



GENTIAN VIOLET ADSORPTION ONTO BIOSORBENT CUPCAR: STATISTICAL PHYSICS MODELING AND CONSEQUENT INTERPRETATIONS

**Salah Knani^{1,*}, Ridha Selmi², Abdellah Bouguettoucha³, Nizar Lefi⁴ and
Waad Albalwi¹**

¹Department of Physics

College of Science

Northern Border University

Kingdom of Saudi Arabia

e-mail: saleh.kenani@nbu.edu.sa

²Department of Mathematics

College of Science

Northern Border University

Kingdom of Saudi Arabia

³Department of Engineering Process

Faculty of Technology

Ferhat ABBAS University Setif

19137, Algeria

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*Corresponding author

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⁴Department of Physics
College of Sciences and Arts in Uglat Asugour
Qassim University
Buraidah, Kingdom of Saudi Arabia

Abstract

A cost-effective and environmental-friendly modified blend of wild carob and *Cupressus sempervirens* with H_3PO_4 (Cupcar- H_3PO_4) was developed for the extraction from aqueous solutions of cationic dye, crystal violet (CV). The capacity of adsorption was estimated to be 117.26mg/g at 25°C with a pH of 6.22. Isotherm data were fitted using four advanced models to gain insights into the mechanism of CV retention on Cupcar- H_3PO_4 . The multilayer with saturation model emerged as the most suitable advanced statistical physics model, suggesting that CV was adsorbed at Cupcar- H_3PO_4 biosorbent receptor site with the formation of N_C layers. According to the values of the captured crystal violet (CV) per site (n), it was concluded that a multi-molecular ($n > 1$) process is occurred. This model revealed the potential for a varying quantity of CV molecules to be adsorbed at a specific site, emphasizing their adsorption with two distinct energies. Through thermodynamic examination, it is showed that the process of CV dye adsorption was endothermic and linked to physical forces. This analysis affirmed the possibility and natural occurrence of CV pollutant dye adsorption on the surface of this adsorbent. Finally, a pore size distribution (PSD) of Cupcar- H_3PO_4 is investigated.

1. Introduction

Addressing the provision of clean water for a range of crucial human tasks, like drinking, preparing meals, and cleaning, and agricultural irrigation, poses a significant challenge for researchers and professionals worldwide. Freshwater constitutes a mere 2.5% of the planet's total water supply, with a substantial portion (about 97%) trapped within polar ice caps. The additional 0.3% is distributed across rivers, lakes, and exists in the suspended in the air like clouds and fog. However, these sources of water are

not fully accessible for human use, as they are susceptible to contamination from various sources, including pathogenic bacteria, biodegradable waste, nutrients from plants, dangerous chemicals, solid particles, oil, and radioactive materials. Industries that consume significant quantities of water, such as the tanning and textile sectors, primarily use it for both the dye and finishing processes. These industries stand as major contributors to global pollution concerns, mainly because their wastewater becomes contaminated with toxic dyes, even in low concentrations [1, 2]. In fact, the world market offers a staggering array of approximately 100,000 textile dyes produced annually, totaling an estimated 7.105 metric tons. A noteworthy 30% of these dyes are used in quantities exceeding 1000 tons per year, while 90% of textile products consume 100 tons or less annually [3]. It is alarming that 2 to 20% of these dyes ultimately find their way into liquid effluents. The existence of colorants in water, even in trace amounts, raises undeniable and conspicuous concerns [4]. Moreover, they pose significant health risks, including but not limited to skin irritation, cancer, nausea, diarrhea, vomiting, gastritis, allergic skin reactions, and impacts on the kidneys, liver, reproductive system, and central nervous system [5]. In addition, the colored sewage poses significant harm to aquatic organisms through reducing lighting penetration, thereby impeding photosynthetic processes and the disruption of biological processes [6]. In response to this environmental challenge, the treatment of industrial waste laden with such dyes has garnered increasing attention. Various methods, including biological, chemical, and physical techniques, have been explored and implemented for treating dye-laden effluents. These methods encompass flocculation, exchange of ions, filtration through membranes, precipitation, irradiation and ozonation. Nonetheless, these approaches often demand costly technical resources [7, 8]. Therefore, because of its straightforward operation, adsorption remains a widely used method for eliminating dyes [9]. The fundamental concept behind adsorption treatment involves the capture of dyes using a solid material known as an adsorbent. Various solid materials have been explored in the literature for this purpose, including activated

carbon, zeolites, and biosorbents, clays. Recent research efforts have predominantly focused on using affordable adsorbents easily found nearby, biodegradable, and sourced from nature. In this context, biosorbents derived from the lingo-cellulose fractions have gained widespread attention as an effective means of treating colored effluents. This is primarily due to their exceptionally porous structure, high surface area and adsorption capacity.

