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Adsorptive Removal of Methylene Blue by Biomass of *Aspergillus versicolor*: A Mechanistic Study.

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A B S T R A C T

Biosorption is a biocompatible and environment friendly approach for removal of synthetic dyes from industrial effluent. In the present study, dried biomass of *Aspergillus versicolor* was used as an adsorbent for the removal of basic dye Methylene Blue (MB) from its aqueous solution. The optimum pH and temperature for adsorption was found to be 7.0 and 28° C respectively. Scanning electron microscopy (SEM) of the biomass suggested changes in surface topology following MB adsorption, while FTIR studies indicated chemical interaction between the surfaces of the biomass with MB. Kinetics study suggested the adsorption rate was fast initially and reached equilibrium at 4 h following a pseudo-second-order-kinetics. The adsorption isotherm follows Freundlich isotherm model. Our data suggests the dried biomass of *A. versicolor* can be used as a potent bio-compatible adsorbent for the removal of MB.

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Introduction:

Economic and industrial growths are part of human modernization that witnesses sharp increase in the production of effluents [1]. Effluents from industries e.g. textile, paper, dyeing and coloring, pharmaceutical and food contains synthetic dyes. Over 10,000 commercially available dyes are available; with production of over 7×10^5 metric tonnes annually [2, 3]. In a typical dyeing and finishing mill, about 100 liters of water is consumed on an average for each ton of clothes processed [4, 5]. Most of the synthetic dyes possess complex aromatic structure that render them non-biodegradable, stable against oxidation and photodegradation [6]. Presence of dyes leads to increased toxicity of the effluent. The wastewaters that are discharged into natural streams cause grave environmental impact such as reduced sunlight penetration, affecting aquatic life and photosynthesis [7, 8]. Moreover, some of these dyes are carcinogenic and teratogenic [3, 9]. Therefore, effluent treatment for removal of these dyes before disposal in nature is critical.

Adsorption, a surface phenomenon by which a multi-component mixture is attracted to the surface of a solid adsorbent and forms chemical or physical attachments, has been used successfully for removal of dyes from aqueous solution [10]. Till date several adsorbents have been reported for removal of both acidic and basic dyes. Chitosan bead based dye removal is efficient [11]. But it involves high production cost as crude chitin is treated with 40-50% sodium hydroxide in the temperature range of 110-115° C to obtain usable chitosan. Activated carbon based dye adsorption is effective; but it involves high cost, produces additional effluent, and results in considerable loss of the adsorbent. This process is expensive and impractical for use in industrial scale, especially for developing nations as India [12-16]. This has led researchers to search for cheaper, economically viable and efficient alternative materials. This includes fungal biosorbents such as *Mucor rouxii*, *Rhyzopus oryzae*, *Penicillium ochrochloron*, *Aspergillus viridie*, *Pleurotus sajor-caju*, *Termetomysces clypeatus* and *Candida utilis* [17]. Other biomaterials utilized for dye removal are palm ash, chitosan composite, salt-treated beech sawdust,

wheat shells and rice husk [18-23]. Biosoerbents, adsorbents of biological origin have advantage of possible biodegradtion. Methylene blue (MB), a cationic dye used extensively in dyeing and printing industries, on inhalation, may cause diseases of digestive and respiratory systems e.g. diarrhea, nausea, vomiting, gastritis or rapid breathing. Ingestion of MB may lead to trachycardia, a condition with unusual heart rate. So, a suitable biosorbent for MB adsorption for its removal is much needed [3]. In this work, we used dried biomass of the fungus *Aspergillus versicolor* as an adsorbent to remove MB from aqueous solution and studied the physicochemical characteristics of adsorbent, adsroption kinetics and isotherm.

Materials and Methods:

Materials:

Methylene Blue (MB) (C.I. 52015) was purchased from Sigma-Aldrich, Co., USA. The absorption maximum of this dye is 668 nm as validated by the spectrophotometric scan from 200-800 nm (not shown). Microbiological media (Potato Dextrose Broth) and ingredients (agar) were procured from Himedia, India.

The fungus *Aspergillus versicolor* (MTCC 280) was kindly provided by Dr. L. G. Roy, Jadavpur University, Kolkata, India. The strain was maintained on Potato Dextrose Agar (PDA) slants. Organisms were sub cultured at intervals of 15-20 days to secure viability.

