Dye Biosorption from Aqueous Solutions by Fomitopsis Pinicola (Sw.) P. Karst.

Ilgaz AKATA¹, Ali SINAĞ²*, Cemil İŞLEK³

¹ Ankara University, Science Faculty, Department of Biology, 06100 Ankara, TURKEY
² Ankara University, Science Faculty, Department of Chemistry, 06100 Ankara, TURKEY
³ Niğde University, Science and Art Faculty, Department of Biology, 51100 Niğde, TURKEY

Received: 30.03.2010 Revised: 10.05.2010 Accepted: 12.07.2010

ABSTRACT

Methylene Blue adsorption by Fomitopsis pinicola (Sw.) P. Karst. collected from Kızılcahamam Işık Mountain, Ankara (Turkey) was investigated. Different initial dye concentrations, adsorbent doses, initial pH and temperature levels of the adsorption capacity of Fomitopsis pinicola were tested in order to reveal the stability and adsorption capacity of the fungus. The effect of the experimental parameters on the adsorption process was also described. The equilibrium binding was described in terms of Langmuir isotherm depending on the dye concentration. Desorption studies were also conducted. The results obtained from the batch experiments revealed the ability of the fungus to remove methylene blue. Thermodynamic parameters, i.e., Gibbs free energy, enthalpy and entropy changes were also calculated. From the calculated kinetic parameters, it can be concluded that adsorption data were also fitted to the pseudo-second-order kinetic model. From the results obtained, it can be suggested that Fomitopsis pinicola can be used as a low-cost biosorbent in wastewater treatments.

Key Words: Fomitopsis pinicola; Methylene Blue; Adsorption; Biosorption.

1. INTRODUCTION

Waste materials from the dying and final treatment in the textile industry are known to include colour [1]. Colour is a visible pollution. The resource of such pollution brings about the rapid increase in the use of synthetic dyes [2]. Biosorption of colours is an important technology for treatment of different types of industrial wastewater containing dyes. Nevertheless, most of the dyes are stable to light and oxidizing agents in wastewater. The traditional methods for treating dye-containing wastewaters are coagulation and flocculation, reverse osmosis, and activated carbon adsorption [3-5]. Currently, activated carbon is an effective adsorbent for dye removal [6]. However, due to the high cost of activated carbon, an alternative, environmental friendly and low cost material is needed. Thus, there is a growing interest in utilising easily available materials for the adsorption of dye colors. Many researches have studied the applicability of using low cost biomaterials [7]. Using waste biomass for preparing new biosorbents is particularly advantageous. Fungi are recognized as a promising class of low-cost adsorbents for removal of colour from aqueous waste solutions [8].

Fungi have many advantages for biosorption; Fungal biosorption has been studied more comprehensively due to the availability of large amounts of waste fungal biomass from fermentation industries [9]. Most of the fungi species have low nutritional requirements, comprehensive in physical growth conditions, dead

*Corresponding author, e-mail: sinag@science.ankara.edu.tr
biomass can be exposed to physical and chemical treatments to increase its performance, and the particle size is optimal [8-11].

*Fomitopsis pinicola* is inedible due to its woody texture, one of the most conspicuous and saprotrophic polytype with a worldwide distribution in temperate and boreal forests. It attacks both conifers and hardwoods causing a cubical brown-rot. The fruiting bodies are perennial. It commonly grows living and dead conifers but has also been also recorded in numerous other living and dead hardwoods [12,13].

Methylene blue (MB) was selected as an adsorbate because it is one of the most important and widely used cationic dye in the textile and paper industries. Thus, the effluents emanating from these industries are often colored due to MB and require proper treatment prior to their discharge [14]. MB has long been used as a model compound for the adsorption of organic pollutants from aqueous solution [6, 15].

MB is an heterocyclic aromatic chemical compound with molecular formula: \( C_{16}H_{18}ClN_{3}S \). The structure of MB was given in Figure 1. At room temperature, it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water.

