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Research paper

Removal of Methylene Blue by Red Macro Alga Euchema Spinosum Sp.: Pretreatment and Desorption Assessment

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Abstract

Red algae species, *Euchema Spinosum (ES)* in Malaysia possesses excellent biosorbent properties in removing dyes from aqueous solutions. Studies had been made on the effect of pretreatment and reusability of this species as a biosorbent for economic viability. In the present study, physical and chemical pretreatments processes were employed on the ES. Desorption using seven different eluents (hydrochloric acid (HCl), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), potassium hydroxide (KOH), sodium chloride (NaCl), nitric acid (HNO_3 and deionized water). Caharacterization of ES biosorbent was conducted using FTIR to investigate the active functional group responsible in the biosorption process. It was observed that the pretreatment process does not enhance the uptake capacity of *ES*. Among of the six eluents used, it is suggested HNO_3 as an effective eluent with 51% desorption efficiency. Through regeneration study, HNO_3 as eluent can promote four times of biosorption-desorption cycles. FTIR confirm the functional groups such as –OH, –NH and –COO^- are responsible for the MB dye biosorption. The experiment displays that the *ES* does not require any pretreatment procedure to improve biosorption efficiency and has the capability of regeneration hence suggesting that *ES* is indeed an economical biosorptive material for MB dye removal.

Keywords: *Biosorbent, Pretreatment, Desorption, Reusability, Methylene Blue*.

1. Introduction

In recent years, sorption technology has received due attention for dye remediation owing to its simple operational condition that promotes cost-effectiveness, eco-friendliness and eco-safety[13]. The development of green and low-cost adsorbent has increased interest among researchers since the application of commercial adsorbent such as activated carbon has several limitations, namely due to their high production cost and poor regeneration ability [14], [15]. Adsorption using biomass material, known as biosorption, is considered as a novel approach offering cheap material, effective adsorption and competitiveness with commercial adsorbents [15], [16]. However, it is worth noting that most biomass that has been utilised as biosorbent such as coffee husk [17], rejected tea [18], vegetable residues [19], palm oil ash [20], [21] and banana [22] requires large quantities for a real field application. Moreover, it has been reported that biomass has low sorption capacities, hence, modifications that incur additional costs are necessary to improve the sorption capability [3], [23].

Algae have been used as potential biosorbent as they are abundance in nature, low cost and possesses high biosorption uptake towards dyes [1]–[4]. The presence of numerous functional group in algae cell walls such as hydroxyl, carboxylate, amino and phosphate play a significant role to remove pollutants from aqueous solution [5], [6]. It has been reported in the literature that modification methods have been utilised either through physical and chemical pretreatment to maximise the adsorption capacity of algae [7], [8]. The findings revealed that such modifications might result in the increase or decrease of the sorption capabilities. For example, the pretreatment of alga for removal of Reactive Blue 4 (RB4) from HCl-treated *Amphiroa foliace a*(red alga) [9] and removal of MB dye using H_2SO_4-treated *Laminaria japonica* biomass (brown alga) [10] demonstrated considerable increase in biosorption capacity. On the other hand, removal of acid orange II dye by chemically modified *Stoechospermum marginatum* (brown alga) by different chemical treatments has shown to significantly decrease the biosorption capacity [11].

On our previous study, we have studied the capability of various indigenous species of local macro alga to removed MB dye, and ES has performed on top of others[12]. Since the used of ES has never been reported either for dye removed or pretreatment and reusability studies, this study is worth to be revealed. Therefore, the main motivation behind the study is to expands the body of knowledge of *ES* on the capability of the aforesaid biosorbent to undergo pretreatment and its ability to be reused with regards to its economical viability for real industrial application.

2. Experimental Section

2.1. Material and Reagent

Euchema Spinosum (ES) from red macroalga species is collected from factory of algae in Kunak, Sabah. The collected ES are washed with tap water three times followed by rinsing with deionized water to remove irrelevant debris and salts on the surface of ES. The wet ES are then dried in an oven (UFB500, Memmert) at 60 °C for 24 hours. Finally, dried ES is crushed and then sieved. The crushed ES are sieves into particle size of 0.6 to 1.18 mm and stored in tight plastic as shown in **Fig 1**

Fig 1: preparation of biosorbent

Methylene Blue (MB) dye was prepared by dissolving a weighed 1g of MB powdered into 1L of deionized water and kept as stock solution and a serial of dilution was made for desired working solution. All chemicals were used as received without further purification.