Preparation of biosorbents:

Potato Dextrose Broth was used for the cultivation of *Aspergillus versicolor*. The media was distributed in aliquots of 50 ml in 250 ml Erlenmeyer flasks and sterilized. The media were inoculated with ~10^6 spores of *A. versicolor* and incubated under rotation (130 r.p.m.) at 28° C for 72 h. The biomass of *A.versicolor* was harvested by filtration using a vacuum pump and washed with de-ionized water. The biomasses were either air or oven dried and grounded.

Optimization of biomass, pH and temperature on biosorption:

For optimization of the amount of biomass required for adsorption, harvested fungus was subjected to two methods of drying: air drying and oven drying at 60° C. Increasing amounts of the dried samples (at 4, 8 and 12 g/L of dye solution), were used for adsorption of the dye from a 25 ml solution of MB (50mg/L) in a 50ml Erlenmeyer flask. After 24 h of incubation, the control and test solutions were filtered to get rid of the spent fungal biomass and optical density of the filtrate was taken at 668 nm in a UV-Vis Spectrophotometer (Multiskan GO, Thermo Scientific).

For pH studies, *A. versicolor* biomass was incubated for 2 h with continuous shaking in buffer solutions of required pH (4.0 to 10.0) under optimal conditions. This experiment was repeated by varying incubation temperature of 28, 37 and 50° C, with pH remaining constant throughout at pH 7.0 to study the effect of temperature on biosorption.

Physico-chemical characterization of the adsorbent:

The biosorbents were subjected to scanning electron microscopy (SEM) analysis to study the changes in surface topology before and after adsorption of dye (JEOL JSM-6390LV, Tokyo, Japan). Fourier Transform Infrared (FTIR) analysis was done for determining the changes in surface exposed functional groups (spectra recorded from 4000-400 cm^{-1}) (Perkin Elmer 1000 FT-IR). Energy Dispersive X-ray spectroscopic (EDX) analysis was done to study the changes in the elemental composition of the samples respectively using the instrument JEOL-JSM 6390, Japan.

Adsorption kinetics and isotherm study:

The rate of MB adsorption was observed at particular intervals of time ranging from 15-480 minutes, using different concentration of dye (10, 20, 30, 40 and 50 mg/L) at pH of 7.0 and temperature of 28° C. Kinetic studies of adsorption was undertaken at various concentrations of MB wherein the extent of adsorption was investigated as a function of time. q_t (mg/g), depicting the amount of adsorption at time 't' was calculated by the equation,

$$q_t = \frac{(C_0 - C_t)V}{W}$$

where C_0 and C_t (mg/L) denote the liquid phase concentrations of the dye at initial and at time 't' respectively. V is the volume of the solution and W is the mass of the dry biosorbent used.

The isotherms were calculated based on the kinetics results. The q_e (mg/g), depicting the amount of adsorption at equilibrium, was calculated by,

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where, C_e (mg/L) denote the liquid phase concentration of the dye at equilibrium.

Results and discussion:

Biosorbent characterization:

SEM micrographs provide a visual imprint of the changes that have occurred in the surface topology after adsorption of dye [6, 24]. The SEM micrograph of the *A. versicolor* biomass after MB adsorption exhibited significant changes in surface topology (Figure 1A). The lattice-like structure found in the pristine biomass was covered partially by the dye molecules attributing to the heterogeneous compactness of the structure. The heterogeneous compactness of the biomass surface indicates a non-uniform adsorption process. Similar changes in surface topology were reported for adsorption of Rhodamine B by *Rhizopus oryzae* or MB by coconut bunch waste [13, 18].

