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Methylene blue dye removal using *Sphagnum palustre* L. Bog-moss as a reusable biosorbent

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Abstract

In this study, *Sphagnum palustre* L. Bog-moss (SPM) was used as a reusable and economical biomaterial for the removal of methylene blue (MB). The effects of different pH, temperature, time, static/shaking conditions, adsorbent amount and concentration of dye were investigated. We evaluated that moss can almost completely remove (99.5 %) MB at low (50 mg L⁻¹) concentration within 1 h, while 85 % dye removal was observed at approximately higher concentration 500 mg L⁻¹. The adsorption isotherm data were fitted well to the Langmuir isotherm. Furthermore, reusability tests showed that *S. palustre* could be used in at least six decolorization steps with high removal efficiency. After the 6th reuse step, the decolorization rate of the MB was found to be 65 ± 0.2 %. As a result, *Sphagnum* moss could be applicable for the decolorization due to their versatility and reusability.

Key words: Decolorization, dye, isotherm, moss, reusability

Metilen Mavisi Boyasının Giderilmesinde Tekrar Kullanılabilir Biyosorbent Olarak *Sphagnum palustre* L. Karayosununun Kullanılması

Öz

Bu çalışmada, *Sphagnum palustre* L. karayosunu (SPM) metilen mavisi (MB) gideriminde tekrar kullanılabilir ve ekonomik bir biyomateryal olarak kullanılmıştır. Farklı pH, sıcaklık, zaman, statik / çalkalama koşulları, adsorban miktarı ve boya konsantrasyonunun boyar madde giderimine etkileri araştırılmıştır. Karayosunu, düşük konsantrasyon boya maddeyi (50 mg L⁻¹) 1 saat içinde neredeyse tamamını (% 99,5) giderirken, 500 mg L⁻¹ yüksek konsantrasyonu %85 oranında giderdiği belirlenmiştir. Adsorpsiyon izoterm verilerinin Langmuir izotermi ile uygun olduğu bulunmuştur. Bu duruma ilaveten, tekrar kullanılabilirlik deneyleri *S. palustre*'nin en az altı renk giderimi işleminde yüksek giderim verimi ile kullanıldığını göstermiştir. Altıncı tekrar kullanılabilirlik testinde, metilen mavisinin renk giderim verimi % 65 ± 0.2 olarak bulunmuştur. Bu sonuçlar, çok yönlülüğü ve yeniden kullanılabilirliği nedeniyle *Sphagnum*'un renk giderimi uygulamasında kullanılabileceğini önermektedir.

Anahtar kelimeler: Renk giderimi, boya madde, izoterm, yosun, tekrar kullanılabilirlik

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1. Introduction

Significant amount of wastewater has been released into the environment after industrialization and urbanization period (Saeed et al., 2009; Malik, 2014; San Keskin et al., 2015). Synthetic dyes/pigments in many industries such as textile, plastics, leather tanning, paper production, cosmetics, and hair colorings are major causes of environmental pollution (Zaghbani et al., 2007; Turabik and Gozmen, 2013). After dye applications, about 2-50 % of the dyestuff released into the environment via industrial wastewater (Atafar et al., 2010). Even above the concentration of 1 mg L⁻¹ of dye is enough to be visible by human eye, in general, textile wastewaters contain 10 to 50 mg L⁻¹ of industrial pigments. Dyes affect photosynthesis processes and change the biological cycles. At present, several technologies such as chemical precipitation, ion exchange, solvent extraction, membrane separation and adsorption have been developed to remove dyes from wastewater (Raghu et al., 2009; Saeed et al., 2010; Lee et al., 2011; Kazemi et al., 2013; Ghaedi and Mosallanejad, 2014; Hajati et al., 2014; Soni et al., 2014; Toor et al., 2015). Adsorption is considered as an efficient approach due to its low cost, and easy operation among various other water treatment methods (Chakraborty et al., 2005; Wang et al., 2005). Thus, decolorization technologies such as adsorption are utilized. Several low cost adsorbents such as sawdust (Garg et al., 2003), rice husk (Gupta et al., 2009) and ash (Marrakchi et al., 2017) have been examined on the possibility study to lower dye concentrations and used to water treatment.

