# Highly efficient adsorption of dyes by biochar derived from pigments-extracted macroalgae pyrolyzed at different temperature

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## ARTICLE INFO

## ABSTRACT

Biochar is known to efficiently adsorb dyes from wastewater. In this study, biochar was derived from macroalgae residue by pyrolysis, and the influence of varying temperature (from 400 °C to 800 °C) on biochar characteristics was investigated. Among the biochar samples tested, macroalgae-derived biochar possessing highly porous structure, special surface chemical behavior and high thermal stability was found to be efficient in removing malachite green, crystal violet and Congo red. The biochar derived by pyrolysis at 800 °C showed the highest adsorption capacity for malachite green (5306.2 mg g$^{-1}$). In this study, the transformation of microalgae residue into a highly efficient dye adsorbent is a promising procedure for economic and environmental protection.

## 1. Introduction

Algae are promising sources of nutrition and biofuel because of their pigment and lipid content. Moreover, they can be cultivated in wastewater, do not require fertile land, do not compete with food crops, and reduce greenhouse gases from the environment (Chen et al., 2017). Researches have recently been focusing on both nutritional and pharmaceutical applications of algal pigments. However, the cost of algae cultivation and harvesting is high, which limits the downstream application of biodiesel production. Numerous studies indicate that residual algal biomass can be used as a substrate for bioethanol and biogas, as well as for animal/poultry/fish feed and fertilizer (Rashid et al., 2013). Since the cultivation of macroalgae is relative effortless, and the biochar derived from this source has a high absorbability of pollutants, macroalgae-derived biochar (MDBC) is drawing more and more attention as a promising potential candidate of low-cost adsorbent. Notably, MDBC can efficiently remove both organic and inorganic environmental contaminants because of its high surface area, stable structure, negative surface charge, high ion exchange capacity and the presence of various value-added surface functional groups (Ho et al., 2017). Jung et al. (2016) also demonstrated that MDBC was a good fertilizer after adsorbing phosphate. Zheng et al. (2017) suggested that biochar from *Chlorella* sp. Cha-01 has a high potential to remove p-nitrophenols in wastewater treatment or emergency water pollution control. Nautiyal et al. (2016) utilized the residual biomass of *Spirulina platensis* to remove up to 82.6% of Congo red (CR) dye.

Dye-containing wastewater is one of the most serious water pollution issues in textile, paper, plastic, leather and other industries. It is difficult to estimate the discharge of various dyes in the environment accurately (Lee and Pavlostathis, 2004). Most dyes not only destroy aquatic organisms but also harm humans because of carcinogenic, mutagenic and teratogenic properties and respiratory toxicity (Luan et al., 2016; Sharifpour et al., 2018). Malachite green (MG) is widely applied in the paper and spinning industries and used for biological control. Crystal violet (CV) is always applied for textile dyeing as a biological stain (Saeed et al., 2010). CR is a textile industry released dye, almost 15% of which flows into wastewater (Chatterjee et al., 2010). Therefore, it is necessary to find effective ways to remove dyes from effluents. The most common methods of removing dyes from industrial effluents are biological oxidation, flocculation, chemical precipitation and activated carbon adsorption. Being simple and effective, the adsorption treatment method is a promising way to remove dyes and organic compounds from aqueous effluents (Fontoura et al., 2017). To date, amounts of studies focus on the dye removal by biochar, but there is still no study on the dye removal by the biochar from pigments-extraction macroalgae.

The aim of this work was to investigate whether MDBC can be efficiently used for functional biochar production, as well as for the identification of surface chemical behavior and the definition of dye sorption mechanisms. In this study, MDBC was initially obtained

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through pyrolysis. The capacity of MDBC for removal of various dyes, such as MG, CV and CR, was investigated at different pyrolysis temperatures. The adsorption kinetics, sorption isotherm and corresponding dye removal mechanisms were studied under optimal conditions. In addition, physicochemical properties and adsorption mechanisms of MDBC before and after adsorption were studied by analyzing the change in surface chemical behavior through elemental analysis (EA), scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), fourier transform infrared spectroscopy (FTIR) and Brunauer-Emmett-Teller (BET). The knowledge created from this study can be used to conclude whether biochar produced from macroalgae is an efficient adsorbent for dyes, which makes the proposed method a promising way to treat macroalgae residue.

## 2. Materials and methods

### 2.1. Macroalgae preparation

*Ulothrix zonata* algae from south of Taiwan, Pingtung, were collected after being rinsed and extracted with distilled water at 60 °C for 4–5 h to extract fucoxanthin. Then algae filaments were used as an adsorbent in this research after being dried for 48 h at 40 °C. Chlorophyll and carotenoids were extracted from macroalgae biomass which was mixed with acetone by ultrasonic destruction for 5 times, and 20 min for each time. Finally, the macroalgae residue was dried for 12 h at 105 °C.

