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Study of the Kinetics, Thermodynamics and Isotherm of Adsorption of Diamine

green B dye using biocatalyst Laccase @Fe-BTC

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Abstract:

In this study, isotherm, kinetics and thermodynamic properties of Diamin green B dye adsorption were investigated using enzymatic metal organic frameworks. First and second-order kinetic models and alovich kinetic model as well as Langmuir and Freundlich isotherm models were also used to evaluate the data. According to previous studies, dye adsorption efficiency by this material was investigated by examining the effects of contact time, adsorbent value and primary dye concentration. The most optimized adsorption conditions for this nano adsorbent were also obtained at time of 45 minutes and 5 g/l of adsorbent. The calculated values for the thermodynamic variables ΔG , ΔH and ΔS indicate that the adsorption of the tested dye onto the enzymatic organometallic adsorbent is spontaneous, endothermic and in the direction of increasing disorder. The process data were described by Alovich kinetics. Several isotherm models were also fitted to the experimental data and the Freundlich Isotherm model provided the best fit.

Keywords: Diamine Green B dye, Fe-BTC, Dye Removal, Laccase Enzyme, Kinetics Thermodynamic Isotherm.

1. Introduction

Metal-organic frameworks (MOFs) are bi or tridimensional nano porous materials, generally crystalline, formed by either metal ions or metal clusters linked by multidentate organic ligands. One of the most recent applications of MOFs focuses on the immobilization of enzymes. Moreover, the hybrid organic-inorganic character of certain MOFs seems to favor the interaction of these materials with enzymes, since solid active biocatalysts can be formed by just contacting both species, even when the material does not contain enough large pores to host the enzyme

The aromatic sections in the structure of dyes increase their toxicity and make their biodegradability impossible. Diamin green B dye has a closed molecular formula of C34H22N8Na2O10S2 and is a anionic azo dye and is used for dyeing fibers. The surface adsorption is one of the process for removing dyestuffs. Nanostructured adsorbents, with their high surface-to-volume ratio, have greater adsorption capacity than conventional adsorbents. The higher porosity in these materials increases their adsorption capacity. Nanostructured adsorbents produce less waste that can be collected. Also, the reusability of the adsorbent justifies the use of this process from an economic perspective. Among mesoporous silica adsorbents, the Mobil Composition of Matter (MCM) and Santa Barbara Amorphous type materia (SBA) families of molecular sieves have attracted attention due to their high surface area, high porosity, homogeneous pore size distribution, and controllable surface area. In order to increase the applications, changes

can be made inside the channel walls or the attachment of functional groups on the surface of these materials. New structures have also been prepared using nonionic surfactants in acidic media. One of the most recent applications of MOFs focuses on the immobilization of enzymes. Enzymes are catalytic proteins that facilitate chemical reactions within a living organism. They are widely used in a variety of industries due to their high specificity, catalytic power, and environmental safety(Singhania et al., 2015).enzymatic immobilization techniques are employed to protect of Enzymes can be easily obtained from a variety of sources, and they are widely used in biotechnological processes due to their ability to catalyze oxidation reactions using only atmospheric oxygen as an electron acceptor, unlike other cofactor-dependent oxidases, making them attractive for application in bioremediation processes, bio sensing and many other applications that will be further discussed (Barrios-Estrada et al., 2018b; Orlikowska et al., 2018).

Several materials and nanomaterials can be used to immobilize enzymes, including natural polymers such as collagen, alginate, chitosan, and cellulose and inorganic materials such as zeolites, ceramics, silica, charcoal, and glass (Datta et al., 2013). Enzymes are immobilized into these carriers by adsorption, covalent linkage, pore entrapment, encapsulation, crosslinking, or ligand affinity. Many techniques can be utilized to synthesize and/or prepare such materials in which to anchor enzymes including electrospinning, matrix-assisted pulsed laser evaporation (MAPLE), soft plasma polymerization, 3D and laser printing, and the use of cross linked enzyme aggregates, nano flowers and, of course, MOFs (Alvarado-Ramírez et al., 2021).

