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Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. *cylindracea*

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Abstract

Caulerpa racemosa var. *cylindracea* is one of the well-known invasive species in the Mediterranean Sea. In the present study, dried biomass of *C. racemosa* var. *cylindracea* was shown to have adsorption capacity for methylene blue. The adsorption reached equilibrium at 90 min for all studied concentrations (5–100 mg/L). The pseudo-second-order model is well in line with our experimental results. There was a sharp increase in the adsorbed dye amount per adsorbent amount from 3.3 to 16.7 g/L, then a slight increase up to 66.7 g/L was observed. Langmuir and Freundlich's models were applied to the data related to adsorption isotherm. According to Langmuir's model data, the observed maximum adsorption capacity (q_m) was 5.23 mg/g at 18 °C. The enthalpy of adsorption was found to be 33 kJ/mol, which indicated a chemical adsorption between dye molecules and *C. racemosa* var. *cylindracea* functional groups.

Keywords: Biosorption; *Caulerpa racemosa* var. *cylindracea*; Dye removal; Methylene blue; Waste waters

1. Introduction

Caulerpa racemosa var. *cylindracea* is a green marine macroalga and is one of the well-known invasive species in the Mediterranean Sea. Since 1991, this species showed invasive property in Mediterranean Sea. Eleven Mediterranean countries are still threatened by this species (Verlaque et al., 2003). In as much as there is no valid eradication method and also no well-consumers for this species, *C. racemosa* var. *cylindracea* has gone on its dangerous invasion in Mediterranean since 1991 (Verlaque et al., 2003). Many of Turkish coastlines are also invaded by *C. racemosa* var. *cylindracea* (Cavas and Yurdakoc, 2005a,b). This species can be easily collected from shallow waters (0.5–1 m) from Seferihisar (Turkey) coastlines. Dyes used in textile industry are important causes of pollution in aquatic ecosystems. Dyes generally consist of complex aromatic complexes which provide stability against biodegradation in aquatic ecosystems. The dyes which are released into the aquatic environment without any treatment inhibit development of aquatic animals and plants by blocking sunlight penetration (Raghuvanshi et al., 2004). Therefore, removal of dyes from the effluents of textile industries is of paramount importance for the proper maintenance of the health of the ecosystem. Over 7×10^5 tons dyes and about 10,000 different types are produced in the world. Unfortunately, about 10–15% of the total produced dyes is released into the aquatic ecosystems without being removed from the effluents (Senthilkumaar et al., 2006; Hoda et al., 2006; Bukallah et al., 2007). Methylene blue (MB) has lots of application areas such as coloring paper,dyeing cottons,wools and coating for paper stocks (Vadivelan and Vasanth Kumar, 2005). Although MB is not considered to be a very toxic dye, it can reveal very harmful effects on living things. After inhalation, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans (Bhattacharyya and Sharma, 2005). MB is generally used to test the adsorption capacity of various sorbents inasmuch as this dye has a reasonably simple structure which allows examination of the adsorption mechanism. It also permits a quantitative comparison

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between the adsorption capacities of various sorbents. There are a few reports in the literature on the adsorption capacities of genus *Caulerpa*. Pavasant et al. (2006) studied the biosorption characteristics of dried *Caulerpa lentillifera* for some heavy metals such as Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}. According to their research, they have concluded that *C. lentillifera* could be used for removal of heavy metals from low strength waste water. Marungrueng and Pavasant (2006) have investigated the adsorption of a dye, astrazon blue FGRL, onto *C. lentillifera* from aqueous solution. The adsorption capacity of *C. lentillifera* was 49.26 mg/g. Marungrueng and Pavasant (2007) in their another report showed that *C. lentillifera* exhibited greater sorption capacities than activated carbon for some basic dyes such as Astrazon Blue FGRL, Astrazon Red GTLN and methylene blue.

