Sugarcane Bagasse-based Adsorbent as an Alternative to Enhance the Harvesting Process of *Chlorella vulgaris* Biomass

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**ABSTRACT**

This research brightens a new approach to enhance *Chlorella vulgaris* biomass harvesting process using low-cost sugarcane bagasse-derived adsorbents in the optimized culture medium. Sugarcane bagasse-derived adsorbents were activated using different chemical concentration. Acid modified sugarcane bagasse-derived adsorbents of 1.5 M resulted the highest adsorption capacity of 66%. Point of zero charge was carried out the explained the reasons. The samples viewed under SEM showed 1.5M acid modified sugarcane bagasse-derived adsorbents have highest microalgae adsorption. Different sizes (710µm, 1mm, 2mm and 4mm) of 1.5M acid modified sugarcane bagasse-derived adsorbents were tested and 4mm-sized sugarcane bagasse-derived adsorbents gave the best adsorption.

**Keywords:** Chemical activations, harvest, microalgae biomass, sugarcane bagasse-derived adsorbents

1. Introduction

Recently, culturing microalgae for biodiesel production purpose has gained significant attention and interest around the globe. Microalgae biomass is the potential source of renewable energy source via conversion into biodiesel [1]. They are microorganisms that usually cultivate in water and possessed similar photosynthetic action followed by higher order of plants [2]. It is confirmed that microalgae growth under the controlled condition is able to crop 20 times oil per hectare more than the telluric oil seed yield [3]. Such microalgae can provide essentially more biodiesel than existing oil seed crops while using lesser water and land.

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The cultured microalgae will undergo harvesting process after achieving stationary growth phase. This harvesting process involves separation or detachments of microalgae from the culture medium [4]. The most common method used for microalgae harvesting involve flocculation, sedimentation as well as electrophoresis. The life cycle assessment (LCA) studies of late showed humongous energy was needed to grow, harvest and dry the microalgae biomass [5]. The harvesting cost has encompassed about 20%-30% of total production [6]. Thus, for mass biodiesel production, an effective harvesting method is necessary in ensuring economical viability [7].

Chlorella vulgaris strain was cultured as mother stock and sugarcane bagasse precursor was prepared as the derived adsorbents for this experiments. Recently, many adsorbent studies have been done to solve the separation issues. The adsorbents were derived from agricultural by-products or food wastes such as rice husk [8], rice straw [9], sawdust [10], sea mango [11], etc. Thus, it is believed that by introducing adsorbents, in this particular case is sugarcane bagasse, is able to enhance and fasten the harvesting process of microalgae biomass via thickening for the production of biodiesel in downstream process. The usage of low-cost, agricultural waste material has been proposed as a replacement for the nowadays costly procedure [12].

Microalgae adsorption was tested by using raw and modified (acid and base) sugarcane bagasse derived adsorbents. Acid modified adsorbents were the most suitable one. Next, six different concentrations of acid modification were tested on the following experiment and the point of zero charge of each adsorbents was identified. Also, the characterization of the adsorbents was studied. Next, the experiment of different sizes was carried out. The use of sugarcane bagasse-derived adsorbent is not only economical, but it also can reduce the waste generated from sugarcane industries. Therefore, the purpose of this research is to verify the potential of sugarcane bagasse-derived adsorbent used to thicken microalgae biomass.

2. Materials and Methods

A. Microalgae Culture Preparation

Potassium nitrate and sodium phosphate were used as the nutrient source in the culture medium following Bold’s Basal Medium (BBM). The weighted chemicals were put into 1-L volume conical flask. Next, 100ml of mother culture stock of C. vulgaris microalgae were introduced into the same conical flask and the rest volume were added with tap water up to 1000ml. The initial pH was adjusted to 3 with 0.1M of either NaOH or HCl.

B. Sugarcane Bagasse Derived Adsorbents Preparation

The collected raw sugarcane bagasse precursors were cut into small pieces, boiled and washed thoroughly to eliminate the impurities according to the method proposed by Azmi et al. [13]. Then, the sugarcane bagasse was dried in the oven to the constant weight at the temperature of 104-105ºC to discard the moisture. The dried bagasse were ground with 0.5 mm blade of grinder machine and then activated chemically. Next, the adsorbents were sieved by mechanical sieve shaker.

