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TREATMENT OF METHYLENE BLUE IN WASTEWATER USING *Scirpus grossus*

(Rawatan Metilena Biru dalam Air Sisa Menggunakan *Scirpus grossus*)

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Abstract

Phytoremediation is an emerging technology that should be considered for the remediation of contaminated sites because of its aesthetic advantages and long-term applicability. The possibility of *Scirpus grossus* for degradation of a basic dye, methylene blue (MB) was investigated. The effect of the operational parameter of different dye concentrations (0, 200, 400, 600, 800 and 1000 mg/L) was determined, and the water quality parameters namely pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) were monitored. The UV-Visible absorption confirmed the degradation of MB within 72 days. The removal efficiency of methylene blue dye from synthetic wastewater was determined to be in the range of 86 – 38% for all treatments at different concentrations (200 – 1000 mg/L) respectively. Furthermore, the highest removals for BOD, COD in 400 mg/L and TOC in 200 mg/L MB were 69, 58 and 63% respectively.

Keywords: phytoremediation, *Scirpus grossus*, methylene blue, decolourisation, water quality

Abstrak

Fitopemulihan merupakan teknologi baru yang perlu dipertimbangkan untuk pemulihan tapak tercemar kerana kelebihan estetik dan kebolehgunaan bagi jangka panjang. Kemungkinan *Scirpus grossus* untuk degradasi pewarna asas, metilena biru (MB) telah dikaji. Kesan parameter operasiiaitu kepekatan pewarna yang berbeza (0, 200, 400, 600, 800 dan 1000 mg/L) ditentukan dan parameter kualiti air iaitu pH, oksigen terlarut (DO), permintaan oksigen biokimia (BOD), permintaan oksigen kimia (COD) dan jumlah karbon organic (TOC) dipantau. Penyerapan UV cahaya nampak mengesahkan degradasi MB dalam masa 72 hari. Kecekapan penyingkiran pewarna metilena biru daripada air sisa sintetik telah ditentukan dalam lingkungan 38 – 86% untuk semua rawatan dalam kepekatan yang berbeza (200 – 1000 mg/L) masing-masing. Tambahan pula, penyingkiran tertinggi bagi BOD, COD dalam 400 mg/L dan TOC dalam 200 mg/L MB masing-masing adalah 69, 58 dan 63%.

Kata kunci: pemulihan-fito, Scirpus grossus, metilena biru, penyahwarnaan warna, kualiti air

Introduction

Major progress in textile industry has caused serious environmental problems, since the textile industries use dyes to colour their products and, as a result, generate a considerable amount of coloured effluents causing water pollution. These dyes can be mutagenic, carcinogenic and can impart toxicity to aquatic life [1]. Discharge of dye-bearing wastewater poses a severe problem. In textile industries, about 10 – 15% of the dye gets lost in the effluent during the dyeing process [2]. Effluents containing dye produce wastewaters having a high chemical oxygen demand

(COD), biological oxygen demand (BOD), and other toxic chemical compounds [3]. The values of COD, BOD and TOC in textile effluents are 276 – 1379, 99 – 350 and 74 – 530 mg/L, respectively [4]. Various techniques like adsorption, coagulation, ozonation, and electrolysis are used for the purification and decolourization of dyeing wastewater [5]. Due to low biodegradability of dyes, a conventional treatment process such as the physical-chemical method is not very effective. Moreover, all these methods have different colour removal capabilities, incur high costs, and have low efficiency [6].

In recent years, microorganisms have been reported for degradation of textile dyes [7–10]. The knowledge that plants can also be used to clean up contaminated soil has opened up new avenues of research, and has provided a basis for the present-day use of constructed wetlands for treating municipal and industrial waste streams. In this study, constructed wetland systems (CWs) employing horizontal subsurface flow were set up in a greenhouse, with and without *Scirpus grossus.* We aim to study the role of a native Malaysian plant, *Scirpus grossus* (*S. grossus*)*,* in a subsurface batch system to remove textile dyes containing methylene blue dye (MB) at different concentrations (200, 400, 600, 800 and 1000 mg/L) from synthetic wastewater. *S. grossus* is an aquatic species with a high growth rate, and has the ability to degrade contaminants, giving an insight into the involvement of bacteria and the prediction of metabolic pathways behind the degradation of the dye. This technology has received attention lately as an innovative and cost-effective alternative to the more established treatment methods used at hazardous waste sites [11]. Thus, the phytoremediation potential of the plant for the synthetic dye of MB was evaluated.

