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BIOSORPTION OF METHYELEN BLUE FROM AQUEOUS SOLUTION USING WASTES MICELIUM OF FUNGAL BIOMASS TYPE WHITE ROT FUNGI

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Abstract: A waste dried mycelium of fungal biomass type *white rot fungi* was used to remove methylene blue dye from aqueous solution in batch mode. The equilibrium isotherm and kinetics have been investigated. Several parameters such as pH, contact time, dye concentration and biosorbent dosage were evaluated to determine the adsorption capacity and analyze the suitability of biosorption process. The equilibrium of the process was modeled using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich(D-R) isotherms, while kinetic data were fitted by pseudo-first-order and pseudo-second-order kinetic models. Kinetic experiments indicated a better fit of process to a pseudo second order model, while the equilibrium isotherm data fitted well to Langmuir isotherm with maximum biosorption capacity of 23.69 mg/g and determination coefficient R^2 equal 0.9909 compared with other isotherm models. The values of heat of sorption b_T 0.6062 KJ/mol from Temkin model and mean free energy of sorption E 0.7847 KL/mol from D-R model indicated that the biosorption process was endothermic and physisorption in nature. The results show that dead biomass derived from waste of *white rot fungi* can be used as a good biosorbent material for removal of methylene blue from wastewater due to its low cost and high efficiency.

Keywords: *Biosorption, Methylene blue, White fungi, Kinetics, Isotherm models.*

الامتزاز الحيوي لصبغة المثلين الزرقاء في المحلول المائي باستخدام مخلفات جذور فطر العفن الابيض

الخلاصة: مخلفات جذور الفطر الجاف الحيوية نوع فطرالعفن الابيض تم استعمالها لازالة صبغة المثلين الزرقاء من المحلول المائي في اسلوب نظام الدفعات. تم بحث عملية الاتزان الحراري وديناميكية التفاعل . لقد تم تقييم عدة متغيرات مؤثرة على عملية الامتزاز الحيوي مثل الدالة الحامضية، وقت التلامس ، التركيز الابتدائي للصبغة في المحلول ومقدار الجرعة المستخدمة للمادة الحيوية المازة وذلك من اجل تحديد سعة الامتزاز وايجاد التحليل المناسب لعملية الامتزاز الحيوي.لقد تم تحديد عملية الاتزان باستخدام الموديلات التالية : لانكماير ، فريندليش، تومكن و دوبنن- رادوشكيفيج، بينما عمليات حركية التفاعل تمت باستخدام الموديلات من النوع: المرتبة الاولى الوهمي والمرتبة الثانية المزيف. لقد اثبتت تجارب حركية التفاعل على تطابق واضح مابين النتائج العملية وموديل المرتبة الثانية الوهمي بينما تجارب عمليات الاتزان كانت متطابقة مع موديل لانكاير حيث كانت اكبر سعة امتزاز تم الحصول عليها هي 23.69 mg/g و معامل تحديد مقداره 0.9909 مقارنة مع بقية الموديلات المستخدمة. لقد كانت قيمة المعامل الحراري b_T في موديل تومكن هو 0.6062 kj/mol ومتوسط الطاقة الحر E لعملية الامتزاز في موديل دوبنن- رادوشكيفيج هو 0.7847 kj/mol وهذا يدلل على ان عملية الامتزاز كانت طاردة للحرارة وان الامتزاز كان فيزياويا في طبيعته. لقد اظهرت النتائج العملية : بان المادة الحيوية الجافة المستخدمة من مخلفات جذور الفطرالعفن البيضاء بالامكان استخدامها بصورة فعالة كمادة امتزاز جيدة في عمليات ازالة صبغة المثلين الزرقاء من الماء الملوث وذلك بسبب كفاءتها العالية وقلة كلفتها

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1. Introduction

Dye pollutants are an important source of contaminates from industrial wastewater which causes extensive damage to the environment [1].

They pose serious environmental problems because of their color, low biochemical oxygen demand (BOD) and high chemical oxygen demand (COD) [2, 3]. Dyes are widely used in textiles, paper, wood, rayon, silk, plastics and rubber, leather, cosmetic, pharmaceutical and food industries [4], they are mostly non-biodegradable and resistant to destruction by conventional wastewater treatments [5].

The releasing of dyes to the environment can cause acute and/or chronic effects on the exposed organisms, adsorb or reflect sunlight entering into water, and thus result in change of food chain [6].

Several methods exist for reducing the color in industrial effluent streams such as adsorption, reduction or oxidation, ion exchange, biosorption, membrane filtration, reverse osmosis, electrochemical treatment, evaporation recovery, chemical precipitation, chemical lime coagulation and solvent extraction , among these methods, sorption processes appear to be preferable techniques [7].

Biosorption is a process that utilizes biological materials as adsorbents, this method has been studied by several researchers as an alternative technique to conventional methods for heavy metals and dyes removal from wastewater [8]. Waste materials from natural biological, agriculture and industry represent potentially more economical alternative bioadsorbents [9].

The major advantages of biosorption system for water pollution control are good removal performance, less investment in terms of initial cost, flexibility, simplicity of design, easiness of operation and insensitivity to toxic pollutants as compared with the conventional process treatment [10].