2.2 Pretreatment

For chemical pretreatment using acid, briefly, 1g of *ES* biosorbent and 50mL of HCl were added to 100 mL capped Erlenmeyer flask. Several solutions were prepared at different HCl concentrations (0.5, 0.6, 0.8, 1.0, 1.2 M). Flasks were shaken in an orbital shaker at 200 rpm for 1 h to increase the contact between the solution and the biosorbent. The treated biosorbent was separated from the mixture by filtration. The same procedure described was repeated for pretreatment using base (KOH).

For physical pretreatment using thermal effect, 1 g of biosorbent is placed in each porcelain dish. The porcelain dishes were kept for 1 h in a furnace at various temperatures (100 ºC, 250 ºC, 350 ºC, 450 ºC). The samples were then cooled at room temperature. All treated biosorbent were washed with deionised water and oven dried at 60 ºC for 24 h, crushed and sieved.

For control specimen, *ES* was prepared by washed with deionised water and directly oven dried at 60 ºC for 24 h, and referred to as untreated biomass.

2.3 Biosorption-Desorption Experiments

Based on optimization study, a maximum predicted MB removal of 95.9 % (qe= 398.09 mg/g) was obtained at optimised conditions set as follows: 300 mg/L of MB, biosorbent dosage of 0.72 g/L at pH6.9. Therefore, the biosorption study was conducted according to the optimal condition. Hence, batch study was done by adding 0.025g of biosorbent into 250mL MB solution. . For uniform mixture, the sample was shake at 130 rpm at 27 °C for within equilibrium time using shaker then centrifuged at 4000rpm for 60s. The residual dye concentration was estimated using the UV–vis spectrophotometric technique at optimum wavelength of 640 nm wavelength. The flowchart of overall biosorption experiment is presented in **Fig 2**

The MB dye biosorption capacities (q_e, mg/g) and the percentage removal (R,%) of MB dye were calculated based on equation (1) – (2):

MB dye biosorption capacity, qe (mg/g) $:\frac{(c_i - c_f)\forall}{M}$ (1)

MB dye removal, R(%) $:\frac{C_i - C_f}{C_i} \times 100$ (2)

Where, Ci and Cf (mg/L) are the initial and final MB dye concentration in the solution respectively, M(g) is the biosorbent mass and V (L) is the MB solution volume.

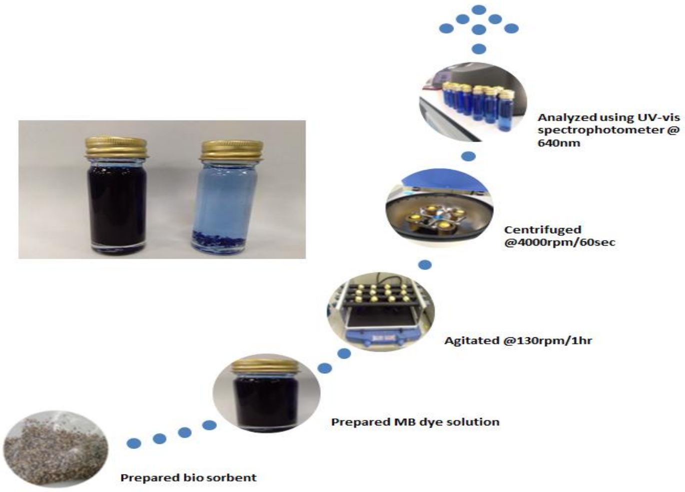

Fig 2: flowchart of the biosorption process

The reusability of biosorbent is the most important aspect as an indicator of good biosorbent. Six different chemical reagents (KOH, NaCl, NaOH, HCl, HNO_3 and H_3PO_4) and deionized water were used as an attempted to screen the most effective eluent for ES biosorbent**.** Therefore, desorption study were carried out by adding 5 mg of ES biomass rich in MB dye into 250 mL conical flask containing 0.5M of eluent. The biomass was kept in orbital shaker at 130 rpm for 2 h, centrifuged at 4000 rpm for 1min, filtered using whatman filter, washed with deionized water and oven dried for 24h. Each single cycle comprises of biosorption-desorption procedure. The desorption efficiency was given by the following equation (3):

MB dye desorption, (%) $:\frac{amount\ of\ desorbed\ dye\ ion}{amount\ of\ biosorbed\ dye\ ion} \times 100$ (3)

2.4 Instrument

All of the equipment were accurately calibrated followed the instructions by manufacturer. pH value was measured using pH meter (Mettler Toledo). The agitation speed was set at 130 rpm using orbital shaker (Excella E1, Edison, New Jersey, USA). The solutions were centrifuged by using centrifuge (Centrifuge 2420, Japan). **Fig 3** shows the wavelength for MB dye set at 640 nm by using a UV–vis spectrophotometer (UV–vis spectrophotometer, DR5000, Arachem). The characteriszation of *ES* sample were examined for functional group using Fourier Transform Infrared Spectrophotometer (FTIR, spectrum 100 Perkin-Elmer).

