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Removal of methylene blue from aqueous solutions by brown alga *Cystoseira barbata*

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ABSTRACT

The removal of dyes from wastewater is crucial and considered an environmental challenge. Biosorption is an alternative technology to conventional processes aiming at the removal of toxic metals and dyes from polluted waters. In this study, *Cystoseira barbata* (Stackhouse) C. Agardh was used to remove the methylene blue (MB) from aqueous solution. The effects of solution pH, contact time and initial MB concentration at different temperatures were investigated. The adsorption reached to equilibrium in 25 min and the pH did not have an important role on the biosorption. The Freundlich isotherm model showed slightly stronger correlation than Langmuir isotherm model especially at 25°C. The maximum adsorption capacity (q_m) increased in parallel to the rise of temperature and reached to 14.97 mg/g at 45°C. *C. barbata* can be successfully used for the removal of MB from aqueous solution.

Keywords: C. barbata; Methylene blue; Biosorption

1. Introduction

Environmental pollution has become a significant problem to all living organisms by the rapid increase in industrialization and technology [1,2]. Synthetic dyes are one of the main pollutants causing health disorders and damages in human life [3]. For example, methylene blue (MB) is an organic and common type of colorants, usually used to dye cotton, wool and other materials. MB may also cause serious health problems such as vomiting, hard breathing and mental disorder [4] and even very low concentration of the dye in water is not desired [5,6]. Direct discharge of these effluents into wastewater plants and/or environment may cause different problems [7]. In this respect, the removal of dyes from wastewater is important.

There are several treatment methods for the removal of colorants [8] such as chemical coagulation, ion-exchange and adsorption [9–11]. Bioadsorption or biosorption among these techniques is an alternative method since it is easier, faster, more economic and efficient compared to conventional techniques [12,13]. In this technique, however, especially solution pH and contact time are of high influence on biosorption capacity [14]. Several organisms such as fungi, bacteria and algae have been suggested as biosorbents in biosorption studies, among which macroalgae (seaweeds) were found to be capable of efficiently adsorbing various water polluting agents including dyes [15,16]. There are many studies on macroalgae treated with different colorants to find out the adsorption capacities [17–19]. Brown alga *Cystoseira barbata* (Stackhouse) C. Agardh is a common species mostly found in temperate regions such as the Mediterranean Sea, Indian and Pacific Oceans. Algae have carboxyl, hydroxyl, sulphate and amino groups in cell wall polysaccharides, which act as binding sites responsible for the biosorption [20]. As for brown algae, carboxyl and sulphate groups are active compounds as binding sites since the cell walls generally contain cellulose, alginic acid and sulphated polysaccharides [21].

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The aim of the study was to evaluate the removal of MB from aqueous solution using *C. barbata*. The effects of solution pH, contact time and concentration of MB solution were also tested. The experimental data were fit to different isotherm models namely the Langmuir and the Freundlich. FTIR and SEM analyses were utilized to characterize and compare MB loaded and unloaded *C. barbata*.

2. Experimental

2.1. Biomass

Brown alga *C. barbata* (Stackhouse) C. Agardh was collected from the Dardanos Campus of Canakkale Onsekiz Mart University. The biomass was rinsed to remove some impurities and dried in an oven at 60°C until constant weight was reached. Dried biomass was ground and sieved.

2.2. Reagent and equipment

All chemicals used were analytical grade (Merck). All the solutions were prepared with distilled water. For biosorption experiments, stock MB solution (1,000 mg/L) was used and different concentrations of MB (5, 10, 20, 50, 100, 150, 200, 250 and 300 mg/L) were prepared from stock solution using distilled water. The MB concentration in the solution was measured with a spectrophotometer (Rayleigh Vis-7220 G). The pH values of aqueous solutions were adjusted using 0.1 M HCl or 0.1 M NaOH. Samples were filtered through Millipore Millex-HV hydrophilic PVDF 0.45 μm syringe filter. A Wise Bath WSB-30 model shaker was used for the adsorption experiments.

2.3. Biosorption experiments

The batch adsorption technique was employed to assess the adsorption of MB from the aqueous solution. *C. barbata* (100 mg) was put into a 50 mL falcon tube and treated with 10 mL of a MB solution. All the biosorption experiments were carried out using 10 mL aqueous MB solutions. The test solutions were shaken at 250 rpm at room temperature for 60 min, centrifuged at 3,000 rpm and the supernatants were filtered through the syringe filters. The adsorbed amount of MB was calculated following the spectrophotometrically measurement of supernatant at 665 nm.

