue MB ($C_{16}H_{18}ClN_3S$ 99.9% – China), sodium hydroxide (NaOH 99.5% – China), potassium hydroxide (KOH 99.5% – China), acid hydrochloric (HCl 36.5% – China), deionized water (DI) was purified through a milipore system with a resistivity of 18.2 MΩ/cm.

2.2. Adsorption studies experiment

The activated carbon sample was treated with KOH at a mass ratio of KOH to activated carbon of 1:4. The resulting mixture was dried at 110 °C for 24 hours, after which the dried solid was subjected to pyrolysis in a tube furnace at 700 °C for 60 minutes under a nitrogen gas flow (99.99%) [7]. After pyrolysis, the solid was washed multiple times with distilled water until the wash water had a neutral pH. The solid was then dried again at 110 °C for 24 hours to obtain the treated activated carbon. The synthesized materials were analyzed for surface morphology and structural characteristics using X-ray diffraction XRD (D2 Phaser, Bruker, Germany), scanning electron microscopy SEM (Hitachi S-4800, Japan), the BET specific surface area was analyzed using the nitrogen adsorption/desorption method at 77.35 K (PMI's BET Sorptometer, India). The kinetics and isotherms of methylene blue adsorption onto activated carbon were investigated under varying conditions, including the pH of the methylene blue aqueous solution, as well as key factors such as adsorption time, the KOH pretreatment ratio (from 1:2 to 1:5), and the initial concentration of the methylene blue solution (from 100 to 200 ppm). The residual methylene blue concentration after the adsorption process was measured using a colorimetric method with a UV-Vis spectrophotometer (wavelength λ = 640 nm). From this, the methylene blue adsorption capacity of the activated carbon was calculated and is expressed by the following equation:

$$Q_e = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

Where, m is the mass of activated charcoal, C_t and C_0 are the concentrations at the sampling time and the initial concentration of methylene blue, V is the volume of the solution.

2.3. Simulation method

Accelrys' Materials Studio software is used to model the molecular structure of activated carbon and methylene blue. The optimization structure performed with selected parameters is the orbital polarization function (DNP), a generalized slope approximation (GGA) optimization method with

a high-precision Perdew-Burke-Emzerhof (PBE) function in the description of van der-Waals forces. The simulation was performed on the forcite module by configuring the simulation on the amorphous cell module. COMPASS force was used to assign partial charge to the atoms and the equations of motion for every 1 ps were integrated [9].

2.4. Mean square displacement

The mean squared displacement measures the deviation of a molecule's position from its reference point over time. This value serves as a system-level measurement of the spatial extent of random motion, helping to determine the molecule's diffusion behavior within a particle [10]. The mean squared displacement is calculated by measuring the positional deviation at a random time from the molecule's initial position, as shown in equation (2):

$$MSD = \left\langle \left| r(t) - r(0) \right|^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \left| r_i(t) - r_i(0) \right|^2 \quad (2)$$

Where N is number molecules; r(t) is Cartesian position vector of the molecules at the time t; r(0) is the initial position vector of the molecules.

2.5. Radial distribution function

The radial distribution function in a system of molecules moving within a homogeneous environment describes how the molecular density changes with distance from a reference particle [11]. It is given by the following expression:

$$g(r) = \frac{n(r)}{2\pi r p} \quad (3)$$

Where r is distance between molecules; n(r) is time average number; p is number density of molecules.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the activated carbon

The X-ray diffraction patterns of the initial activated carbon and the treated carbon sample are presented in figure 1.

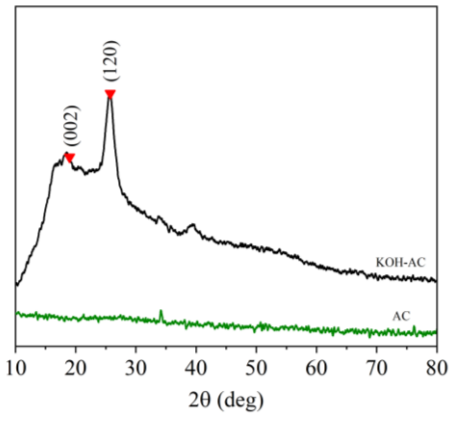

Figure 1. *X-ray diffraction patterns.*

The X-ray diffraction results reveal two peaks at 19° and 26° in the pattern of the treated activated carbon, corresponding to the miller planes (002) and (120) of the remaining carbon crystals, while the other components are amorphous and lack a crystalline structure [12]. This can be attributed to the predominance of the amorphous phase in the initial carbon sample. After surface modification, conditions became favorable for the transformation into a crystalline structure.

