Biochemical Engineering Journal 67 (2012) 35–44

Contents lists available at SciVerse ScienceDirect

Biochemical Engineering Journal

journal homepage: www.elsevier.com/locate/bej

Textural characteristics, physiochemical properties and adsorption efficiencies of Caribbean alga *Turbinaria turbinata* and its derived carbonaceous materials for water treatment application

S. Altenor[a], M.C. Ncibi[a,*], E. Emmanuel[b], S. Gaspard[a]

[a] *Laboratoire COVACHIMM, EA 3592 Université des Antilles et de la Guyane, BP 250, 97157 Pointe à Pitre Cedex, Guadeloupe*
[b] *LAQUE, Université Quisquéya d'Haïti, Port-au-Prince, Haiti*

ARTICLE INFO

Article history:
Received 5 July 2011
Received in revised form 24 April 2012
Accepted 19 May 2012
Available online 29 May 2012

Keywords:
Alga
Activated carbons
Characterization
Adsorption
Modeling
Waste-water treatment

ABSTRACT

The adsorptive removal capacities of highly available *Turbinaria turbinata* alga and its derived carbonaceous products (i.e. pyrolyzed, physically and chemically activated carbons) were investigated in this study. Several textural and chemical characterizations were performed on the alga and its activated carbons (ACs). Besides, kinetics and isotherms assays were performed and modeled in order to monitor the sorption capacities and dynamic behaviors.

The main results showed that the raw Turbinaria biomass has a non porous structure. Then, after thermo-chemical treatments, a porous matrix starts to develop and the total pore volume drastically increased from 0.001 cm^3/g for the algal precursor (turb-raw) to 1.316 cm^3/g for its derived chemically AC (turb-P1). As well, the specific surface area improved from m^2/g for (turb-raw) to 1307 m^2/g for (turb-P1). Consequently, the maximum sorption capacity went from 63 mg/g for the algal biomass up to 411 mg/g for the chemically ACs.

Moreover, the removal rate was taken into consideration in order to set a more reliable and realistic approach to figure out the most efficient AC.

Thus, based on those criteria, it was found that the chemically activated carbon "turb-P1" is the most efficient Turbinaria-derived sorbent to adsorb and remove methylene blue (MB) molecules from aqueous solutions with 169 g of the dye using 1 kg of raw alga (considering an AC production yield of 49%).

1. Introduction

One of the most abundant and highly available natural resources in tropical ecosystems is alga. Along with its industrial valorization in the pharmaceutical, cosmetics and food industries, the use of alga for environmental decontamination is an interesting field of research and development. Indeed, based on their rich biochemical composition, the algal biomass is a very promising material to be used as adsorbent to remove various kinds of pollutants from contaminated water and wastewaters.

Several pollutants were successfully removed from aqueous media using alga such as *Ulva fasciata* and *Sargassum* sp. for copper uptake [1], *Ulva lactuca* and *Sargassum* sp. [2,3] for chromium removal and *Sargassum filipendula*, *Laminaria hyperborea*, *Bifurcaria bifurcata*, *Sargassum muticum* and *Fucus spiralis* [4,5] for cadmium, zinc and lead ions adsorption. Besides, many algae were studied for synthetic dyes removal like *Enteromorpha* spp. [6], *U. lactuca* [7], *Caulerpa racemosa* [8]. As well, phenol and phenolic compounds could be removed from aqueous solutions by adsorption onto alga such as *Caulerpa scalpelliformis* [9] and *Lessonia nigrescens* and *Macrocystis integrifolia* [10].

In this study, the sorption capacities of highly available, low-cost and renewable brown alga, *Turbinaria turbinata* and its derived activated carbons were investigated for the removal of methylene blue (MB); a model compound for organic molecules. To the best of our knowledge, the use of this algal biomass, widely distributing in the Caribbean, to remove pollutants using the adsorption technique has never been reported, along with its conversion into activated carbons (ACs). Thus, in this research, we will examine the sorption capabilities of this marine biomass starting with the raw alga, then with the pyrolyzed biomass and different kinds of activated carbons (physically and chemically activated) through kinetic and isotherm studies.

Several theoretical models were tested in order to fit the experimental data and to understand the possible physicochemical interactions involved in the sorption phenomenon between the biomass surface and the dye molecules. Besides, a comparative

* Corresponding author. Tel.: +590 590 48 30 50; fax: +590 590 48 30 72.
E-mail address: ncibi_mc@yahoo.com (M.C. Ncibi).

1369-703X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.bej.2012.05.008

study on the sorption performances of Turbinaria and its derived ACs with other sorbents was also carried out.

2. Experimental

2.1. Biomass preparation

Brown alga *T. turbinata* (turb-raw) was harvested in St. Francois, Guadeloupe. It is composed of 20.5% carbohydrate, 8% proteins, 0.2% lipids, 13% water, 16% ash, and 41% fibers content [11]. First, the biomass was washed with tap water to remove dirt and sand, then with deionized water to remove salt. After that, it was dried in the sun for a week before dividing the whole lot into two parts: one will be used for the biosorption experiments and the other for the preparation of activated carbons.

For the algal biomass to be used in the sorption assays, it was dried (after a week of sun exposure) in an oven at 50 °C until constant weight. After drying, it was crushed and then sieved. The fraction of particles size ranging between 0.4 and 1 mm were chosen to perform all experiments.