2.4. Determination of optimum pH

Four pH values (3, 5, 7 and 9) were tested in the trial. Accordingly, 100 mg dried *C. barbata* was put into the Falcon tubes filled with 10 mg/L MB solutions at different pH values. The tubes were shaken at room temperature for 60 min at 250 rpm. The samples were centrifuged, filtered and the absorbance of the supernatant was measured.

The percentage of MB removal (% *R*) from the aqueous solution was calculated as follows:

$$\% R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where C_0 is the initial MB concentration (mg/L) and C_e is the equilibrium concentration of MB (mg/L).

2.5. Determination of optimum contact time

Dried biomass (100 mg) was added into 10 mL of MB (10 mg/L) solution and the pH was adjusted to 5. Falcon tubes were shaken at room temperature for different time intervals (10, 25, 50, 100, 150, 200 and 300 min). Samples were centrifuged, filtered and the absorbance of the supernatant measured with the spectrophotometer.

The amount of MB uptake, q_t (mg/g), at each interval was calculated using the following equation:

$$q_t = \frac{(C_0 - C_e)}{M} \times V \quad (2)$$

where C_0 (mg/L) is the initial MB concentration, C_e (mg/L) is the concentration of MB solution at a given time, V (L) is the volume of metal solution and M (g) is the mass of biosorbents (dry weight).

2.6. Adsorption isotherms

10 mL MB test solutions (pH 5) were prepared at different concentrations (5, 10, 20, 50, 75, 100, 150, 200, 250 and 300 mg/L) and added into the Falcon tubes each containing 100 mg of dry biomass. The test solutions were shaken for 25 min at 25°C and 45°C. The amount of MB adsorbed was calculated using Eq. (2). In the equation q_t is substituted with q_e.

2.7. Characterization of biomass

Fourier transformed-infrared spectroscopy (FTIR) spectra were obtained using a Perkin-Elmer FTIR Spectrometer (Spectrum BX-II). Biomass of *C. barbata* was dried to a constant weight at 60°C and 1 mg of the biomass was then pelleted with 100 mg KBr. FTIR analysis was performed in the range of 400–4,000 cm^{-1} for the characterization of biomass.

Morphological features of algal biosorbent particles before and after the adsorption were obtained using the Scanning Electron Microscope (SEM, Jeol JSM 7100F) at accelerating voltages of 5 and 7 kV attached to an X-ray energy dispersive spectrometer (EDX). Before the scanning process, all samples were dried and coated with gold to enhance electron conductivity. SEM micrographs were taken at different magnifications.

3. Results and discussions

3.1. Determination of optimum pH

The trials were conducted from pH 3 to 9 since the pH of the solution is critically important in the adsorption process [22,23]. In the range mentioned above, the effect of pH on the biosorption of MB by *C. barbata* was negligible as shown on Fig. 1. The MB concentrations adsorbed were almost constant at different pH values.

3.2. Determination of optimum contact time

Fast response of sorbents to the chemicals, or in other words, fast sorption equilibrium is very important in an adsorption process. The relationship between contact time and biosorption of MB onto *C. barbata* was given in Fig. 2.

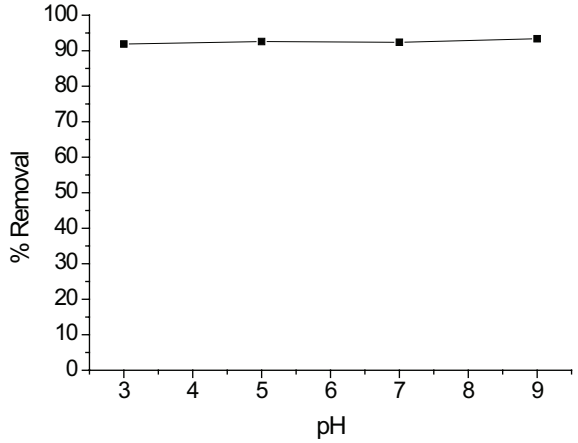

Fig. 1. Effect of pH on the biosorption of MB.