C. Chemical Activation Methods

15g of adsorbents were activated by using 0.5M sulphuric acid & 0.5M sodium hydroxide respectively in 1L working volume and stirred for 24 hours. Then, the adsorbents were dried in the oven at 105º C for overnight. The adsorbents were tested by putting it into 1L of microalgae culture.
The experiments were run with acid-activated adsorbents, base-activated adsorbents and raw adsorbents without activation. The absorption (Abs) reading was recorded by using UV-VIS spectrophotometer (SHIMADZU, UV-2600) within wavelength of 650-700 to measure the microalgae biomass concentration. Adsorption capacity is calculated using equation (1).

\[
\frac{(a-b)}{a} \times 100
\]

\(a\) = final concentration of microalgae without adsorbents
\(b\) = final concentration of microalgae with adsorbents

\[\text{(1)}\]

**D. Different Chemical Concentration Activation**

Based on chemical activation result, only acid modified adsorbents can absorb microalgae. Hence, six different concentrations of sulfuric acid were selected; 0.1M, 0.5M, 1.0M, 1.5M, 2.0M and 2.5M to choose the best concentration of acid modification. These selected concentrations were prepared in 1L conical flask with 15g of adsorbents and stirred for 24 hours. Next, the adsorbents were put into 1L of microalgae culture to identify the suitable concentration. The absorption (Abs) readings were taken daily by using UV-VIS spectrophotometer (SHIMADZU, UV-2600) within wavelength of 650-700 to measure the microalgae biomass concentration.

**E. Point of Zero Charge Determination**

The \(pH_{pzc}\) of sugarcane bagasse-derived adsorbents was resolved by solid addition method [12]. A series of 250ml conical flasks were prepared and 45 ml of 0.01 M of KNO3 solution of decided concentration was transferred. The pH value of the solution in each flask was roughly adjusted from pH 2 to 9 by adding either 0.1 M of HCl or NaOH with pH meter (Vernier, PH-BTA). Next, the total volume of each flask was added to 50 ml by adding KNO3 of the same concentration. The pHi of the solution in each flask was precisely recorded and 0.1 g of sugarcane bagasse-derived adsorbents of different concentration were put inside each flask respectively and securely capped. The flasks then were manually shaken and equilibrate for 48 hours with periodic manual shaking. The final pH value of each solution was noted. The difference between the initial and final pH values (\(\Delta pH = pH_i - pH_f\)) was plotted against the pHi and the point of intersection of pH=0 gave the \(pH_{pzc}\).

**F. Characterization of Adsorbents**

Scanning Electron Microscope (SEM) analysis was used to view the surface morphology of the adsorbents. Meanwhile, the samples consisted of adsorbent and microalgae were freeze-dried and coated before view under SEM.

**G. Different Sizes Determination**

After selecting the suitable concentration for adsorbents modification, the next step was to select the suitable sizes of adsorbents. The adsorbents of 1.5M acid modification with four different sizes were chosen; 710\(\mu\)m, 1mm, 2mm and 4mm. 100ml of microalgae was taken from mother culture stock and put inside 250ml conical flask. 0.5g of adsorbents of different sizes were added into the conical flasks respectively and securely capped. Next, shake the flasks at 200 rpm with and the reading was taken before putting the adsorbents 0h, 2h, 5h, 8h, 11h, and 28h.
3. Results and Discussions

A. Chemical Activation Method

Three different adsorbents were tested in 1L microalgae culture medium. The readings were taken daily using UV-VIS spectrophotometer and the Abs readings of microalgae biomass concentration were recorded. The Abs readings were converted in form of concentration (g/L). Fig. 1 below shows the result.

![Fig. 1. The suspended concentration of microalgae biomass after being tested with three different adsorbents](image)

The adsorption of base-modified adsorbents and raw adsorbents showed the lowest adsorption of microalgae biomass. Both base-modified adsorbents and raw adsorbents gave high concentration value of 1.081 g/L and 0.994 g/L respectively. These values showed less microalgae being absorbed through based-modified and raw adsorbents sugarcane bagasse. Plus, these adsorbents took the shortest time to achieve stationary phase and the adsorption capacity was negligible.

