



Characterization and application of bio-chars from liquefaction of microalgae, lignocellulosic biomass and sewage sludge



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ABSTRACT

Three bio-chars from liquefaction of spirulina (SP), rice straw (RS), and sewage sludge (SS) were characterized with an elemental analyzer, Fourier transformation infrared spectrometer, thermogravimetric analyzer, scanning electron microscope, and surface area analyzer and used as adsorbents for methylene blue (MB) removal. The analyzed characteristics of enriched oxygen-functional groups, thermally stable and porous structure on the surface may qualify the mesopores bio-chars to be potential adsorbents. In the MB removal experiments, the effects of pH and initial MB concentration on MB adsorption capacity were investigated. The equilibrium adsorption data were well fitted to Langmuir isotherm. MB adsorption may be described to be a monolayer “chemisorption” process. The maximum MB adsorption capacities were found to be 144.2, 128.6, and 160.5 mg/g for SS char, SP char, and RS char, respectively, which exceeded pyrolytic bio-chars reported by other researchers (12–130 mg/g), quantifying the liquefaction bio-chars to be suitable adsorbents for MB removal.

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1. Introduction

Considering the global fossil fuel diminution, the excessive petroleum price increase and the environment and energy security concern, there is growing tendency for biofuel production employing biomass resources including lignocellulosic biomass (e.g. rice straw, RS), microalgae (e.g. *spirulina*, SP), energy crops, aquatic plants, animal wastes, sewage sludge (SS), and cooking wastes [1–5]. The conversion of biomass to biofuel can be achieved via thermal processes, with hydrothermal liquefaction or liquefaction and pyrolysis be the two major focused ones [2,3]. Recently, liquefaction has been demonstrated to be one of the promising processes to produce bio-oil and has undergone a sudden increase in the number of publications [4–7]. Bio-oil, the main product of the biomass liquefaction, has a great potential to be used as high-quality biofuel [1,8], while bio-char, the main by-product of liquefaction process, can be used for soil remediation [9], carbon sequestration [10], and for the removal of pollutants as

modification-free adsorbent [11,12], and thus has good economical and environmental prospects [13,14].

Thermal decomposition of biomass can result in complex bio-char surface with less extractable organic compounds left in the char, rendering the char to be potentially used as competitive adsorbent for wastewater treatment. Bio-char can have quite different physical and chemical characteristics depending on the thermal technology (e.g., pyrolysis, gasification, hydrothermal liquefaction) used for its production [15]. Recently, the application of char from these thermal conversion technologies for adsorption has been focused mainly on char from high-temperature pyrolysis [13,16–20]. However, during the high temperature pyrolysis, most volatile compounds in the matrix were lost, and the surface area and ash increased, but surface functional groups that can provide exchange capacity decreased [21]. While, a large amount of polar groups was detected on the surface of liquefaction bio-char after hydrothermal treatment [22]. Therefore, although char from hydrothermal liquefaction had relatively lower surface area, its adsorption capacity for copper was much higher than pyrolytic char [12]. Thus bio-char, the main by-product from liquefaction process, may be a competitive candidate for adsorption application.

Our previous study [1] carried out liquefaction experiments at identical condition investigating the effect of distinct compositions and structures of SP, RS, and SS on the distributions and properties of

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liquefaction products. The purpose of this preliminary research is to systematically characterize and evaluate the feasibility of liquefaction bio-char from different biomass as adsorbent and to develop a value-added utilization for the bio-char.

2. Materials and methods

2.1. Materials

Bio-chars in this study were obtained from SP, RS, and SS by liquefaction from the previous study [1]. Briefly, 7.89 g of dried feedstock and 100 ml of ethanol were loaded into a 500 ml stainless autoclave, which was then sealed and heated to 350 °C with electric resistance heating. The reaction was held at 350 °C for 20 min and then cooled down to room temperature. The matrix was rinsed from the autoclave by washing with acetone, and then vacuum filtration was implemented to separate the solid and liquid products. The solid product was recovered as bio-char. The char was dried in an oven at 105 °C for 24 h and then ground to less than 75 μm and kept in a desiccator for use. The yields of bio-char were determined to be 45.73%, 25.41%, and 20.33% of the feedstock for SS, RS, and SP, respectively [1].

2.2. Char characterization

The elemental compositions of SS, SP, and RS feedstock were analyzed by a CHNOS elemental analyzer (Elementar, Vario EL III, Germany) in the previous study [1]. The elemental compositions of bio-chars and the moisture content, combustibles and ash in bio-chars were analyzed by the method reported in reference [1].