### 2.2. Preparation and characterization of macroalgae-derived biochar

MDBC (10 g) was prepared by pyrolysis of pigments-extracted macroalgae residue, which was annealed for 90 min at 400 °C (MDBC400), 600 °C (MDBC600) and 800 °C (MDBC800) under a nitrogen atmosphere, while the pyrolysis heating rate was set at 15 °C min$^{-1}$. The biochar ash was annealed under an air atmosphere at 600 °C for 120 min (Ho et al., 2017). The C, H, N and O contents in MDBC were measured with an elemental analyzer (Bruker, Germany). Also, the percentage of oxygen was determined by the mass balance via Eq. (1).

$$O(\%) = 100(\%) - C(\%) - H(\%) - N(\%) - Ash(\%) \quad (1)$$

Micro-morphological images of MDBC were acquired by SEM (TM3030, Hitachi, Japan) and EDS. FTIR (SPECTRUM one, PerkinElmer, USA) was used to confirm the MDBC surface functional groups ranging from 400 cm$^{-1}$ to 4000 cm$^{-1}$ wavenumber. After being degassed for 6 h at 150 °C, the surface area, pore volume and average pore diameter of biochar was measured by BET (JW-BK132F, JWGB SCI & TECH, China). UV spectrophotometer (UVmini-1240, Shimadzu, Japan) was applied to measure the MG, CR and CV concentrations at the absorbance wavelengths of 617 nm, 502 nm and 582 nm, respectively. The pH of MDBC was confirmed at the solid-to-liquid mass ratio of 1:10.

### 2.3. Determination of dye metal removal

Solutions (10 mL) of MG (500 mg L$^{-1}$), CV (200 mg L$^{-1}$) and CR (100 mg L$^{-1}$) were placed in a 30 mL glass reactor, followed by the addition of 0.005 g MDBC. MDBC and dye solutions were mixed in a shaker at 200 rpm and 25 °C for 14 h. To measure the residual dye by UV spectrometry, 0.45 μm membrane was used to filter the suspension. The influence of pH was investigated before and after dye removal. Before the adsorption process, the initial pH of the solution was set at 2, 4, 6, 8 and 10 for studying the pH effect by 1 M NaOH or 1 M HNO$_3$ solutions. The dye-laden biochar was dried at 105 °C and analyzed using FTIR and SEM-EDS to study the dye removal mechanism.

### 2.4. Adsorption isotherm models

To identify the adsorption mechanism, the equilibrium adsorption isotherms need to be built to describe the relationship between adsorbate and adsorbent. The effect of different temperatures (288 K, 298 K and 308 K) was investigated for the adsorption process. In this study, the dye adsorption process by MDBC800 was described by the Langmuir and Freundlich isotherm, respectively. The Langmuir model describes the adsorption process when the adsorbent has a homogeneous monolayer surface and possesses energetically equivalent sites for adsorbate interaction. The adsorbate molecules do not transmigrate on the adsorbent after the formation of a monolayer (Chen et al., 2018). The Langmuir model can be expressed as:

$$\text{Lamgmuir isotherm:} C_e/Q_e = C_e/Q_m + 1/Q_m K_L \quad (2)$$

where $C_e$ is the balanced concentration of dye (mg L$^{-1}$), $Q_e$ is the amount of dye adsorbed per mass of MDBC800 (mg g$^{-1}$), $Q_m$ is the maximum adsorption capacity of MDBC800 (mg g$^{-1}$), and $K_L$ is the Langmuir constant (L mg$^{-1}$).

The exponentially decaying adsorption site energy distribution can be described by the Freundlich isotherm model. Heterogeneous surfaces and multilayer sorption which is non-ideal can be expressed by this model (Tang et al., 2014). The Freundlich model is described as:

$$\text{Freundlich isotherm: } logQ_e = logK_F + 1/nlogC_e \quad (3)$$

where $K_F$ is the Freundlich adsorbent capacity, and $n_F$ is the heterogeneity factor.

### 2.5. Adsorption kinetics models

Pseudo-first-order and pseudo-second-order kinetic models were used to investigate the dye adsorption kinetics on MDBC800. The models expressions are as follow:

$$\text{Pseudo - first - order model } q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (4)$$

$$\text{Pseudo - second - order model } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \quad (5)$$

where $t$ is the contact time (min); $q_e$ and $q_t$ represent dye adsorption capacity (mg g$^{-1}$) at equilibrium and at time $t$ (min), respectively. $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the pseudo-first-order rate constant and the pseudo-second-order rate constant, respectively.

To describe the mechanism of adsorption, the intra-particle diffusion rate model, proposed by Weber and Morris (1963), was adopted, of which expression is:

$$q_t = k_p t^{0.5} + C \quad (6)$$

where $k_p$ is the intra-particle diffusion rate constant (mg g$^{-1}$ min$^{-0.5}$), and the thickness of the boundary layer (mg g$^{-1}$) is represented by C. Higher C values mean that other mechanisms besides pore diffusion may be involved as rate-determining steps.

## 3. Results and discussion

### 3.1. Elemental composition and surface morphology of macroalgae-derived biochar

To analyze the chemical process of the adsorption, the main characteristics of MDBC produced at three temperatures (Table 1). The biochar yield percentage for MDBC was 46.2% at 400 °C, but declined to 22.6% at 800 °C. The amount of surface functional group elements, e.g. H, O and N, were reduced because volatile matter was vanished with increasing pyrolysis temperature (Table 1). The molar ratios of H/C and O/C are the main parameters for carbonization degree, which is generally used to characterize the organic compound aromaticity in