Methylene Blue (MB) is selected as the dye studied in order to evaluate the capacity of the biosorbent material for the removal of MB from its aqueous solution. Besides its significant usage in the manufacturing industry, MB has a significant function in the medical field and is used in large amounts.

Though MB is not extremely hazardous, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans [11].

Fungal systems appear to be most appropriate biological agent in the treatment of colored and metallic effluents [12, 13]. Important fungal biosorbents include Aspergillus[14], Penicilium[15] and rhizopus[16].

In this study, the use of locally fungal waste mycelium biomass type white rot fungi for removal methylene blue dye from industrial effluents was evaluated as low cost biosorbent dye removal technology to obtain better understanding of biosorption mechanisms, the kinetic and isotherm, also, the effect of various parameters such as pH, initial dye concentration, biosorbent dosage and contact time were analyzed on dye adsorbate capacity and removal efficiency.

2. Materials and Methods

2.1. *Biosorbent Preparation*

Waste mycelium of biomass type white rot fungi obtained from industrial farms at the end of harvested of mushroom. This type of mushroom was cultured locally at the north-west of Iraq, the waste of fungi was grounded, sieved to a particle size of 150-300 μm , washed several times by portable and distilled water for removing dust, dried for 48 h in an oven at 65 ^{o}C and stored in an air tight plastic bottle for further use. Table 1 shows the physical properties of waste of biomass mycelium of fungi type *white rot fungi*

Table 1. Properties of the dead mycelium of fungal biomass type white rot fungi

Particle size (mm)	0.15-0.3
Color	Light-Brown
Appearance	Granular or Powder
Solubility	Insoluble in Water
Durability	Excellent
Bulk density (kg/m^3)	525.6
Real density (kg/m^3)	1935.4
BET surface area (m^2/g)	3165
Bed porosity %	72.33
Particle porosity %	81.69
Ash content	Below 4

2.2. *Dye solution Preparation*

Methylene Blue ($C_{16}H_{18}ClN_3S.2HO$; molecular weight: 319.86) is cationic dye purchased from Fisher Scientific. The MB was chosen in this study because of its known strong adsorption onto solids [17]. The maximum adsorption wavelength of this dye is 661 nm. The structure of MB is shown in Fig.1.

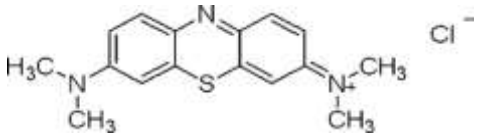

Figure 1. Chemical structure of Methylene Blue dye

Stock solution of methylene blue was prepared by dissolving 1.00 g of Methylene Blue powder in 1 L of distilled water to prepare the stock solution with concentration of 1000 mg/L. Solutions of different concentrations (10-100 mg/L) used in experiments were obtained diluting a stock solution of MB with distilled water to a desired concentration.

2.3. *Dye concentration Analysis*

Standard curves were developed through the measurement of absorbance of the dye solutions at maximum wavelength λ=661 nm by UV/Visible Spectrophotometer

(Shemadzu model UV-160A ultraviolet/visible spectrophotometer)

2.4 *Batch biosorption experiments*

Batch mode experiments were carried out to investigate the effects of various process parameters such as pH, biosorbent dose, contact time and initial concentration of solution on the biosorption of methylene blue by dead fungal biomass as biosorbent.

Each batch adsorption experiment was carried out in 50 mL of a known concentration of methylene blue with appropriate weights of waste dried biomass of white rot fungi as biosorbent in 250 mL stoppered conical flasks. The samples were placed in the shaker in a constant speed of 200 rpm at room temperature (25°C). After determined a contact time, then reached to equilibrium state, 1 ml of the supernatant was taken and analyzed using a UV-Vis spectrophotometer to determine the concentration of dye remaining in the sample at the maximum wavelength of the MB obtained at 661 nm. All experiments were duplicated and only the mean values are reported, the maximum deviation observed was less than $\pm$ 3%.

The amount of dye adsorbed per unit weight of fungi at equilibrium; q_e (mg /g) or at time t; q_t (mg/g) were calculated according to the following relations [18]:

$$q_e = (C_o - C_e) \times \frac{V}{m} \qquad (1)$$

$$q_t = (C_o - C_t) \times \frac{V}{m} \qquad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of dye (mg/L) respectively; C_t is the concentration of dye at any time t ; V is the volume of dye solution (L) ; and m is the amount of biosorbent used (g). To determine the percentage of dye removal, equation (3) is used:

$$\%Removal = \frac{C_o - C_e}{C_o} \times 100 \qquad (3)$$

For kinetic studies, all experiments were carried out at room temperature. The solutions were then subjected to magnetic stirrer for proper adsorption. Samples were withdrawn from the stirrer at different time intervals. Then the adsorbent was separated from the sample by using filter paper (0.42 µm). The absorbance was measured for supernatant solution using UV-Spectrophotometer. The final concentration of dye was estimated with the help of these absorbance data.

For determining the uptake of the dye, all sets of experiments were performed at different parameters such as time intervals (5, 10, 20, 30, 60, 90, 120, 150, and 180 minutes) and pH (2, 3, 4, 5, 6, 7, 8, 9, 11, and 12). A range from 0.1g to 2.0 g of adsorbent dose was also used to perform these experiments.

