Journal of Environmental Chemical Engineering 5 (2017) 5076–5084

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Defatted microalgal biomass as biosorbent for the removal of Acid Blue 161 dye from tannery effluent

Juliana Tolfo da Fontoura[a,*], Guilherme Sebastião Rolim[a], Bianca Mella[a], Marcelo Farenzena[b], Mariliz Gutterres[a]

[a] Laboratory for Leather and Environmental Studies (LACOURO), Chemical Engineering Post-graduated Program (PPGEQ), Federal University of Rio Grande do Sul (UFRGS), Av. Luiz Englert s/n°, Porto Alegre, RS, 90040-040, (51)3308-3954, Brazil

[b] Laboratory of Process Control and Integration (LACIP), Chemical Engineering Post-graduated Program (PPGEQ), Federal University of Rio Grande do Sul (UFRGS), Av. Luiz Englert s/n°, Porto Alegre RS, 90040-040, (51)3308-3954, Brazil

ARTICLE INFO

Keywords:
Biosorption
Defatted microalgae
Scenedesmus sp.
Azo dye
Acid Blue 161
Tannery wastewater

ABSTRACT

The present study investigates the use of defatted microalgal biomass – DAB (waste from microalgal biofuel) as an alternative proposal adsorbent of leather dyes. The biomass was characterized by analytical techniques of Zeta Potential, FTIR, SEM, BET and BJH. The sorption experiments were performed using aqueous dye solutions of Acid Blue 161 (AB-161) and the equilibrium studies were carried out by variation in different parameters, i.e., pH (2–11), biosorbent dosage (0.005–0.040 g), contact time (0–540 min), temperature (25–40 °C) and dye concentration (200–1500 mg L^{-1}). In the evaluation of the kinetic mechanism that controls the adsorption process examined at 200 and 400 mg L^{-1}, it was observed that data fitted quite well with general order kinetic model. Freundlich isotherm model showed the best fit of the equilibrium data at boths experimental temperatures. The maximum amounts of AB-161 dye adsorbed were 75.78 mg g^{-1} at 25 °C and 83.2 mg g^{-1} at 40 °C. For treatment of real tannery wastewater, the results show that DMB significantly reduced the dye concentration (76.65%), TOC (50.78%) and TN (19.80%). From the thermodynamic parameters for the adsorption of AB-161 with DMB indicated a spontaneous endothermic process with a physical reaction by electrostatic interaction. Therefore, defatted microalgal biomass showed to be a promising material for adsorption of dye from tannery effluent.

1. Introduction

Algae are promising sources of biofuel due to their lipid content, as well as ability to utilize wastewater for cultivation, besides non requirement of fertile land, do not compete with food crops and reduce greenhouse gas from the environment [1,2]. However, after lipid extraction about 70% of the microalgae biomass remains intact [3]. It is estimated that approximately 2.4 kg of waste is generated for each liter of biodiesel produced from microalgae [4].

Recent research has been focusing on practicality and sustainability of algal biofuels. The use of the residual biomass is a way to maximize the production of energy obtained through the microalgae and reduce the total costs of the processes and waste treatment. Numerous studies include the use of residual biomass as a substrate for bioethanol, biogas in addition to be used as animal/poultry/fish feed and fertilizer [5]. A suitable economical use of defatted microalgal biomass (DMB) is its application as an adsorbent for the removal of dyes from industrial wastewater.

Dye pollution has grown rapidly due to increased use of synthetic dyes [6,7]. The leather industry is one of the great contributors to this, as uses dyes and other chemicals to give leather the sensory characteristics of surface and deep coloring and uniformity [8].

The discard of wastewater containing dye into water bodies, affect adversely the aquatic environment by impeding light penetration and, as a consequence, inhibiting photosynthetic activity [9,10]. Moreover, most of these dyes can cause serious problems to human health.

The most commonly used methods for dye removal from industrial effluents are coagulation and flocculation [11], biological oxidation and chemical precipitation [12] and activated carbon adsorption [13,14]. The adsorption treatment method has shown promise for the removal of dyes and organic compounds from aqueous effluents [15–19] due its simplicity and high efficiency, as well as the availability of a wide range of adsorbents that can be applied [20–22].

Activated carbon is the most commonly used adsorbent for the removal of dyes because of its high surface area and adsorption capacity. However, there is a growing interest in using low cost, commercially

* Corresponding author.
E-mail addresses: jutolfo@enq.ufrgs.br (J.T. da Fontoura), mariliz@enq.ufrgs.br (M. Gutterres).

http://dx.doi.org/10.1016/j.jece.2017.09.051
Received 14 June 2017; Received in revised form 8 September 2017; Accepted 23 September 2017

