The feasibility of macro alga *E.spinosum* for colour removal from real textile wastewater

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Abstract. Industrial textile wastewater usually contains high chemical substances, suspended solids and a very conspicuous intense colour. The complexity of textile wastewater had urged for an effective treatment method. This paper studies the feasibility of red macro alga, *Euchema Spinosum* as a natural and low-cost biosorbent for the removal of colour in real textile wastewater. The characterization of aforesaid biosorbent was analysed for its physical and chemical properties using Brunauer-Emmett-Teller (BET) and X-ray Fluorescence Spectrometer (XRF). The effect of dosage and contact time on colour removal was analysed using batch biosorption experiments. The BET result confirmed that surface area of biosorbent is relatively small suitable for biosorbent characteristic. The result shows that at optimum dosage of 15g/L within 48 hours, *E. spinosum* was able to remove 93.71% of colour from textile wastewater. Therefore, *E. spinosum* was found to be highly effective in treating real textile.

1. Introduction

Textile industry is continuously growing to the extent that it has become the eleventh biggest exports in Malaysia. Even though the industry helps to boost the country's economy, at the same time the industry is imposing negative effects too. Textile industries discharge huge amounts of dye and other chemical waste to waterbody, thus polluting the water resources and imposing great threat to humans, animals, and aquatic life. The effluent contain considerable amount of suspended solids, intense dyes color, detergents, salt and other chemicals which makes it difficult to be treated[1]. The discharge of those effluents will severely contaminate river, lake, sea or any other waterbodies. It also affect the ecosystem by hindering sunlight from entering a waterbody, preventing water plants to carry out photosynthesis thus increasing chemical oxygen demand (COD) in a waterbody [2].

Therefore, several efforts have been made to remove dyes from the wastewater. It comprises of physical and chemical methods, electrochemical treatments and biological treatments. The techniques include coagulation-flocculation [3], microbiological discoloration [4], electrochemical [5], advanced oxidation processes [6], membrane filtration [7], ozonation [8] and adsorption[9]. Among all, adsorption is known to be effective in terms of adsorption capacity and cost effectiveness. Adsorption of dye by activated carbon is widely practiced. Activated carbon is very good in adsorbing dyes in wastewater and it has been widely used in many industries to treat wastewater. However, it has been identified that activated carbon is not economical and favourable as it requires a high operating cost as well as energy, generate toxic sludge and it is not suitable to be used for large scale treatments [10].

In recent years, a considerable number of studies have focused on low-cost biomaterial alternatives for adsorption process; so called biosorption for dye removal[11], [12]. Biosorption method is favored as it offers a more eco-friendly and economic alternative. Biosorption using macro algae is one of the most economic and environmental friendly solution to treat dyes in waste water because it is readily available and it does not pollute the environment or generate any dangerous by-products [13]. Macro algae also offer an abundance of tiny pores, which provide a large surface area to adsorb dye molecules. It possesses various functional groups at its cell wall such as the hydroxyl (-OH), amine (-NH), carboxyl (-COOH), *etc* which are responsible for biosorption of dye molecules [14]. Macro algae belong to one of several groups of multicellular algae categorized into red, green and brown algae.

Previous literatures had reported excellent performance of macro algae as biosorbent for synthetic dyes [15]–[19]. The results of our previous study [10]revealed that some functional groups of *E. spinosum* such as hydroxyl (-OH), amine (-NH), carboxyl (-COOH) were mainly involved in the biosorption of Methylene Blue dye from aqueous solution. However, no study reveals the potential of aforesaid biosorbent in real application using textile wastewater. Little study was done on biosorption of real textile wastewater onto biomass such as filamentous fungi Aspergillus carbonarius M333[20]and palm shell-based activated carbon [21].

In biosorption study, the efficiency of biosorption in an industrial scale as well as laboratory scale is very much depend on the factors such the biosorbent dosage, the contact time between the biosorbent and the dye molecule, the dye concentration in the wastewater, the solution pH and the temperature of the solution[22]. Since dye concentration, temperature and pH of solution cannot be control in actual industrial operation, the contact time and biosorbent dosage can be set to work at optimum level to achieve desired rate of removal. In addition, factor of time and dosage gives a huge impact on cost effectiveness of the entire industrial operation.