![Figure 1. Structure of methylene blue.](image)

In the present study, the ability of *Fomitopsis pinicola*, a fungus to adsorb dye from aqueous solution of MB was investigated. MB was selected as a model compound in an attempt to use *Fomitopsis pinicola* as an adsorbent for the removal of dye from wastewater. Effects of the initial MB concentration, adsorbent amount, contact time, temperature and pH of the medium on the results were investigated.

2. EXPERIMENTAL

2.1. Preparation and Characterization of *Fomitopsis pinicola*

The surface of the fungus is more or less smooth, at first orange-yellow with a white margin, later dark reddish to brown and then frequently with orange margin. The pore surface of the fungus is pale yellow to leather-brown with 3-4 pores per mm. It grows on live and dead coniferous or (less common) deciduous trees.

The BET surface area of the fungi was determined using a Quantachrome NOVA 2200 series volumetric gas adsorption instrument. Initially moisture and gases such as nitrogen, oxygen that were adsorbed on the solid surface or held in the open pores, were removed under reduced pressure at 130°C for 5 h. The BET surface area of the fungus was found as 348 m²/g while the average pore diameter of the fungus was around 30 nm.

*Fomitopsis pinicola* was collected on dead wood from Kızılıkaya Işık Mountain. The fruit body of *Fomitopsis pinicola* was isolated from the tree with using knife (1 cm outside of layer of the tree), so there were not any woody particles on the samples. In the experiments, fungus samples were dried at 40°C for 48 h to remove moisture, then ground and sieved to 0.5 mm particle size, and finally washed with distilled water to remove any non-adhesive impurities and small particles.

2.2. Preparation of MB Solution

Standard solutions involving 10 – 150 mg L⁻¹ of MB were prepared by dilution of dye stock solution containing 0.1 mg L⁻¹ of fungus. All experiments were performed by using beakers of 100 mL capacity containing 0.1 g L⁻¹ of fungus suspended in 30 mg L⁻¹ of dye solution. The initial pH adjustments were carried out either by hydrochloric acid or sodium hydroxide solutions before adding the biosolid and recorded as pH. The suspensions were mixed at predetermined periods (30 - 1440 min) at constant temperature (35°C) in a shaker at 140 rpm until equilibrium was reached. The beakers were capped during the stirring. The solution reaction mixture was centrifuged at 5000 rpm for 2 min and the absorbance of dye solution was determined by Cecil 5000 Model 5200 C U.V. spectrophotometer at a 665 nm wavelength, at which the maximum absorbency occurred. \( \lambda_{max} \) of MB in all pH is 665 nm. The amounts of dye adsorbed were calculated from the concentrations in solutions before and after adsorption.

2.3. Experimental Methods and Measurements

**Adsorbent Dosage**

Dosages of Fungus samples used in the experiments were 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1 g L⁻¹. In these experiments, concentration of Initial MB solution was 30 mg L⁻¹ at 35 °C.

**Initial dye concentration**

0.1 g of Fungus as adsorbent with 100 mL of dye solution was kept constant for batch experiments. Initial MB solution concentrations of 10, 30, 50, 70, 90, 110, 130, 150 mg L⁻¹ were performed at 25°C on a rotary shaker operated at 140 rpm for 24 h. The beakers were capped during the stirring. Then optimum initial dye concentration was identified. The effects of adsorbent, adsorbent dosage, pH and temperature were conducted.

**pH**

Initial pH of solution was adjusted to 2, 4, 6, 8, 10, and 12, at optimum conditions of dye concentration (30 mg/L), temperature (35 °C), fungus amount (0.1 g), and contact time (8 hours).
Effect of temperature on the adsorption process was investigated at temperatures ranging between 25 - 45°C.

Desorption studies
Desorption of MB from _Fomitopsis pinicola_ was carried out using 100 mg of fungus loaded with 1.00 mg of dye using 1 M H₂SO₄, 1 M HCl, 1 M HNO₃, 1 M NaOH and distilled water based on previous studies [16, 17]. After desorption, the biosorbent was washed several times with deionized water, with the regenerated biosorbent reused for the next cycle. These cycles of biosorption followed by elution were repeated three times, and the biosorbent capacity was then evaluated.

