Removal of methylene blue from aqueous solution by Artist’s Bracket fungi: kinetic and equilibrium studies
Daryush Naghipour, Kamran Taghavi and Mehrdad Moslemzadeh

ABSTRACT
In this study, adsorption of methylene blue (MB) dye onto Artist’s Bracket (AB) fungi was investigated in aqueous solution. Fourier transform infrared and scanning electron microscopy were used to investigate surface characteristic of AB fungi. Influence of operational parameters such as pH, contact time, biosorbent dosage, dye concentration, inorganic salts and temperature was studied on dye removal efficiency. With the increase of pH from 3 to 9, removal efficiency increased from 74.0% to 90.4%. Also, it reduced from 99.8% to 81.8% with increasing initial MB concentration from 25 mg L\(^{-1}\) to 100 mg L\(^{-1}\), whereas it increased from 54.7% to 99.9% with increasing biosorbent dosage from 0.5 g L\(^{-1}\) to 2 g L\(^{-1}\) and with increasing temperature from 25°C to 50°C, respectively. Isotherm studies have shown adsorption of MB dye over the AB fungi had a better coefficient of determination (R\(^2\)) of 0.98 for Langmuir isotherm. In addition, the maximum monolayer adsorption capacity (q\(_m\)) was 100 mg g\(^{-1}\). Also, the MB dye adsorption process followed pseudo-second-order kinetic. In general, AB fungi particles can be favorable for removal of MB dye from dye aqueous solution with natural pH and high temperature.

Key words | Artist’s Bracket, equilibrium, fungi, kinetic, methylene blue

INTRODUCTION
Artist’s Bracket (AB) (applanatum lucidum) is a white-rotting fungus that can degrade wood components such as lignin and cellulose because of its special enzymatic system. This fungus has a reddish brown color and a fibrous texture (Matos et al. 2007).

The white-rotting group show good potential bioremediation (Joo et al. 2008). Also, they were used for the biosorption of contaminants such as metals and dyes from wastewater and aqueous solution Khoo & Ting (2001), Aksu & Balibek (2007), Bayramoglu & Arca (2007) and Arca & Bayramoglu (2007).

Many industries including textile, rubber, paper, leather, plastic, cosmetic, printing, etc., are producing a high volume of dye wastewater as a result of use of synthetic dye in various dyeing operations. Every year over 7 million tons of dyes worldwide are commercially available while over 10,000 tons of dyes are used in industries. According to research, approximately 15% of the dye stuffs are lost as the industrial effluents (Mahmoodi et al. 2011). Discharging the dye wastewater in the aquatic ecosystem is dangerous for both toxicological and aesthetical reasons (Tan et al. 2007). Methylene blue (MB) is a cationic dye that is more toxic than anionic dyes (Hao et al. 2000). Although the MB is not drastically hazardous, it can causes eye burns which may be responsible for permanent injury to human and animal eyes (Tan et al. 2007). On inhalation, it can create breathing difficulties and may causes nausea, vomiting, profuse sweating, diarrhea, gastritis and mental confusion (El-Latif et al. 2013). Hence, an increased interest resulted in the development of wastewater treatment technologies for eliminating dyes from the wastewater. Poor biodegradable characteristics of dye led to a difficult treatment of wastewater containing dyes by conventional biological treatment processes, such as activated sludge and anaerobic digestion (Vimonses et al. 2009). So far, many technologies have been used to remove dye contaminants such as adsorption by Hameed et al. (2007b), coagulation/flocculation by Moghaddam et al. (2010), electrochemical (Vlyssides et al. 1999), and biological processes (An et al. 1996).

Among the treatment technologies, adsorption is a reasonable treatment technique. Because of availability,
low initial cost, simplicity of design and ability to remove dyes in the higher concentrations, the adsorption process appears to be more effective than other techniques (Mahmoodi et al. 2011). Thus, AB fungi as a parasite for trees can be used as a cheap and suitable source for adsorption of dye.

In this study, AB fungus was used as a biosorbent to remove the MB from aqueous solution. The effects of different variables including pH, contact time, biosorbent dosage, dye concentration, inorganic anions (salt) and temperature were investigated on the dye removal. Kinetic and isotherm studies were conducted to evaluate the adsorption capacity of AB fungi.

**MATERIAL AND METHODS**

**Chemical**

The MB dye, provided its chemical characteristics in Figure 1, was purchased from Ciba laboratory and other chemicals such as potassium nitrate (KNO₃) and sodium chloride (NaCl) were from Merck. The pH of solutions was adjusted using HCl or NaOH.