In this study, synthetic dye methylene blue (MB) is selected as model contaminants which is used MB is used as a coloring agent like paper, cottons, hair, wools and paper stock (Du et al., 2016) in order to evaluate the sorption efficiency of the Turkish *S. palustre* moss from aqueous solutions. Due to its characteristic as a highly porous, polar material, having cellulose and lignin as its main components, moss has been reported as a low cost sorbent for efficient removal of dye water pollutants (Contreras et al., 2007; Gupta et al., 2009).

Removal of MB dye was investigated under batch conditions with various process parameters, such as pH of solution, temperature, static/shaking conditions, adsorbent amount, concentration and contact time, were considered. Finally, the reusability of SPM was tested. To understand the mechanism of dye sorption using

moss as the adsorbent, the sorption data were tested fitted to a number of isotherm models.

2. Materials and Methods

Sphagnum includes approximately 120 species, commonly known from boggy wetland habitats (Daniels and Eddy, 1985). Currently, 24 taxa in *Sphagnum* have been recorded for Turkey (Ören et al., 2017). *Sphagnum* species in Turkey were usually known from eastern Black Sea region. Nevertheless, using blunt-leaved bog moss (*Sphagnum palustre* L.) in this research was collected from the swampy lands near to alpine meadows at Sogucak plateau, alt. c. 1075 m, (40° 36' 21" N, 30° 11' 27" E), (1075 m) on 28 May 2015, in Samanlı Mountains where extend from western edge of the Armutlu Peninsula in Yalova province to Geyve gorge of Sakarya province in north-western of Turkey. Voucher specimens were deposited in Ankara Hacı Bayram Veli University, Polatlı Science and Literature Faculty, Department of Biology (AHBV BRY 1146).

Batch adsorption experiments were performed in by shaking the required amount of moss (0.5 g) with 100 mL MB aqueous solutions, at a 25 ± 1 °C. After a specified contact time period, residual concentration of MB in solution was spectrophotometrically at λ = 665 nm (UV-VIS Spectrophotometer, Shimadzu) (San et al., 2014).

The decolorization experiments in batch mode were accomplish at various contact time (0-5 hours), different pH (pH 2-pH 12), different temperatures vary on 25 °C to 40 °C, static/shaking conditions such as 0 rpm, 100 rpm, 200 rpm, adsorbent amount of 0.1 g to 2 g and dye concentrations 50 ppm to 500 ppm. After inoculation, every 30 minutes, aliquots of the culture solution were withdrawn and used for analysis. Experiments were repeated in triplicates.

Decolorization percentage was calculated from below formula:

$$\% \text{ Decolorization} = \frac{\text{Initial absorbance value} - \text{final absorbance value}}{\text{Initial absorbance value}} \times 100$$

The amount of MB adsorbed by moss, q_e (mg g⁻¹), was calculated by the following equation:

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

where C_0 is initial and C_e is equilibrium concentrations of dye solution. V is the total volume of the dye solution, and m is the mass of moss used (Balan et al., 2009).

When the system is a state of equilibrium, determining the distribution of MB between moss surface and the liquid phase is important for establishing the capacity of the moss. The adsorption equilibrium data were fitted into four different isotherm models using Isofit software (Wagner et al., 2005).

Small moss sample was prepared for SEM analyses. The samples were coated with 5–10 nm layer of gold-palladium and analyzed using SEM microscopy (FEI Instruments, USA).

The reusability of the moss was performed 6 times at 200 rpm and 25 °C for 1 hour. Dye concentrations were measured at the beginning (0 h) and at the end of 1 h.

