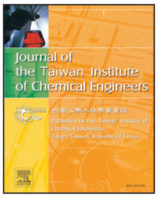
Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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



Removal of methylene blue by chemically modified defatted brown algae *Laminaria japonica*

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ARTICLE INFO

Article history:
Received 13 October 2016
Revised 11 August 2017
Accepted 12 August 2017
Available online xxx

Keywords:
Laminaria japonica biomass
Adsorption
Methylene blue
Modification

ABSTRACT

Defatted *Laminaria japonica* biomass (DLB) was modified by sulfuric acid to produce a low cost adsorbent (Labeled as DLB-S) for removal of methylene blue (MB) from aqueous solutions. DLB and DLB-S were characterized by FT-IR, SEM and BET. And then various factors, such as adsorbent dose, initial pH, contact time, temperatures and initial MB concentrations were systematically investigated. The optimum conditions for the maximum dye removal were found to be about pH 6, low biosorbent dose of 0.6 g/L, quasi-equilibrium reached within 60 min and temperature of 308 K. The maximum MB adsorption capacities of DLB and DLB-S were 418.41 mg/g and 549.45 mg/g in these conditions, respectively. The equilibrium adsorption could be well described by Langmuir models and Sips models. Batch kinetic experiments showed that kinetics was better described by the pseudo-second order kinetic model. In addition, thermodynamic parameters indicated that the adsorptions were spontaneous, endothermic processes. The adsorption of MB onto DLB-S mainly involved electrostatic interaction and complexation. The adsorption capacity of DLB-S was enhanced and the organic content leaching from DLB-S was effectively decreased after DLB was modified by sulfuric acid.

1. Introduction

Nature or synthetic dyes are important colorants extensively employed for industries, including textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals and food [1–3]. The effluents of these industries are highly colored and may be toxic and even carcinogenic. Therefore, removal of these colored agents from aqueous effluents is of significant environmental importance [4,5]. The conventional methods include coagulation and flocculation, reverse osmosis, electroflotation, membrane filtration, irradiation, ozonation, microbiological degradation and active carbon adsorption [6–8]. However, due to the high capital investment and operating costs, the above-mentioned methods have restricted their extensive application [9,10]. Therefore, there is a growing interest in innovative methods to remove the dyes based on low cost, easy operation, and simple maintenance. Biosorption has provided an alternative treatment of industrial effluents from that of the traditional physic-chemical methods, because of simplicity in operation, low cost, flexibility and high adsorption efficiency for low concentration pollutants [2,11,12]. Considering that economical reasons and most synthetic dyes resist degradation, biosorption is a new approach and practical significance in recent years.

Laminaria japonica is a renewable brown algae natural resource and abundance of the biomass in China, which is considered to be a cost-effective and efficient biosorbent for the removal of dyes from industrial wastewaters, due to the functional groups (amino, carboxyl, sulfate, hydroxyl, *etc.*) on the cell wall [4,13–18]. These functional groups play an important role in the biosorption process. However, brown algae contain a high amount of organic substances, such as carbohydrates, protein, lips, and pigments; some of them can inevitably dissolve in the aqueous solutions during the biosorption process [19,20]. The organic leaching from the biosorbent can lead to a secondary pollution and retard the biosorption technology in wastewater treatment [21]. Therefore, it is important to modify the raw brown algae to avoid the organic leaching but not to affect the sorption capacity. Some researchers have worked on modification of algae biomass by sulfuric acid, calcium chloride, polyethylene mine, formaldehyde and glutaraldehyde to increase the stability of the biosorbent material and increase their adsorption potential for the removal of dyes and metals from waste water [22–25]. The adsorption capacities of methylene blue onto *Scenedesmus dimorphus,* defatted algal biomass and sulfuric acid pre-treated defatted algal were 6.0 mg/g, 7.73 mg/g and 18.24 mg/g, respectively [26]. However, only a limited number of studies have been focused on the use of defatted

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http://dx.doi.org/10.1016/j.jtice.2017.08.023

Please cite this article as: H. Shao et al., Removal of methylene blue by chemically modified defatted brown algae *Laminaria japonica*, Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2017.08.023

brown algae *Laminaria japonica* as adsorbent for dye molecules removal from wastewater [26,27].

The aim of the present study was to modify raw *Laminaria japonica* for the prevention of organic leaching and the enhancement of dye removal. Defatted *Laminaria japonica* biomass (DLB) obtained by pretreating with ethanol as a low-cost adsorbent for removal of methylene blue (MB) from aqueous solutions. In order to enhance the adsorption capacity of DLB and reduce the leaching of organic compounds from adsorbent, the adsorption capacities of DLB modified (DLB-S) were tested. The morphologies of DLB and DLB-S were characterized by FT-IR, SEM and BET. The adsorption properties of the biosorbents as functions of initial pH, biosorbent dose, contact time, temperatures and initial MB concentrations were systematically investigated. The equilibrium kinetic data and thermodynamic parameters were also explored to understand the adsorption mechanism of MB on DLB-S.

2. Materials and methods

2.1. Materials

Laminaria japonica was obtained from Weihai, Shandong Province. Analytical reagent grade Methylene blue ($C_{16}H_{18}ClN_3S$, $\geq$ 82%) was supplied from Tianjin Co. Ltd. A stock solution of MB (1 g/L) was prepared by dissolving MB in distilled water; desired concentrations were obtained by diluting the stock solution with distilled water. All chemicals were of analytical grade. Deionized water was used to prepare aqueous solution. The pH value of the solution was adjusted by 0.1 M HCl and 0.1 M NaOH.