**Preparing Bracket fungi particles**

AB was collected from a local forest in the north of Iran. The fungi was first washed to remove the adhering dirt and then it was dried, crushed, and sieved. After drying, it was sieved through a 3.36 mm mesh. Last, the fungi particles were washed with deionized water and again were dried on 105°C for 24 h. In the following, AB fungi and MB were signified by abbreviation of AB and MB, respectively.

**Adsorption experiments**

Adsorption experiments were conducted by investigation of different variables including initial pH of solution, contact time, biosorbent dose, initial dye concentration and temperature as effective parameters on the adsorption of MB onto the AB fungi. Also, adsorption kinetics and adsorption isotherm were studied.

The experiments were carried out as follows. First, a fresh stock solution of MB was prepared by dissolving 1 g of MB in deionized water. In the next step, 100 mL of MB solution with initial concentration of 50 mg L⁻¹ was spilled in 250 mL conical flasks and their pH were adjusted in the range of 3, 5, 7 and 9 using NaOH and HCl solutions and were mixed with various dose of AB fungi particles (0.5, 1, 1.5 and 2 g L⁻¹) for 210 min. The pH was measured with a pH meter (Aqualytic AL15). To investigate the effect of initial dye concentration effect, the experiments were carried out at various MB concentrations (25, 50, 75 and 100 mg L⁻¹) by using AB particles’ optimum dose (1.5 g L⁻¹) at pH 7 and temperature of 25°C for 210 min. To study inorganic salt effect, experiments were conducted at concentration of 160 mg L⁻¹ of potassium nitrate (KNO₃) and sodium chloride (NaCl) at optimum condition.

**Analysis**

After centrifuging the samples, MB residual concentration was measured using a UV-visible spectrophotometer (DR 5000, Hack, America) in λ = 665 nm (Way 2012). Percentage reduction of MB concentration during adsorption onto AB fungi was calculated by Equation (1).

\[
\text{% Adsorption} = \frac{C_0 - C_t}{C_0} \times 100
\]  

(1)

The amount of dye adsorbed onto AB fungi particle biomass at time t, qₜ (mg g⁻¹), was calculated by Equation (2)

\[
q_t = \frac{(C_0 - C_t)V}{m} 
\]  

(2)

where (C₀, Cₜ, V and m) are the initial dye concentration (mg L⁻¹), the concentration of dye at time (t), the volume of solution (L) and the mass of AB fungi particles (g), respectively.

**Isotherm experiments**

The equilibrium adsorption studies were carried out by testing 100 mL of dye solutions with different initial concentrations (25, 50, 75 and 100 mg L⁻¹) with 0.15 g of AB particles in 250 mL conical flasks for 4 h which was more than sufficient to equilibrium time.
Theory

The adsorption isotherm was used to investigate distribution of adsorbate molecules onto the adsorbent in equilibrium. The relationship between the concentration of adsorbate in solution and removed dye was determined using the Langmuir and Freundlich isotherms (Gupta et al. 2014).


\[
\frac{C_e}{q_e} = \frac{1}{K_aq_m} + \frac{C_e}{q_m}
\]  

(3)

The Langmuir constants (\(q_m\), \(K_a\) and \(C_e\)) related to maximum adsorption capacity (mg g\(^{-1}\)), the energy of adsorption (L mg\(^{-1}\)) and equilibrium concentration of dye in solution (L mg\(^{-1}\)), respectively, are calculated from the plot \(C_e/q_e\) versus \(C_e\).

\(R_L\) that is separation factor, is defined by Equation (4).

\[
R_L = \frac{1}{1 + K_aC_0}
\]  

(4)

where \(R_L\) is dimensionless constant and \(C_0\) is the initial dye concentration (mg L\(^{-1}\)).

Freundlich isotherm. Freundlich isotherm model evaluates the multilayer absorption of adsorbate on the absorbent surface. It also assumes that adsorption occurs on heterogeneous surfaces and can be expressed via Equation (5) (Mahmoodi et al. 2011).

\[
\log q_e = \log K_f + \frac{1}{n} (\log C_e)
\]

(5)

The parameters \(K_f\) and \(n\) are Freundlich constants are adsorption capacity (mg g\(^{-1}\)) and the adsorption intensity of the system determined from the plot \(\ln q_e\) versus \(\ln C_e\).