In this regard, the feasibility of *E. spinosum* for the remediation of real textile wastewater from batik industry from Kuantan, Pahang was investigated. The key target of the present study is to examine (1) the physical and chemical characteristics of *E.Spinosum* using Brunauer-Emmett-Teller (BET) to measure the average pore size and pore size distribution and XRF for elemental analysis (2) the removal of real textile wastewater using *E.spinosum* as biosorbent. The efficiency of the *E.spinosum* was evaluated in terms of decolourization (color intensity and percentage removal).

2. Methodology

2.1. Real textile wastewater

Samples of real textile wastewater were collected from a batik printing process industry in Kuantan, Pahang, Malaysia. It was collected from the equalization tank. Portable Multi-parameter (Multi 340i, Germany), was used to characterize the in-situ parameter of the wastewater such as temperature and pH. Other parameters were also measured including total suspended solids (TSS), color and COD. The characteristics of the real textile wastewater are tabulated in Table 1. The effluent is compared with Standard B Environmental Quality (Industrial Effluent) Regulations 2009.

Table 1. Characteristic of real textile wastewater as compared with acceptable conditions for discharge of industrial effluent or mixed effluent of Standards B Environmental Quality (Industrial Effluent) Regulations 2009.

Parameters	Value	Standard B
pH value	4.89	5.5-9.0
TSS (mg/L)	11030	100
COD (mg/L)	7680	250
Colour (ADMI)	8900	200

2.2. Preparation of biosorbent
Macroalga used in this experiment is from red species of E. spinosum. *E. spinosum* was collected from a coastline located at Kunak, Sabah. Wet algal material was washed with distilled water to remove salt and debris. Then the material was oven dry at 60°C for 24 h prior to drying process[23]. Dried materials were blended and grinded with mortar and pestle and sieved according to the desired particle size similar to commercial activated carbon size.

2.3. Biosorbent characterization
The specific surface area of *E. spinosum* was measured by using BET method (Micromeritic ASAP 2020, USA). BET was used to determine the specific surface area of seaweed biosorbents [24]. Firstly, the samples were degassed at 110°C for 3 h under P/Po=0.99 to remove any contaminants that adhere to the surface. The specific surface area was determined by fitting the linear portion of the BET plot to BET equation, and pore size distribution was calculated based on the desorption plot of N_2 adsorption–desorption isotherm using the Barrett–Joyner– Halenda (BJH) method (Micrometrics ASAP 2000, USA). Moreover, WDXRF spectrometer (Wavelength Dispersive X-ray fluorescence, Rigaku ZSX primus II, Japan) was used to determine the chemical compositions of the biosorbents.

2.4. Analytical measurements
Decolorisation process was analyzed using spectrophotometer UV-VIS (Shimadzu U 1800) based on the method adopted by ADMI (American Dye Manufacturers Institute), and recorded as ADMI values [25]. The decolorisation was performed at wavelength range of 200 to 900 nm. The samples were filtered with membrane filter before running with UV-Vis. The UV-vis consists with sources (UV and visible), wavelength selector (monochromator), sample containers, detector, signal processor and readout was used for analysis.

2.5. Biosorption experiment
To test the effect of contact time and dosage against the adsorption capacity, a mixture of *E. spinosum* and real textile wastewater was prepared. The mixture had been prepared in a vial for 25 mL of volume. Various dosages of 5 g/L, 10 g/L, 15 g/L, 20 g/L, 25 g/L and 30 g/L were studied. The removal of color was investigated at every interval of contact time (2, 4, 6, 24, 26, 28, 30, 48, 50, 52 and 54 hours). The pH value of the sample was maintained as it is. The mixture was then left under normal room temperature for biosorption to take place without inducing any force or motion. This is to allow biosorption and settlement of the sediment. The colour intensity was monitored according to the specified time interval. Percentage removal was calculated as shown Equation (1).

$$\textit{Percentage removal (R)} = \textit{(Initial ADMI value-Final ADMI value)/initial ADMI value} \quad (1)$$