FTIR spectral changes can significantly imply adsorption process [24, 25]. Figure 1B shows the FTIR spectra of *A. versicolor* before (a) and after (b) MB adsorption. Strong bands at the region 1750-1735 cm^{-1} are characteristic of C=O stretching vibrations, in ester group or a saturated aliphatic group. The appearance of a strong peak at 1745.83 cm^{-1} after adsorption of dye indicate strong C=O stretch after adsorption of MB; indicating chemical interaction between the adsorbent and the adsorbate. The appearance of medium peak at 1465.70 cm^{-1}, is indicative of C-H bend involving alkane group. The medium peak changes in the 1500-1400 cm^{-1}, denote C-C stretch (in ring). This may involve interaction of the aromatic structure of the dye with that of the surface functional groups of the fungus. Vibration of C-N stretching was observed in the region of 1250-1020 cm^{-1} with a medium peak at 1116.75 cm^{-1} following adsorption of MB. This might indicate interaction of the N moiety in the MB structure with the functional groups in the fungal surface. These change indicated possible participation of those functional groups on the surface of *A. versicolor* in the process of dye uptake.

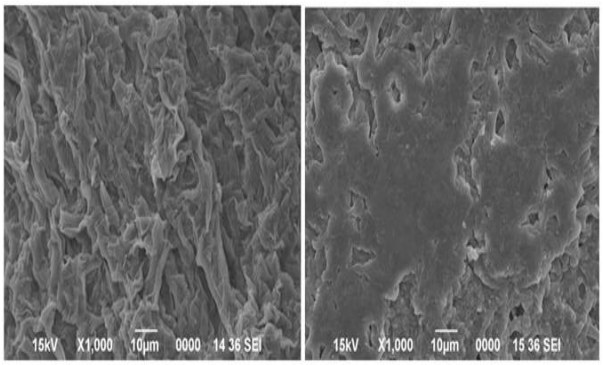

Figure: 1A. The SEM micrographs of *A. versicolor* biomass before (left panel) and after (right panel) MB adsorption;

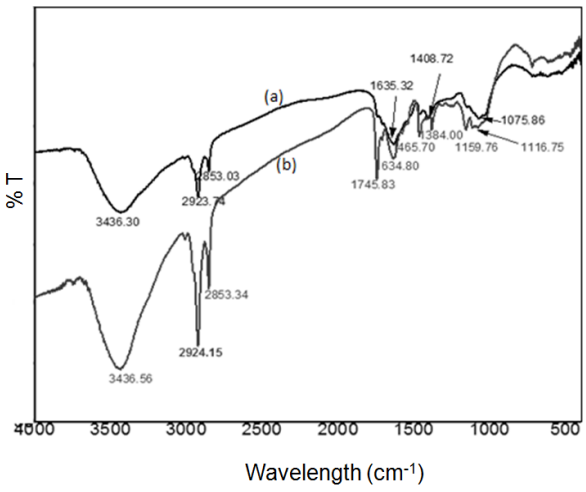

Figure: 1B. The FTIR spectra of pristine (a) and dye-adsorbed biomass (b) of *A. versicolor.*

EDX profile of the *A. versicolor* biomass is shown in Table 1 for elemental analysis of the sample surfaces pre- and post-adsorption. As expected, carbon was found most abundant of the elements as it is the main constituent of chitin present in fungal biomass. However, the amount of carbon increased after adsorption which may be attributed to adsorption of MB as MB possess a carbon based structure; hence the increased detection of carbon post dye adsorption. Minor changes in composition of other elements were found following adsorption of MB which may indicate adsorption of MB on the fungal surface.

Table1: EDX profile of *A versicolor* before and after adsorption with MB

Element	Before adsorption		After adsorption	
	Weight%	Atomic%	Weight%	Atomic%
C K	47.31	54.60	55.09	62.28
O K	51.65	44.84	43.84	37.21
Na K	0.64	0.39	0.44	0.26
P K	0.03	0.01	0.24	0.11
Cl K	0.31	0.12	0.29	0.11
Ca K	0.07	0.03	0.09	0.03
Fe K	0.09	0.02	0.00	0.00
Total	100	100	100	100

Optimization of biomass, pH and temperature for adsorption:

Drying of adsorbents augments adsorption of the dissolved dyes from the aqueous solution. To study the effect of adsorbent drying technique on adsorption, fungal biomasses were air or oven dried (60°C). Biomasses dried by either technique successfully adsorbed MB (50 mg/L), but the efficiency of adsorption with oven-dried samples were better than the air dried samples at low biomass amount (Figure 2A). As adsorbent amount was increased to 12 g per liter of dye, both air and oven dried biomasses showed similar adsorption efficiency (Figure 2A).