Various biosorbents have been employed for dye removal, including date kernels [10], apple pulp [11], kernels of olive [12], peach kernels [13], corncobs [14], coffee beans [15], bagasse [16], coconut shells [17], chitosan [18], and new materials such as shell coconut and ash charcoal, Cassia fistula seed ash [19] and fibers from *Stipa tenassicima* [20], carob wild [21]. More recent developments like pectin, are obtained from residues in the fruit-orange juice industry [22], chitosan vermiculite beads [23], and orange rind treated with H_3PO_4 [24]. Crystal violet, also known as gentian violet, is commonly used for printing paper, coloring textiles, dyeing leather and in some cases for dermatological applications. Alongside many other pollutants, this dye carries toxicity potential, capable of causing skin irritation upon inhalation or ingestion [25].

This study focuses on the removal of dye (CV) crystal violet using a blend of cost-effective and readily available materials, specifically the *Cupressus sempervirens* (Cupcar- H_3PO_4) and wild carob. This mixture is known for its capability to adsorb cationic dyes effectively. Furthermore, we studied the pollutant removal performance of variants of *Cupressus sempervirens* (Cupcar- H_3PO_4) and wild carob biomass [26] using modeling procedure. We show that this developed material, termed Cupcar- H_3PO_4 , was scrutinized for its efficacy in treating wastewater. We provide new insights for CV adsorption onto the biosorbent using four models based on statistical physics approach. These models may retrieve helpful and fruitful information to explain the adsorption process that cannot be provided from the use of classical adsorption models.

2. Materials and Methods

2.1. Materials

The research employed a mixture of local *Cupressus sempervirens* and wild locust bean. The chemicals, such as phosphoric acid (H_3PO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH), as well its salts such as NaCl and Na_2SO_4 , and humic acid, were procured from Sigma-Aldrich for research purposes.

2.2. Adsorbent preparation

The blend of wild carob and the *Cupressus* species has undergone thorough purification process. It has been repeatedly cleaned with tap water and subsequently rinsed with purified water over a period of 48 hours to eliminate extraneous substances. The cleaned biomass was then kilned at 60°C until a constant mass is obtained. Following this, the dry biomass was sifted through a sieve with a mesh size less than 0.5mm and surface treated with H_3PO_4 . A powdered blend comprising 10 grams each of *Cupressus sempervirens* and carob was combined with a 100ml phosphoric acid solution (0.5mol/L) and stirred at room temperature for 24 hours. Then, the solid phase was separated through filtration and rinsed repeatedly with distilled water to eliminate any surplus modifier. Subsequently, it was allowed to dry at room temperature for an additional 24 hours. The modified compound, processed using 0.5M of phosphoric acid, was identified as Cupcar- H_3PO_4 . In this study, crystal violet dye, also recognized as basic violet 3 or gentian violet, bearing the IUPAC designation Tris[4-(dimethylamino)phenyl]methylium chloride, was chosen for wastewater decolorization. Its structural formula is $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$ (Figure 1), and its molecular weight is about 407.98g/mol. The dye, obtained from Sigma-Aldrich with the purity 99.99%, was initially prepared in the form of a solution of concentration 50mg/L, which could be further diluted as needed. pH adjustments for the solutions were made by adding 0.1M HCl or 0.1M NaOH solutions.

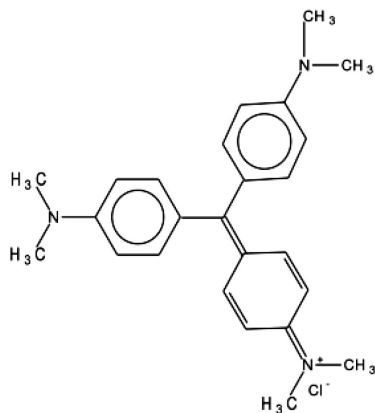


Figure 1. Structure of crystal violet.