3. RESULTS AND DISCUSSION

3.1. Effect of Contact Time on the Adsorption

Amount of dye adsorbed (mg/g) versus contact time for different initial MB concentrations of 10, 30, 50, 70, 90, 110, 130 and 150 mg/L was presented in Figure 2.

![Graph of adsorption vs. contact time for different initial concentrations of MB](image)

According to this figure, the amount of dye uptake increased with contact time at all initial dye concentrations. A significant increase in the sorption rate was observed by increasing the initial dye concentration from 10 to 150 mg/L. The adsorption rates of dyes with the initial concentration of 130 mg/L and 150 mg/L were more rapid compared to those at other initial concentrations for the first 12 h of contact time. At longer contact times than 12 h, a slight increase in the sorption rate was observed and the reaction of adsorption almost reaches equilibrium within 12 h. After this equilibrium period, the amount of adsorbed MB did not significantly change with time with the exception of initial concentration of 130 mg/L of MB, which show a slight decrease up to 20 h.

The binding of MB molecules to the surface of _Fomitopsis pinicola_ during the initial stages of contact time might be the reason of the enhancement of adsorption. Another reason of the enhancement in sorption rate is the strong attractive forces between the dye molecules and the adsorbent.

Further increase in contact time leads to the observation of lower sorption rates due to the interior penetration of dye molecules into the fungal as explained by Low et al. [18].
3.2. Effect of Temperature on the Dye Removal

Figure 3. Effect of temperature on the removal of the dye at the different contact times (Initial concentrating of 30 mgL$^{-1}$, adsorbent dosage of 0.1 gL$^{-1}$).

Figure 3 shows the effect of temperature on the dye removal. The system attains the equilibrium at a contact time of 18 h. Increasing the temperature reduces the dye removal for contact times between 15 h and 24 h. Actually, temperature has an important effect on the adsorption process. As the temperature increase, the rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increases [19]. The introduction of changes to the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [20]. It can be concluded that the remarkable effect of temperature on the removal of MB was seen above 16 h of contact time.

3.3. Effect of pH on the adsorption

Figure 4. Effect of pH on the adsorption at the different contact times (Temperature : 35$^\circ$C, $C_0$ : 100 mg/L, V : 100 mL).
Variation of pH with the adsorption of MB on fungal for different contact times was given in Figure 4. A distinct influence of pH on the adsorption rate was observed for the contact times due to the chemical characteristics of both adsorbate and adsorbent. Negative charge density of biosorbents, such as fungus in the aqueous phase, was reported by Kapoora et al. [21]. According to this study, at low pH (less than 4.0), the higher concentration of protons compared to higher pH values in the solution leads to an increase in positive charge density on metal binding sites and the sorption rate decreases. Increasing pH leads to the deprotonation of the metal binding sites leading an increase in negative charge density on the cell surface. Thus, the biosorption rate is increased at higher pH values. This observation is consistent with our findings.

3.4. Effect of Adsorbent Dosage on the Dye Removal

![Figure 5](image)

Figure 5. Effect of adsorbent dosage on the dye removal at different contact times (10 of pH, 25°C of temperature, 30 mgL⁻¹ of initial concentration).

Influence of adsorbent mass on the removal of MB dyes was investigated at different contact times for various adsorbent dosages of 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 1.0 and 2.0 gL⁻¹. Results were given in Figure 5. A regular increase in dye removal with increasing adsorbent dosage at different contact times was observed due to the increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the adsorbent.

3.5. Biosorption Isotherms

![Figure 6](image)

Figure 6. Langmuir isotherm (Speed 140 rpm, 480 min., 35 °C, concentration of fungus 0.1 g L⁻¹, concentration of dye 30 mg L⁻¹).
In order to understand the mechanism of the sorption, the equilibrium isotherm is of significant importance for the design and optimization of the adsorption system for the removal of dye from aqueous solution. Among the several isotherm equations available in the literature, two isotherms, Langmuir and Freundlich, were used to evaluate the experimental data in this study.