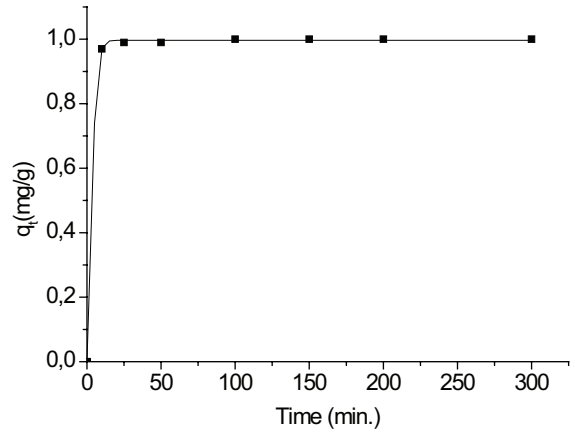

Fig. 2. Effect of contact time on the biosorption of MB.

The results showed that the adsorption reached to equilibrium within 25 min while the fastest part was observed in the first 10 min due to the effective interaction between MB dye molecules and active sites on the surface of grounded biomass [3]. MB amount adsorbed did not increase anymore and kept almost constant at 1.00 mg/g for the periods longer than 25 min.

3.3. Adsorption isotherms

The equilibrium data at different temperatures were analyzed with Langmuir and Freundlich isotherms. The monolayer of the adsorbate on the adsorbent surface was predicted with the Langmuir model while the multi-layer adsorption isotherm, the Freundlich model, was applied to the heterogeneous surfaces. The Langmuir model was shown below [24]:

$$\frac{C_e}{q_e} = \frac{1}{q_m a_L} + \frac{C_e}{q_m} \tag{3}$$

where q_e (mg/g) is the amount of MB adsorbed at equilibrium, C_e (mg/L) is the equilibrium concentration of the MB solution, q_m (mg/g) is the maximum adsorption capacity and a_L is the Langmuir constant related to the energy of adsorption.

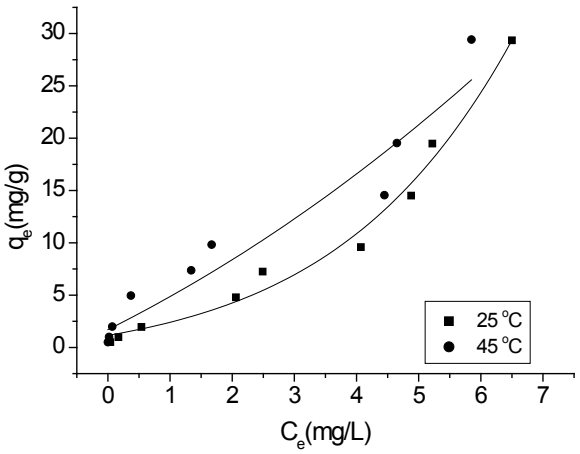

Fig. 3. Sorption isotherm curves for biosorption of MB at 25°C and 45°C.

Table 1
Langmuir and Freundlich isotherm models of *C. barbata* for MB at different temperatures

Temperature (°C)	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	a_L	R_L^2	n_f	K_f (mg/g)	R_F^2
25	12.78	0.43	0.8525	1.46	3.67	0.9875
45	14.97	1.79	0.9614	2.56	6.94	0.9809

A linear form of the Freundlich equation was given below [25]:

$$\log q_e = \log K_f + n \log C_e \tag{4}$$

where K_f (mg/g) is related to adsorption capacity and n is an empirical parameter that varies with degree of heterogeneity.

Fig. 3 shows the adsorption isotherms used to characterize the interaction between MB and algal biomass. According to the results of the experiment, MB amount adsorbed by *C. barbata* increased in higher solution concentrations. The maximum adsorption capacities (q_m) of *C. barbata* were 12.78 and 14.97 mg/g at 25°C and 45°C, respectively. In this study, Freundlich isotherm model showed a better fit than the Langmuir isotherm model for all the temperatures studied (Table 1). A comparison of the q_m of *C. barbata* and some selected adsorbents were presented in Table 2. The q_m value of *C. barbata* in MB solution was higher than that of *Posidonia oceanica* and a commercial product zeolite.

3.4. Characterization of biomass

3.4.1. FTIR

The FTIR spectroscopy method is largely used to characterize the mechanism of binding on algal surfaces with the help of the hydroxyl, carboxylic acid, amine, amino, sulfonyl and phosphate functional groups found in the structure of

Table 2
Maximum MB adsorption capacities of different adsorbents

Adsorbent	q_m (mg/g)	Temperature (°C)	References
Raw *Posidonia oceanica* (L.) fibres	5.56	30	[26]
Petalonia fascia	28.50	25	[27]
Gracilaria corticata	95.41	30	[28]
Ulva lactuca	40.20	25	[29]
Ulothrix sp.	86.10	25	[10]
Daucus carota stem	55.50	30	[30]
Kappaphycus alvarezii	74.40	30	[31]
Zeolite	12.70	25	[32]
Casuarina equisetifolia	110.80	25	[33]
Peat	111.00	25	[34]
Peat	143.90	70	[35]
Artocarpus odoratissmus skin	184.60	25	[36]
Cystoseira barbata	12.78	25	This study
Cystoseira barbata	14.97	45	This study