Materials and Methods

Plant source of *Scirpus grossus*

S. grossus was collected from a freshwater lake, Tasik Chini in Pahang, Malaysia for propagation for one month until the first generation was produced.

Concentration and analysis of dye in synthetic wastewater

This experiment was conducted in a greenhouse at Universiti Kebangsaan Malaysia (UKM), under subsurface batch system (SSF) using *S. grossus* plants on various dye concentrations for 72 days. 33 aquarium glasses were used in this study, 15 aquaria containing synthetic wastewater contaminated with MB, and each concentration with three replicates (R1, R2, R3). There were another three aquaria-containing MB-contaminated wastewaters, only without plants as contaminant controls (CC1, CC2, CC3) for each concentration of MB. The last three acquiria acted as plant controls (PC1, PC2, PC3), as illustrated in Figure 1a.

Each aquarium was layered from top to bottom with 8 cm of gravel with a size of Φ10–20 mm, 3 cm of gravel with a size of Φ 1–5 mm and 10 cm of sieved fine sand of Φ 2 mm (Figure 1b). Each aquarium was filled with 7 L of synthetic wastewater prepared by mixing tap water with MB (R&M Chemicals Marketing, UK) at different concentrations (200, 400, 600, 800 and 1000 mg/L). An aliquot of 10 mL of decolourised solution of the dye was centrifuged at 4000 rpm for 10 min to remove all particulate matter using Eppendorf Centrifuge (AG 22331 Hamburg, Germany), and then the absorbance of the solution was measured at 665 nm wavelength using UV/vis spectrophotometer (DR 3900 HACH). The decolourisation percentage for the respective dyes was calculated using equation 1 based on initial and final absorbance:

$$\text{Decolorization (\%)} = \frac{(\text{Initial absorbance at 0 h}) - (\text{Observed absorbance at t})}{(\text{Initial absorbance at 0 h})} \quad (1)$$

Monitoring and analysis of operational parameters

The operational parameters were determined during 72 days of exposure with sampling performed on days 0, 7, 14, 28, 42 and 72. The parameters of pH temperature (T, $^{\circ}$C), dissolved oxygen (DO, mg/L) and oxidation reduction potential (ORP, mV) were recorded to observe the physicochemical changes in water using a Metrohan multi-probe of (Model 877, Swiss) for the pH, ORP and temperature measurements. For dissolved oxygen, the YSI sensor (Model 550A, USA) was used.