3. Results and Discussion

3.1. *Effect of pH*

The pH of the aqueous solution is an important parameter in the adsorption of dyes on biosorbents [19]. The effect of pH on the sorption removal of methylene blue dye

from wastewater using waste fungal biomass type white rot was investigated over the range from 2.0 to 12.0 (Fig. 2).

From this figure, it is clear that the adsorption capacity increases from 13 to 15.2 with increase in pH from 2 to 6, and then remains approximately constant with increase in further pH of the solution.

The influence of pH on the adsorption of methylene blue can be explained on the basis that the surface of the biosorbent is positively charged at the lower values of pH and the amount of MB ions sorbed increased with the increase in the pH value.

At lower values of pH, the presence of a higher concentration of H^+ ions from acidic solution will be competing with the MB ions for the sorption sites.

The uptake continuously increases with the increase in pH value since the surface of the adsorbent becomes negatively charged and there exists a strong electrostatic attraction of dye cations with the adsorbent leading to the increased in adsorption process. The highest uptake was observed at pH range from 5.5 to 7.5. In work were carried out at initial pH value of 6.0.

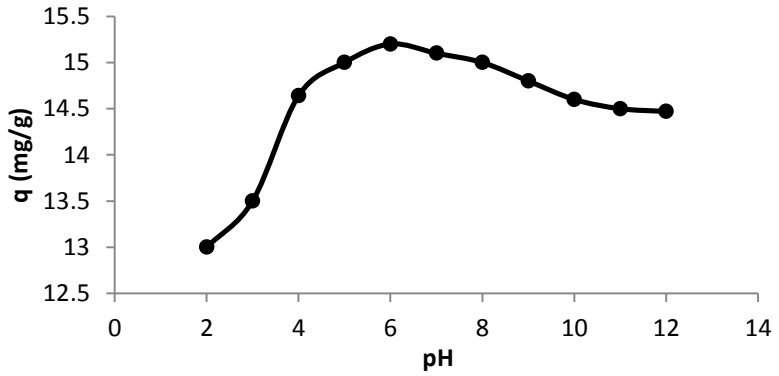

Figure 2. Effect of initial pH of the solution on the biosorption of MB at 25°C [I.C.=50mg/L, biosorbent dose= 0.3 g, agitation speed =200 rpm, contact time=180 min]

3.2. *Effect of Adsorbent Dosage*

The effect of dead mycelium fungal biomass type white rot fungi on the adsorption of methylene blue was studied using dye concentration of 50 mg/L, by varying the biosorbent dosage in the range 0.01 to 1.0 g/100ml. From Fig. 3, it is clear that the dye removal increases from 7 to 82.5% with increase in adsorbent dose from 0.01 to 0.25 g/100 ml of dye solution.

The reason for the increased adsorption may be attributed to greater surface area and large number of active sites. It was observed that the optimum dye removal of methylene blue (15.33 mg/g (92%)) took place at a dosage of 0.3 g.

The result is agreement with that obtained from [20, 21], they study the effect of the dose on biosorption of MB and found a higher biosorption when dose is increased.

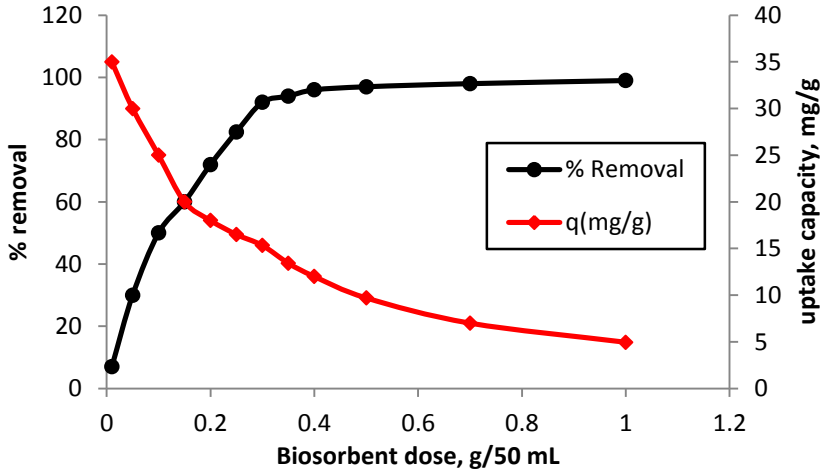

Figure 3. Effect of waste fungi biomass type white rot on the (a) biosorption capacity and (b) percentage removal of MB at 25°C [C_o=50mg/L, pH=6.0, biosorbent dose= 0.3 g, agitation speed =200 rpm, contact time=90 min]

3.3. *Effect of Initial Dye Concentration and Contact Time*

The effect of initial ion concentration was performed at initial concentrations of 25,50, 75 and 100 mg/L at 25°C for the biosorption of methylene blue ions onto dead fungal biomass 0.3 g/50 mL at pH=6.0 using different contact time as shown in Fig.4. The adsorption increases from 7.92 to 23.1 mg/g with increase in initial methylene blue concentration from 25 to 100 mg/L .

This is due to the fact that with increase in initial concentration of MB, presence of MB at the biosorbent interface also increases, then increases the amount of biosorption. This happened due to higher probability of collision be each investigated ion and the biosorbent particles [22]. The biosorption process will be reached to the saturated limit when the active sites in the surface of biosorbent are fully covered.