3. Results & Discussions

3.1. Characteristic of biosorbent

3.1.1. Brunauer-Emmett-Teller(BET). BET analysis provides data of the porous nature of the biosorbent. The surface area of biosorbent recorded was 7.2036m^2/g which demonstrated that the surface area of biosorbent is relatively small (Table 2). Previous research had reported similar surface area for natural materials as biosorbent which included spirulina (2.7958m^2/g) [26], Sargassum Tenerrimum (4.06m^2/g) [27], micro-fungi Penicillium glabrum (6.31 m^2/g), Aspergillus carbonarius (5.07 m^2/g) [28], and Thamnidium elegans cells (10.76m2/g) [29]. The pore volume was recorded as 0.003427cm3/g while adsorption average pore diameter was 19.0297 Å. Most dyes have an average size of 1–2 nm. Hence preventing the molecules to access a large proportion of the total surface area [24].

Table 2. Physical analysis using BET.

Parameter	Value
BET surface area (m^2/g)	7.2036
Pore Volume(cm^3/g)	0.003427
Average Pore diameter(Å)	19.0297

3.1.2. X-ray Fluorescence Spectrometer (XRF). The results of XRF analysis for determination of *E. Spinosum* characterization are listed in Table 3. Significant amount of CO_2 (74.4%), SO_3 (15.9%) and K_2O (5.35%) were found in *E. spinosum* species. *E. spinosum* has an enormous capacity for CO_2 as they capture and release oxygen while growing [30]. SO_3 was derived from S and O that are found as typical mineral class of marine macro algae [30]. Therefore, it can be inferred that the biosorption will be mainly adsorbed by SO_3 and K_2O. *E. spinosum* also contains silica and alumina in a least percentage. Previous literature reveal the significant amount of silica and alumina in adsorbent such as fly ash [31], LECA [32], oil palm ash [33] and alkali-activated sand [34] due to strong interaction with soil[35].

Table 3. Elemental analysis using XRF.

Constituent	Weight (%)
CO_2	74.40
Na_2O	1.77
MgO	0.95
Al_2O_3	0.0094
SiO2	0.0406
P2O5	0.19
SO3	15.90
Cl	0.34
K2O	5.35
CaO	0.74

3.2. Batch biosorption experiment

3.2.1. Effect of contact time and dosage. Profiles for colour reduction at various dosages and contact times are shown in Figure 1. Result showed that the optimum contact time for *E. spinosum* to exhibit its maximum color reduction is 48 h. At any particular dosage, almost no remarkable improvement was observed after 48 h contact time, which means that equilibrium state had been achieved. At equilibrium condition, aggregation happen when biosorption sites has fully occupied by higher amount of dye molecules resulted in a decrease of total biosorbent surface area available [34].