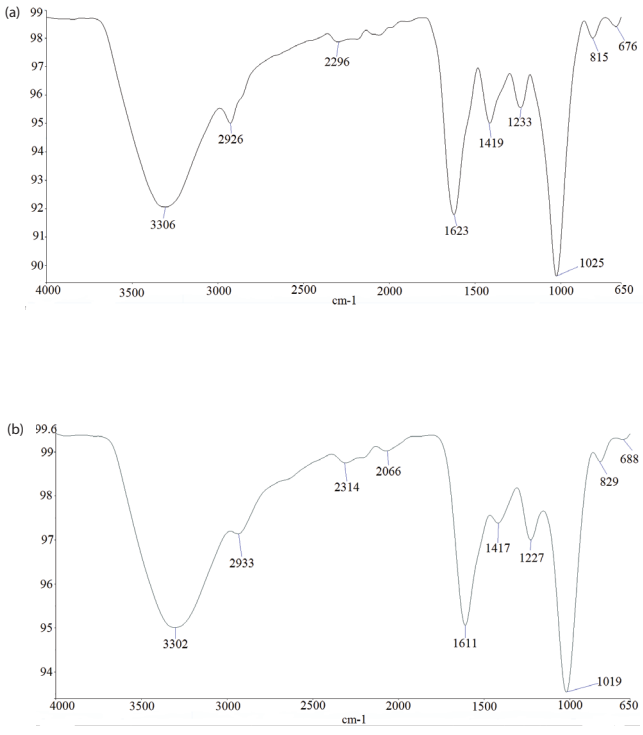

Fig. 4. FTIR spectra of *C. barbata* unloaded (a) and loaded with MB (b).

algae [12,37,38]. The FTIR spectra of *C. barbata* were given in Fig. 4. It was seen that MB was generally attached to hydroxyl, amine and carboxyl groups of biomass, which were given in Table 3 together with the other functional groups of the biomass. Similar results were also reported in some studies carried out with MB [28,31].

Table 3
Functional groups observed in FTIR of *C. barbata*

Functional group	Wavenumber (cm^{-1})	
	Unloaded	Loaded with MB
–OH and – NH streching	3,306	3,302
–CH stretching	2,926	2,933
–OH	2,296	2,314
C = O groups in amide	1,623	1,611
C-O stretching	1,419	1,417
C-O carboxyl	1,233	1,227
S=O stretching	1,025	1,019
S-O stretching	815	829

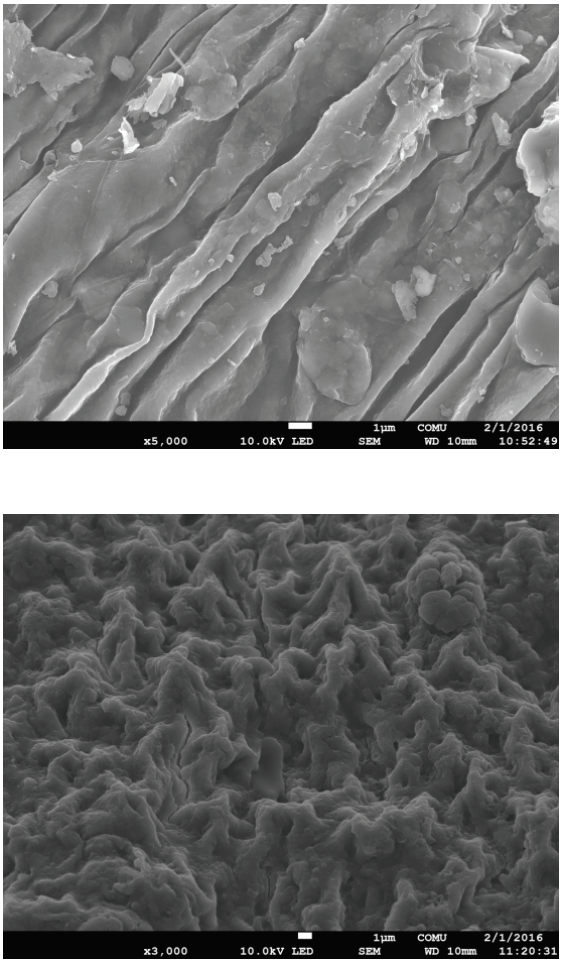

Fig. 4. SEM images of C. barbata unloaded (a) and loaded with MB (b).