Also, the amount of methylene blue ion removed sharply increases with time in the initial stage (0-60 min range), and then gradually increases to reach an equilibrium value in approximately 80-100 min.

This mechanism happened due to presence of large number of vacant surface sites for biosorption during initial stage, while when reached to equilibrium stage, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between solute molecules on solid and bulk phases [23].

The equilibrium time required for the maximum removal of methylene blue by dead fungal biomass was 90 min for all experiments.

The percent MB removal at equilibrium time was found to be 96% and 70% for the MB concentrations of 25 and 100 mg/L respectively. Consequently, the extent of methylene blue ion uptake decreases significantly with increase of contact time, depending on the decrease in the number of vacant sites on the surface of biosorbent material as shown in Fig. 5.

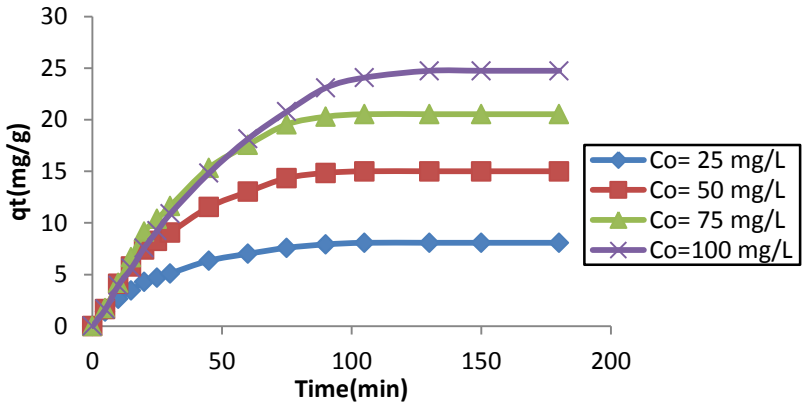

Figure 4. Effect of initial concentration of solution on uptake capacity of MB ions using fungal dead biomass type white rot at 25°C

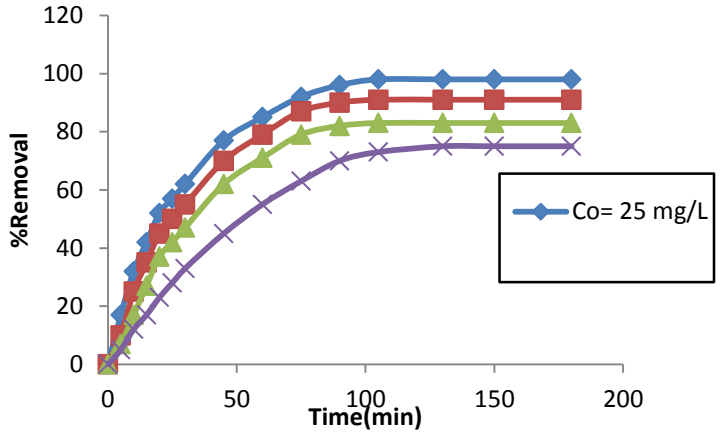

Figure 5. Effect of initial concentration of solution on percentage removal of MB ions using fungal dead biomass type white rot at 25°C

3.4. *Biosorption Isotherm*

Analysis of adsorption isotherms described the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the biosorbent's surface at a certain condition, named an isotherm. Many adsorption isotherm models are used to describe equilibrium data, but in the present study, Langmuir, Freundlich, Temkin and Dubnin-Radushkevich isotherm model (D-R) models were chosen to describe the relationship between the amount of MB adsorbed on dead waste fungal biomass and its equilibrium concentration.

The equilibrium data was obtained by varying the solute concentration while the biosorbent dose was kept constant under optimized operating conditions. The applicability of the isotherm models was determined by knowing the value of correlation coefficient R^2.

3.4.1. *Langmuir isotherm model*

The Langmuir adsorption isotherm is based on the assumption, that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent

surface with no later interactions between sorbed molecules. The model takes the following relations [24]:

$$q_e = \frac{q_m b C_e}{1+bC_e} \quad (4)$$

Increasing above equation gives:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (5)$$

where b is the equilibrium constant in (L/mg) and q_m is maximum adsorption capacity when the surface is completely covered with dye molecules in (mg/g). Data obtained from experimental work for the sorption of MB dye in the concentration range 10 to 100 mg/L are fitted to the Langmuir isotherm (Fig. 6) [24]. A plot of C_e/q_e versus C_e gave a straight line, the slope and the intercept of which corresponding to q_m and b respectively as shown in Fig.7, confirming that this expression is indeed a reasonable representation of chemisorption isotherm. Table 2 shows the numerical values of constants q_m and b, where the value of b is 0.33689 L/mg and q_m is 23.69 mg/g with regression coefficient (R^2=0.9909). The linear plots show that the adsorption obeys Langmuir isotherm and indicates the monolayer coverage of methylene blue molecules at the outer surface of dead fungal biomass.

The Langmuir model can express by dimensionless constant called equilibrium parameters R_L [25]:

$$R_L = \frac{1}{1+bC_o} \quad (6)$$

where, Co is the highest initial MB dye ion concentration in (mg/L). The value of R_L indicates the type of isotherm. As shown from the values of R_L appeared in Table 2. All the values of R_L were found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of dye ions [25].