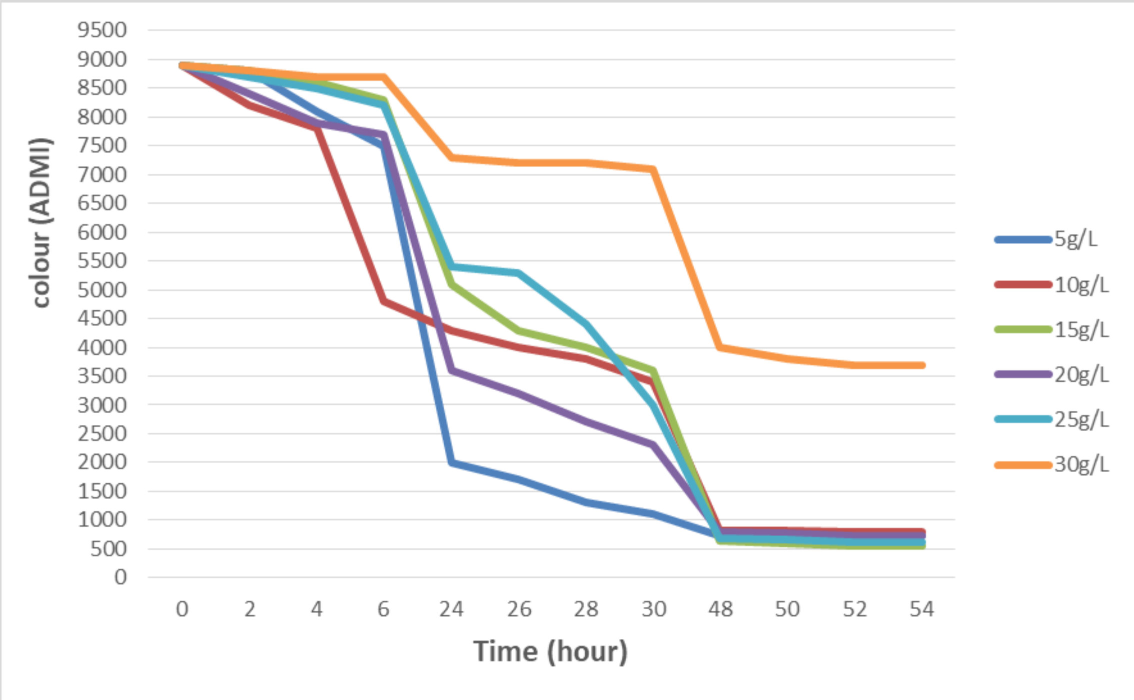

Figure 1. Effect of contact time at different dosage against color intensity.

3.2.2. Effect of dosage. The effect of dosage at 48 h contact time was summarized in Figure 2. Experiments were performed by varying the biosorbent dosage in the range of 5 to 30g/L. The optimum dosage of biosorbent was found at 15g/L with 93.7% of colour removal. This can be attributed to an increase in surface area of the biosorbent that promote more binding sites. At higher biosorbent dosage, the aggregation of the biosorption sites resulted in a net decrease of total biosorbent surface area available for dye biosorption [34]. Figure 3 illustrates the before and after biosorption on the samples. The figure shows the effect of decolourization of effluent at different dosage. Clear supernatant was noticed at dosage 5 to 20g/L indicating success decolorization of real textile wastewater effluent.

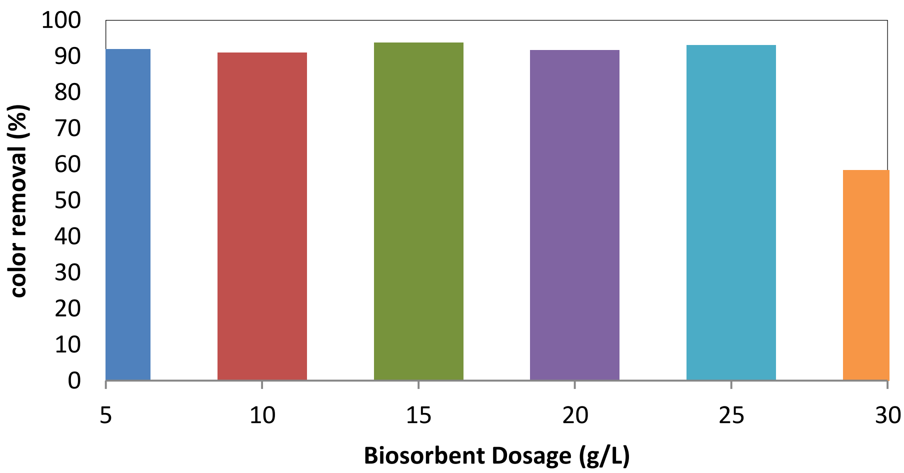

Figure 2. Effect of different dosage on the biosorption of real wastewater sample onto biosorbent (Experimental condition: pH: 4.89; time: 48 h; temperature: room temperature).