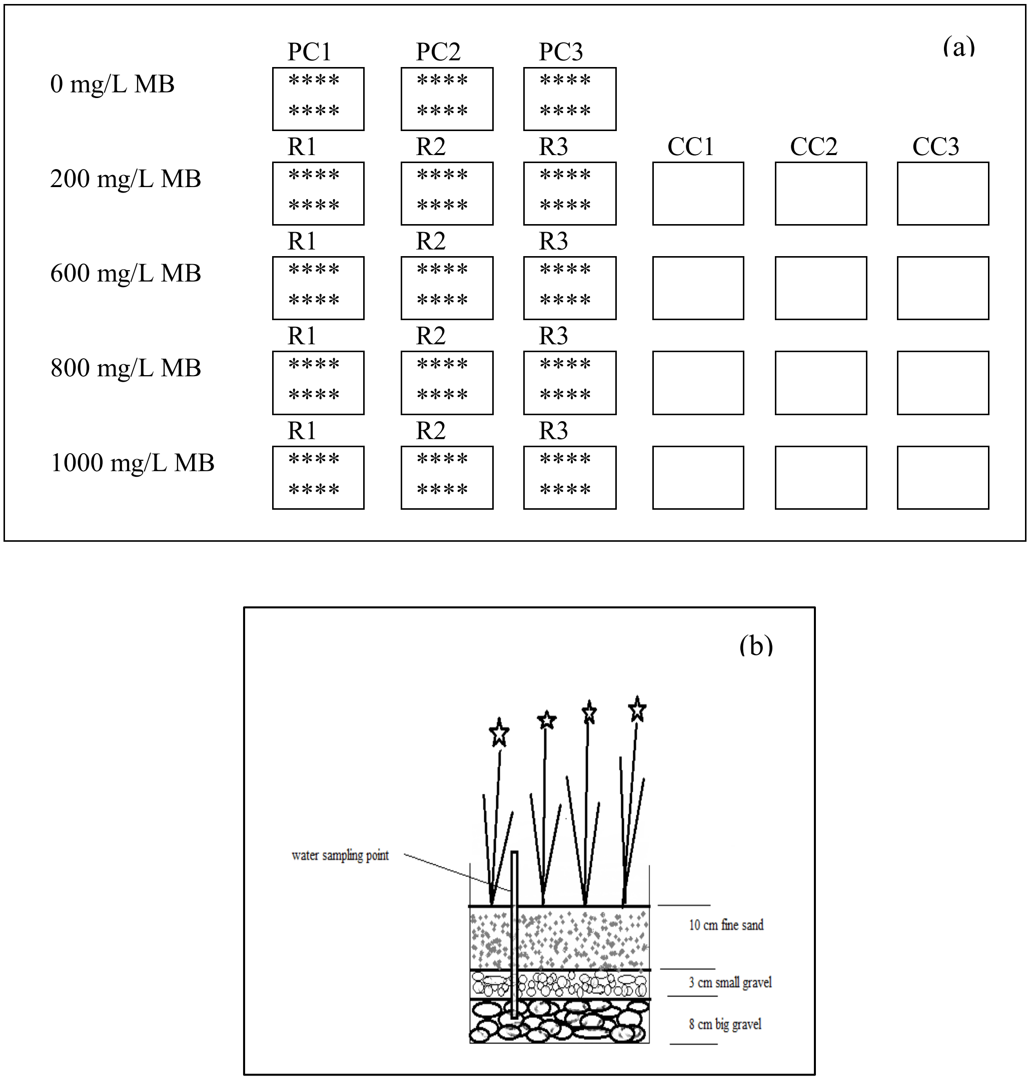

Figure 1. (a) Experimental set-up of the phytotoxicity experment, (b) Schematic diagram of an aquarium for the phytotoxicity test

Analysis of water quality parameters (BOD, COD, TOC)

BOD, COD and TOC of the MB contaminated water were determined. The COD and TOC values were determined using a spectrophotometer (DR3900 HACH, Germany). The BOD value was determined by measuring the dissolved oxygen levels in the sample before and after incubation for five days, according to Winkler's iodometric method [3]. BOD was calculated using equation 2 as follows:

$$\mathrm{BOD}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) = \frac{D_0 - D_5}{P} \quad (2)$$

where D_0 is define as initial DO concentration in the sample, D_5 is DO concentration after five days and P is decimal volumetric fraction of sample used.

Results and Discussion

Variation of operational parameters for different dye concentrations

The physical parameters (i.e. T, pH, DO and ORP) were recorded throughout the phytotoxicity test, as shown in Table 1. For treatment with plants and without plants at different concentrations of MB dye (200, 400, 600, 800 and 1000 mg/L), the range of temperature with plants was between 28.3 – 29 ^{o}C, while the temperature without a plant was 29 ^{o}C. The pH ranged between 8.2 – 8.6 in the aquarium with plants; for the aquarium without plants, the pH ranged between 9 – 10, with increasing pH during the treatment of 72 days. With regard to DO, the average value range between 4.3 – 4.7 mg/L in the aquarium with plants, indicating that the organism used oxygen for MB degradation. The average value of DO in the aquarium without plants was between 2.7 – 3.4 mg/L. The ORP range value was between -201till -139 mV for the aquarium with plants, while the values of ORP in the aquarium without plants was -184 till -172 mV, with the reading increasing with time. The negative values of ORP throughout the MB dye treatment show that the condition was under anaerobic conditions [12]. However, for the aquaria with plants, the conditons were less anaerobic and became more aerobic with treatment duration.