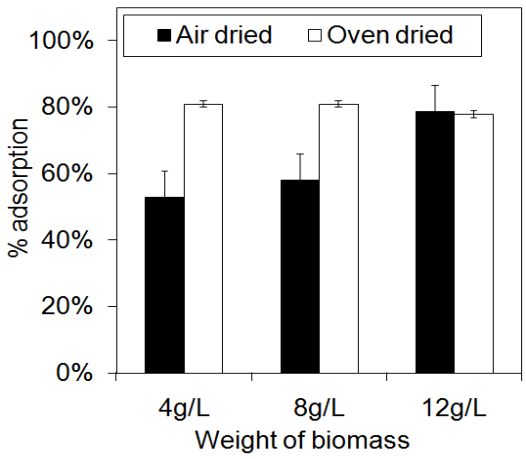

Figure: 2A. Optimization of biomass amount for efficient MB adsorption

pH alterations are known to alter the surface charges of the biosorbent, thereby playing a critical role in the adsorption process [5, 26-28]. In the present study, we determined that highest adsorption of MB on

A. versicolor biomass was at pH 7.0 (Figure 2B). Since MB is a basic dye, increased adsorption is expected with the rise in negative surface charge of the biosorbent. But, decrease in dye uptake was observed after pH 8.0. It is thus possible that, along with the electrostatic force of attraction, factors such as chemical interaction between dye molecules and surface functional groups of the biomass or physical forces of attraction also play a role in the biosorption process.

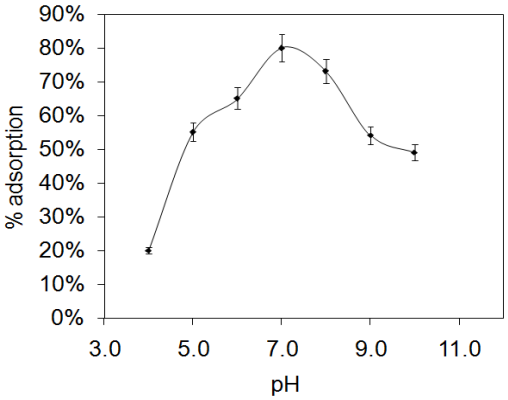

Figure: 2B. The effect of pH on adsorption of MB by *A. versicolor* biomass

Rise in temperature is associated with increase in internal energy of the system leading to heightened molecular vibrations; thus playing a decisive role in adsorption. Adsorption by biosorbents can be dependent or independent of temperature [29-32]. Figure 2C shows the impact of temperature on adsorption of MB by *A. versicolor* biomass. Among the temperatures studied, 28° C was found to be most efficient for adsorption. The adsorption declined after 18 h at this temperature. This may be attributed to decreased surface activity with increased temperature. This was also noted by Aksu and Tezer for adsorption of Remazol Black B reactive dye by *R. arrhizus* biomass [28].

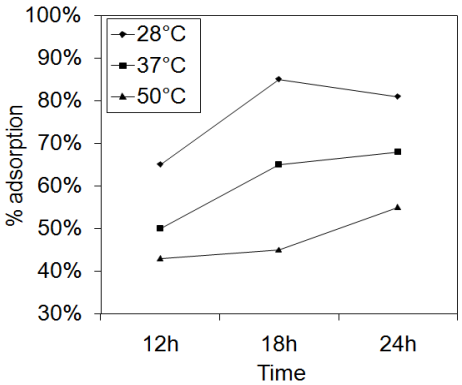

Figure: 2C. Effect of temperature on adsorption of MB by *A. versicolor* biomass

Effect of initial dye concentration on dye adsorption:

At a constant adsorbent amount of 12 g per liter of dye, we studied the effect of initial dye concentration on adsorption. As shown in Figure 3, the amount of MB adsorbed at equilibrium (q_e) significantly increased per g of biomass as the initial concentration of the dye was increased from 10 to 50 mg/L. The initial concentration of the adsorbate provides for a vital driving force needed to overcome all mass transfer resistances between the adsorbent and the adsorbate. Hence, a higher initial concentration of dye increases or enhances the adsorption process. Equilibrium was reached earlier at lower concentrations, whereas, it was delayed for relatively higher concentrations.