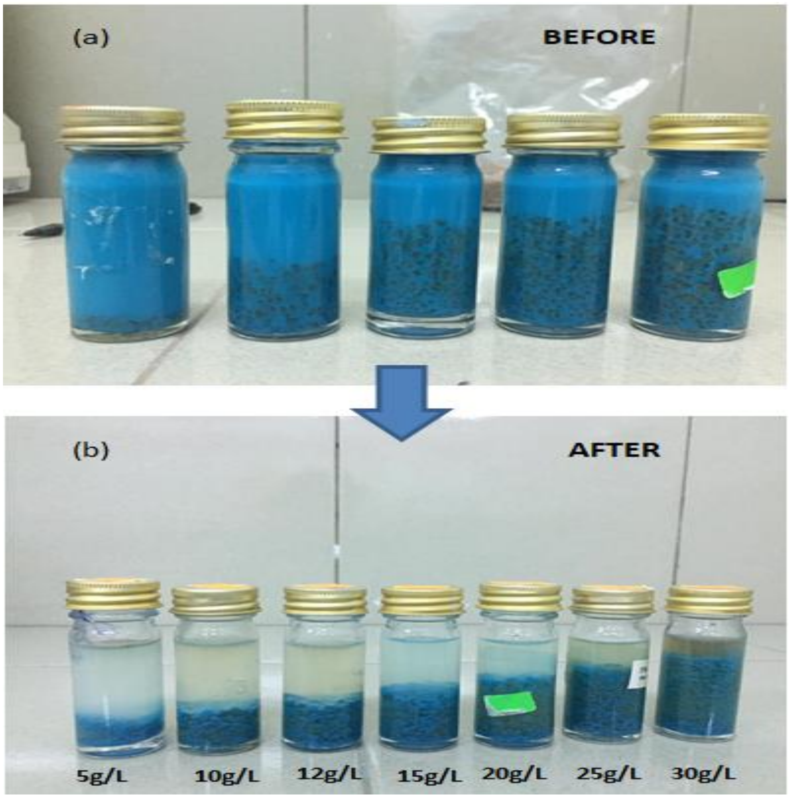

Figure 3. Effect of biosorption of real textile wastewater samples onto biosorbent at different dosage; (a) before biosorption; (b) after biosorption at 48 h.

3.2.3. Effect of contact time

Profile for colour removal was presented in Figure 4. The biosorption increased with time with slow progress at initial time of 0 to 24 h, followed by a gradual increase during 24 to 48 h until finally reached equilibrium state at 48 to 54 h of contact time. The equilibrium state of colour removal was obtained approximately 92% of the colour removal. The raw sample of real textile wastewater contained high TSS and complex substances remain above the limit set by Standard B Environmental Quality (sewage and Industrial Effluents) Regulation 2012 under the Environmental Quality Act 2012. This may contribute to lower removal efficiency of the dye thus require higher contact time in order to achieve equilibrium state. Further elimination of these latter substances is needed to achieve maximum biosorption. Similar finding on a decolourization study using real textile wastewater was done by Kumar et al. [36] used coconut fibre as a natural biomaterial whereby 87% decolourization was observed after 90 h.