2.3. Adsorption studies

2.3.1. Advanced models

In this study, four statistical models: the single layer with one energy (M_1), single layer with two energies (M_2), double layer with two energies (M_3), and multilayer model with saturation (M_4) are employed as theoretical models to analyze CV uptake dynamics. Modeling is essential to provide a supplementary tool to understand the mechanism underlying adsorption of CV on the material Cupcar- H_3PO_4 . The theoretical treatments serve as crucial tools to better elucidate and comprehend the process involved. If we denote by Q ($\text{mg}\cdot\text{g}^{-1}$) the adsorbed quantity, n the number of CV molecules per site, N_m ($\text{mg}\cdot\text{g}^{-1}$) the receptor site density, and $C_{1/2}$ (mgL^{-1}) the concentration at half-saturation, the adsorbed quantity of CV onto Cupcar- H_3PO_4 versus the concentration C according to monolayer adsorption can be written as [27]:

$$Q = \frac{nN_m}{1 + \left(\frac{C_{1/2}}{C}\right)^n}. \quad (M_1)$$

If we suppose that the adsorption can be occurred in monolayer adsorption onto two types of receptor sites, the adsorbed quantity takes the

following form [27]:

$$Q = \frac{n_1 N_{m1}}{1 + \left(\frac{C_{S1}}{C}\right)^{n_1}} + \frac{n_2 N_{m2}}{1 + \left(\frac{C_{S2}}{C}\right)^{n_2}}, \quad (M_2)$$

with n_1 and n_2 being the numbers of CV molecules for the first and second types of sites, respectively. N_{m1} and N_{m2} denote the densities of the receptor sites for the first and second types, and C_{S1} and C_{S2} are the concentrations at which the first and second types of receptor sites reach half-saturation, respectively.

The adsorption can be extended to double layer, so the adsorbed quantity takes the form [27]:

$$Q = n \cdot N_m \frac{\left(\frac{C}{C_{L1}}\right)^n + 2 \cdot \left(\frac{C}{C_{L2}}\right)^{2n}}{1 + \left(\frac{C}{C_{L1}}\right)^n + \left(\frac{C}{C_{L2}}\right)^{2n}}, \quad (M_3)$$

with C_{L1} and C_{L2} being the half-saturation concentrations for the initial layer and the second layer, respectively.

When the adsorption takes place with, in addition of the first layer, N_2 layers where the initially adsorbed molecules serve as receptor sites for the others, the adsorbed quantity can be written as [28]:

$$Q = nN_m \frac{\frac{-2(X_1)^{2n}}{1 - (X_1)^n} + \frac{(X_1)^n(1 - (X_1)^{2n})}{(1 - (X_1)^n)^2} + \frac{2(X_1)^n(X_2)^n(1 - (X_2)^{nN_2})}{(1 - (X_2)^n)} - \frac{N_2(X_1)^n(X_2)^n(X_2)^{nN_2}}{(1 - (X_2)^n)} + \frac{(X_1)^n(X_2)^{2n}(1 - (X_2)^{nN_2})}{(1 - (X_2)^n)^2}}{\frac{(1 - (X_1)^{2n})}{(1 - (X_1)^n)} + \frac{(X_1)^n(X_2)^n(1 - (X_2)^{nN_2})}{(1 - (X_2)^n)}} \quad (M_4)$$

with

$$X_1 = \frac{C}{C_{L1}} \text{ and } X_2 = \frac{C}{C_{L2}}.$$

3. Results and Discussion

3.1. Isotherm modeling with advanced models

Table 1 illustrates the determination coefficient R^2 which measures by its value the goodness of the fit. The best fit is obtained when R^2 values are close to 1. In Table 1 and Figure 2, it is shown that among the statistical physics models considered, the multilayer model with saturation (M_4) stood out as the most suitable to adjust the experimental data of CV biosorption on Cupcar- H_3PO_4 . According to this model, the CV pollutant molecule exhibited adsorption on two distinct sites within the Cupcar- H_3PO_4 biosorbent. Moreover, it suggested variability in the number of CV molecules, designated as ' n ', that have the probability to be adsorbed in each site. This purpose derived from that CV underwent adsorption with two different energies, result of the formation of N_C layers on the surface of the Cupcar- H_3PO_4 biosorbent.

Table 1. Values of the determination coefficient R^2 of fitting

T (K)	Monolayer single-energy (M_1)	Monolayer two-energies (M_2)	Double-layer two-energies (M_3)	Multilayer model with saturation (M_4)
283	0.967	0.976	0.989	0.991
298	0.964	0.996	0.948	0.989
303	0.988	0.998	0.976	0.997