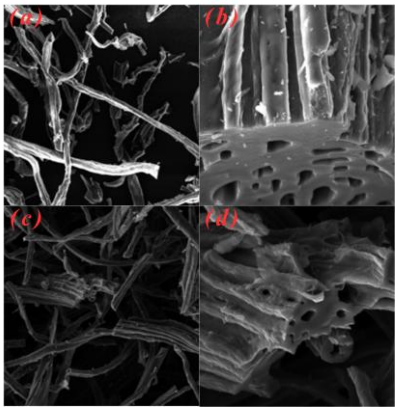

Figure 2. *SEM image of AC (a, b) and KOH-AC (c, d).*

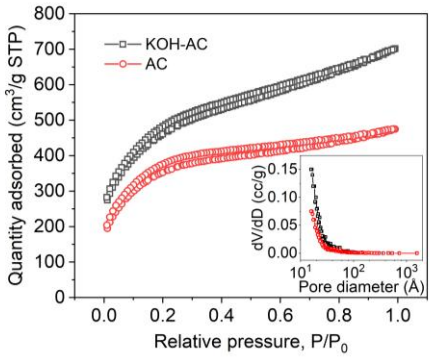

Figure 3. *N_2 adsorption – desorption isotherm.*

The SEM images of the material samples (figure 2) reveal that both the activated carbon and KOH-activated carbon exhibit structures composed of fibers arranged in a random and uneven manner. These fibers have a cylindrical shape with internal voids, contributing to the material's enhanced porosity. BET analysis of nitrogen adsorption-desorption isotherms indicates that the specific surface area of the KOH-activated carbon sample is 1581 m²/g. The interaction between KOH and the surface of the activated carbon promotes the development of active sites, resulting in an increased surface area. Despite this modification, the porous structure remains largely intact, as evidenced by the similarity in the adsorption isotherm curves.

3.2. Adsorption of methylene blue by activated carbon

3.2.1. Adsorption kinetics

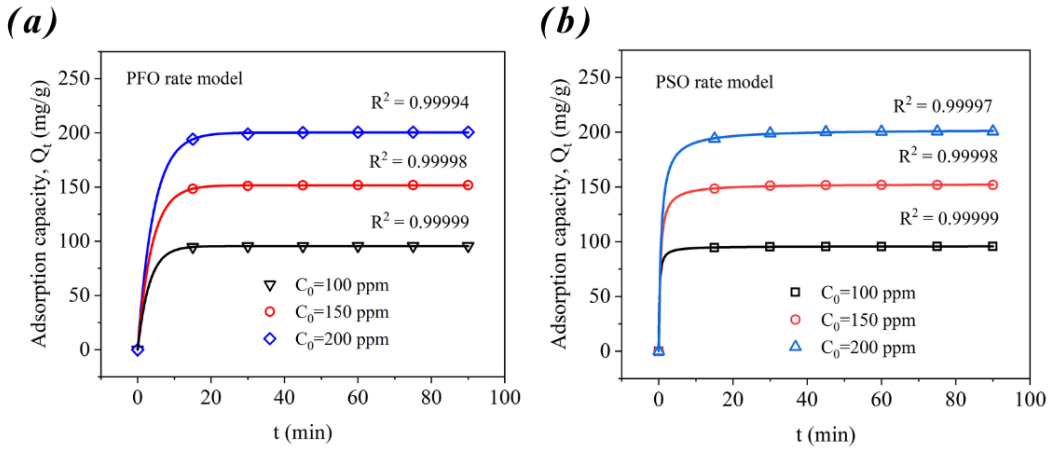

Figure 4. *Adsorption kinetic models (V = 400 mL, m = 0,4 g, pH = 7).*

The results of the methylene blue adsorption kinetics study on activated carbon are presented in figure 4.

The results of the experimental study show that as the initial concentration increases, the adsorption capacity also increases, reaching a maximum value of 200.71 mg/g after 90 minutes of reaction when the initial concentration is 200 mg/L. This explains the positive charge portion of the methylene blue molecule's ability to be rapidly adsorbed onto the surface containing functional groups, making it easier to form adsorption bonds. An increase in the initial concentration leads to a higher methylene blue molecular density, which creates favorable conditions for the equilibrium

shift in favor of the reaction. The reaction process occurs quickly within the first 15 minutes and then gradually reaches a saturation state.