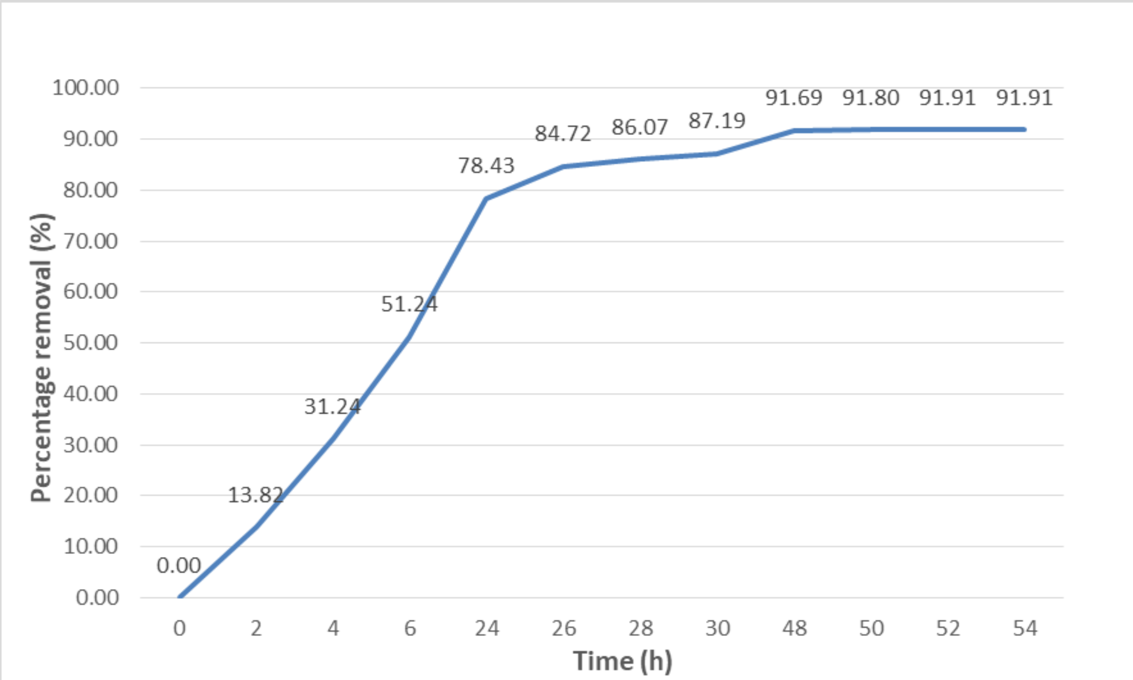

Figure 4. Effect of contact time on the biosorption of real wastewater sample onto biosorbent (Experimental condition; pH: 4.89; dosage: 15g/L; temperature: room temperature).

There is relatively less study on biosorption that utilizes real textile wastewater as a sorbate. Moreover, most of the previous studies were limited to synthetic dyes [12], [37]–[41]. Biosorbent origin can be varied from organism, natural earth sources, plant species, nano-material and sludge. Table 4 lists down some literatures that reported the use of various types of biosorbent for the treatment of real wastewater application. From the literatures, the successful used of biosorbent as colour removal is quite significant. However, the contact time was vary between studies.

Table 4. Previous literature on biosorption performance on the treatment of real textile wastewater using different biosorbent.

Biosorbent	Contact time	Color removal	References
Coconut fiber	90 h	87%	[36]
Alkali-activated sand	3 min	70%	[34]
Aspergillus carbonarius M333	2 h	91%	[20]
E.spinosum	48 h	94%	*This study*

3.3. Removal of TSS and COD using E. spinosum

By adopting the optimum contact time of 48 h and dosage of 15 g/L, the experimental work was done onto COD and TSS removal. As results, biosorbent has successfully removed TSS and colour as much as 98% and 93.71% respectively; however not for COD which gave negative values (-31%) (Table 5). The biosorbent unable to remove COD from textile wastewater was probably due to electrostatic repulsion force. Electrostatic repulsion force happens when the charge of binding site of *E.spinosum* is the same dye molecules [42]. When charges of two mediums are alike, they could not attract to each other, instead they experience repulsion when getting near each other. Foreign impurities and substances in textile wastewater such as oil, wax, and mordant have positive charge, same as the charge of macroalga, thus they were moving apart from each other [21]. These chemicals were inert, refused to been oxidized. These chemicals also further reacted with other unknown substances in the solution, thus creating more by-product with complex chemical composition which were difficult to be oxidized, thus increasing the chemical oxygen demand in the solution [43]. To summarize, none of the experiment results reach the minimum requirement as set by Standard B. Hence, it is suggested that, preliminary treatment need to be introduce before biosorption process since biosorption normally act as polishing treatment [10].

Table 5. Comparison of real textile wastewater effluent before and after biosorption with acceptable conditions for discharge of Industrial effluent or mixed effluent of Standards B Environmental Quality (Industrial Effluent) Regulations 2009.

Parameters	Standard B	Effluent before biosorption	Effluent after biosorption	% removal
COD	250 mg/L	7680 mg/L	10070 mg/L	-31%
TSS	100 mg/L	11030 mg/L	220 mg/L	98%
Colour	200	8900 ADMI	560 ADMI	94%

4. Conclusion

The present investigation demonstrates the promising performance of macroalga *E.spinosum* as biosorbent for decolourization of textile wastewater sample. The characterization study confirmed the presence of small surface area suitable for biosorption of dye molecules. The surface area of biosorbent was recorded 7.2036 m^2/g with average pore diameter of 19.0297 Å. XRF reveal that, with the least amount of silica and alumina as main constituent for adsorbent, *E.spinosum* can still performed well as biosorbent with the present of other chemical element such as CO_2, SO_3 and K_2O. The biosorption study revealed that *E.spinosum* achieved 94% decolorization after 48 h. This indicates the applicability of the biosorbent derived from macroalga biomass for treating textile wastewaters as polishing treatment at low cost impact.

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