3. Findings

Hemmati et al., (2017) used acid modified Spagnum as a biosorbent for removal of malachite green. In response to this, *S. palustre* was used directly in our studies with no further preparations.

SEM image of the pore structure of *S. palustre* is shown in Figure 1. Due to highly pore structure, *S. palustre* has the unique ability to hold up to 20 times its weight in water (Schofield, 2001). These structures provide moss to extremely large surface area, and hold water/moisture well.

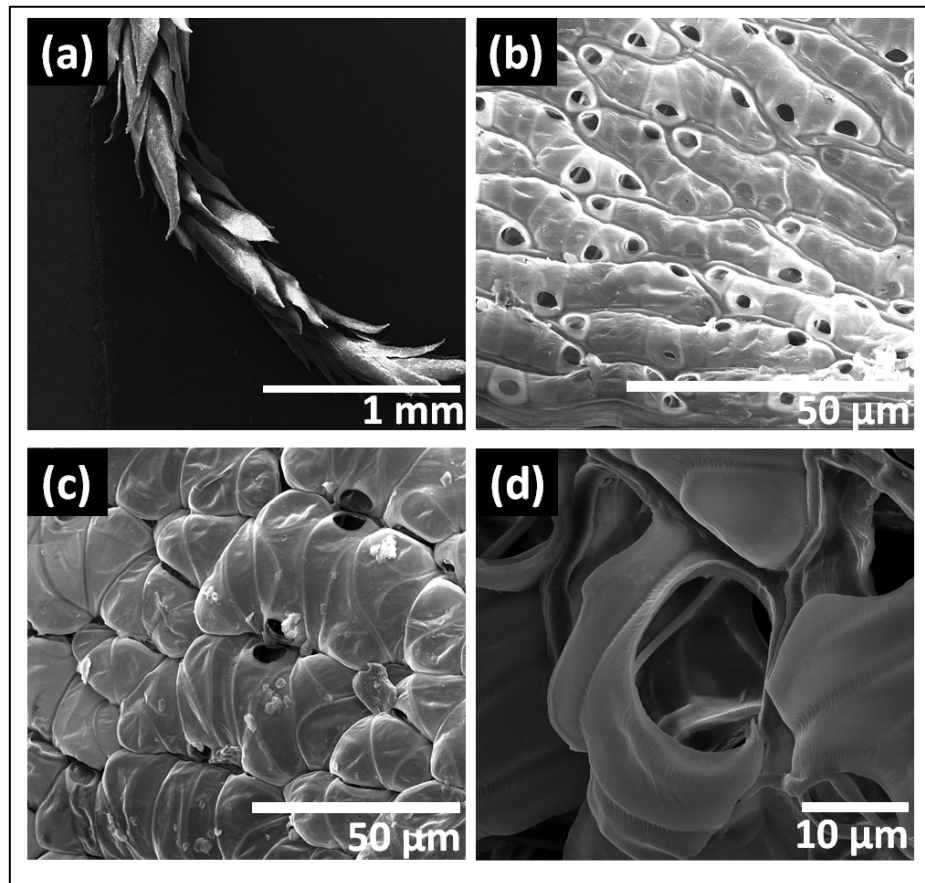


Figure 1. SEM images of the pore structure of *S. palustre* collected from Samanlı mountains.

Selecting the appropriate pH, contact time, static/shaking conditions, temperature and amount of moss for achieving maximum efficiency in the decolorization of dye by adsorption might be essential. After 1 h incubation, pH value effect on dye decolorization was determined. The experiments were performed at pH 2.0–12.0. As shown in Fig. 2a,

the lowest uptake yields were observed at pH 2.0 and pH 12, which correspond to strongly acidic and basic conditions respectively. The maximum uptake yield was $99.5\% \pm 0.06$ at pH 4. In addition, decolorization yields were still high at pH 5 and pH 6. As a result, an initial pH in the range of 3.0–6.0 was favorable for the dye removal by the adsorbent.