Table 1. *Fitting parameters for the adsorption kinetic data of MB on activated carbon.*

Models	Equation	Parameters	Unit	C_0 = 100 ppm	C_0 = 150 ppm	C_0 = 200 ppm
PFO rate model	$Q_t = Q_e(1-e^{-k_f t})$	k_f	1/min	0,32	151,69	200,32
		Q_e	mg/g	95,59	0,26	0,23
		R^2	-	0,9999	0,9998	0,9994
PSO rate model	$Q_t = \frac{tk_sQ_e^2}{1+tk_sQ_e}$	k_s	g/ (mL.min)	5,6	2,38	1,59
		Q_e	mg/g	95,91	152,86	202,63
		R^2	-	0,9999	0,9998	0,9997

To explain the occurring kinetics, first-order and second-order kinetic models were selected for the study. The methylene blue adsorption process on activated carbon best fits the second-order kinetic model, with high fitting coefficients ($R^2 > 0.9997$) in all investigations. The kinetic parameters in the study are presented in table 1.

3.2.2. Adsorption isotherms

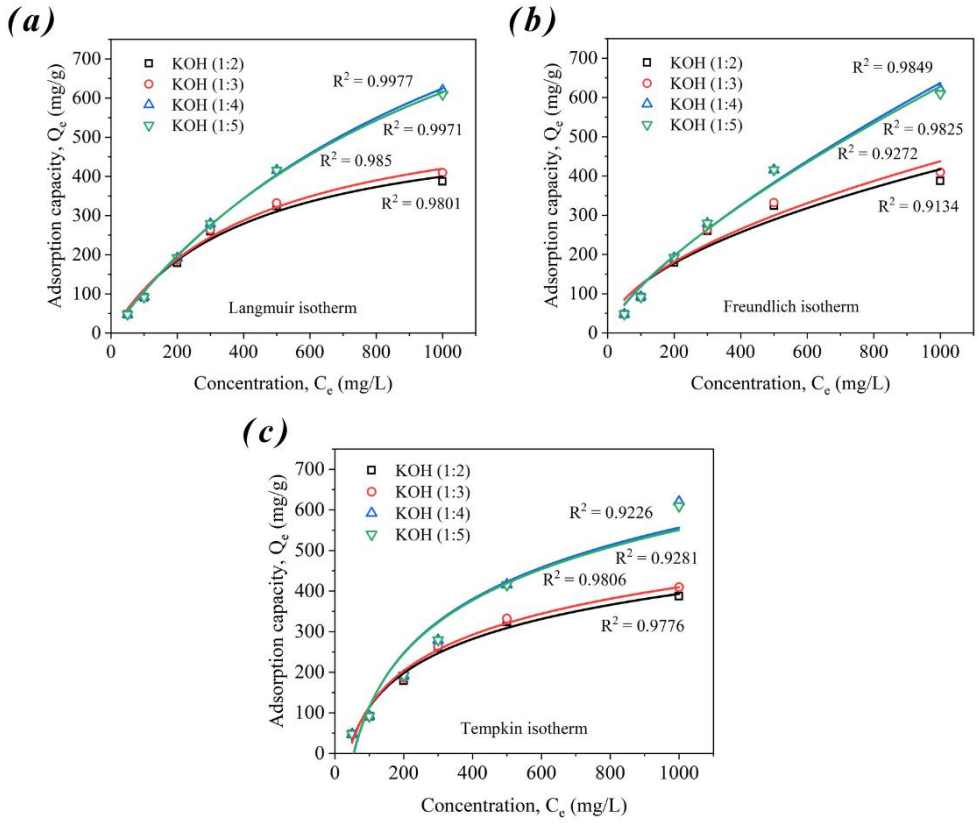

Figure 5. *Adsorpiton isotherm models*
(V = 25 mL, m = 0,025 g, t = 180 min, pH = 7).