The MOF materials possess pores reaching the 'meso' range (diameter larger than 2.0

nm) could encapsulate certain small enzymes. Moreover, the hybrid organic-inorganic character of certain MOFs seems to favor the interaction of these materials with enzymes, since solid active biocatalysts can be formed by just contacting both species, even when the material does not contain enough large pores to host the enzyme. Laccase is a multi copper oxidoreductase enzyme that can oxidize organics such as dye compounds. Laccases appear to be unstable at room temperature, and their conformation often changes in a strongly acidic or alkaline environment, making them less effective. Therefore, rationally linking enzymes with supports can effectively improve the stability and reusability of native enzymes. However, in the process of immobilization, many factors may le3933ad to a decrease in enzymatic activity. Therefore, the selection of a suitable support can ensure the activity and economic utilization of immobilized catalysts. Metal-organic frameworks (MOFs) are porous and simple hybrid support materials. Moreover, the characteristics of the metal ion ligand of MOFs can enable a potential synergistic effect with the metal ions of the active center of metalloenzymes, enhancing the catalytic activity of such enzymes.

In this study, laccase enzyme was coated on a Metal organic nanostructure adsorbent. In these cubic nanoparticles, half of the octahedral sites and one-eighth of the tetrahedral sites are filled with trivalent iron ions. By adding laccase enzyme to these nanoparticles, cluster-shaped materials capable of removing dyes from industrial wastewater will be produced. Nanostructured materials with magnetic and electrical properties are converted into magnetically coated materials. Metal-organic frameworks (SMOF), also known as porous coordination polymers, have attracted the attention of many researchers in recent years. These structures are a new class of porous materials, which are formed by

connecting metal ions or clusters to polydentate allylic ligands through covalent bonds. Co-coordination polymers, compared to Other porous compounds such as zeolites, silica, and activated carbon have been proposed as multi-purpose materials with different requirements due to their ability to regulate the pore surface, size, shape, and functional groups of their pores. Magnetic metal-organic nanocomposites have the ability to adsorption and destroy the dye in photo degradation processes and even in the absence of light. In this study, a cheap enzyme was used in the sequential processes of removing the Diamin green B dye. This ability is due to the easy separation of metal-organic materials under a magnetic field, which is very effective in reducing costs. Laccase catalyze the single-electron oxidation of compounds with molecular oxygen as an electron acceptor and create active radicals that destroy dye molecules [1-8].

2. Experimental

2.1. Materials

The ingredients in this research were laccase enzyme based on Aspergillus nager, Diamin green B dye, benzene tricarboxylic acid (H3BTC), solvent N,N-dimethyl formamide, ethanol, methanol, iron nitrate (Fe(NO3)3.9H2O), nitric acid, sodium hydroxide and hydrochloric acid. All chemicals were purchased from Sigma-Aldrich, Finland. (Enzyme-enhanced metal-organic nanoadsorbents made using (improved) laccase enzyme and characterized by SEM and x-ray methods were used in previous research by this group [1]).

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2.2. Methods

2.2.1. Synthesis of Laccase @Fe-BTC powder

Fe-BTC powder was prepared by solvo thermal method as described in our previous work. Briefly 1.0 g of H3BTC was dissolved in 30 mL of DMF; the resulted solution was mixed with a solution made of 2.0 g of Fe(NO₃)₂·9H2O and 20 mL of DMF. The mixture was sonicated for 15 min and then heated in an oven at 110 °C for 6 h. The resultant material was filtered and washed then dried overnight. Then 7 gr of the dried adsorbent was chemically enzymatically treated for 48 h in a hot bath containing 1 ppm laccase, dissolved in 0.1 mM sodium phosphate buffer.[Figure 1]



Figure1: Schematic of prepare Lc@FeBTC

In order to prepare and analyze the samples, a spectrophotometer, a Philips x-ray device with a wavelength maximum of 1.54056 angstroms, 40 kV,35 mA ,is used to determine the crystallinity and the structural composition of the synthesized material. IR spectra were recorded on a (Bruker-ertex 70, Germany) Spectrometer at the wave number range of 4000-400cm-1 Scanning Electron Microscope (FESEM). The BET analysis for specific surface area, Functional group, pore size distribution and specific pore volume of the prepared samples were determined (TriStar II 3020 Micrometrics, USA).