The Freundlich isotherm model is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. The Langmuir adsorption isotherm assumes that adsorption can only occur at a fixed number of definite localized sites, each site can hold only one adsorbate molecule (monolayer), and the sites were homogeneous. The equations were given in a previous study [22]. The Langmuir isotherm was given in Figure 5 and its parameters were given in Table 1 along with regression coefficients since the Langmuir isotherm gives a better representation of adsorption of MB on fungus compared to the Freundlich isotherm.

Table 1. Langmuir constants for the adsorption of methylene blue dye by different dosages of fungus (stirrer speed 140 rpm, 480 min., 35°C, concentration of dye 30 mg L\(^{-1}\)).

<table>
<thead>
<tr>
<th>Adsorbent dosage (g)</th>
<th>0.05</th>
<th>0.06</th>
<th>0.07</th>
<th>0.08</th>
<th>0.09</th>
<th>0.1</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>0.266</td>
<td>0.336</td>
<td>0.393</td>
<td>0.643</td>
<td>0.698</td>
<td>0.739</td>
<td>2.194</td>
<td>3.136</td>
</tr>
<tr>
<td>K(_L)</td>
<td>5.780</td>
<td>6.849</td>
<td>7.143</td>
<td>11.904</td>
<td>11.629</td>
<td>10.869</td>
<td>48.454</td>
<td>75.758</td>
</tr>
<tr>
<td>R(_L)</td>
<td>0.111</td>
<td>0.090</td>
<td>0.078</td>
<td>0.049</td>
<td>0.046</td>
<td>0.043</td>
<td>0.015</td>
<td>0.011</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.978</td>
<td>0.980</td>
<td>0.973</td>
<td>0.982</td>
<td>0.980</td>
<td>0.976</td>
<td>0.996</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The observed linearity in Fig. 6 was evidenced by the higher R\(^2\) values, which indicate the applicability of the Langmuir adsorption isotherm and the monolayer coverage on the adsorbent surface. The monolayer adsorption capacities of the adsorbents show that it possesses high adsorption capacity, and hence, it could be employed as a low-cost adsorbent for the removal of MB, as seen from Table 1.

The calculated R\(_L\) values at different initial methylene reveal that sorption of MB on fungus was more favorable at higher concentrations. According to Table 1, the value of R\(_L\) lying between 0.011 and 0.111 at all initial dye concentrations confirms the favorable uptake of the MB molecules. Higher R\(_L\) values at lower dye concentrations indicated that the adsorption was more favorable at lower dye concentrations. Lower b values representing the ratio of adsorption/desorption rates was evident that a good correlation for adsorption between the adsorbent and the adsorbate was found. Table 2 showed the maximum adsorption capacities of the various adsorbents related to Langmuir isotherm model.

Table 2. Comparison of maximum adsorption capacities of various materials for MB.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Equilibrium contact time</th>
<th>q(_{max}) (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giant duckweed</td>
<td>32</td>
<td>8</td>
<td>48 h</td>
<td>145.00</td>
<td>[7]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>32</td>
<td>8</td>
<td>48 h</td>
<td>40.60</td>
<td>[24]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>25</td>
<td>7±0,5</td>
<td>30 min</td>
<td>238.00</td>
<td>[25]</td>
</tr>
<tr>
<td>Caulerpa entilifera</td>
<td>25</td>
<td>7±0,5</td>
<td>30 min</td>
<td>417.00</td>
<td>[25]</td>
</tr>
<tr>
<td>Posidonia oceanica fibres</td>
<td>30</td>
<td>6</td>
<td>3 h</td>
<td>5.56</td>
<td>[26]</td>
</tr>
<tr>
<td>Oil Palm Fibre Activated carbon</td>
<td>30</td>
<td>6,5</td>
<td>24 h</td>
<td>277.78</td>
<td>[27]</td>
</tr>
<tr>
<td>Yellow passion fruit waste</td>
<td>25</td>
<td>8</td>
<td>48 h</td>
<td>44.70</td>
<td>[28]</td>
</tr>
<tr>
<td>Cystoseira barbatula</td>
<td>35</td>
<td>6,4</td>
<td>210 min</td>
<td>38.61</td>
<td>[29]</td>
</tr>
<tr>
<td>Caulerpa racemosa var. cylindracea</td>
<td>18</td>
<td>7</td>
<td>90 min</td>
<td>5.23</td>
<td>[30]</td>
</tr>
<tr>
<td>Trametes versicolor</td>
<td>25</td>
<td>11</td>
<td>8 h</td>
<td>-</td>
<td>[31]</td>
</tr>
<tr>
<td>Granular Muntingia calabura</td>
<td>-</td>
<td>6</td>
<td>3 h</td>
<td>20.00</td>
<td>[32]</td>
</tr>
<tr>
<td>Fomitopsis pinicola</td>
<td>35</td>
<td>10</td>
<td>12 h</td>
<td>24.68</td>
<td>This study</td>
</tr>
</tbody>
</table>
3.6. Thermodynamic Parameters