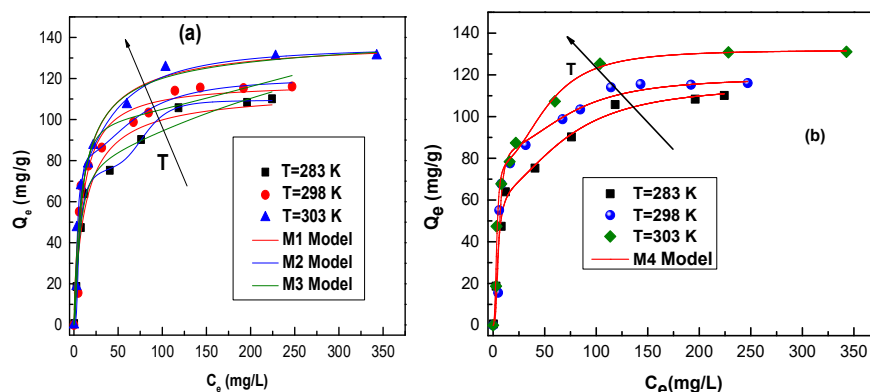


Figure 2. Statistical physics simulation of models: (a) single layer with one energy (M_1), single layer with two energies (M_2), double-layer with two energies (M_3) and (b) multilayer model with saturation (M_4).

3.2. Steric interpretations

Using the multilayer saturation model (M_4), the physicochemical parameters influencing the interaction between CV and Cupcar- H_3PO_4 will be identified and examined. The value of the n parameter characterizes the orientation (horizontal or vertical) and means (multi-docking or multi-molecular) of adsorbing CV onto the Cupcar- H_3PO_4 surface. When n is less than 1, it represents one horizontal orientation and multiple anchoring mechanism. Conversely, when n is greater than 1, it indicates a vertical orientation and multi-molecular interaction [28, 29]. The values of the steric parameters n , N_m , N_C and Q_{sat} are indicated in Table 2, and their evolution versus temperature is depicted in Figure 3. According to Table 2 and Figure 3(a), at the examined temperatures, the steric parameter, n is consistently greater than 1, suggesting that CV biosorption on the various Cupcar- H_3PO_4 material sites occurred in multimolecular process. This fact signifies that one receptor site is occupied by more than two molecules of CV (multi-molecular anchorage).

Table 2. Parameter values adjusted using the multilayer model for adsorption of CV on the Cupcar-H₃PO₄ system

T (K)	283	298	303
Q_{sat} (mg/g)	115.184	121.03	131.04
N_m (mg/g)	28.49	28.73	27.95
n	2.218	2.51	2.79
N_C	1.761	1.685	1.681
C_1 (mg/L)	4.523	5.750	3.456
C_2 (mg/L)	72.03	75.094	52.465

The values of n were 2.218, 2.51 and 2.79 at 283, 298 and 303K, respectively. This process indicates an accumulation of n -molecules on the Cupcar-H₃PO₄ material with rising temperature. The contrasting characteristics observed in the evolution of n parameter may stem from the variability in active sites within the Cupcar-H₃PO₄ material. This result may be connected to how active groups participate in the adsorption process of CV on Cupcar-H₃PO₄. The distribution of the N_m parameters against temperature variations is depicted in Figure 3(b). We can see according to Figure 3(b) and in Table 2, a growth in temperature from 283 to 303K corresponds to a decrease in the N_m parameter from 29.49 to 27.95mg.g⁻¹. Consequently, the temperature escalation unveiled a diminishing trend in the behavior of N_m parameter. The decrease in N_m might be associated with the clustering of molecules of CV on receptor sites like ($C = O$) and the diminished involvement of the active sites within the novel biosorbent Cupcar-H₃PO₄ in eliminating molecules of CV. So, the bio-adsorbing process of the molecule of CV involves employing various functional groups present in the Cupcar-H₃PO₄ material, including ($C - O$, $C = C$, $C - H$).

Figure 3(c) presents the variation of the global number of formed layers for the CV deposited on Cupcar-H₃PO₄ systems, which is ranging between 1.76 and 1.68. This variability suggests that the adsorption of CV

necessitates the development of one or possibly two adsorbate layers. As the rise in adsorption temperature, there is a decrease in the number of layers. It was theorized that this reduction in the number of layers could be attributed to the heightened interaction energies associated with the process. In practical application, a process multilayer adsorption helps alleviate the decreasing in the number of available active sites for CV adsorption on the Cupcar- H_3PO_4 adsorbent's surface.