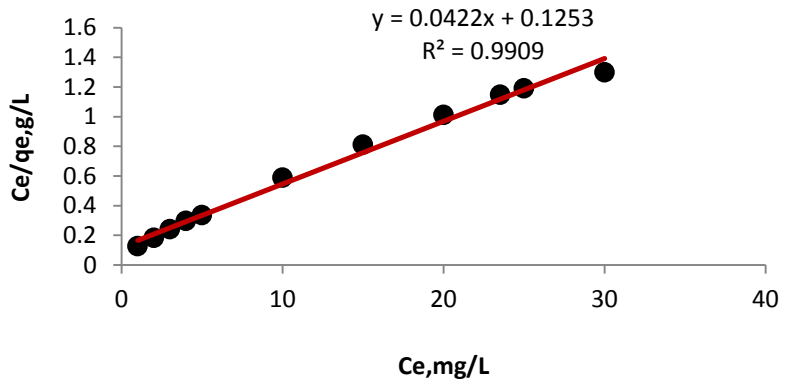

Figure 6. Langmuir isotherm plots for the sorption of MB dye onto waste fungal at 25°C

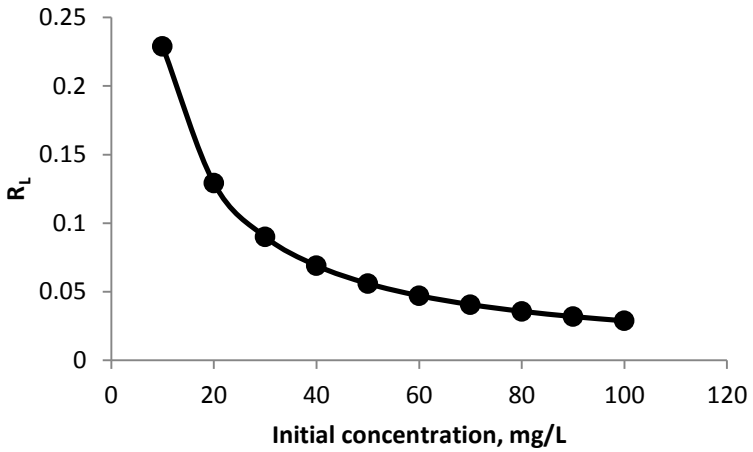

Figure 7. Equilibrium constant versus methylene blue initial concentrations

3.4.2. *Freundlich isotherm model*

Freundlch equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces, .the concept of equation is: if the concentration of solute in the solution at equilibrium C_e was raised to the power n , the amount of solute adsorbed being q_e, then C_e^n/q_e was a constant at a given temperature[24,25].

$$q_e = k_f {C_e}^n \qquad (7)$$

The Freundlich equation can be written in logarithmic form as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (8)$$

where K_f is constant indicator of the relative sorption capacity of dead fungal biomass (mg/g) and *1/n* is the constant indicator of the intensity of the sorption process. A plot of log q_e gives a slope of *1/n* and intercept of log k_f.

The results of this application in present experiment were present in Fig.8 and given in Table 2. It can be seen from these data that the Freundlich intensity constant *(n)* are greater than unity.

This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between methylene blue ions and dead fungal biomass [26]. (1/n) is the slope of the line, its value is 0.2786 < 1. This is favorable biosorption. A regression coefficient (R^2= 0.977) is obtained with the Freundlich isotherm.

The values of k_f and n are 8.8189 mg/g and 3.589 respectively (n is between 1 and 10, the adsorption is favorable). In general, results indicate that the biosorption of methylene blue by dead fungal biomass type *white rot fungi* depends on Langmuir isotherm.

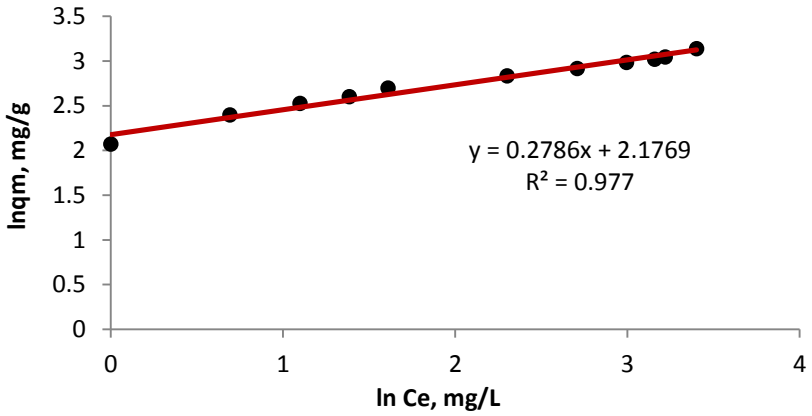

Figure 8. Freundlich isotherm plots for the sorption of MB dye onto waste fungal at 25°C

3.4.3 *Temkin isotherm model*

Temkin isotherm model was used to determine the heat of adsorption and the interactions between adsorbate and the adsorbent on the adsorption process.