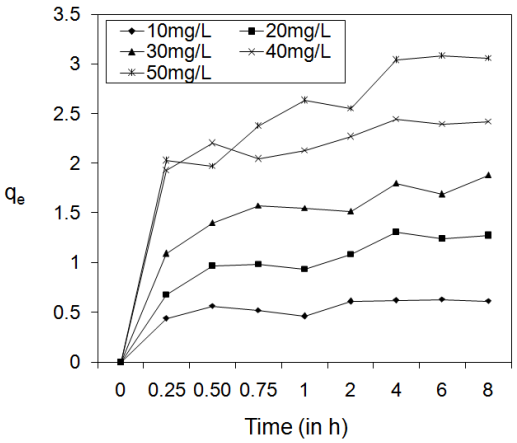

Figure: 3. Adsorption kinetics corresponding to different initial concentration of MB.

Adsorption kinetics:

The pseudo-second-order kinetics can be expressed in a linear form as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where the dye adsorbed at equilibrium (q_e) and the second order constants k_2 (g/mg h) can be determined from the slope and intercept of plot t/q_t vs t [3, 37-38]. Figure 4A represents the pseudo-second-order sorption kinetics of MB on *A. versicolor* biomass. The values for k_2 and q_e (both experimental and calculated) are represented in Table 2. We observed clear agreement between values of q_e experimental and q_e calculated for the pseudo-second-order-model. Hence, pseudo-second-order model was able to explain the adsorption kinetics. Such phenomenon has also been observed in the adsorption of MB by bamboo based activated carbon, hazelnut shells and wood sawdust, activated carbon from rattan sawdust and coconut bunch waste [3, 33-35].

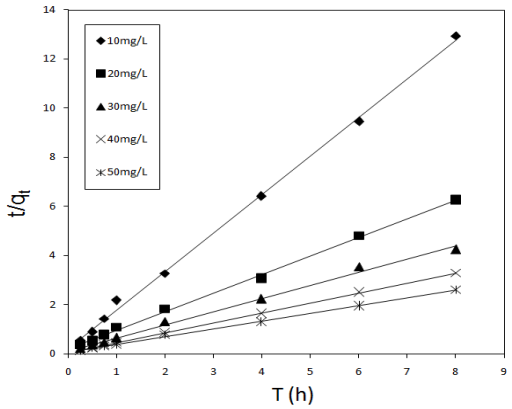

Figure: 4A. Pseudo second-order sorption kinetics plot of MB adsorption on *A. versicolor*

Table 2: Pseudo second-order model parameters for adsorption of MB on *A. versicolor* biomass

Initial conc. (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-second-order kinetic model		
		K_2 (g/mg h)	$q_{e,cal}$ (mg/g)	R^2
10	0.6181	10.7226	0.6382	0.99
20	1.2773	2.7216	1.3227	0.99
30	1.8853	2.2996	1.8726	0.99
40	2.4268	3.8334	2.4631	0.99
50	3.0661	1.2324	3.1847	0.99

The initial adsorption rates h (mg/g min) was calculated from the pseudo-second-order model by the following equation:

$$h_{0,2} = k_2 q_e^2$$

and the results were plotted in Figure 4B. The plot further confirmed that the initial rate of adsorption was directly proportional to the initial MB concentration, which, however decreased at a very high concentration. This could be attributed to heterogeneous type of adsorption with limited site of adsorption on fungal biomass surface, that was saturated easily and negating the effect of rise in initial concentration. This data is in contrast to increase in initial rate of adsorption by coconut bunch waste upon raising the initial concentration of methylene blue as reported by Hameed et al. [3].

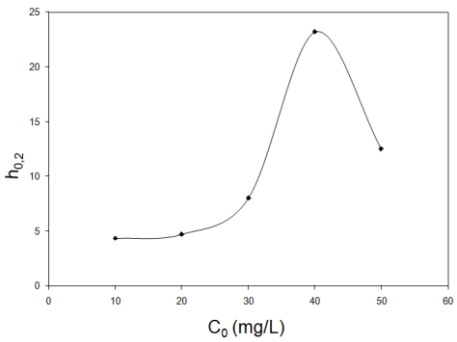

Figure: 4B. Variation of initial rate of adsorption with the initial MB concentration

Sorption mechanism:

To understand the mechanism and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intra-particle diffusion model [36] expressed by the equation,

$$q_t = k_{id} t^{1/2} + C$$

where C is the intercept and k_{id} is the intra-particle diffusion rate constant (mg/g $h^{1/2}$). k_{id} is calculated from the slope of the linear plot of q_t versus $t^{1/2}$ as shown in Figure 5. The intercept is directly proportional to the contribution of the surface sorption in the rate controlling step. k_{id}, C and R^2 values were calculated and enumerated in Table 3. When regression of q_t versus $t^{1/2}$ is linear and passes through origin, intra-particle diffusion is considered as the sole rate-limiting step. However, the linear plots of each concentration did not pass through the origin and associated with low regression co-efficient (Table 3). Thus, intra-particle diffusion may not be controlling factor for adsorption in this study. Similar observations were reported for MB adsorption by coconut bunch waste [13].

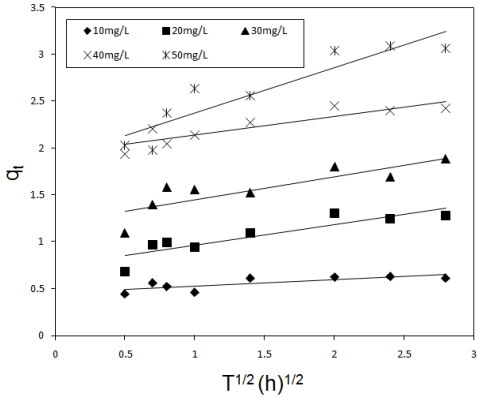

Figure: 5. Plot of intra-particle diffusion rate constant for sorption of MB on *A. versicolor* biomass.

Table 3: Intra-particle diffusion constants

Initial Concentration (mg/L)	K_{id}	C	R^2
200	0.482	1.898	0.84
300	0.196	1.950	0.79
400	0.244	1.211	0.71
500	0.219	0.745	0.79
600	0.069	0.459	0.60

Adsorption isotherms:

Adsorption isotherm study is done to establish a relation between the adsorbate concentration in the solution and the adsorbed amount at the adsorbent interface under constant temperature. There are a number of isotherm models available to analyze the adsorption process [11]. We analyzed the isotherm results using Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm model assumes that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface, with no lateral interaction between the

adsorbed molecules [24]. The Langmuir equation in expressed in linearized form by the equation

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where Q_0 is the highest amount of the dye adsorbed per unit mass of the adsorbent that forms a complete monolayer on the surface bound at *Ce*, and b is the constant related to the affinity of the binding sites (L/mg). The Langmuir plot of C_e/q_e (specific adsorption) versus equilibrium concentration (C_e) showed that adsorption did obey Langmuir model; as the R_L value was found to be 0.625, well within the favorable range of $0<R_L<1$ (Figure 6A). This observation was negated however by a low correlation coefficient (R^2 = 0.349) (Table 4).

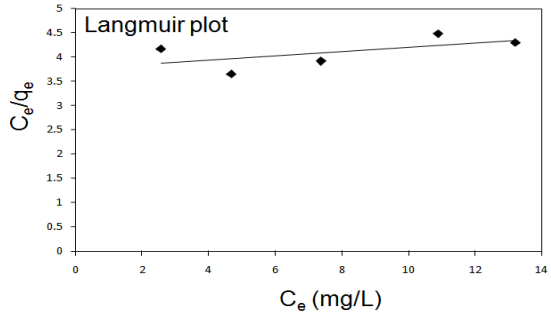

Figure 6A Langmuir isotherm plot for adsorption of MB on *A. versicolor* biomass

Table 4: Langmuir, Freundlich and Temkin isotherm constants and correlation coefficients for adsorption of MB on *A. versicolor*

Isotherm Parameters	Values
Langmuir isotherm	
Q_o (mg/g)	22.72
b (L/mg)	0.012
R^2	0.349
Freundlich isotherm	
K_f	0.049
n	1.058
R^2	0.986
Temkin isotherm	
A	0.256
B	1.428
R^2	0.971

The Freundlich isotherm model describes heterogeneous adsorption process (3, 6). The linear form of the Freundlich equation is expressed by the equation,

$$lnq_e = lnK_F + \left(\frac{1}{n}\right) lnC_e$$

Where K_F and n are Freundlich constants with K_F $(mg/g(L/mg)^{1/n})$ being the adsorption capacity of the sorbent and n indicating favorability of adsorption process. We calculated the values of K_F and n from the plot of $\ln q_e$ against $\ln C_e$ shown in Figure 6B. The n of 1.058 fulfilled the criterion (n>1) satisfying the fact that the present adsorption study followed Freundlich adsorption isotherm model with a high correlation coefficient (R^2= 0.986).