Table 3. Thermodynamic parameters for adsorption of methylene blue by fungus.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>ΔS (kJ mol⁻¹.K)</th>
<th>ΔG (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>-1.368</td>
<td>-1.236</td>
<td>-3.761</td>
</tr>
<tr>
<td>298</td>
<td></td>
<td></td>
<td>-4.239</td>
</tr>
<tr>
<td>308</td>
<td></td>
<td></td>
<td>-2.561</td>
</tr>
<tr>
<td>318</td>
<td></td>
<td></td>
<td>-2.644</td>
</tr>
<tr>
<td>328</td>
<td></td>
<td></td>
<td>-2.727</td>
</tr>
</tbody>
</table>

ΔH and ΔS values calculated from the slope and intercept of the linear variation of lnK with the reciprocal of temperature (1/T) were given in Table 3. All of the ΔG values calculated at different temperatures are negative, which indicates the feasibility of the process and spontaneous nature of the adsorption. The values of ΔH and ΔS for the adsorption of MB on the fungus are also negative, which elucidates the exothermic behavior of the adsorption process.

3.7. Desorption Studies

Desorption of dye from the fungus in various media such as HCl, Ethanol, H₂SO₄, HNO₃, distilled water and NaOH was investigated at different contact times. A higher desorption rate in the acids was observed compared to the other eluents, as seen in Figure 7.

![Figure 7. Desorption of dye-loaded fungus following treatment with HCl, Ethanol, H₂SO₄, distilled water and NaOH.](image)

Among the solvents used for desorption experiments, HNO₃ was found to be effective in desorbing and recovering dye from the fungal surface at higher contact times. The surface of the fungus was protonated in the presence of acids and charged positively, due to the replacement of protons by the dye molecules. This positively charged surface causes the repulsion of MB molecules from the fungal surface, resulting in an increased desorption rate. This ion-exchange mechanism cannot easily proceed in the presence of alcohol, water and NaOH solutions due to the insufficient number of protons available for ion exchange in the media.

3.8. Kinetic Models

Predicting the rate at which adsorption takes place for fungus-MB system was one of the important factors in adsorption system design. This is the reason why a series of kinetic calculations were being conducted in the present study.
The uptake of copper from...of methylene blue from val...of acids, and greatly contributes to the desorption of dye...

From the desorption experiments, it can be concluded that an ion exchange mechanism proceeds in the presence of acids, and greatly contributes to the desorption of dye from fungus. The second order kinetic model was well fitted to the MB-fungus system, representing the rate-controlling step during the adsorption.

REFERENCES


4. CONCLUSION

The experiment results showed that the Fomitopsis pinicola could be used as an alternative low cost adsorbent in the removal of MB. The adsorption isotherm data is fitted with the Langmuir isotherm. The contact time, adsorbent dosage and pH affected the adsorption of MB.

The adsorption process was chemical in nature, according to the results. Thermodynamic parameters showed that the adsorption process was exothermic and spontaneous. From the desorption experiments, it can be concluded that an ion exchange mechanism proceeds in the presence of acids, and greatly contributes to the desorption of dye...