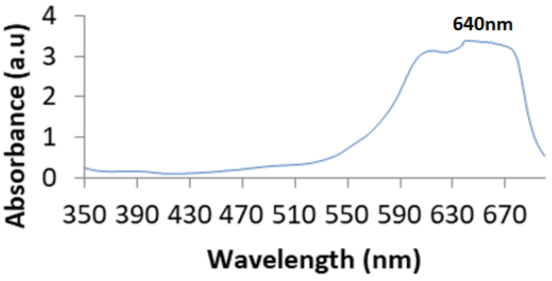

Fig 3: MB wavelength using UV-Vis spectrophotometer

3. Result and Discussion

3.1. Pretreatment

Table **1** summarises the effect of pretreatment onto ES. Oven heating at 60ºC prior to primary drying method was treated as a control sample and labelled as untreated. It is apparent that by heating the sample over 60ºC, the moisture content of macroalga was observed to be close to 0% [61].

Physical pretreatment has been carried out onto the ES biosorbent through the use of furnace heating with effect of various heats (100, 200, 250, 350, 450ºC). The result shows that removal efficiency decreases significantly with the increase of heat. At a temperature above 250ºC, the biosorption capacity of MB dye onto ES was decreased significantly, where removal was recorded as low as 1.74% (qe <0.66 mg/g). The major destruction of the physical structure of the macro-alga was a consequence of the heating effect at high temperature. This may cause a significant rupture to the cell wall, and the functional groups exist in the cell walls. Furthermore, the essential organic matter may also decompose and hence decreasing the biosorption capability.

MB dye biosorption capacity onto of different macroalgae (brown, red and green) of different species was studied by Daneshvar [5]. The authors reported a similar finding, where treatment using oven dry heating at 100ºC has no significant effect on the biosorption capacity. The degradation of red seaweed occurred as early as 100ºC is associated to the evaporation of water and the functional groups such as glycerol and the significant degradation after 200ºC was due to decomposition of agar [13]. As agar is the primary cell wall component in red alga which protects alga against extreme temperatures, pH and salinity, the rupture of this main component decreases the biosorption capability of *ES* onto MB dye molecules [14]. Chemical pretreatment using base and acid has been adopted onto the *ES*. The effect of base (KOH) at different concentrations (0.5, 0.6, 0.8, 1.0 and 1.2 M) has been studied, and the result shows a decrease on MB dye removal as compared to control sample (84.36%). At the concentration of 1.0 M, the removal decreased significantly (y =29.39%, q_e =21.31mg/g). High KOH concentration gives negative effect in the removal efficiency due to agglomeration and decreased number of active binding site. Pretreatment of macro-alga using KOH has never been reported previously, but KOH has been applied for activation of various agricultural waste product such as of rambutan [15], seed hull [16], grape seed [17] and marine fibrous biomass, *Posidonia oceanica* [18]. Although it has been reported that the biosorption capacity increases with the pretreatment process via KOH in various agricultural waste product, the pretreatment of macro alga using KOH shows a decreasing trend. This observation is similar to the findings made by [5] in which the pretreatment using potassium iodide (KI) has decreased the efficiency of macro alga, indicating that the potassium inhibited the biosorption process.

Table 1: Effect of pretreatment onto *ES*

Pretreatment	Method	Biosorption capacity,qe (mg/g)	MB dye removal,y(%)
Untreated	Oven heating at 60°C	59.48	84.36
Physical	Furnace heating 100°C 200°C 250°C 350°C 450°C	52.93b 49.64b 1.49a 0.66a 1.63a	73.66b 69.13b 2.90a 1.74a 3.09a
Chemical	Potassium hydroxide (KOH) 0.5M 0.6M 0.8M 1.0M 1.2M	47.98b 56.29b 47.41b 21.37a 28.41a	66.00b 77.44b 65.23b 29.39a 39.09a
	Hydrochloric acid (HCl) 0.5M 0.6M 0.8M 1.0M 1.2M	5.63a 6.82a 1.98a 2.75a 4.10a	7.74a 9.38a 2.73a 3.78a 5.64a