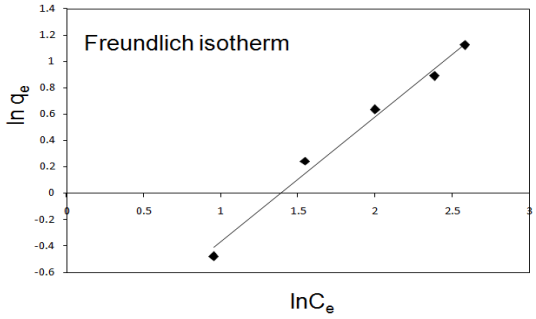

Figure 6B Freundlich isotherm plot for adsorption of MB on *A. versicolor* biomass

Temkin model suggests that because of adsorbent-adsorbate interaction, the heat of adsorption will decrease linearly with coverage. The Temkin isotherm has been generally applied in the following linearised form:

$$q_e = BlnA + BlnC_e$$

Where $B = RT/b$, A is the Temkin isotherm constant (L/g), R is the gas constant (8.314J/molK), T is the absolute temperature (K) and b is the Temkin constant related to heat of sorption (J/mol). Therefore, we plotted q_e versus lnC_e to determine the other constants which are listed in Table 4. Fig 6C suggests the adsorption also follows Temkin isotherm with a R^2 value of 0.971.

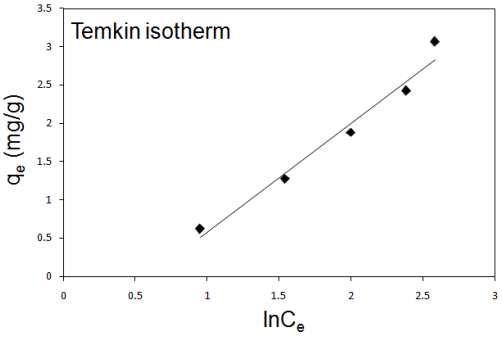

Figure: 6C Temkin isotherm plot for adsorption of MB on *A. versicolor* biomass

A higher correlation coefficient (R^2) of Freundlich isotherm plot (0.986) compared to Langmuir (0.349) and Temkin (0.971) depicts that Freundlich isotherm model was better fit for describing the adsorption of MB on dried *A. versicolor* biomass. The isotherm constants from Langmuir, Freundlich and Temkin isotherm models are listed in Table 4. The value of n being greater than unity (n>1) suggested favorable adsorption of MB on *A. versicolor* biomass. As Freundlich isotherm explains the adsorption process better than Langmuir and Temkin isotherm model, the current study indicates that surface heterogeneity of *A. versicolor* is responsible for this multi-layered

adsorption. This may be because of the presence of energetically heterogeneous adsorption sites on the fungal surface.

Conclusion:

This study investigated the efficiency of the dried biomass of *A. versicolor* to remove MB from aqueous solution. Fungal biomass can adsorb dye molecules through electrostatic interaction, complexation, chemical binding, or by combination of all processes. SEM images of pristine and dye-adsorbed biomass showed distinct changes in the structure of the surface topology post adsorption. EDX data suggested nominal changes in the surface of biomass following adsorption of MB, indicating adsorption. FTIR analysis indicated changes in functional groups post adsorption of MB by the fungal biomass suggesting chemical interaction (chemisorption) of the dye molecules with the surface functional groups. Kinetics study revealed that the adsorption is proportional to initial concentration of dye possibly because of the increase in driving force at higher concentration. The present adsorption study follows pseudo-second-order kinetics. Adsorption isotherm was well described by the Freundlich isotherm model with 'n' value of 1.058. *A. versicolor* dried biomass, thus, appeared to be an efficient biosorbent in removing MB from aqueous solutions.

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Conflict of interest:

The authors declare no conflict of interests.

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