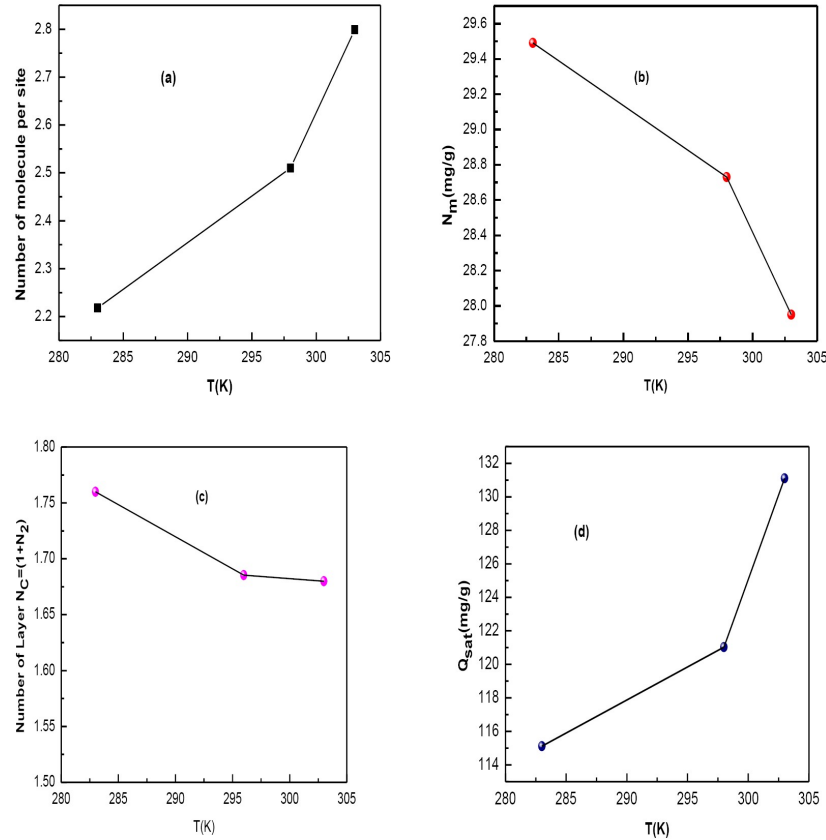


Figure 3. Evolution of n (a), N_m (b), N_C (c) and Q_{sat} (d) versus temperature for CV adsorption onto Cupcar- H_3PO_4 .

Finally, in Figure 3(d), we show the influence of temperature on the evolution of Q_{sat} . We can observe that the process of aggregation of CV on

the adsorbent Cupcar-H₃PO₄ increases with temperature. This phenomenon could be linked to the trend observed in steric parameters (n , N_m and N_C). While n values rise with temperature, N_C and N_m coefficients decrease. This behaviour indicates that product adsorption capacities increase with temperature. Consequently, N_m emerged as the main factor influencing the CV uptake capacity of the Cupcar-H₃PO₄ adsorbent.

3.3. Energetic interpretations

The multilayer model (M_4) is employed to estimate the energy of CV adsorbed to the Cupcar-H₃PO₄ surface. This model characterizes the adsorption behavior, providing crucial insights into the strength of bounds between the adsorbate and adsorbent. As per the (M_4) equation, the adsorption energies ($-\Delta E_1^a$) and ($-\Delta E_2^a$) associated with the specific concentrations (C_1 and C_2) are determined using the following expressions. These estimations play a key role in establishing their relationship with temperature [28, 29]:

$$\Delta E_1^a = R.T.\ln\left(\frac{C_s}{C_1}\right), \quad (1)$$

$$\Delta E_2^a = R.T.\ln\left(\frac{C_s}{C_2}\right). \quad (2)$$

Here, C_s denotes the CV dye molecule's solubility value (g/L), R stands for the universal gas constant ($8.314 \times 10^{-3} \text{kJK}^{-1} \text{mol}^{-1}$), and T signifies the temperature value (K).

The various adsorption energies that were found are illustrated in Table 3. As previously stated, the bonds between the CV molecules and the Cupcar-H₃PO₄ surface are associated with the 1st energy of adsorption (ΔE_1^a), whereas the interactions between the subsequent layers of CV molecules are characterized by the 2nd energy of adsorption (ΔE_2^a). The initial energy (ΔE_1^a) ranging from 18.91kJ/mol to 20.22kJ/mol is higher

than the second energy because of the weak interactions between CV-CV molecules (ΔE_2^a) ranging from 12.40kJ/mol to 14.07kJ/mol.

Table 3. Adsorption energies of CV molecule on Cupcar-H₃PO₄ at 283K, 298K and 303K

T (K)	ΔE_1^a (kJ/mol)	ΔE_2^a (kJ/mol)
283	18.911	12.399
298	19.316	12.924
303	20.226	14.074

The model-predicted adsorption energies remained below 30kJ/mol, indicating the prevalence of physisorption mechanisms driven by van der Waals specified by London dispersion forces. Moreover, the positive values of the adsorption energies reinforce the endothermic nature of CV adsorption onto the investigated adsorbents. This rise in average active site energy was attributed to the effect of temperature, which caused the site atoms to become agitated. It is possibly allowing the adsorbed molecule to fit easily into the volume of the Cupcar-H₃PO₄ receptor site. This can be described by the fact that the increase of temperature is accompanied by availability of active sites having great energy, and so CV molecules adsorbed onto sites with higher affinity. Once these sites are occupied, CV molecules adsorbed are then adsorbed on sites with lower adsorption energy values.