Kinetic experiments

To study the mechanism of adsorption, the transient behavior of the dye adsorption process was analyzed using the pseudo-first-order and pseudo-second-order kinetics which are explained in the following.

Pseudo-first-order kinetic. Linear form of pseudo-first-order kinetic is expressed by Equation (6) (Gupta et al. 2014).

\[
\log (q_e - q_t) = \log (q_e) - \left(\frac{k_1}{2.303}\right)t
\]

(6)

where \((q_e, q_t,\) and \(k_1)\) are the amount of adsorbed dye at equilibrium (mg g\(^{-1}\)), the amount of adsorbed dye at time \(t\) and the equilibrium rate constant of pseudo-first-order kinetic (min\(^{-1}\)), respectively. The \(k_1\) is obtained from drawing \(\log (q_e - q_t)\) versus \(t\).

Pseudo-second-order kinetic. Linear form of pseudo-second-order kinetic is shown in Equation (7) (Ho & Chiang 2001).

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

(7)

From plot of \((t/q_t)\) versus \(t\) the values of the pseudo-second-order rate constants \((k_2)\) (g mg\(^{-1}\) min\(^{-1}\)) and \(q_e\) (mg g\(^{-1}\)) can be calculated.

The initial adsorption rate \((h)\) was calculated at zero time, in Equation (8):

\[
h = k_2q_e^2
\]

(8)

pH at point zero charge

To determine pH at point zero charge (pHpZC) for biosorbent particles, the following steps were performed.

In the first step, a sufficient amount of 0.1 M NaNO\(_3\) solution was spilled into 250 mL flasks and the pH was adjusted in the range from 2 to 11 by either 1 M HCl or NaOH. In the next step, the total volume of the solution in each flask was adjusted to 100 mL by adding NaNO\(_3\) solution of the same known concentration, at the same time the initial pH values of the solutions was accurately noted. In the next step, 0.15 g of AB biosorbent was added to the flasks and the suspensions were shaken and allowed to equilibrate for 24 h with a shaker. In the final step, the final pH values of the supernatant liquids were noted. The analyzed results were presented as in Figure 2, where the pHZPC of the AB biosorbent was found to be 3.5.

Fourier transform infrared absorption spectra analysis

Fourier transform infrared (FTIR) spectra of AB particles was recorded by FTIR absorption spectrophotometer using KBr disc method. The particles were thoroughly mixed with KBr, powdered and disc was formed by applying the
pressure. FTIR absorption spectra were recorded in the region of 400–4,000 cm\(^{-1}\).

**Scanning electron microscopy analysis**

Scanning electron microphotograph (SEM) of the particles were recorded using scanning electron microscope at different magnifications operating at 15 kV.

**RESULT AND DISCUSSION**

**FTIR study**

The functional groups on the biosorbent surface were studied by FTIR (Figure 3). Several peaks can be seen in Figure 3 indicating various functional groups for AB particles which can be responsible for bonding with MB. Spectra at 3,378.72 cm\(^{-1}\) related to the -OH group, 1,700.37 cm\(^{-1}\) contribute to the C=O stretch and 1,293.25 cm\(^{-1}\) indicating C-N and C-O bands (Schmitt & Flemming 1998; Dawood & Sen 2012).

**SEM analysis**

The SEM microphotograph was shown the particle shape, porosity and appropriate size distribution of the biosorbent. Scanning electron micrographs of AB fungi particles before and after the dye adsorption process are shown in Figure 4. As can be seen in Figure 4(a), there are numerous pores on the surface of the biosorbent. As shown in Figure 4(b), the absorbent sites were occupied by MB dye molecules.

**Effect of operational parameters**

**Effect of initial pH**

Figure 5 shows the MB removal efficiency at various pH values. The dye removal efficiency increased with time as well as with the increasing pH value. The removal efficiency increased from 74.0% at pH 3 to 90.0% at pH 9 (Figure 5). It is usually expected that the cationic dye adsorption increases with increasing pH in higher pH\(_{ZPC}\) because of the increasing negative surface charge of the adsorbent. Hence, with the increase of pH from 3 to 9, the dye removal
efficiency increased. Moreover, the high percentage of dye removal at higher pH is also due to the presence of less H⁺ ions competing for sorption sites on the biosorbent. On the other hand, in the low pH because of more H⁺ ions the surface of AB biosorbent acquires positive charge that decreases adsorption of cationic dye (Vadivelan & Kumar 2008; Kumar et al. 2013). A similar result was reported for adsorption of MB on oak sawdust by El-Latif et al. (2013).