It is based on the assumption that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbent interactions according to the following linear forms [27]:

$$q_e = \frac{RT}{b_T}(\ln A + \ln C_e) \qquad (9)$$

$$q_e = B \ln A + B \ln C_e \qquad (10)$$

where $\frac{RT}{b_T}$=B, R is the universal gas constant (8.314 J/mol.K) and T is the absolute temperature (K). Here, B will represent the heat of adsorption, while A represents Temkin equilibrium binding constant ((L/g)), b_T(J/mol) is related to the heat of sorption [28]

By plotting q_e versus $ln\, C_e$, linear plots can be found and the values of A and B can be estimated from the intercept and the slope of the line as shown in Fig.9.

The values of parameters are listed in Table 2.The linear correlation coefficient (R^2) is
0.9893, that is mean, the distribution of binding energy arise is uniform due to the interaction of dye molecules.

The parameter b_T was determined as 0.6062 Kj/mol this value is less than 8, that means the interaction between methylene blue dye and dead white rot fungi is weak, indicating that the process is physicosorption [29],

also the value of A is 6.988 L/g, so the variation of energy was very low and positive showing that the adsorption process was physicosorption and endothermic in nature [30].

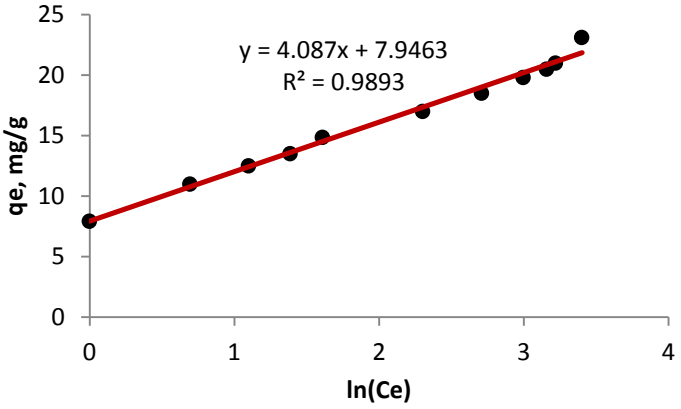

Figure 9. Temkin isotherm plots for the sorption of MB dye onto waste fungal at 25°C

3.4.4. *Dubnin-Radushkevich isotherm model (D-R)*

D-R adsorption isotherm model is used to characterize the nature of sorption processes, it is based on the assumption that there is no homogeneous surface or constant biosorption potential and may distinguish between physical and chemical adsorption. The general form of D-R equation is [31]:

$$q_e = q_m \exp(-\beta\varepsilon^2) \qquad (11)$$

the linear form is:

$$lnq_e = lnq_m - \beta\varepsilon^2 \qquad (12)$$

where:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (13)$$

where q_e *is* the amount of MB dye ions biosorbed per unit mass of biosorbent (mg/g), q_m is the maximum biosorption capacity (mg/g), β is the isotherm constant related to sorption energy (mol^2/K J^2), ε is the Polanyi potential represents the work required to remove a molecule from its location, R is the gas constant (8.314 *10 $^{-3}$KJ/mol K), T is the absolute temperature (K). The mean free energy of sorption E (KJ/mol) is calculated in order to give more information about the nature of biosorption process as physisorption or chemisorption; it is calculated from constant β as [31]:

$$E = (-2\beta)^{-0.5} \qquad (14)$$

When the value of E lies between 1 and 8 KJ/mol the adsorption process would be physisorption, while when $E > 8$ KJ/mol the process would be chemisorption. The linear plot of the D-R isotherm was shown in Fig.10. Where plotting ln q_e versus ε^2 gives β as gradient and q_m as the intercept. The parameters q_m, β, R^2 and E are presented in Table 2.The correlation factor R^2 of 0.7606 pointed to the fitness of the isotherm model in describing the equilibrium data. The maximum sorption capacity q_m is (18.145

mg/g and the value of *E* calculated is 0.7847 KJ/mol, the sign and magnitude of *E* indicated that the sorption process endothermic and physisorption mechanism in nature.

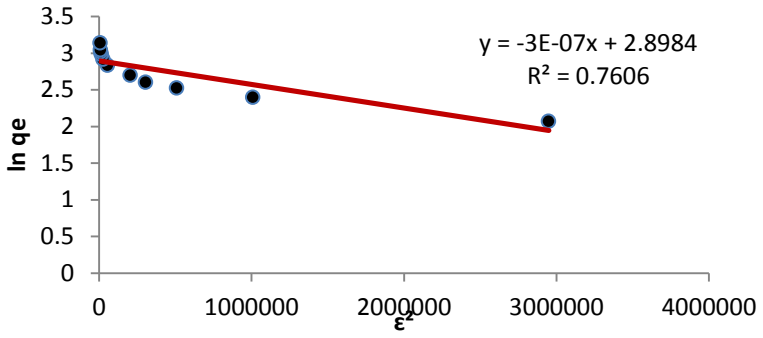

Figure 10. D-R isotherm plots for the sorption of MB dye onto waste fungal at 25°C

Table 2. Isotherm parameters for methylene blue ions adsorbed onto waste of biomass type white rot fungi with correlation coefficient

Model	Parameters	Values
Langmuir (Eq.5)	q_m(mg/g)	23.69
	b(1/mg)	0.3368
	R_L	0.0319
	R^2	0.9909
Freundlich (Eq.8)	K_f(mg/g)(1/mg)$^{1/n}$	8.8189
	n	3.5893
	R^2	0.9770
Temkin (Eq.10)	A(L/g)	6.988
	B	4.087
	b_T(kJ/mol)	0.6062
	R^2	0.9893
Dubinin-Radushkeich (Eq.12)	k_{ad}	-3.00E-07
	β (mol²kJ⁻²)	0.8119
	q_m(mg/g)	18.145
	E(KJ/mol)	0.7847
	R^2	0.7606

Figure 11 below, shows the comparisons of uptake capacity of methylene blue between experimental data and that obtained from using Langmuir and Freundlich models.