4. Thermodynamic Potential Functions

By employing model (M_4), we were able to extract vital thermodynamic functions. These functions involve the internal energy (E_{int}), the configuration entropy (S_a) and the free energy of Gibbs (G_a). The utilization of these key functions significantly contributes to characterizing the adsorption mechanism of CV dye onto Cupcar-H₃PO₄-based adsorbents operates, as detailed in the subsequent discussion. The starting point to calculate thermodynamic potentials is the grand canonical partition function Z_{gc} which describes the microscopic states of the system

following the physical situation in which this system is placed. The Z_{gc} used to obtain model (M_4) is given by [30]:

$$Z_{gc} = 1 + e^{\beta(\varepsilon_1 + \varepsilon_2 + 2\mu)} \frac{1 - e^{\beta(\varepsilon_2 + \mu)N_2}}{1 - e^{\beta(\varepsilon_2 + \mu)}} \quad (3)$$

with ε_1 and ε_2 being the adsorption energies in the first and the other layers, respectively. $\beta = \frac{1}{k_B T}$ denotes the Boltzmann factor and μ is the chemical potential.

4.1. Internal energy calculation

In general, the internal energy is deduced by using the model of adsorption with a variable number of layers. This approach provides a thermodynamic interpretation of the CV adsorption process. The internal adsorption energy equation is given as follows [30]:

$$E_{int} = -\frac{\partial \ln(Z_{gc})}{\partial \beta} + \frac{\mu}{\beta} \left(\frac{\partial \ln(Z_{gc})}{\partial \mu} \right). \quad (4)$$

Figure 4 depicts the change in internal energy of adsorption (E_{int}) versus the concentration for different temperature values. We can observe that all recorded values of internal adsorption energy (E_{int}) demonstrate negativity across the range of temperatures investigated. This signifies the spontaneous evolution of the CV-Cupcar- H_3PO_4 system, as it releases energy. Additionally, concerning CV adsorption, the absolute value of internal energy (E_{int}) grows with higher temperatures. This is likely due to the intensified interaction between CV molecules and the surface of Cupcar- H_3PO_4 , a result of heightened thermal collisions between CV molecules and the adsorbent surface. Consequently, when a CV molecule adheres to adsorbent surface receptor sites or to functional groups, the released energy contributes to endothermic processes of adsorption of CV on Cupcar- H_3PO_4 .

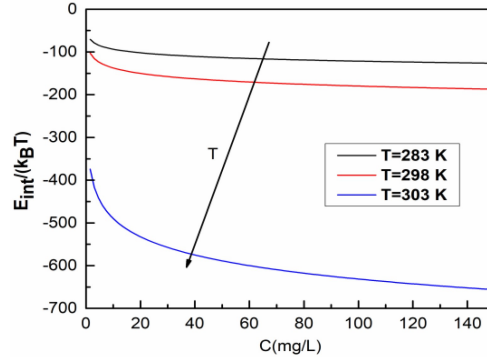


Figure 4. Internal energy of adsorption (E_{int}) versus the equilibrium concentration of CV onto the Cupcar- H_3PO_4 -based adsorbent.

4.2. Free energy of Gibbs

The free energy of Gibbs (G_a) describes a specific potential function which is used to predict the feasibility of the process and its spontaneity in the systems under analysis. Its determination can be achieved through the following equation [31]:

$$G_a = \mu \times Q. \quad (5)$$

In this equation, Q stands for the adsorbed quantity, while μ represents the chemical potential of an individual receptor site. Figure 5 depicts the concentration-dependent free energy of Gibbs (G_a) fluctuations at different temperatures.

The insights from Figure 5 reveal a distinct trend: as the concentration remains low, G_a experiences a steep decrease with increasing concentration. Additionally, all G_a values are negative, signifying the spontaneous thermodynamic evolution of CV adsorption onto Cupcar- H_3PO_4 . Furthermore, the absolute magnitude of G_a rises with temperature, suggesting an enhanced feasibility of the adsorption process within the (CV/Cupcar- H_3PO_4) system at higher temperatures.