2.2.2. Adsorption Experiments

Decolorization efficiency and amount of dye adsorbed on the MOF adsorbent in mg/g (Absorbent capacity) was calculated using equations 1 and 2 respectively. In this study, the important conditions affecting the adsorption process, including dye concentration, adsorbent amount, and contact time, were investigated using the experimental design method. In these equations, Ce is the equilibrium concentration and C0 is the initial concentration of the dye in ppm, qe is the adsorption capacity in mg/g, and M is the ratio of the weight of the adsorbent in grams to the volume of the solution. In these equations, C0 is the initial concentration of the dye (mg/l), Ce is the equilibrium concentration (mg/l), M is the amount of adsorbent in (g/l), and V is the volume of the solution (Li).

$$\mathbf{R}(\%) = \frac{(C_0 - C_e) \times 100}{C_0}$$
)1(
(q_e) = $\frac{(C_0 - C_e) \times 100}{M}$ (2)

3. Results and Discussion

3.1. Adsorbent characterization

The x-ray method was used to determine the qualitative properties and crystal orientation, the presence of sharp peaks, purity, crystallinity and single-phase nature of the material. With the information of the intensity and average peak width, the diameter of the crystal particles is calculated from the Scherrer equation. In equation 3, L is the average particle diameter, K is the Scherrer constant (0.9), λ is the X-ray wavelength (1.54060 angstroms), θ is the diffraction angle of each peak and β is the peak width at half maximum height (radians). By comparing the x ray image of the enzyme-containing and

enzyme-free nanoadsorbent, there is a significant difference in the intensity of the xray image peaks of most of the Fe-BTC with the enzyme [Figure 3]. The average crystal size D was obtained using Equation 3 to be 41.4 nm.

 $L = K \lambda / \beta Cos\theta \quad (3)$



Electron microscope images of Fe-BTC Include Scanning electron microscope show that the structure of the Fe-BTC metal organic adsorbent is in the form of clusters and agglomerates or clumps of irregular particles that have a nanometer size (Figures5and 6) which according to the particle size distribution result of these samples By dynamic light scattering method(DLS) have an average diameter of 30-36 nanometers (Figure 7).

Figure 5: SEM image of Fe-BTC

Figure 6: SEM image of LC @Fe-BTC

Figure 7: Particle size intensity distribution The Fe-BTC sample (DLS method) has an average particle size of 30-36 nm

Table1.Immobilization efficiency and catalytic performance of the in-situ biocatalysts LC@Fe-BTC-x (x is the

Biocatalyst Enzyme	Enzyme immobilizeda/ %
Lac@Fe-BTC-10 min	98
Lac@Fe-BTC-1h	99
Lac@Fe-BTC-4h	100
Lac@Fe-BTC-22h	100

synthesis preparation time)

3.2. Response surface statistical method(RSM)

The analysis was performed using the response surface statistical method at three levels and three variables, and with a design type of central composite. Variables include dye

concentration, time, and amount of enzymatic adsorbent.(Table 2)

Variable	Symbol	Low	Medium	High	
		-1	0	+1	
Times (min.)	А	5	32.5	60	
Dye Concentration (mg/L)	В	90.7	397.15	611.39	. 0
Adsorbent (g/L)	C	3	3	5	
				60	

Table2: Range of variables in CCD method.

3.2.1. Modeling the removal of the desired dye using an enzymatically functionalized adsorbent using ultivariate linear regression(MLR)

The multivariate linear regression method was used to model the absorption of the desired dye. The design variables were calculated from the quadratic regression equation (Equation 4), where: Bi: linear coefficient, Bii: squared coefficient, Bij: interaction coefficient (coefficients that are fitting constants), Xi, Xi2, Xi.Xj: independent variables, B0: width from the origin and Y is the response. According to the values determined by the model, 15 experiments were conducted for each factor.

$$Y = B_0 + \sum B_i \cdot X_i + \sum B_{ii} \cdot X_i^2 + \sum \sum B_{ij} \cdot X_i \cdot X_j \quad (4)$$

The number of test points is obtained from Equation 5, in this equation K is the number of variables and C0 is the number of center points, both values are set to 3 in this study.

$$N=2K(K-1)+C0$$
 (5)

According to the values determined by the model, 15 experiments were conducted for each factor, the characteristics of which are given in (Table 3).

The selected software designs the experiments, the model obtained is shown by Equation 4, and the diagram of the effect of the primary factor, the interaction of the factors, and

the response surface is drawn based on the ANOVA analysis of variance table. Design Expert software was used for modeling using the MLR method.