Note:a: significantly decreased, b: non-significant

The pretreatment of alga by HCl at various concentrations (0.5, 0.6, 0.8, 1.0 and 1.2 M) shows a significant decrease on the removal efficiency of MB dye from 84.26% (control sample) to 7.74%, 9.38%, 2.73%, 3.78%and 5.68%, respectively. A similar finding was also reported by Daneshvar [5] and Zeraatkar [8] using different species of algae in which the pretreatment using acid caused an opposite effect on the biosorption capacity. Strong mineral acid like HCl decreases the negative charge on the algae surface hence reducing the electrostatic attraction between biosorbent and cationic MB dye molecules. The amine group in the cell wall has been protonated by HCl that makes the surface positively charged, hence reducing the biosorption efficiency [19]. It is apparent from the present study that the pretreatment process either by means of physical or chemical processes have significantly deteriorated the removal efficiency of MB dye onto the *ES*. Hence, it is evident that no pretreatment is required to enhance the MB dye uptake onto *ES*.

3.2. Desorption and Reusability

Regeneration is a process that offer a reduction of processing cost in biosorption process in which, biosorbent can be used up to several time with great removal efficiency. Therefore, biosorbent biosorption-desorption study was carried out to investigate the biosorbent potential for regeneration.

3.2.1 Screening of the Best Eluent

The observation suggests that *ES* exhibits high desorption using HNO_3 (51%). From **Fig 4,** it can be seen that the maximum and minimum desorption efficiency of MB were obtained from HNO_3 and NaCl which are 51% and 7.02%, respectively. The low of desorption efficiency of MB by NaCl solution might be due to aviolet-colored complex configuration between eluent and desorbed MB dye in the test solution [20]. In addition, the high of desorption efficiency of MB dye is because of repulsion of electrostatic that occur between cationic dye molecule and positively charged located on the biomass [21]. As a result, nitric acid (HNO_3) was selected as the most effective eluent and used for further experiment to determine the reusability of the macroalga**.**

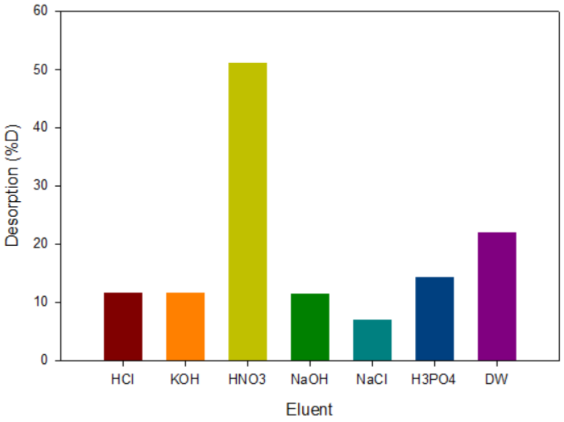

Fig 4: Screening of potential eluent

3.2.2 Biosorption-Desorption Cycle

The regeneration of ES biosorbent was reused for up to four successive biosorption-desorption cycles (**Fig 5**). After 4 consecutive adsorption/desorption cycles, *ES* capable in removing MB dye from aqueos solution (94.5%,74.5%, 62.26% and 48.5%). The decrease in the biosorption uptake with the number of regeneration cycles was attributed by the strongly attached of MB molecules onto *ES* surface at previous cycle. This observation is similar to findings reported by previous study for MB dye removal using Chitosan clay composite[22]. The significant decreased of removal efficiency using reused biosorbent was 46% probably due to measurably biomass lost and structural deficiency of the aforesaid biosorbent

The desorption efficiency reduce from 51% to 23.4% after four cycle which probably due to strong chemical interaction of sorbate/biosorbent that prevent desorption of MB dye [23]. Based on the result obtained, it indicated that low desorption efficiency than biosorption efficiency is probably due to some heterogeneity present on the surface of ES [20].