The results of the methylene blue adsorption isotherm on activated carbon are shown in figure 5. The results above show that the adsorption capacity increases rapidly as the concentration varies in the study from 50 to 1000 mg/L, reaching a maximum value of 619.92 mg/g for the sample

pretreated with KOH (ratio of 1:4). When the activated carbon undergoes activation, it triggers a reaction between KOH and the molecules in the carbon chain, thereby expanding the micropore surface area, which increases the adsorption sites that favor the formation of bonds with methylene blue molecules. This value decreases when the amount of KOH in the activation process is increased to a ratio of 1:5, at which point excess KOH reduces the specific surface area and pore structure of the activated carbon due to the destruction of the micropore structure. The adsorption isotherm study using the Langmuir, Freundlich, and Tempkin models reveals that the methylene blue adsorption process on activated carbon best fits the Langmuir model, with the maximum adsorption capacity calculated by the model being 1371.42 mg/g.

Table 2. *Fitting parameters for the adsorption isotherm data of MB on activated carbon.*

Models	Equation	Parameters	Unit	KOH (1:2)	KOH (1:3)	KOH (1:4)	KOH (1:5)
Langmuir isotherm	$Q_e = \frac{k_L Q_m C_e}{1 + k_L C_e}$	Q_m	mg/g	561,41	604,39	1371,42	1301,51
		k_L	L/mg	0,0025	0,0023	0,00084	0,00089
		R^2	-	0,9801	0,9853	0,9977	0,9971
Freundlich isotherm	$Q_e = k_F C_e^{1/n}$	k_F	$mg^{1-n}.L^n/g$	10,63	9,93	4,05	4,31
		n	-	1,88	1,82	1,37	1,34
		R^2	-	0,9234	0,9272	0,9849	0,9825
Tempkin isotherm	$Q_e = \frac{RT}{b_T}\ln(K_T C_e)$	RT/b_T	mg/g	121,36	127,89	191,95	189,29
		K_T	g/mg	0,026	0,025	0,018	0,018
		R^2	-	0,9776	0,9806	0,9226	0,9281

The obtained data serve as a basis for evaluating the effect of the activated carbon surface structure on its adsorption capacity, which will be presented in the subsequent study.

3.3. Molecular simulation results

3.3.1. Effect of surface structure on activated carbon

The previously obtained experimental results will be evaluated to assess the influence of the surface structure of activated carbon on its adsorption capacity for methylene blue. The simulation results are compared with experimental data and are presented in figure 6.

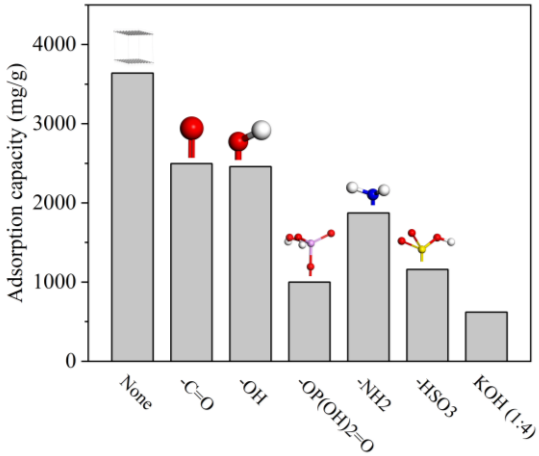

Figure 6. *Adsorption capacity with different structures.*

The results obtained indicate that the activated carbon sample in this study has a surface structure containing oxygen-containing functional groups. Its adsorption capacity is similar to that of the simulated structures featuring $-HSO_3$ and $-OP(OH)_2{=}O$ functional groups. According to the

simulation, activated carbon with an inert surface, devoid of functional groups, exhibits the highest adsorption capacity. The considerable differences in adsorption capacity among the structures suggest that the pore size of activated carbon plays a critical role in its ability to adsorb methylene blue. Bulkier functional groups reduce the pore space, leading to a lower capacity for methylene blue molecule adsorption within the pores [13]. To better understand the adsorption process, this study conducted molecular dynamics simulations to examine the adsorption behavior of methylene blue on the surface of activated carbon.

3.3.2. Diffusion coefficient – mean square displacement

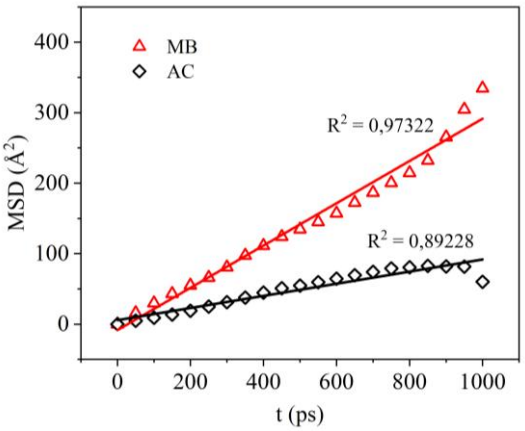

Figure 7. *Mean square displacement.*

The mean square displacement was determined using the molecular dynamics method as a function of pressure. The parameters of Brownian motion are illustrated in figure 7, where n represents the number of spatial dimensions in the model, which in this case is n = 3.