No	Time(min) A	Dye (mg/liter) B	Adsorbent(g/liter) C	
1	5	300	5	
2	5	399	1	
3	5	100	3	
4	60	300	1	
5	5	500	3	
6	32.5	500	1	
7	60	500	3	
8	32.5	100	5	
9	32.5	300	3	
10	60	100	3	
11	32.5	300	3	
12	32.5	500	5	
13	60	300	5	
14	32.5	300	3	
15	32.5	100	1	

Table3: Characteristics of dye solution and other components in experiments.

The equation obtained from fitting the response surface for the parameter R is as Equation 6.

 $R = 87/61 + 10.32A - 3.99B + 18.32C - 0.61AB - 0.90AC + 5.33C - 6.51A^{2} - 1.84B2 - 9.22C^{2}$ (6)

Statistical evaluation (equation 6) was performed by performing F test, which is a measure of the deviation of the data from the mean, and ANOVA analysis of variance of the quadratic response surface model. The ANOVA data confirms the accuracy of this model. The F value (equal to 73) is very high for this model, indicating that the model

predicted the test results well. The numerical value of P is also less than 0.05, indicating the significance of this model. In this model, the parameters BC, C2, A2, C, B and A are indicators.

Also, the equation obtained from fitting the response surface for the parameter q is in the form of equation7. ipt

q=101.63+16.48A+65.67B-50.71C+10.23AB-15.44AC-23.94BC-3.80A²-

 $13.44B^2 + 23.17C^2$ (7)

In this model, P is less than (P<0.0001) and F is equal to 56.45. Parameters C^2 and BC, AC, C, B, are effective in this model. Statistical evaluation (equation 6) of was done by performing F test and ANOVA analysis of variance of the quadratic response surface model and its results are given in Table 4. ANOVA data confirms the accuracy of this quadratic model. The F parameter is a measure of the deviation of the data from the mean. For a model that successfully predicts the test results, a very high F and P less than 0.05 indicate the significance of the model. The of R^2 adj and R^2 pred values are 0.9786 and 0.9333 respectively, which are in agreement and indicate good accuracy of the model used.

Parameter F Value P Value Model 72.07 0.0001< А 103.90 0.0002 В 42.11 0.0013 С 389.41 0.0001< AB 0.33 0.5929 AC 0.42 0.5464 BC 24.98 0.0041

Table4: P and F response values obtained from surface response analysis for response %R

A ²	20.00	0.0066
B ²	4.25	0.0942
C ²	40.01	0.0015

Table5: P and F response values obtained from surface response analysis for response q

Parameter	F Value	P Value	
Model	56.50	<0,0001	
A	16.00	0/0002	
В	258.44	0,0102	
С	153.39	<0,0001	
AB	3.2	01,0001	
AC	7.16	0/1339	
BC	17.52	0.0450	
A2	0/40	0/0088	
B2	4.64	1/0839	
C2	15.99	0/0119	

Based on the results obtained by increasing the contact time of the adsorbent with the dye, the removal percentage increases and after 45 minutes, due to the filling of the empty places of the adsorbent, the trend becomes constant. On the other hand, the increase in the removal percentage with increasing the amount of adsorbent can be justified in accordance with the increase in the active sites of the adsorbent.

Also, in investigating the effect of the amount of enzymatic adsorbent, different amounts of organometallic enzyme adsorbent were used under the condition of initial dye concentration of 10 mg/L. The highest removal of dye was with the amount of 5 g/L of the adsorbent and after 45 minutes, with increasing the amount of adsorbent, the removal percentage remained constant.(Figure 8)

Figure 8: Effect curve of adsorbent amount and time on adsorption capacity.

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Also, with increasing solution concentration, the percentage of removal decreases. This decrease in adsorption can be explained by the fact that with increasing solution concentration, the ratio of the adsorbent's empty sites to the amount of dye decreases and a lower percentage can be absorbed. The relationship between the initial concentration and the removal of the dye substance is correlated. The effect of the removal amount was related to the initial concentration of the dye substance, the number of enzyme sites on the adsorbent surface, and with increasing dye substance concentration, the removal amount increased. With increasing the contact time of the adsorbent and dye. Also, with increasing the concentration of the solution, the removal percentage decreased. [1]

3.3. Adsorption Kinetics

Adsorption kinetics study was conducted to investigate the effect of contact time and obtain parameters derived from adsorption kinetics. The adsorption kinetics results were investigated using three kinetic models: pseudo first order, pseudo second order, and alovich.