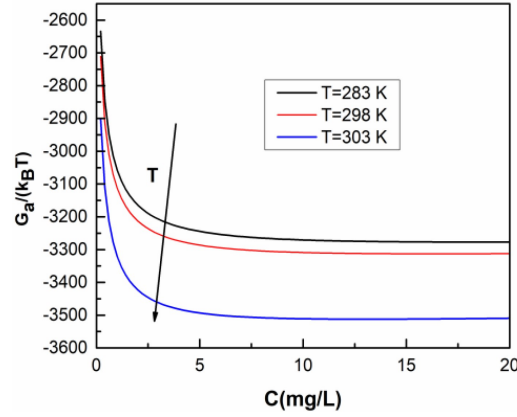


Figure 5. Free enthalpy of adsorption of Gibbs (G_a) depending on the equilibrium concentration C of CV on the surface of the Cupcar- H_3PO_4 adsorbent.

4.3. Adsorption entropy calculation

The entropy of adsorption, also called entropy of configuration (S_a) holds valuable insights as it delineates the evolution of disorder among crystal violet adsorption. The equation defining the entropy (S_a) is elucidated as follows [30, 32]:

$$\frac{S_a}{k_B} = -\beta \frac{\partial \ln(Z_{gc})}{\partial \beta} + \ln(Z_{gc}). \quad (6)$$

The changes in this parameter with concentrations for a range of temperature values are illustrated in Figure 6.

The entropy of configurational adsorption (S_a) exhibits a consistent pattern across the entire temperature range. Notably, the trend of S_a concerning equilibrium concentration displays two peaks, aligning with the first (C_1) and (C_2); the two specific concentrations. Specifically, as the adsorption initiates, S_a begins from zero, subsequently surging to its peak near or at the first concentration ($C \leq C_1$ or $C = C_1$). This indicates that

the highest degree of disorder ($C = C_1$) is reached when half of the sites ($N_m/2$) of the first layer is occupied. Indeed, in the early stages, the CV molecule has many choices for linking to an unoccupied site, to be adsorbed. Then, as all the receptor sites involved in adsorption to the first layer are fully occupied, the entropy of configuration (S_a) is reduced. Beyond the concentration C_1 and for the first layer, we found that the number of vacant receptor sites, accessible for CV molecules, becomes limited. However, entropy of configuration continues to rise as the other changing number of formed layers (N_2) starts to be occupied by CV molecules, resulting in the lowest value of entropy (S_a) not reaching zero. Secondly, the configurational adsorption entropy (S_a) exhibits the same characteristics as those observed at C_2 around C_1 , with the additional consequence that the first adsorbed layer is utilized as an adsorbent receptor site for the subsequently formed N_2 layers. Finally, the entropy (S_a) attains zero, when saturation is complete, and adsorption too is complete.

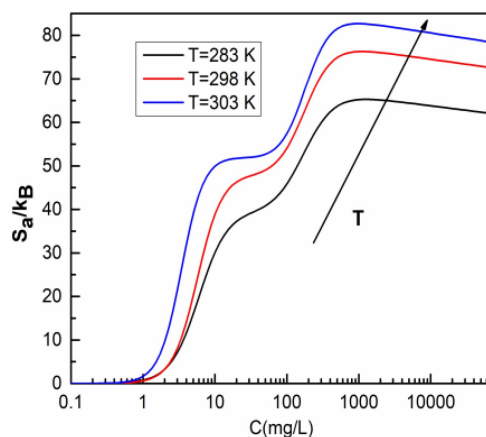


Figure 6. Adsorption configurational entropy (S_a) depending on concentration for adsorption of CV dye on Cupcar- H_3PO_4 at different temperatures.

5. The Pore Size Distribution (PSD)

The PSD can be estimated using the Kelvin equation in relationship with the solubility C_s and the pore radius (r), and promising the statistical physics model (M_4), CV adsorption isotherms on the Cupcar- H_3PO_4 . The PSD, which can be expressed as follows, was therefore derived using the statistical physics formula and the Kelvin's law in the liquid phase [33, 34]:

$$\ln\left(\frac{C}{C_s}\right) = \frac{-2\gamma V_m}{rRT}, \quad (7)$$

$$\frac{C}{C_s} = e^{\frac{-2\gamma V_m}{rRT}} = e^{-\frac{K_k}{rRT}}, \quad (8)$$

where T represents the absolute temperature, R is defined by the universal gas constant, r is the pore radius of molecular sieves, $K_k = 2\gamma V_m$ is specified as the Kelvin constant and V_m denotes the molar volume of the crystal violet molecule merged into the solution. When M is taken to be the molar mass and $\gamma = 44.2 \cdot 10^{-3} \text{N.m}^{-1}$ denotes the surface tension, considering the contact angle θ to be zero.