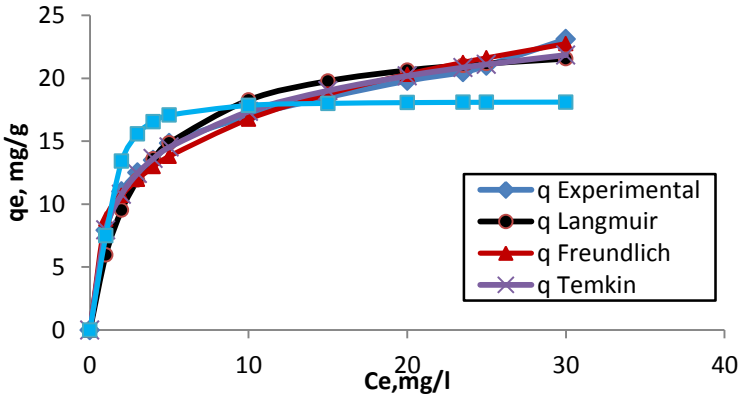

Figure 11. Comparison between the measured and modeled isotherm curves for biosorption of MB ions onto dead fungal biomass type white fungi at 25°C, [I.C.=50mg/L, pH=6.0, biosorbent dose= 0.3 g, agitation speed =200 rpm, contact time=90 min]

3.5. *Biosorption Kinetics*

Important information can be obtained for designing batch adsorption systems when knowing the adsorption rate. This information about kinetics of solute removal is required for selecting the optimum operating conditions for full-scale batch process. Kinetic studies are necessary to determine the equilibrium time of adsorption and for scale up of adsorption systems. Two mechanisms controlled dye adsorption were taken into account on dye adsorption systems called external diffusion and internal diffusion. In our experiments, two kinetic models were used to analyze the kinetics of the adsorption data, pseudo-first-order and pseudo-second-order, which important in predicting the reactor volume [31].

3.5.1. *Pseudo-first-order kinetic model*

Contact time process, the pseudo-first –order kinetic equation is written [31, 32]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (15)$$

where qe and q_t are the amount of dye adsorbed (mg/g) at equilibrium and given time t respectively. K_1 is the rate constant of adsorption (1/min).
By integration and taking the boundary conditions: at t=0 $(q_e - q_t) = 0$

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad (16)$$

By plotting ln(q_e-q_t) vs. t , gives a straight line containing the intercept of ln q_e and slope of (-k_1 t). Value of q_e can be calculated and then compared with that obtained from experimental work. Figure 12 showed the plot of linearized form of pseudo first order kinetic model at several concentrations of dye studied (25, 50, 75 and 100 mg/L). From this figure, we determined the values of k_1 and $q_{e,\,cal.}$. The calculated rate constants, experimental and predicted q_e with corresponding correlation coefficient values are presented in Table 3. From Figure 12, the plots are expected to yield straight lines if this model is applicable. Since straight lines are not obtained, the values of slopes are negative and R^2 values vary from 0.9852 to 0.9584, it has been concluded that this model is not applicable. According to values of slope and $R^{2,}$ this model is not useful to explain the kinetics of sorption of methylene blue ions.

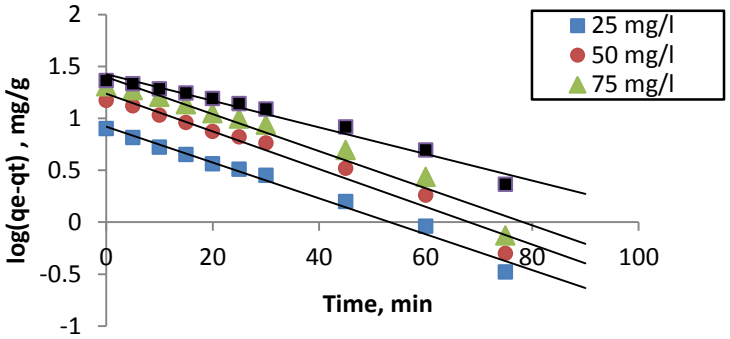

Figure 12. Pseudo first-order kinetic plots for sorption of MB dye onto waste fungal biomass at different initial dye concentrations, pH=6, adsorbent dose=0.3 g, temperature=25°C

3.5.2. *Pseudo-second-order kinetic model*

This model was found by Ho and McKay; it is based on solid phase adsorption and external diffusion. It was expressed as [31, 33]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (17)$$

where k_2 is the pseudo second order rate constant (min. g/mg). The linear form is:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \qquad (18)$$

The kinetic data were analyzed using above equation. The values of the k_2 and q_e presented were determined from the intercept and slope of the plot t/q_t vs. t and the corresponding R^2 values are given in Table 3.
K_2 can be used to compute the initial adsorption rate named *h*.

$$\text{at } t \to 0 \qquad h = k_2(q_e)^2 \qquad (19)$$

The initial sorption rate increased with an increase in initial dye concentration.