2.2. Preparation of adsorbents

Raw Laminaria japonica (RLB) was firstly washed with the tap water and distilled water several times to remove sand and other impurities, respectively, and then the washed materials were dried at 333 K for 12 h, finally crushed to 100 mesh size for further studies.

The lipids were extracted from the dry RLB with ethanol for 12 h at 361 K using Soxhlet extractor. The Defatted *Laminaria japonica* biomass (DLB) was used for further studies.

DLB-S was prepared by treating DLB using 96% sulfuric acid according to the previous study [23]. DLB (5 g) was mixed with 30 mL of 96% H_2SO_4 and stirred for 24 h at 373 K. The product was filtered, neutralized with 2% sodium bicarbonate solution, and washed with distilled water until neutral pH, then dried for 6 h at 333 K, and finally crushed to produce particles of 100–150 μm in diameter, hereafter abbreviated as DLB-S.

2.3. Characterization

The Fourier transform infrared (FTIR) spectroscopy was measured on a Nicolet FT-IR 6700 spectrophotometer (Madison, USA) over the wave number range from 4000 to 400 cm^{-1} at room temperature. The morphologies of RLB, DLB and DLB-S were characterized by a ZEISS Ultra 55 scanning electron microscope (SEM) (Carl Zeiss, Germany). And the specific surface area was measured on an ASAP 2020 adsorption apparatus using the Brunauer-Emmett-Teller (BET) method. The point of zero charge (pH_{pzc}) was determined by solid addition method.

2.4. The organic leaching from the biosorbent

The total organic carbon (TOC) of solution after biosorption was a direct measurement of the organic pollution that was caused by the organic leaching from the biosorbents, the main compositions of which were organic [22]. In order to evaluate the degree of organic leaching during adsorption process, the TOC concentration in the solution with RLB, DLB and DLB-S were measured as follows: Dried 12 mg of biosorbent powders were equilibrated with 20 mL of distilled water at pH = 2, 4, 5, 7, 9 and 10, respectively, by shaking at 308 K for 12 h in a thermostated shaker. Then TOC concentration of the filtrate was measured by using a TOC analyzer (Shimadzu TOC Analyzer Model 5000A, Japan). All samples were filtrated using 0.45 µm membrane filters before measuring TOC.

2.5. Batch adsorption studies

Adsorption studies were conducted in 50 mL Erlenmeyer flasks. The initial pH of the dye solution was adjusted to 6.0 by using 0.1 M HCl or 0.1 M NaOH solution. Biosorption experiments were carried out by mixing 12 mg DLB (DLB-S) in a series of Erlenmeyer flasks containing 20 mL of MB solutions of initial concentration 20, 40, 60, 80, 100, 150, 200 and 250 mg/L at various temperatures (298, 308 and 318 K).The flasks were kept in a thermostated shaker at a speed of 180 rpm for 4 h. After shaking, the solution was centrifuged at 3500 rpm for 10 min. Then the dye concentration in the supernatants was determined using a UV-spectrophotometry (UV-3100 PC, Mapada) at a wavelength of 664 nm [17].

Kinetic experiments were conducted by mixing 12 mg DLB (DLB-S) in a series of Erlenmeyer flasks containing 20 mL of MB solutions of initial concentration 65 mg/L at different time intervals. The amount of dye adsorbed at equilibrium, q_e (mg/g) was evaluated by using the following mass balance equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of MB, respectively. V is the volume of solution (L), W is the mass of adsorbent (mg).

3. Results and discussion

3.1. Characteristics of adsorbent

3.1.1. SEM and BET

The surface morphologies of RLB, DLB, MB-loaded DLB, DLB-S and MB-loaded DLB-S in the present study were characterized by SEM. The RLB showed comparatively compact and smooth surface (Fig. 1(a)). Compared to RLB, DLB appeared as a rough and corrugated surface (Fig. 1(b)), which indicated the process of solvent extraction for defatting. After DLB was further treated with sulfuric acid, the surface of DLB-S was finely granular to increase porosity and specific surface area (Fig. 1(d)). After MB biosorption, the surfaces of MB-loaded DLB (Fig. 1(c)) and MB-loaded DLB-S (Fig. 1(e)) appeared flattened in comparison to DLB and DLB-S sample, respectively.

The BET surface area of RLB, DLB and DLB-S were 0.0171 m^2/g, 0.191 m^2/g and 23.748 m^2/g, respectively. Compared with RLB and DLB, the higher surface of DLB-S could provide more adsorption sites for MB [28]. The results revealed that the sulfuric acid treatment could destroy the cell structure to increase the surface area of the DLB-S.

3.1.2. FTIR

The FT-IR spectrums of RLB, DLB, MB-loaded DLB, DLB-S and MB-loaded DLB-S were shown in Fig. 2. For RLB (Fig. 2a), –OH and –NH stretching vibrations around 3334 cm^{-1} were overlapped to form a broad peak [29]. The peaks around 2922 cm^{-1} and 2852 cm^{-1} were corresponded to the $-CH_2$ and $-CH_3$ antisymmetric stretching vibration and symmetric stretching vibration [17], respectively. The peaks at 1597 cm^{-1} and 1412 cm^{-1} could be

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