Effect of biosorbent dose

Concentration of adsorbent is an important variable in the adsorption process because it prepared active sites for contaminant adsorption. Figure 6(a) shows MB removal efficiency at different biosorbent dose. An increase in the adsorbent dose from 0.5 to 2 g L⁻¹ led to the increase of the MB removal efficiency from 54.0 to 98.0%. A similar behavior have been reported for MB adsorption on the rice husk by Sharma (2009) and for Congo red adsorption on the cashew nut shell by Kumar et al. (2010).

Effect of initial MB concentration and contact time

Figure 6(b) shows the effect of initial dye concentration and contact time on the adsorption of MB dye at different initial dye concentration onto AB biosorbent. The dye removal efficiency increased from 81.0 to 99.0% with decreasing initial concentration of MB dye from 100 to 25 mg L⁻¹ (Figure 6(b)). Also, the MB removal efficiency is rapid in the initial stages of contact time and then become slowdown with time. In constant dosage of biosorbent the removal of MB dye depends on the initial concentration of MB because with the increase of the concentration of dye available adsorption sites of biosorbent became fewer (Sen et al. 2011). A similar behavior was observed for adsorption of MB on oak sawdust by El-Latif et al. (2010).

Effect of monovalent salts (NaCl and KNO₃)

The addition of ions can cause improve or scavenge adsorption of dyes, or can be insensitive to the addition of ions (El Boujaady et al. 2014). To clarify the role of salts (NaCl and KNO₃) on the adsorption system, experiments were carried out at a concentration of 160 mg L⁻¹ of potassium...
nitrate (KNO₃) and sodium chloride (NaCl). In Figure 6(c), the addition of potassium nitrate had little effect on the adsorption efficiency while the sodium chloride salt had more remarkable effect than potassium nitrate. Nevertheless, these results indicate that the presence of external electrolyte, such as, KNO₃ and NaCl have a limited effect on the binding between AB biosorbent and MB. K⁺ ion of KNO₃ and Na⁺ of NaCl salt may complete with MB dye for binding on the adsorbent surface, decreasing adsorption efficiency. Mahmoodi *et al.* (2011) have reported a similar behavior.

**Effect of temperature on dye adsorption**

The adsorption experiments were conducted at different temperatures (25, 35 and 50°C). As shown in Figure 6(d), the removal efficiency increased with the increase of temperature which indicates the adsorption is an endothermic process. It perhaps occurred due to an increase in the mobility of the dye molecules with increase of temperature (Dawood & Sen 2012). Similar phenomenon have been observed for adsorption of MB, Malachite green and Crystal violet by carbon prepared from waste apricot by Önal (2006). Also, Sharma (2009) studied the adsorption of MB on a low-cost activated carbon and observed that MB removal efficiency increased with increasing the temperature.

**Langmuir and Freundlich isotherms**

Figure 7(a) shows Langmuir isotherm for AB biosorbent and its results are presented in *Table 1*. Langmuir isotherm fittings for AB biosorbent have good coefficient of determination ($R^2 = 0.98$). Also, Langmuir constants $q_m$, $K_a$ and $R_L$ are obtained in 100 mg g⁻¹, 2 mg g⁻¹ and 0.013 mg g⁻¹, respectively. The $R_L$ is taken to the relative volatility in vapour–liquid equilibrium. It is easy to verify that, for a favorable equilibrium, $R_L$ lies between 0 and 1; it is larger than 1 for an unfavorable equilibrium (Sen *et al.* 2011). In this study, $R_L$ values lie between 0 and 1 which indicates a favorable adsorption system.

The adsorption data were analyzed using Freundlich isotherm and results are presented in *Table 1*. Freundlich constants $K_F$ and $n$ are calculated from the plot of ln$q_e$ vs. $\ln C_e$.
versus InC_e, not provided here, which are 12.3 mg g\(^{-1}\) and 3.4 mg g\(^{-1}\), respectively; also, coefficient of determination \((R^2)\) for Freundlich isotherm is 0.1 (Table 1). The value of \(n\) is larger than 1 which indicates a favorable adsorption system and a physical process.

From Table 1 it can be concluded that the adsorption of MB onto the AB biosorbent has a better coefficient of determination \((R^2)\) of 0.98 for Langmuir isotherm than Freundlich isotherm, indicating the Langmuir isotherm suitability. In a number of past studies, such as adsorption of MB onto activated carbon prepared from rattan sawdust (Hameed et al. 2007a) and adsorption of MB onto jute fiber carbon (Senthilkumaar et al. 2005), it has been observed that Langmuir model describes well adsorption isotherms.