The effect of time on the decolorization process were studied from 15 minutes to 5 hours at 50 mg L⁻¹ initial MB at pH 4.0 at 25 °C. As seen in Figure 2b, the decolorization increased during the first 1 h and 99.5 ± 0.06 % of MB was removed from the solution at 200 rpm. After 1h, reached a constant value when equilibrium was established for both 100 rpm and 200 rpm. For static condition (0 rpm) equilibrium reach to constant value after 180 minutes of incubation. Optimum shaking time found 1h, which was used for all further adsorption studies. Adsorbent decolorization ability was significantly enhanced to 98.8 ± 0.06 % for 100 rpm and 99.5 ± 0.06 % for 200 rpm.

Due to direct effect on adsorption process, temperature is significant physico-chemical process parameter. The simultaneous decolorization of MB at different temperatures

such as 25 °C, 30 °C and 40 °C was shown in Figure 2c. Whereas the percentage of removal after 1 h was found to be comparatively low at 40 °C, it increased to a higher level at 30 °C and reaches maximum rate 99.6 ± 0.06 % for 25 °C. Temperature analysis indicates that the adsorption is an exothermic process (Argun et al., 2008). When temperature increase adsorptive forces between the dye and adsorbent surface-active sites decrease as a result of decreasing the amount of adsorption. The results of the dependence of MB adsorption on the amount of moss was shown in Figure 2d.

Data showed that, there is parallel relationship between amount of dye and dye concentrations cause dyes adsorption increased with increasing the amount of moss. At the end, value reached a constant value when equilibrium was established. 0.5 g was found to be the optimum amount that used for all further experiments.