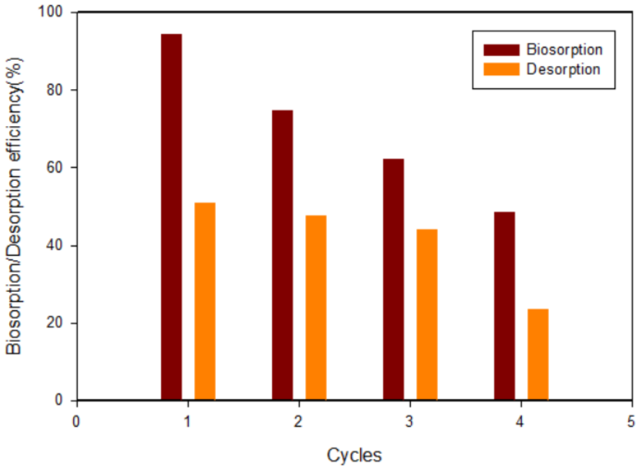

Fig 5: Regeneration of ES biosorbent using HNO_3 eluent

3.3 Characteristization of *ES*

Fig 6 shows the FTIR spectrum of *ES* biosorbent before and after MB dye biosorption. The changes in vibration frequency were characterised using IR spectroscopy in order to explain the interaction between the biosorbent and MB dye. The spectrum obtained is presented in Table **2**. Typical characteristic peaks of polysaccharide can be detected at the following wavenumber, 1020 cm^{-1}, 1230 cm^{-1}, 1400 cm^{-1}, 1540 cm^{-1}, 1650 cm^{-1} and 3200 cm^{-1} which correspond to glycosidic linkage (C-O-C), phospho- or sulpho- diester (P=O and S=O), bending hydroxyl (–OH), bending amine (–NH), asymmetric carboxylate ($-COO^-$) and stretching –NH and –OH, respectively.

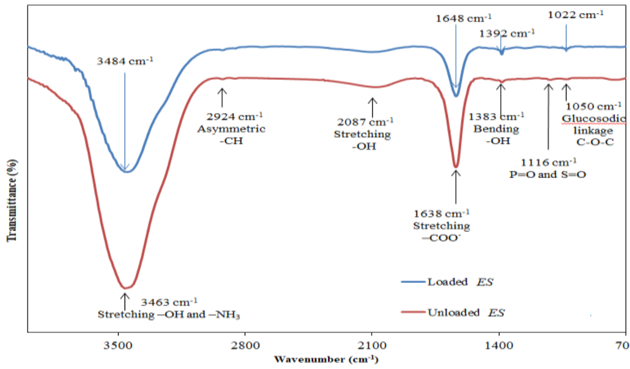

Fig 6: FTIR spectra of ES (a) before biosorption and (b) after biosorption in the wavenumber of 700-4000 cm^{-1}

The interaction between biosorbent and MB dye can be observed based on changes in wavenumber or peak intensity. The results reveal that *ES* biosorbent contained various functional groups to behave as the binding site such as –OH, –NH and $–COO^-$ which are responsible for the MB biosorption. Apparently, adsorption band for —OH, –NH and $–COO^-$ observed at the wavenumber 1383 cm^{-1}, 1638 cm^{-1}, 2087 cm^{-1} and 3463 cm^{-1} exhibit a decrease in peak intensity after the biosorption. This might suggest that chemical interaction has occurred between the MB dye and the sorption sites. On the other hand, adsorption band at 1116 cm^{-1} assigned to P=O or S=O has disappeared which indicate the involvement of these group in the biosorption process.

Table 2: List of FTIR vibrational frequency of ES species before and after biosorption.

Vibrational mode	Wavenumber (cm^{-1})		References
	Unloaded ES	Loaded ES	
Bending C-O-C (1,4-beta-d glucoside)	1050	1022	[13]
P=O and S=O	1116	n.a	[24]
bending–OH	1383	1392	[13]
Asymmetric $–COO^-$	1638	1648	[25]
Stretching –NH and -OH	3463	3484	[25]

Note: n.a=not available

4. Conclusion

In this study, the pretreatment of *ES* biosorbent by using physical(heat) and chemical(acid and base) result in the decreased of biosorption capability. Therefore, untreated ES biosorbent was used for further biosorption study. Reusability of ES was performed using acid eluent (HNO_3) and results shows capability of *ES* to be regenerate up to four cycles. The obtained results indicated that the ES could be effective and green biosorbent in practical application for dye removal as proved for its excellent biosorption capability without incur additional cost of pretreatment. At high initial concentration, ES capable to be reused up to four-cycle indicates the great potential of reusability in real dye wastewater that normally appear in low concentration (<100mg/L), hence promote no secondary pollutant. Therefore, ES is technically fullfill the requisite characteristics of eco-friendly and low cost biosorbent for real industrial application.

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