3.4.2. SEM

SEM is a useful tool to examine the surface structure of the biosorbent. In this study, the surface microstructures of *C. barbata* samples were analyzed by the SEM/EDS technique (Fig. 5). The SEM micrographs indicated the presence of rough and flat surfaces on unloaded samples (Fig. 5(a)).

Fig. 5(b) showed how the surface structure changed when the sample loaded with MB. After the biosorption process, the surface of the algal sample appeared roughed and more porous compared to the unloaded raw sample.

4. Conclusion

In this study, the effect of various parameters such as pH, contact time and initial MB concentration were investigated on the adsorption of MB by *C. barbata*. The findings were further supported by FTIR and SEM analyses to see the differences after biosorption. In this study, the effect of contact time and initial MB concentration were more effective on the biosorption capacity than that of pH. The biosorption reaction reached equilibrium within the first 25 min and the maximum adsorption capacity (q_m) was 14.97 mg/g at 45°C. Freundlich isotherm model showed a better fit than the Langmuir isotherm model. The possible functional groups in *C. barbata* responsible for binding of MB were proven hydroxyl, amine and carboxyl groups. The biomass can be modified by crosslinking with various chemicals to further increase the q_m. As a result, *C. barbata* can be used as an alternative and low-cost material for the removal of MB from aqueous solution.