The diffusion coefficients of methylene blue and activated carbon were determined to describe their kinetic characteristics in an aqueous environment. For activated carbon, the diffusion coefficient is smaller due to the influence of large molecular size, as these molecules tend to adsorb methylene blue molecules, thereby reducing thermal motion. Methylene blue molecules tend to approach the surface of activated carbon, characterized by a high diffusion coefficient of D = 0,3 (Å^2/ps).

Table 3. *The parameters of the diffusion model.*

Parameters	MSD model	MB	AC
Intraparticle diffusion coefficient D (Å^2/ps)	MSD = 2nDt (Å^2)	0,3	0,086
Coefficient of determination R^2		0,97322	0,89228

The models achieved a high fitting coefficient R^2, indicating their suitability for evaluating molecular distribution based on a multilayer surface mechanism. The distribution of methylene blue molecules in water, including their mutual interactions, will be further elucidated through the cross-distribution density function.

3.3.3. Radial distribution functional methylene blue and with respect to activated carbon

The radial distribution function was computed to analyze the interactions and the likelihood of locating methylene blue molecules within a mixture of methylene blue, activated carbon, and water (figure 8).

The methylene blue molecules are most likely to be found at a distance of r = 4.01 Å, with the maximum measured g(r) value of 5.07. This value represents the distance from the activated carbon

surface to the methylene blue molecules, which are adsorbed in a horizontal geometric arrangement. Furthermore, as illustrated in figure 5, an additional value is observed at r = 7.11 Å, with a corresponding g(r) value of 3.57, which signifies the multilayer adsorption of methylene blue molecules on the surface of activated carbon. The probability of locating methylene blue molecules decreases as the radial distance increases, indicating that the adsorption process remains stable. At equilibrium, the molecules undergo oscillations in the aqueous environment, forming a unified structure, as shown in figure 9.

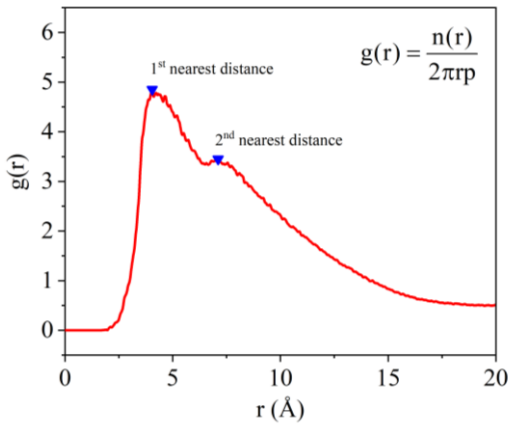

Figure 8. *Radial distribution functional of adsorption methylene blue on activated carbon.*