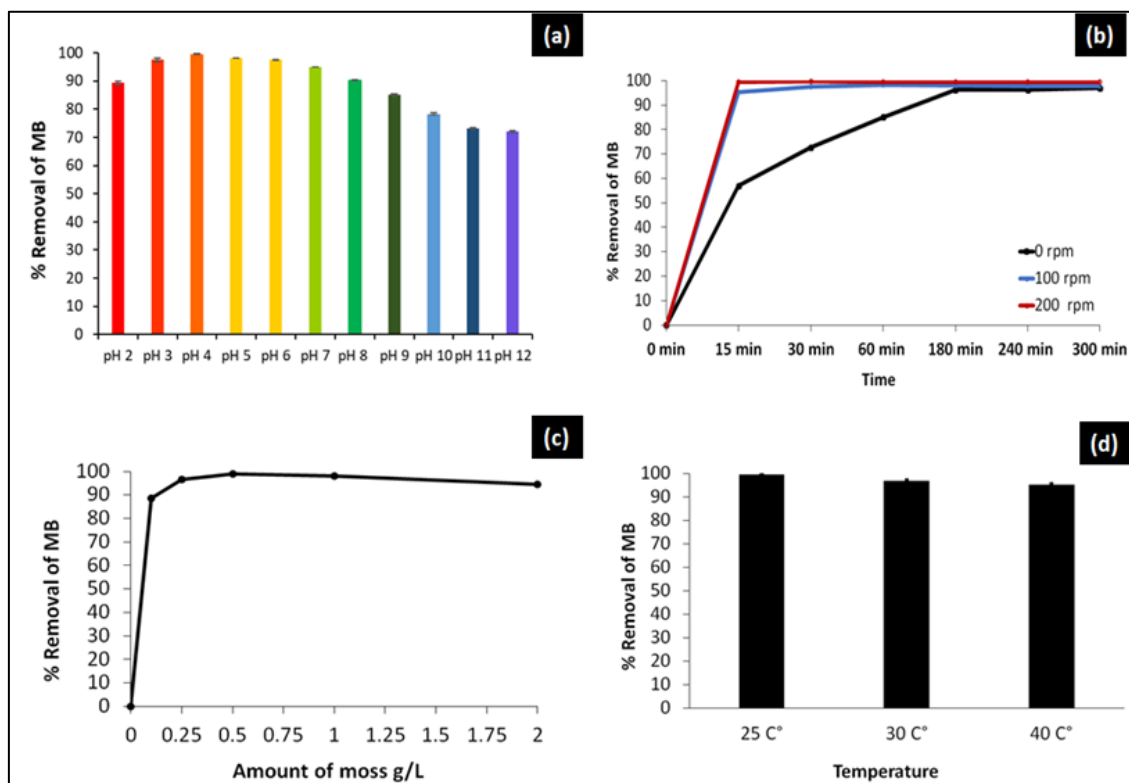


Figure 2. The effect of (a) pH (b) contact time and static/shaking conditions (c) amount of moss and (d) temperature on the decolorization yield of the moss in the 50 mg L⁻¹ MB dye.

Initial dye concentration effect on the decolorization process was explored by using different dye concentrations such as 50, 100, 250 and 500 mg L⁻¹. As given in Figure 3, MB decolorization was achieved 97.04 ± 0.1 % decolorization at 100 mg L⁻¹. For 250 mg L⁻¹ dye concentration, the decolorization capacity was

96.23 ± 0.2 %. When dye concentration was increased up to high concentration as 500 mg L⁻¹, the decolorization capacity was decreased to 85 ± 1.9 %. As it was clearly seen in Figure S1 that after decolorization process, decolorization yields of the moss cells were still significantly higher.

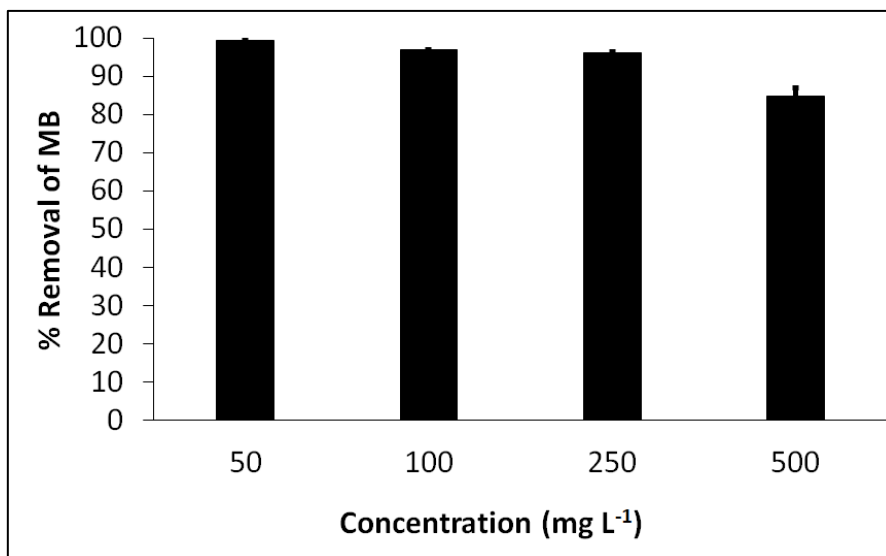


Figure 3. The effect of initial dye concentration on the decolorization yield of the moss in the 50 mg L⁻¹ dye of MB (pH 4; Temp: 25 °C; stirring rate: 200 rpm).

From the point of view of bioremoval research it was essential to study the reusability of the microorganisms. Moss dye decolorization capability was tested for six cycles of reuse (Figure 4). Figure 4a showed the MB decolorization efficiency for cycles. At the end of the first cycles, % removal of dyes was observed as 96.5 ± 0.02 %. For the 3th cycle, the dyes decolorization decrease to 89.4 ± 0.5 %.

The cycle numbers of reusability are a significant issue for applications. 65.09 ± 0.2 % of the dye decolorization was obtained for the 6th cycle for MB which suggests that Sphagnum can continue to decolorization under several cycles of reuse. For this reason, moss may be use constantly for decolorization of wastewater. Figure 4b shows the remaining colors at the end of each reusability experiment.