Thermogravimetric analysis (TGA) of bio-chars was performed with an integrated thermal gravimetric analyzer (EXSTAR, TG/DTA 7300, Japan) in a nitrogen atmosphere (purity of 99.99%). Bio-char samples were heated from 40 °C to 800 °C with a constant heating rate of 10 °C/min. The gas flow rate was 100 ml/min. Fourier transform infrared (FTIR) spectra of the biomass and bio-char samples were recorded on a FTIR spectrometer (WQF-410, China) at room temperature in the 400–4000 cm⁻¹ wavenumber range to determine their functional groups. Boehm titrations were applied for quantifying the total oxygenated groups on these bio-chars according to Boehm [23]. Briefly, a given amount of bio-char was added to the 0.1 M sodium ethoxide (NaOC₂H₅) solution and the mixture was shaken for 48 h at 150 rpm. Then the supernatant was drawn and back titrated with 0.1 M HCl [23,24]. The surface morphology was studied by scanning electron microscope (SEM) on FEI-Quanta200 (Holland). The Brunauer–Emmett–Teller (BET) surface area was measured using nitrogen as an adsorbate at 77 K in an automatic apparatus ASAP 2020 Micromeritics (USA). And the Dubinin–Radushkevich method was employed to determine the micropore volume of the samples and the meso- and macropore volumes were obtained using the Barrett–Joyner–Halenda method.

The points of zero charge for bio-chars were determined by the solid addition method reported in reference [25]. Briefly, 20 cm³ of 0.01 M NaCl solution was placed in a closed vessel and the pH was adjusted to a value from 3 to 10 with 0.1 M HCl or 0.1 M NaOH. Then, 0.10 g bio-char was added and the solution pH after 24 h of agitation was measured. The points of zero charge is the point where the curve ΔpH = pH (final) – pH (initial) = 0.

2.3. Adsorption experiment

Methylene blue adsorption is representative for the adsorption of medium-sized organic contaminants from aqueous solution [14,26]. And MB is often used to describe meso-porous materials for it is accessible to the pores with diameters larger than 1.5 nm [16,26].

Stock MB solution (150 mg/L) was prepared by dissolving MB in 1000 ml ultra-pure water. Different concentration solutions were prepared by diluting stock solution. After the adsorption equilibration

was achieved in each experiment, the solution matrix was separated and the MB concentration in the solution was determined by an Ultraviolet–Visible (UV–Visible) spectrophotometer (Shimadzu, Model UV-200S, Japan) at 665 nm. The UV–Visible spectrometer was calibrated with six MB standards range from 0.5 to 5.0 mg/L. Solutions were diluted to ensure that their concentrations remained within the linear calibration range.

The adsorption experiments were conducted under the same condition (adsorption temperature, 30 °C; adsorption time, 12 h (equilibrium time during preliminary experiment); agitation speed, 160 rpm) unless noted specifically. All experiments were duplicated with maximum errors of less than 5%, and only the average values were reported. The effect of initial pH on MB adsorption capacity (q_e : mg/g) was investigated over the pH range of 3.0–10.0. The pH value was adjusted by 0.1 M HCl or 0.1 M NaOH solutions. The effect of initial adsorbate (MB) concentration on the MB adsorption capacity was investigated with different MB concentration range from 10 to 150 mg/L, and the initial pH values in solution were controlled at 7.0 ± 0.1. MB adsorption capacity was calculated from the difference between the initial concentration and the final equilibrium one by the following equation:

$$q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

where C_o and C_e are the initial and equilibrium concentration of MB in solution, respectively, mg/L; V is the volume of solution, L; m is the adsorbent mass, g.

3. Results and discussions

3.1. Chemical composition analysis

As shown in Table 1, the yields of ash in SS and SS-derived bio-char were much higher than the others, which may be attributed to the abundance of metal elements and metal oxides originated from the raw SS. The metal oxides in SS may subsequently result in the retention of oxygen in SS bio-char for the metal oxides would be inactive during liquefaction [1]. Considerable higher carbon content in SP bio-char and RS bio-char were obtained, which may be due partly to the formation of coke for carbon existed in chars mainly in the form of coke [1], and partly to the difference of the reaction mechanisms of the components of each feedstock during liquefaction [1,2].

3.2. Thermogravimetric analysis

As shown in Fig. 1, the decomposition of RS, SS, and SP mainly occurred from 200 °C to 400 °C with 51.7%, 29.7%, and 52.3% weight loss, respectively. The residues of RS, SS, and SP after 800 °C were 28.1%, 49.1%, and 24.2%, respectively. The RS and SP derived bio-chars

Table 1
Elemental analysis and proximate analysis (wt.%) of raw feedstocks and bio-chars.

Sample	Elemental analysis (daf)				Proximate analysis		
	C	H	N	O ^a	M _{ad}	VM _{ad} + FC _{ad}	A _{ad}
<i>Raw feedstocks^b</i>							
SS	43.38	5.91	3.18	47.53	5.6	57.4	37.0
SP	43.17	8.53	8.91	39.39	3.3	88.4	8.3
RS	45.04	5.05	1.06	48.85	7.6	81.6	10.8
<i>Bio-chars</i>							
SS bio-char	54.18	4.07	6.93	34.82	0.7	27.8	71.5
SP bio-char	70.35	4.48	9.19	15.98	1.4	58.4	40.2
RS bio-char	78.48	5.07	2.72	13.73	1.2	67.5	31.3

M: moisture; VM: volatile matters; FC: fixed carbon; A: ash; daf: dry and ash-free base; ad: air dry base; d: dry base.

^a Calculated by difference.

^b Cited from Ref. [1].

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