Table 1. Average operational parameters in phytotoxicity test with and without *Scirpus grossus* in MB contaminant

Parameters	With *Scirpus grossus*	Without *Scirpus grossus*
Temperature (^{o}C)	28.4 ± 0.4	29 ±0.3
pH	8.2 ± 0.4	9.4 ± 0.6
DO (mg/L)	4.5 ± 0.2	3.2 ± 0.4
ORP (mV)	-171 ± -24	-180 ± -8

Decolourisation of MB dye by *S. grossus*

In the screening experiments, the decolourisation of MB by *S.grossus* at different dye concentrations showed different decolourisation patterns. The decolourisations of 86, 52, 47, 34 and 38% were observed for 200, 400, 600, 800 and 1000 mg/L respectively, at the end of 72 day exposure. The maximum decolourisation occurred at 200 mg/L (86%); whereas the minimum decolourisation was obtained for 800 mg/L (34%). The increasing MB concentration caused decreasing percentages of MB decolourisation values monitored throughout 72 days (Figure 2), indicating some toxicity effects on the plants. The low percentage of decolourisation at higher concentrations of dye was due to the inhibitory effects of the dye transformation process (Figure 2). As for the comparison with the control aquaria without plants, the decolourisations of MB were only 31% (200 mg/L), 15% (400 mg/L), 19% (600 mg/L), 2% (800 mg/L) and 19% (1000 mg/L). These results confirm the ability of *S. grossus* plants to decolourise MB dye. In previous studies, 98% MB was removed using *Limna minor* after six days [13], while a removal effiency of 65.7–89.30% was obtained by [14] through an adsorption process using *peat* with MB concentration of 19–134 mg/, which is comparable with our results.

Monitoring of BOD, COD and TOC

BOD, COD and TOC are widely used methods to determine organic matter in wastewater [15]. The BOD, COD and TOC values of synthetic wastewater for different dye concentrations were found to decrease in the test samples treated with *S. grossus* for 72 days, as depicted in Figure 3. The highest efficiency removal of BOD was 69% for 400 mg/L dye concentration; while the lowest was 21% for 800 mg/L. The BOD removals were 46, 25 and 37% for 200, 600 and 1000 mg/L respectively. Similarly, the highest efficiency removal of COD was 58% for 400 mg/L and the lowest was 21 % for 800 mg/L, while the COD removals were 40, 30 and 26 mg/L for 200, 600 and 1000 mg/L respectively. As for the TOC, the highest removal was 63% for 200 mg/L while the lowest was 26% for 1000 mg/L. 49, 36 and 39% were obtained for 400, 600 and 800 mg/L respectively. The results obtained for BOD, COD and TOC removal indicated that *S. grossus* has the ability to decolourise MB in contaminated water.

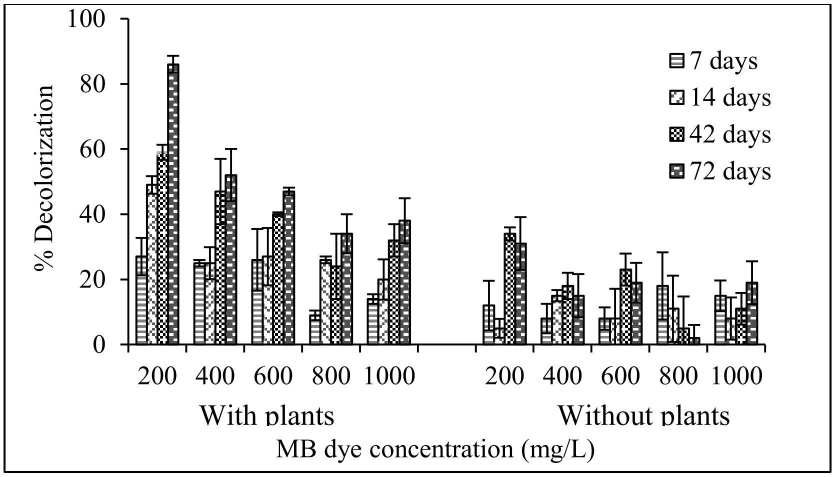

Figure 2. Effect of increasing concentrations of MB (200, 400, 600, 800 and 1000 mg/L) on the percentage of decolourisation monitored at 7, 14, 42 and 72 days with and without *S. grossus*