### Adsorption kinetics

In this study, the applicability of the pseudo-first-order and pseudo-second-order models were tested for the adsorption of MB onto AB fungi particles. Pseudo-first-order model gives a very poor coefficient of determination \((R^2)\) (Table 2). In addition, pseudo-first-order kinetic model predicted a significantly lower value of the equilibrium adsorption capacity \((q_e (\text{cal}))\) than the experimental \(q_e\) value that indicates the inapplicability of this model (Table 2). The adsorption data were then analyzed using the pseudo-second-order kinetic model. Figure 7(b) shows pseudo-second-order kinetics as plot \(t/q_t\) versus \(t\) with high coefficient of determination \((R^2)\), indicates pseudo-second-order kinetic is applicable. However, all kinetic parameters, including coefficient of determination \((R^2)\), obtained from model plots with experimental data were provided in Table 3. The values of coefficient of determination \((R^2)\) for pseudo-second-order are very high and the theoretical \(q_e (q_e (\text{cal}))\) values are closer to the experimental \(q_e\) values (Table 3). In a number of past studies such as absorption of MB onto rice husk (Vadivelan & Kumar 2005) and adsorption of MB onto bamboo-based activated carbon (Hameed et al. 2007b) it has been reported that pseudo-second-order

#### Table 1 | Freundlich and Langmuir isotherm parameters for adsorption of MB onto AB biosorbent

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Parameters</th>
<th>Freundlich isotherm</th>
<th>Parameters</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>(q_m) (mg g(^{-1}))</td>
<td>12.3</td>
<td>(K_f) (mg g(^{-1}))</td>
</tr>
<tr>
<td>2</td>
<td>(K_a) (L mg(^{-1}))</td>
<td>3.4</td>
<td>N</td>
</tr>
<tr>
<td>0.013</td>
<td>(R_L)</td>
<td>0.1</td>
<td>(R^2)</td>
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<tr>
<td>0.98</td>
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#### Table 2 | Pseudo-first-order kinetic parameters for the MB adsorption on AB biosorbent

<table>
<thead>
<tr>
<th>System</th>
<th>(q_e) (mg g(^{-1})) experimental</th>
<th>(k_1) (min(^{-1}))</th>
<th>(q_e) (mg g(^{-1})) calculated</th>
<th>(R^2)</th>
</tr>
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<tr>
<td>Initial MB concentration (mg L(^{-1}))</td>
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<tr>
<td>25</td>
<td>24.9</td>
<td>0.04</td>
<td>11.4</td>
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<tr>
<td>50</td>
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<tr>
<td>75</td>
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<td>38.0</td>
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</tr>
<tr>
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<td>87.0</td>
<td>-0.115</td>
<td>6.6</td>
<td>0.5893</td>
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</table>

#### Table 3 | Pseudo-second-order kinetic parameters for the MB adsorption on AB biosorbent

<table>
<thead>
<tr>
<th>System</th>
<th>(q_e) (mg g(^{-1})) experimental</th>
<th>(k_2) (g mg(^{-1}) min(^{-1}))</th>
<th>(q_e) (mg g(^{-1})) calculated</th>
<th>(h) (mg g(^{-1}) min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
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<td>Initial MB concentration (mg L(^{-1}))</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>25</td>
<td>24.9</td>
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<td>25.3</td>
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<tr>
<td>75</td>
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<td>0.0013</td>
<td>86.9</td>
<td>9.8</td>
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</table>
kinetic best describe the adsorption process than pseudo-first-order kinetic.

CONCLUSIONS

In summary, this study shows that the MB dye could be sufficiently absorbed by AB fungi. Considering the pH_{PZC} of AB biosorbent was 5.5, as well as that the dye was cationic, the removal efficiency enhanced with increasing pH from 3 to 9. The removal efficiency reduced because of increasing initial MB concentration, whereas it increased with increasing biosorbent dose. Also, the removal efficiency increased with the increase of temperature, indicating the endothermic adsorption process. Proportionality of the adsorption process with Langmuir isotherm model indicated a monolayer adsorption process. Proportionality of the adsorption process with Langmuir isotherm model indicated a monolayer adsorption process. Proportionality of the adsorption process followed the pseudo-second-order kinetic model. In general, AB fungi particles can be favorable for removal of MB dye from aqueous solution with natural pH and high temperature.

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