The pseudo first order equation form is equation 8, 9:

(dqt/dt) = K1(qe-qt) (8)

 $\log(qe-qt) = \log(qe) - (K1/2.303) * t$ (9)

In equation (9), qt and qe are the adsorption capacity at time t and at equilibrium point in mg/g, respectively. K1 is the rate constant of the pseudo-first-order equation. The linear form of the pseudo-first-order kinetic is given by equation 9. The values of K1 and qe can be calculated using the slope and the width from the origin of the plot of log(qe-qt) versus t.

The pseudo second order equation form is equation 10, 11. In equation 10, K2 is the rate constant of the pseudo-second-order equation and in equation 11. where K and qe can be calculated using the width from the origin and the slope of the t/qt versus t graph..

$$(d(q)t/dt) = K2 (qe-qt) (10)$$

$$(t/q1) = (1/Kq^2) + (1/qe)*t$$
 (11)

The equation of the alovich model is as Equation 12, 13:

$$dqt/dt = \alpha \exp(-bqt)$$
 (12)

$$qt = \left(\frac{1}{b}\right) \ln(\alpha\beta) + \left(\frac{1}{b}\right) \ln(t)$$
 (13)

In equation (12), qt is the amount of substance adsorbed by the adsorbent at t, α is the initial rate of adsorption and represents the rate of chemical adsorption at zero coverage. b is the desorption constant and is related to the amount of surface coverage and the activation energy. The simplified form of the alovich equation is in Mathematical relationship 13. The values of 1/b ln($\alpha\beta$) and 1/b in this equation are the width from the origin and the slope of the qt graph in terms of ln(t).

3.4. Adsorption Isotherm

The adsorption isotherm was investigated using the Freundlich and Langmuir equations.

The Freundlich isotherm is given as Equation 14, 15

$$\log qe = \log kf + (1/n) \log Ce$$
 (14)

$$qe = ((QmKaCe)/(1+KaCe))$$
(15)

In 14 relation, kf is the Freundlich constant and is related to the binding energy. 1/nf is the non-uniformity factor of the adsorbed system. In 15 relation, qe is the adsorption value at the equilibrium point, Qm is the maximum adsorption capacity, Ce is the dye concentration at the equilibrium point, and Ka is the absorption equilibrium constant. The Langmuir model is given in Equation 16, where the values (1/KaQm) and 1/Qm are the width from the origin and the slope of the Ce/qe versus Ce graph.

 $\frac{Ce}{qe} = \frac{1}{KaQm} + \frac{1}{Qm} \times Ce) ($ (16)

The results of the alovich kinetic for the adsorption of Diamin green B dye on the composite nanoadsorbent are shown in Figure 8.

Figure 8: Alovich adsorption kinetic of Diamin green B dye on nanoadsorbent

The quasi-first order kinetic model for the adsorption of Diamin green B dye onto the composite nanoadsorbent was shown in Figure 9.

Figure 9: Pseudo first order kinetic for the adsorption of Diamin green B dye on nanoadsorbent

The results of the pseudo second order kinetic for the adsorption of Diamin green B dye onto the composite nanoadsorbent were shown in Figure 10.

Figure 10: Pseudo second order kinetic for the adsorption of Diamin greene B dye on nanoadsorbent

The Freundlich adsorption isotherm for Diamin green B dye on the composite nanoadsorbent is shown in Figure 11.

Figure 11: Freundlich adsorption isotherm of Diamin green B dye on nanoadsorbent

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The Langmuir adsorption isotherm for the adsorption of Diamin green B dye on the composite nanoadsorbent is shown in Figure 12.

Figure 12: Langmuir adsorption isotherm of Diamin green B dye on nanoadsorbent

3.5 Adsorption Thermodynamic

In the thermodynamic studies of the absorption process, it is necessary to determine three factors, standard enthalpy ΔH° , standard free energy ΔG° , and standard entropy ΔS° . The values of ΔH° and ΔS° are obtained using relations 17 and 18. The standard enthalpy and entropy values can be calculated by plotting ln k versus T–1, with the slope and width being from the origin. The Gibbs free energy can also be calculated using equation 19.