Nomenclature

AB-161	Acid Blue 161 dye
DMB	Defatted microalgal biomass
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy
BET	Brunauer–Emmett–Teller surface area
BJH	Barrett– Joyner–Halenda pore size
q	Amount of dye adsorbed by the adsorbent (mg g^{-1})
C_o	Initial dye concentration put in contact with the adsorbent (mg L^{-1})
C_f	Dye concentration after the batch adsorption procedure (mg L^{-1})
V	Volume of dye solution put in contact with the adsorbent (L)
m	Mass of adsorbent (g)
R^2	Determination coefficient
R^2_{adj}	Adjusted determination coefficient
SD	Standard deviation
$q_{i,\mathrm{mod}\,el}$	Value of q predicted by the fitted model
$q_{i,\mathrm{exp}}$	Value of q measured experimentally
$\bar{q}_{i,\mathrm{exp}}$	Average of q experimentally measured
p	Number of parameter of the fitted model
TOC	Total organic carbon
TN	Total nitrogen
k_f	Pseudo-first-order rate constant (min^{-1})
q_e	Amount of adsorbate adsorbed at the equilibrium (mg g^{-1})
q_t	Amount of adsorbate adsorbed at time t (mg g^{-1})
n	Adsorption reaction order with regard to the effective concentration of the adsorption sites available on the surface of adsorbent
k_s	Pseudo-first-order rate constant (g mg^{-1} min^{-1})
k_N	General-order rate constant (h^{-1}(g mg^{-1})n^{-1})
K_L	Langmuir equilibrium constant (L mg^{-1})
$Q_{\max}$	Maximum adsorption capacity of the adsorbent, langmuir isotherm (mg g^{-1})
C_e	Dye concentration at the equilibrium (mg L^{-1})
K_F	Freundlich equilibrium constant (mg g^{-1}(mg L^{-1})$^{-1/nF}$)
n_F	Dimensionless exponent of the freundlich equation
pH_{pzc}	Point of zero charge
ΔH^0	Standard enthalpy change (kJ mol^{-1})
ΔG^0	Standard gibbs free energy change (kJ mol^{-1})
ΔS^0	Standard entropy change (J K^{-1} mol^{-1})

available materials as these are derived from non-renewable sources [23] and are relatively expensive.

Different kinds of alternative adsorbents to remove dyes and other contaminants from the leather industry from aqueous solutions have been reported, such as leather waste samples from the shaving operation of chromium tanned leather [16,19], papaya seed [24], fungal biomass [25], algae [26], cattle hair waste [27], ficus auriculata leaves [28], Sterculia guttata shell [29] and others.

The biomass of microalgae contains a variety of functional groups present in the surface such as hydroxyl, carboxyl, phosphate, sulphate, and other charged groups which can be mediate pollutant binding [21,30]. Biomass algal has been successfully employed to remove heavy metals [31,32], food dyes [33], textile dye [21,26,34,35] from aqueous solutions. Despite of this, were not found report of studies on the use of defatted microalgal biomass for the removal of leather dyes.

In this context, the aim of the present study was to investigate the potential application of defatted microalgal biomass (DMB), cultivated in tannery wastewater, as a biosorbent for the removal of Acid Blue 161 (AB-161) dye, which is largely used in the leather industry. Zeta Potential, FTIR, SEM, Optical microscopy micrographs and BET and BJH, characterized the biosorbent. Influences of pH, kinetics, equilibrium and mechanism studies were carried out in order to elucidate the adsorption process of dye onto DMB. The adsorbents were used for treatment dye aqueous solutions and tannery effluent.

2. Materials and methods

2.1. Solutions and reagents

The dye used as adsorbate Acid Blue 161 (AB-161; C.I. 15706; CAS number 12392-64-2; chemical formula is $C_{20}H_{13}N_2O_5SNaCr$; molecular weight = 394.40 $gmol^{-1}$), was obtained from chemical company Lanxess (São Leopoldo, RS-Brasil) as a commercially available leather dye. It belongs to the azo dye group, whose the molecular structure is shown in Fig. 1. Azo dyes are extensively used in the tannery industry [36]. The stock solution (2.00 g L^{-1}) was prepared by dissolving the dye in distilled water. The working solutions were obtained by diluting the dye stock solution to the required concentrations. To adjust the pH of the solutions, 0.50 mol L^{-1} sodium hydroxide or chloric acid were used.

2.2. Adsorbents preparation and characterization

The adsorbent used in this research was the residual biomass of the microalgae *Scenedesmus* sp. after lipid extraction (defatted microalgal biomass − DMB). The microalgae was cultured in 3 L photobioreactors containing tannery effluent without pretreatment (beamhouse stage effluent) for 20 days. At the end of cultivation, the biomass was recovered by centrifugation and freeze-dried.

Lipid extraction was performed using the organic solvents chloroform:methanol:water (2:2:1.8 v/v). After extraction, the biomass was washed with distilled water, centrifuged and dried in an oven for 12 h at 80 °C. The dry biomass was macerated for homogenization of the biosorbent and was characterized by vibrational spectroscopy in the infrared region with Fourier transform (FTIR). The spectra were obtained with a resolution of 4 cm^{-1} with 100 cumulative scans using a Varian spectrometer, model 640-IR. The surface physical morphology of the biosorbent was observed by a scanning electron microscope (JSM 6060–JEOL) and by microscopy (Olympus SZX16 stereomicroscope). N_2 adsorption–desorption isotherm measurements were carried out at 77 K (−196 °C) using an adsorption analyzer (Gemini 2375 Micrometer), at a relative pressure (P/Po) from 0 to 0.99. The specific surface area were determined from the Brunauer, Emmett and Teller (BET) multipoint method and the pore size distribution were obtained using Barret, Joyner, and Halenda (BJH) method.

Zeta potential measurements were conducted using a Zetasizer

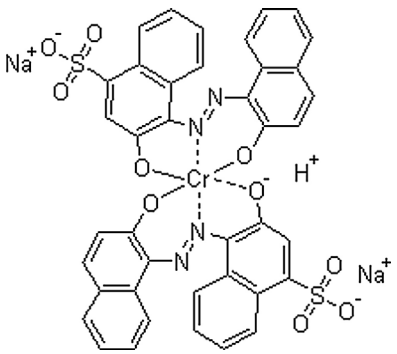

Fig. 1. Chemical structure of the Acid Blue 161.