2.2. Activated carbons preparation

The alga were initially dried at 105 °C for 48 h using a drying oven, then ground and sieved. The fraction with a particle size ranging between 0.4 and 1 mm was retained. In this study, two conventional methods of ACs preparation were used:

(i) For *physical activation*, approximately 15 g of pre-treated *T. turbinata* were initially pyrolyzed in a Barnstead/Thermolyne furnace F-21100 under nitrogen atmosphere at 800 °C for 1 h with a heating rate of 10 °C/min. Charcoals thus prepared "turb-pyr", were then activated with steam under a nitrogen atmosphere at 800 °C for 8 h with a heating rate of 10 °C/min in the same furnace giving sample "turb-H_2O" [12].

(ii) For *chemical activation*, approximately 10 g of *T. turbinata* were impregnated in phosphoric acid (H_3PO_4) 85% for 24 h, in order to facilitate the access of the acid inside the particles [13]. Impregnation ratio; X_P (g H_3PO_4/g precursor) 1:1 is used producing the sample "turb-P1". After impregnation, the sample is dried for 4 h at 105 °C in a drying oven. The sample thus dried is pyrolyzed under nitrogen flow at 600 °C for 1 h. After cooling (i.e. till ambient temperature), the AC thus obtained is washed with distilled water until stabilization of the pH. Then, it was dried overnight using a drying oven at 105 °C [14].

2.3. Sorbents characterization

2.3.1. Textural characterization

The BET surface area and porous properties of each sample were determined from N_2 adsorption experiments. The sorbents were characterized by N_2 adsorption at 77 K using a "Micromeritics" accelerated surface area and porosimetry analyzer model ASAP-2020. The sample was degassed for 24 h at 573 K to remove any moisture or adsorbed contaminants that might be present on the surface. The manufacturer's software provided BET surface area (S_{BET}) of the samples by applying the BET equation to the adsorption data. The microporous surface (S_{micro}) and external surface (S_{ext}), the total pore volume (V_T) and micropore volume (V_{mi}) were evaluated by *t*-plot method. The mesopore volume (V_{me}) was estimated by Barrett–Joyner–Halenda (BJH) method [15]. The mean pore diameter, D_p, was calculated from $D_p = 4V_T/S$ [11], where V_T is the total volume of pores, and *S* being the BET surface area.

2.3.2. Chemical characterization

The surface properties of the sorbents were monitored by XPS (X-Ray Photoelectron Spectroscopy). XPS measurements were conducted on an Axis-Ultra DLD Model from KRATOS, equipped with a hemispherical electron analyzer and a monochromatized Al Kα (1486.6 eV) X-ray exciting source. Based on the high sensitivity of the DLD detector, a source power of 90 W was enough to obtain high quality spectra in a reasonable acquisition time. The XPS allows identification and quantification of the element and the functional groups on/near the surface of sorbents, with a relative sensitivity factor (RSFS) of 1 provided by the KRATOS data basis. Since the samples are conducting materials, no charge correction was applied to the spectra. The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f7/2 line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for Cu 2p3/2 line for metallic copper.

The pH_{PZC} (i.e. pH at the point of zero charge) was measured for the produced ACs. For this purpose, 50 ml of a 0.01 M NaCl solution was placed in a 100 ml Erlenmeyer flask. Then, the pH was adjusted to successive initial values between 2 and 12, by using either NaOH or HCl, and 0.15 g of ACs was added to the solution. After a contact time of 48 h, the final pH was measured and plotted against the initial pH. The pH at which the curve crosses the line pH (final) = pH (initial) is taken as the pH_{PZC} of the tested AC.

The total surface basicity and acidity of the samples were determined by titration with NaOH and HCl using the Boehm titration method [16]. 0.2 g of AC was mixed with 50 ml of 0.05 N NaOH or HCl solutions for 48 h with continuous stirring. Ten milliliters of each filtrate were then titrated against 0.05 N HCl or NaOH, using phenolphthalein as indicator. Capacity for H^+ and OH^- were then measured.

2.3.3. SEM analysis

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray microanalysis (Hitachi S-2500) was used to determine the surface and pore structural characteristics of the experimented sorbents. The Turbinaria and its derived ACs were firstly mounted on an aluminum stub, and for the case of the raw Turbinaria, the biomass was covered with a thin layer of carbon. Then, the microscope was operated at an accelerating voltage of 200 kV and a working distance of 35 mm.

2.4. Adsorption studies

2.4.1. Adsorption experimental protocol

Organic dyes are pollutants commonly found in wastewater. Thus, methylene blue (molecular diameter > 1 nm) [17] was chosen as organic adsorbate to test the adsorptive properties of *T. turbinata* and its derived ACs. All experiments were performed in liquid phase in glass bottles of 200 ml at 25 °C in a thermostatic bath. Synthetic solutions for the adsorbate were prepared by dissolving accurately weighted amount of dye (1000 mg/l) in distilled water and subsequently diluted to obtain the required concentrations.

Spectrophotometric scanning of dilute MB dye solutions was performed and absorbance maxima were fixed at 660 nm using an UV-Visible spectrophotometer (Anthelie Advanced 5 Secoman).

2.4.2. Adsorption kinetic study

Kinetic experiments were carried out in a 600 ml glass vessel at 25 °C. The aqueous solution (500 ml with 40 mg of AC or 100 mg of Turbinaria fibers) was agitated at 200 rpm using a magnetic agitator at 25 °C. The recording time was started when biomass was added to the solution. Aqueous samples (1 ml) were taken from the solution using a calibrated syringe with a 0.45 μm filter at preset time intervals and the concentrations were analyzed using an UV–visible spectrophotometer (Anthelie Advanced 5 Secoman). The amount