Hence, the characterization of Cupcar- H_3PO_4 's pore size distribution, which encompasses structured pores, is achieved by deriving the adsorbed amount (Q) associated with the pore radius, as demonstrated in the following equation [33, 34]:

$$PSD = \frac{dQ}{dr}. \quad (9)$$

From the depicted curve in Figure 7, it is evident that the pore size distribution (PSD) varies across different temperature values.

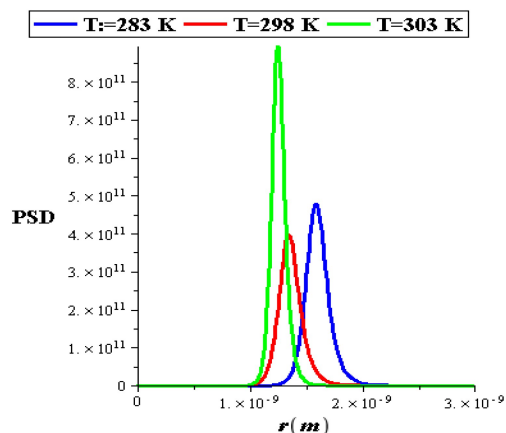


Figure 7. Pore size distribution of the Cupcar-H₃PO₄ at different values of temperature.

It is shown that the adsorption surface's pore radius of Cupcar-H₃PO₄ primarily consists of pores easily penetrable and sized below 2nm. This reaffirms the micro-porous nature expected of Cupcar-H₃PO₄ as an adsorbent. Additionally, with increased thermal agitation, the entire distribution shifts towards smaller pore sizes within Cupcar-H₃PO₄. Moreover, examining the PSD across various temperatures reveals a unimodal distribution, showcasing a predominant peak in the micropore size of the micro-porous Cupcar-H₃PO₄.

At $T = 283\text{K}$, the bigger micro-porous mode has a radius peak of around 1.73nm. This peak has already informed in some studies of pore size distribution of Cupcar-H₃PO₄ micro-porous. Furthermore, several studies have consistently identified a modal distribution within the micro-porous structure of Cupcar-H₃PO₄. Notably, the size of CV particles is measured at $(1.73 \pm 0.25) \times 10^{-9}\text{m}$, suggesting a potential for these CV molecules to penetrate the pore size of Cupcar-H₃PO₄. This penetration likely occurs with a non-parallel anchored orientation, indicating that CV molecules can indeed enter the micro-porous structure of Cupcar-H₃PO₄. The interaction of CV molecules is affected with Cupcar-H₃PO₄ pore surface involved in micro-porous types (between 1nm and 2nm).

6. Conclusion

In our research, an environmental-friendly and low-cost mixture of wild carob and *Cupressus sempervirens* with H_3PO_4 (Cupcar- H_3PO_4) was produced. The adsorption studies were performed in a continuous adsorption system using crystal violet (CV) as a model dye. The multilayer model with saturation proves to be adequate to fit the experimental isotherm curves, showcasing greater thermodynamic efficiency. This model delves into the physicochemical intricacies of the adsorption system, employing the observed characteristics for theoretical analysis. Through numerical simulations, we can grasp the behavior of CV adsorption isotherms and the underlying phenomenon. The experimental isotherm curves serve as a key to understanding the physicochemical aspects linked to the adsorption process. In this study, five crucial physicochemical parameters; density (N_m), two concentrations at half-saturation associated with energetic parameters ($-\Delta E_1^a$) and ($-\Delta E_2^a$) are instrumental in comprehensively defining the adsorption processes. The adsorption capacity, Q_{sat} , displayed variability ranging from 115mg/g at 283K to 131.04mg/g at 303K. Furthermore, the suggested model yields adsorption energies ranging from 12kJ/mol to 21kJ/mol, aligning comparably with those within the band of physisorption. Moreover, this model facilitates the estimation of critical thermodynamic functions governing the adsorption mechanism, such as adsorption entropy, internal energy, and Gibbs free energy. The results elucidate that the adsorption of CV on the Cupcar- H_3PO_4 adsorbent material is both endothermic and spontaneous. The Cupcar- H_3PO_4 exhibits distinct pore size distributions (PSD) outcomes directly derived from statistical physics modeling. These findings serve as valuable tools for the comprehensive physical characterization of the Cupcar- H_3PO_4 -based adsorbent. The PSD facilitates the examination of the adsorbent's porosity, especially in the case of Cupcar- H_3PO_4 acting as a micro-porous adsorbent.

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