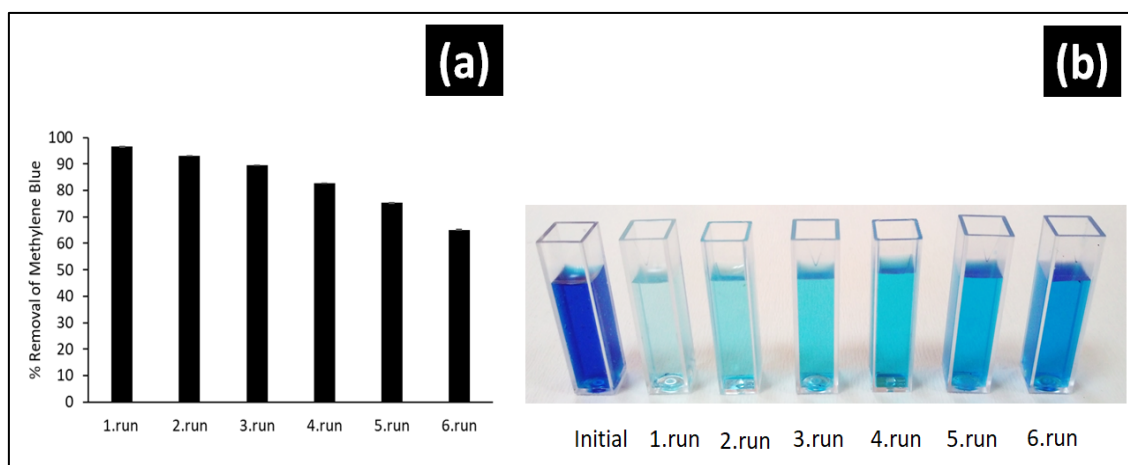


Figure 4. (a) Reusability results of the six cycles of MB decolorization experiments at 50 mg L⁻¹ dye concentrations (b) the photographs of color after reusability experiments.

The Freundlich, Langmuir, Toth and Linear adsorption isotherm models were used for the experimental equilibrium sorption analyses and the best-fit equilibrium model was established based R² that correspond to linear regression correlation coefficients. Adsorption isotherms and their values were listed in Table 1. Results from these experiments were modelled

adsorption isotherm theories with the Langmuir model proving to be the more suitable. The Langmuir isotherm theory presume monolayer coverage of adsorbate over a homogenous adsorbent surface (San Keskin et al., 2015). Similar results was reported by Allen et al., (1988).

Table 1. Dye adsorption kinetics coefficients of *S. palustre* for each isotherm model

Material	Isotherm	Parameters	Values	Ry ² value
<i>S. palustre</i>	Freundlich	Kf	0.015	0.97
		1/n	0.7	
	Langmuir	Q _{max}	2.49	0.98
		b	1.92	
	Linear	Kp	2.5 x10 ⁻²	0.92
Toth	Q _{max}	2.15x10 ⁵	0.93	

4. Result and Discussion

S. palustre moss was utilized as an adsorbent for the decolorization of methylene blue (MB) from aqueous solutions as a function of solution pH value, temperatures, static/shaking conditions, contact time, adsorbent dose and initial dye concentrations. Results obtained from experiments showed that the highest percentages of dye removal were attained using moss from pH 4.0 with MB concentrations below 50 mg L⁻¹.

S. palustre was chosen as a suitable adsorbent which have pore structure that was capable of decolorization of dyes in wastewater. Due to large usage in textile industry MB was chosen as the target contaminant. After dye removal process, moss was reused six cycles and at the end of the last cycle, ~ 65 % of the MB dye decolorization capacity was obtained. 6th cycle reusability suggest that moss utilized repeatedly for dye decolorization in wastewater such as industrial origin.

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Conflict of interest

The authors declare no conflict of interest.

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