In the present study, removal of methylene blue by invasive *C. racemosa* var. *cylindracea* was aimed to investigate from aqueous solutions. To the best of our knowledge, this is the first report related to material development by using invasive *C. racemosa* var. *cylindracea* for removal of methylene blue.

2. Methods

2.1. Seaweed and dye solution preparation

C. racemosa var. *cylindracea* was collected from Seferihisar coastline in September 2006. The depth of the collection area was between 0.5 and 1 m. The map of area where alga material was collected is shown in Fig. 1. Wet algal material was washed with deionised water to remove salt and some epiphytes. Then the material was dried at 80 °C for 14 h. Dried materials were ground with mortar and pestle. The changes in functional groups of *C. racemosa* var. *cylindracea* before and after adsorption were interpreted using fourier transform infrared (FT-IR) spectroscopy technique (Perkin–Elmer, Spectrum BX) and the results are shown in Table 1. The calibration curve was plotted from the dye solution prepared in the concentration range of 1.0–200 mg/L. Dye concentrations were measured at 665 nm in Shimadzu UV–VIS 1601 Spectrophotometer. The effect of pH on the amount of color removal was analyzed from 3 to11. For adjusting pH, 0.1 N NaOH and 0.1 N HCl were used.

Table 1
Changes in the functional groups in the dried *Caulerpa racemosa* var. *cylindracea* before and after methylene blue adsorption

Functional group	Standard wavenumber (Skoog and Leary, 1992) (cm^{-1})	Wavenumber from the pure alga (cm^{-1}) (max values)	Wavenumber from the MB attached alga (cm^{-1})
Hydroxyl; O–H	3250–3700	3409	3403
Amine; NH_2	3300–3500	3409	3403
Carboxyl; COOH	2400–3300	2923	2923
Amine; (–NH bending)	1490–1580	1550	1540
Sulfonyl; S=O	1040–1200	1141	1145
Carbonyl; C=O	1670–1780	1646	1649
S–O	550–650	526	526

2.2. Adsorption protocol and analysis

Experiments were carried out by agitating 0.5 g of alga with 30 mL dye solution of the desired concentration and pH at 105 rpm, 27 °C in thermostated rotary shaker (Memmert). The dye solution was separated from the adsorbent by centrifugation at 4000 rpm for 5 min. Then absorbance of supernatants was measured spectrophotometrically at 665 nm. In order to study the effect of adsorbent dosages, various amounts of adsorbent (0.1–2 g) were agitated with dye solution. The amount of methylene blue adsorbed, q(mg/g), was obtained as follows:

$$q = (C_0 - C_e)V/M \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid phase concentration of methylene blue (mg/L), respec-

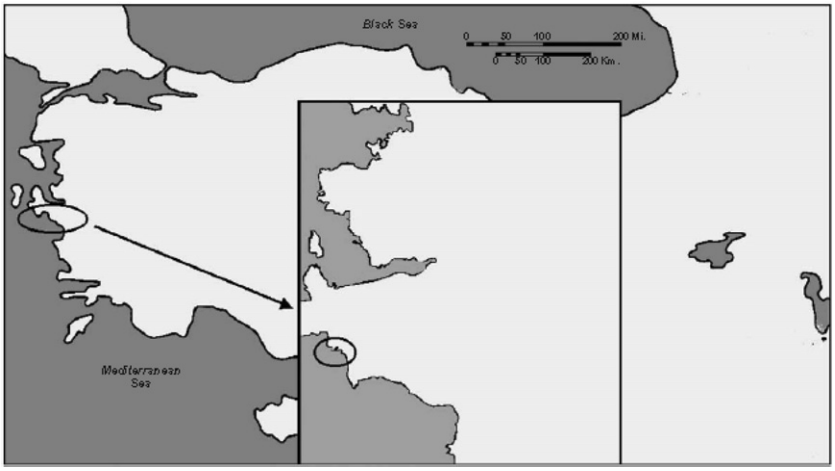

Fig. 1. The map of area where alga material collected.