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References

[1] S. Devi, A. Murugappan, R. Rajesh Kanan, Sorption of reactive blue 19 onto freshwater algae and seaweed, Desal. Wat. Treat., 54 (2015) 2611–2624.
[2] G.Y. Deak, V. Daescu, E. Holban, P. Marinescu, G.S. Tanase, R. Csergo, A.I. Daescu, S. Gaman, Health-environment relation: a key issue of Romanian environmental protection, J. Environ. Protect. Ecol., 16 (2015) 304–315.
[3] A.R. Khataee, F. Vafaei, M. Jannatkhah, Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra* sp.: kinetic, isotherm and thermodynamic studies, Int. Biodeterior. Biodegrad. 83 (2013) 33–40.
[4] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci., 20 (2002) 295–300.
[5] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, J. Hazard. Mater., 177 (2010) 70–80.
[6] K.V.K. Rao, Inhibition of DNA synthesis in primary rat hepatocyte cultures by malachite green: a new liver tumors promoter, Toxicol. Lett., 81 (1995) 107–113.
[7] V.K. Garg, R. Kumar, R. Gupta, Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria,* Dyes Pigments, 62 (2004) 1–10.
[8] W. Tsai, H. Chen, K. Kuo, Surface characterization of dead microalgae-based biomass using methylene blue adsorption, Surface Interface Anal., 43 (2011) 959–963.
[9] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Batch and column studies on biosorption of acid dyes on fresh water macro alga *Azolla Filiculoides,* J. Hazard. Mater. B, 125 (2005) 121–129.
[10] C. Dogar, A. Gurses, M. Acikyildiz, E. Ozkan, Thermodynamics and kinetic studies of biosorpion of a basic dye from aqueous solution using green algae *Ulothrix* sp., Colloid Surface B, 76 (2010) 279–285.
[11] Y.S. Ho, G. Mckay, Sorption of dye from aqueous solution by peat, Chem. Eng. J., 72 (1998) 115–124.
[12] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera,* Bioresour. Technol., 97 (2006) 2321–2329.
[13] D. Kratochvil, B. Volesky, Biosorption of Cu from ferruginous wastewater by algal biomass, Water Res., 32 (1998) 2760–2768.
[14] Y. Cirik, Y. Büyükateş, M. Merdivan, İ. Ak, T. Göksan, Biosorption of Cu (II) and Co (II) ions using *Spirulina platensis* (Cyanophyceae), BIBAD, 5 (2012) 7–12.
[15] R.H.S.F. Vieira, B. Volesky, Biosorption: a solution to pollution?, Int. Microbiol., 3 (2010) 17–24.
[16] M.M. Figueira, B. Volesky, V.S.T. Ciminelli, F.A. Roddick, Biosorption of metals in brown seaweed biomass, Water Res., 34 (2000) 196–204.
[17] Z. Bekci, Y. Seki, L. Cavas, Removal of malachite green by using an invasive marine alga *Caulerpa Racemose* var. cylindracea, J. Hazard. Mater., 161 (2009) 1454–1460.
[18] M.C. Ncibi, A.M. Ben Hamissa, A. Fathallah, M.H. Kortas, T. Baklouti, B. Mahjoub, M. Seffen, Biosorptive uptake of methylene blue using mediterranean green alga *Enteromorpha* spp., J. Hazard. Mater., 170 (2009) 1050–1055.
[19] N. Nagarani, H. Vahitha, A.K. Kumaraguru, Comparative studies on the removal of textile effluents by various eco-friendly adsorbent strategies, Toxicol. Environ. Chem., 94 (2012) 1259–1271.
[20] S.O. Lesmana, N. Febriana, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, Biochem. Eng. J., 44 (2009) 19–41.
[21] E. Romera, F. Gonzales, A. Ballester, M.L. Blazquez, J.A. Munoz, Comparative study of biosorption of heavy metals using different types of algae, Bioresour. Technol., 98 (2007) 3344–3353.
[22] K. Chojnacka, A. Chojnacki, G. Helena, Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue–green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process, Chemosphere, 59 (2005) 75–84.
[23] I. Michalak, A. Zielinska, K. Chojnacka, J. Matula, Biosorption of Cr(II) by microalgae and macroalgae: equilibrium of the process, Am. J. Agric. Biol. Sci., 2 (2007) 284–290.
[24] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.
[25] H. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385.
[26] M.C. Ncibi, B. Mahjoub, M. Seffen, Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia Oceanica* (L.) fibres, J. Hazard. Mater., 139 (2007) 280–285.
[27] Y. Ozudogru Cirik, I. Ak, T. Goksan, Biosorption of Methylene Blue by a Brown Algae, 40 Eme Congres Ciesm, France, 28 August–5 September, 2013.
[28] J. Vijayaraghavan, T. Bhagavathi Pushpa, S.J. Sardhar Basha, J. Jegan, Isotherm, kinetics and mechanistic studies of methylene blue biosorption onto red seaweed *Gracilaria corticata,* Desal. Wat. Treat., 57 (2015) 13540–13548.
[29] A. El Sikaily, A. Khaled, A. El Nemr, O. Abdelwahab, Removal of methylene blue from aqueous solution by marine green alga *Ulva lactuca,* Chem. Ecol., 22 (2006) 149–157.
[30] A.K. Kushwaha, N. Gupta, M.C. Chattopadhyay, Removal of cationic methylene blue and malachite green dyes from aqueous solution by waste materials of *Daucus carota,* J. Saudi Chem. Soc., 18 (2014) 200–207.
[31] J. Vijayaraghavan, T. Bhagavathi Pushpa, S.J. Sardhar Basha, K. Vijayaraghavan, J. Jegan, Evaluation of red marine alga *Kappaphycus alvarezii* as biosorbents for methylene blue: isotherm, kinetic, and mechanism studies, Separ. Sci. Technol., 50 (2015) 1120–1126.
[32] C.D. Woolard, J. Strong, C.R. Erasmus, Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams, Appl. Geochem., 17 (2002) 1159–1164.
[33] M.K. Dahri, M.R. Rahimi Kooh, L.B.L. Lim, Application of *Casuarina equisetifolia* needle for the removal of methylene blue and malachite green dyes from aqueous solution, Alexandria Eng. J., 54 (2015) 1253–1263.

[34] L.B.L. Lim, N. Priyantha, D.T.B. Tennakoon, C.H. Ing, C. Bandara, Sorption characteristics of peat of Darussalam I: preliminary characterization and equilibrium studies of methylene blue-peat interactions, Ceylon J. Sci. Phys. Sci., 17 (2013) 41–51.
[35] C.H. Ing, T. Zehra, L.B.L. Lim, N. Priyanta, D.T.B. Tennakoon, Sorption characteristics of peat of Brunei Darussalam, Environ. Earth Sci., 72 (2014) 2263–2277.
[36] L.B.L. Lim, N. Priyantha, D.T.B. Tennakoon, M.K. Dahri, H.I. Chieng, T. Zehra, M. Sukleung, *Artocarpus odoratissumus* skin as potential low-cost biosorbent for the removal of methylene blue and methyl violet 2B, Desal. Wat. Treat., 53 (2015) 964–975.
[37] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre De Vicente, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium (II) and lead (II) removal: kinetic and equilibrium studies, Environ. Pollut., 142 (2006) 264–273.
[38] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res., 37 (2003) 4311–4330.