$Ln kd = \Delta S^{\circ}/R - \Delta H^{\circ}/RT$	(17)
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Kd = qe/Ce(18)

 $\Delta G^{\circ} = -RT \ln kd \tag{19}$

R is the universal gas constant, T is the temperature (Kelvin), and kd is the equilibrium constant and the ratio of the amount of dyestuff adsorbed on the organometallic adsorbent to the amount of dyestuff remaining in the solution.

Sample	T (k)	∆H KJ/mol	∆S J/mol K	∆G KJ/mol
LC @Fe- BTC	288	11.4	50	-2.918
	298			-3.418
	303			-3.668
Fe-BTC	288	5.2	22	-1.04
	298			-1.26
	303			-3.668

 Table 6: Thermodynamic variables of dye adsorption on enzyme-containing and enzyme-free organometallic adsorbents

The calculated values of the thermodynamic variables of dye adsorption on the adsorbent in Table 6 show that ΔH° has positive values, indicating that the adsorption process is endothermic in nature, which is consistent with previous results based on the increase in the adsorption amount with increasing solution temperature. The positive values of ΔH° also indicate the formation of a strong chemical bond between the dye molecules and the adsorbent surface. It is also observed in Table 6 that another thermodynamic parameter, ΔS° , has positive values, indicating the affinity of the adsorbent for dye adsorption and its

efficiency increases with increasing temperature in the solid-liquid phase during the adsorption process. However, the negative values obtained for the free energy of gypsum, ΔG° , indicate that the dye adsorption reaction is spontaneous.

The increase in negative ΔG° values with increasing temperature from 288 to 303 K may be due to the dehydration effect of both adsorbent, which facilitated the reaction between them and ultimately made adsorption at higher temperatures desirable. The correlation coefficient (R^2) is 0.978 at all three temperatures. It is also observed that ln kd values increase with increasing temperature. This trend indicates a high tendency for the dye to dissolve at high temperatures. The increase in removal with increasing amount of adsorbent is due to the increase in the adsorbent surface and greater access to the adsorption and enzymatic decomposition sites because with increasing the active surface of the catalyst, the amount of bleaching also increases. The reason for this is the overlap of the adsorption sites on the adsorbent surface and enzymatic decomposition in the first phase and then this accumulation of powers leads to stability in the number of adsorption sites and consequently stability in the efficiency and amount of adsorption. With increasing adsorbent, free sites for adsorption increase, and all dye molecules are adsorbed to the enzyme active sites on the adsorbent surface, and further increase in adsorbent (with constant dye concentration) and further increase in free surfaces causes them to remain empty. For this reason, the adsorption percentage remains constant and the equilibrium adsorption capacity (qe) decreases. The results of this study are consistent with Mousavi et al. [9-16] study on the removal of azo orange 7 dye by single-layer carbon nanotube adsorbent and also the results of the study by Sheshmani et al [17-20]. On remoe of azo orange dye by chitosan adsorbent. In this study, with increasing contact

time, the adsorption efficiency of the dye increases, which is due to the number of collisions and the probability of more collisions between the dye and the adsorbent. These results are consistent with the achievements of Hamzeh et al. for the removal of azo orange 7 dye and the study by Gerlock and Hoby K. [21-24] for the removal of Reactive Black 5(RB5) dye. There is a very high correlation between the amount of dye removal and its initial concentration. The effect of the amount of dye removal on the initial concentration is related to the number of enzyme sites available on the adsorbent surface. As the dye concentration increases, the percentage of its removal from the medium decreases, which is due to the reduction of sites available for higher concentration in the enzyme activity of the adsorbent. Therefore, as the dye concentration increases in the efficiency of the process [25-30].

4. Conclusion

The results of the research show that the bio-modified metal organic nanostructure is an effective adsorbent in the adsorption of dyes due to its high surface area and enzymatic process, and the adsorption of dyes on this adsorbent is carried out with greater adsorption power and energy. Adsorption kinetics studies show a complete correlation of the adsorption reaction with the Allovich kinetics. The obtained results also show a good correlation between the isotherm Freundlich model, the adsorption of the tested dye onto the enzymatic organometallic adsorbent is spontaneous, endothermic and in the direction of increasing disorder.

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