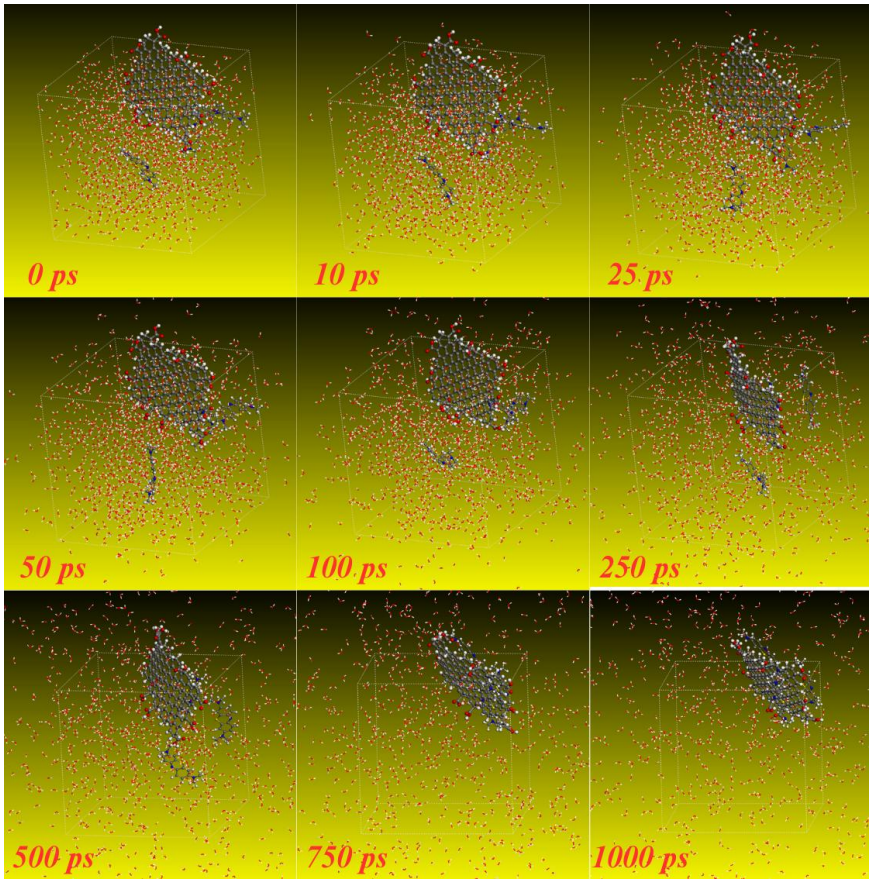

Figure 9. *Snapshots of adsorption methylene blue on activated carbon by MD simulation.*

4. CONCLUSIONS

This research explored the adsorption capacity of methylene blue onto activated carbon in water, utilizing both experimental techniques and molecular dynamics simulations. The activated carbon samples underwent pre-treatment with varying KOH concentrations, resulting in a maximum adsorption capacity of 619.92 mg/g. Kinetic studies of methylene blue adsorption revealed that the process most closely aligns with a second-order kinetic model, exhibiting a high correlation coefficient (R^2). Isotherm analysis showed that the adsorption process is best described by the Langmuir model, with a calculated maximum adsorption capacity of 1371.42 mg/g. Theoretical calculations further suggested that the surface structure of activated carbon predominantly consists of oxygen-containing functional groups, which contribute to its adsorption affinity. The adsorption process follows a multilayer surface bonding mechanism, facilitated by electrostatic interactions between the methylene blue atoms and the functional groups on the activated carbon surface. Additionally, the intraparticle diffusion coefficient, calculated from the model, was found to be 0.3, indicating stable diffusion of methylene blue molecules to the activated carbon surface. These findings offer valuable insights into the potential use of activated carbon for treating persistent organic pollutants in aquatic environments.

Acknowledgment: *This research was supported by the Academy of Military Science and Technology*.

REFERENCES

[1]. Oladoye P.O, Ajiboye T.O, Omotola E.O, and Oyewola O.J, *"Methylene blue dye: Toxicity and potential elimination technology from wastewater"*, Results in Engineering, 16, p. 100678, (2022), https://doi.org/10.1016/j.rineng.2022.100678

[2]. Khan I, Saeed K, Zekker I, Zhang B, Hendi A.H, Ahmad A, Ahmad S, Zada N, Ahmad H, and Shah L.A, *"Review on methylene blue: Its properties, uses, toxicity and photodegradation"*, Water, 14(2), p. 242, (2022), https://doi.org/10.3390/w14020242

[3]. Moorthy A.K, Rathi B.G, Shukla S.P, Kumar K, and Bharti V.S, *"Acute toxicity of textile dye Methylene blue on growth and metabolism of selected freshwater microalgae"*, Environmental Toxicology and Pharmacology, 82, p. 103552, (2021), https://doi.org/10.1016/j.etap.2020.103552

[4]. Mashkoor F and Nasar A, *"Magsorbents: Potential candidates in wastewater treatment technology–A review on the removal of methylene blue dye"*, Journal of magnetism magnetic materials, 500, p. 166408, (2020), https://doi.org/10.1016/j.jmmm.2020.166408

[5]. Kuang Y, Zhang X, and Zhou S, *"Adsorption of methylene blue in water onto activated carbon by surfactant modification"*, Water, 12(2), p. 587, (2020), https://doi.org/10.3390/w12020587

[6]. Fito J, Abrham S, and Angassa K, *"Adsorption of methylene blue from textile industrial wastewater onto activated carbon of Parthenium hysterophorus"*, International Journal of Environmental Research, 14, p. 501-511, (2020), https://doi.org/10.1007/s41742-020-00273-2