Figure 13 showed the plots of linearized form of pseudo second order kinetic model at several concentrations of dye studied.

The plots of t/q_t vs. t yield straight lines indicating that the process follows the pseudo second order kinetics.

From Table 3, the decrease in the values of k_2 for various initial concentrations is quite significant.

The values of equilibrium sorption capacity obtained from plot were vary from the experimental values, indicating non ideal adsorption and that removal of the dye involved number of processes such as adsorption, ion exchange etc.[34], the correlation coefficients R^2 of determination as obtained from the plots were found to be very closely to unity for all initial dye concentrations.

Although the correlation coefficients ($R^{2)}$ at 298 k for the pseudo first order model are quite high (> 0.958) , the R^2 for pseudo second model is greater than that of pseudo first order (> 0.997), the calculated $q_{e,cal}$ value is less accurate than that of the pseudo-second order model, so , the calculated value of sorption capacity q_e($q_{e,cal}$)obtained in the pseudo second-order model perfectly agrees with the experimental values of q_e ($q_{e,\ exp.}$), i.e. straight lines obtained from pseudo second-order kinetic plots suggest the applicability of the pseudo second order kinetic model to fit the experimental data over the all stages of the sorption process compared with pseudo first order kinetic model[35].

These results explain that the pseudo second –order sorption mechanism is predominant. The results show that the rate-limiting step may be the adsorption mechanism.

Table 3. Kinetic parameters for biosorption of methylene blue ions onto fungal dead biomass type white rot fungi at 25°C

		First-order kinetic parameters			Second-order kinetic parameters			
Initial Conc.(mg/L)	$q_{e,exp}$ (mg/g)	K_1 (min^{-1})	$q_{e,cal}$(mg/g)	R^2	K_2(min g/mg)*10^3	$q_{c,cal}$(mg/g)	h(min g/mg)	R^2
25	7.92	0.0398	8.3004	0.9852	6.7407	7.0821	0.3380	0.9988
50	14.85	0.0419	17.3320	0.9647	2.6372	14.2247	0.5336	0.9984
75	20.29	0.0412	25.0553	0.9584	1.3775	20.2021	0.5621	0.9990
100	23.10	0.0294	26.6993	0.9725	0.80402	23.2011	0.4328	0.9924

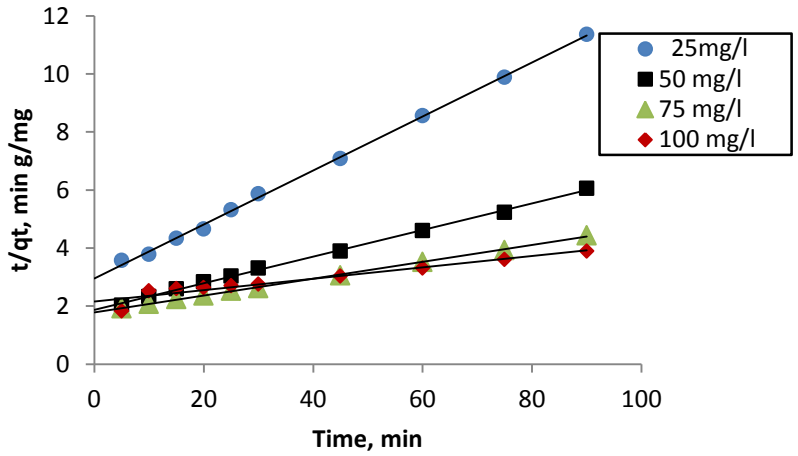

Figure 13. Pseudo second-order kinetic plots for sorption of MB dye onto waste fungal biomass at different initial dye concentrations, pH=6, adsorbent dose=0.3 g, temperature=25°C

4. Conclusions

Results and analysis obtained from this study show that waste mycelium biomass derived from white rot fungi can be used as a success biosorbent for removal of methylene blue from aqueous solutions by an adsorption technique. The amount of MB adsorbed on waste of fungi depends on the initial dye concentration, contact time, adsorbent dose, pH of solution and increases with an increase of these parameters. Where the results show that the best conditions for the uptake of methylene blue are at 50 mg/L, 90 min, pH 6 and 0.3 g adsorbent dose which was conducted on 150 -300 micron size of waste of fungi.

Methylene blue biosorption onto waste of white rot fungi followed the Langmuir isotherm model for all samples studied indicating a monolayer adsorption on a homogeneous surface. The maximum monolayer adsorption capacity is 23.69 mg/g. The values of b_T 0.6062 KJ/mol from Temkin model and mean free energy of sorption E 0.7847 KL/mol from D-R model indicated that the biosorption process was endothermic and physisorption in nature.

Kinetics studies indicated that a pseudo-second order model described the adsorption process well. It's revealed that initially the adsorption process of MB onto waste of fungi followed bulk diffusion and then shifted to intra-particle diffusion. Waste biomass derived from white rot fungi can be used as an alternative low cost adsorbent of dyes from industrial wastewater discharged from dying units. Its cheaply available, friendly environment material and its possible to design and optimize an economical treatment process for the dye removal from industrial effluents.

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