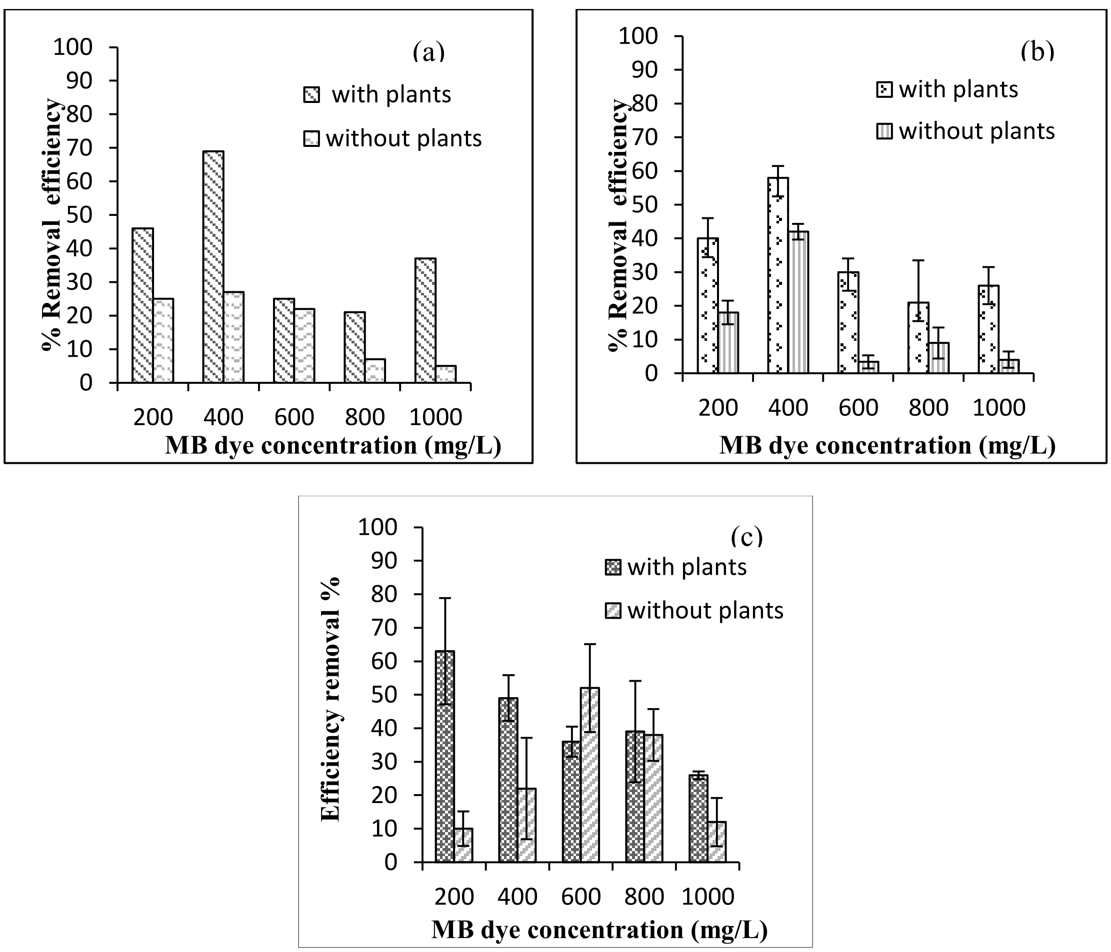

Figure 3. Removal percentages of (a) BOD, (b) COD and (c) TOC for different concentrations of MB dye

Conclusion

We have demonstrated the ability of S. *grossus* to decolourise MB dye at different concentrations (200, 400, 600, 800 and 1000 mg/L) after 72 days in a subsurface batch system. Based on the results, the highest dye removal of 86% and 38% was obtained for MB dye concentrations of 200 and 1000 mg/L respectively. Compared to the results obtained from the aquarium without plants, the dye removals were only 31% and 2% at MB dye concentrations of 200 and 800 mg/L respectively. These results give evidence that *S. grossus* was able to remove dye from wastewater.

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