[7]. El-Bery H.M, Saleh M, El-Gendy R.A, Saleh M.R, and Thabet S.M, *"High adsorption capacity of phenol and methylene blue using activated carbon derived from lignocellulosic agriculture wastes"*, Scientific reports, 12(1), p. 5499, (2022), https://doi.org/10.1038/s41598-022-09475-4

[8]. Jawad A.H, Abdulhameed A.S, Wilson L.D, Syed-Hassan S.S.A, ALOthman Z.A, and Khan M.R, *"High surface area and mesoporous activated carbon from KOH-activated dragon fruit peels for methylene blue dye adsorption: optimization and mechanism study"*, Chinese Journal of Chemical Engineering, 32, p. 281-290, (2021), https://doi.org/10.1016/j.cjche.2020.09.070

[9]. Khnifira M, El Hamidi S, Sadiq M, Şimşek S, Kaya S, Barka N, and Abdennouri M, *"Adsorption mechanisms investigation of methylene blue on the (0 0 1) zeolite 4A surface in aqueous medium by computational approach and molecular dynamics"*, Applied Surface Science, 572, p. 151381, (2022), https://doi.org/10.1016/j.apsusc.2021.151381

[10]. Guediri A, Bouguettoucha A, Chebli D, Chafai N, and Amrane A, *"Molecular dynamic simulation and DFT computational studies on the adsorption performances of methylene blue in aqueous solutions by orange peel-modified phosphoric acid"*, Journal of Molecular Structure, 1202, p. 127290, (2020), https://doi.org/10.1016/j.molstruc.2019.127290

[11]. Narayanaswamy V, Alaabed S, and Obaidat I.M, *"Molecular simulation of adsorption of methylene blue and rhodamine B on graphene and graphene oxide for water purification"*, Materials Today: Proceedings, 28, p. 1078-1083, (2020), https://doi.org/10.1016/j.matpr.2020.01.086

[12]. Surekha G, Krishnaiah K.V, Ravi N, and Suvarna R.P, FTIR, *"Raman and XRD analysis of graphene oxide films prepared by modified Hummers method"*, in Journal of Physics: Conference Series, IOP Publishing, (2020), https://doi.org/10.1088/1742-6596/1495/1/012012

[13]. Yu L, Guo Y, Chen H, Liu B, Xu X, Sheng P, Zeng Z, and Li L, *"Influence of functional groups and pore sizes in porous carbon for methanol acetone adsorptive separation based on molecular simulation"*, Journal of Materials Science, 56, p. 18550-18565, (2021), https://doi.org/10.1007/s10853-021-06549-y

TÓM TẮT

Nghiên cứu quá trình hấp phụ methylene blue trên bề mặt than hoạt tính: Kết hợp nghiên cứu thực nghiệm và mô phỏng phân tử

Nước thải có chứa methylene blue có trong nước thải dệt nhuộm nếu không được xử lý gây ô nhiễm nghiêm trong môi trường nước, phá hủy sinh thái và mang nhiều độc tính đối với sức khỏe con người. Bài báo này đã tiến hành nghiên cứu khả năng hấp phụ methylene blue của than hoạt tính trong nước. Mẫu than hoạt tính được tiền xử lý với các tỷ lệ KOH khác nhau cho dung lượng hấp phụ methylene blue cao nhất đạt được bằng 619,92 mg/g. Nghiên cứu đã tiến hành đánh giá quá trình hấp phụ bằng hệ thống các mô hình động học và đẳng nhiệt hấp phụ cho kết quả quá trình hấp phụ phù hợp nhất với mô hình động học bậc hai và mô hình đẳng nhiệt hấp phụ Langmuir với các hệ số phù hợp R^2 đều ở mức cao. Nghiên cứu cũng tiến hành áp dụng các phương pháp mô phỏng phân tử nhằm làm rõ bản chất của quá trình hấp phụ. Kết quả chỉ ra rằng, cơ chế hấp phụ đa lớp với lực liên kết tĩnh điện đặc trưng cho khả năng tạo liên kết bền vững giữa bề mặt than hoạt tính và các phân tử methylene blue. Từ kết quả của nghiên cứu cho thấy hiệu quả xử lý ô nhiễm nguồn nước bởi methylene blue của than hoạt tính.

Từ khóa: Than hoạt tính; Methylene blue; Mô phỏng phân tử.