Meanwhile, acid-modified adsorbents showed the lowest microalgae concentration. Hence, the highest adsorption capacity. The concentration of acid-modified adsorbents was the lowest which is 0.399 g/L. The value showed the adsorption of microalgae occurred via acid-modified adsorbents. The adsorption capacity was 53%. Acid modified adsorbents showed better adsorption compared to base modified adsorbents and these could be related to the surface charge of microalgae which is known as negative [14]. Also, the acid modification method used to critically improve the adsorption capacity [15].

B. Selection of Suitable Acid Concentration Used for Modification of Sugarcane Bagasse-Derived Adsorbent

Based on Fig. 2 below, acid-modified adsorbents with 2.5M gave the highest concentration of 0.4153 g/L that showed low adsorption of microalgae biomass. Meanwhile, 1.0M and 1.5M acid-modified adsorbents had the lowest concentration values of 0.2932 g/L and 0.2888 g/L respectively. The adsorption capacities were both 66%. The adsorbents treated with H₂SO₄ were increased simultaneously with the increasing acid concentration to a maximum which was at 1.5M and dropped afterwards [16]. The reason could be that high concentration such as 2.0M and 2.5M may have the destructive effects on the modification of adsorbents which make it unable to absorb microalgae biomass. The said concentration may be too strong for the modification of sugarcane bagasse adsorbents. Hence, the optimum concentration that is suitable for the sugarcane bagasse adsorbents was 1.5M acid modified sugarcane bagasse-derived adsorbents.
C. Point of Zero Charge Determination

Based on Fig. 3 below, the pH_{pzc} for each acid concentration for adsorbent modification; 0.1M, 0.5M, 1.0M, 1.5M, 2.0M and 2.5M were 5.5, 5.1, 4.8, 4.5, 4.6 and 4.2 respectively. Acid-activated sugarcane bagasse-based adsorbent with concentration of 1.5 gave the highest adsorption capacity of 108 mg/g.
Fig. 3. Determination of pH_{pzc} for (A) 0.1M adsorbents, (B) 0.5M adsorbents, (C) 1.0M adsorbents, (D) 1.5M adsorbents, (E) 2.0M adsorbents, and (F) 2.5M adsorbents.

D. Characterization of Adsorbents

Scanning Electron Microscope (SEM) analysis: The adsorbents samples were analyzed under SEM to study the surface morphology. Fig. 4 below shows the surface morphology of the modified adsorbents after ran for batch experiments.

Fig. 4 showed the surface morphology of the modified adsorbents after run for batch experiment. There were microalgae attached on the surface of adsorbents. Previously, Fig. 2 showed adsorbents modified with 1.0M and 1.5M concentration absorb the most. It can be seen on the Fig. 4 below that there were many microalgae attached on that concentration.

Fig. 4. (A) Surface morphology of adsorbents modified with 0.1M, (B) Surface morphology of adsorbents modified with 0.5M, (C) Surface morphology of adsorbents modified with 1.0M, (D) Surface morphology of adsorbents modified with 1.5M, (E) Surface morphology of adsorbents modified with 2.0M, (F) Surface morphology of adsorbents modified with 2.5M; all with magnification of x2500, after run batch experiments.
E. Different Sizes Determination

Fig. 5 below showed the microalgae concentration was decreased after putting the adsorbents inside. The initial microalgae concentration on each flask was 3.5 mg/L. The reduction of microalgae concentration was not obvious at the early hours. Based on the above figure, 4mm size of adsorbents gave the best adsorption results with 39.5% of adsorption capacity with 1.4 mg/L reduced from the initial concentration. The 710µm adsorbents absorbed microalgae the least with 7.5% of adsorption capacity and 0.3 mg/L reduction. It shows the bigger the sizes, the capability of adsorption is increasing. This could be 4mm has more porous available on the adsorbents compared to adsorbents with 710µm size. Besides, 4mm sized-adsorbents did not require any special attention and labour during experiment compared to the smaller sizes [17].

![Fig. 5. Determination of sizes of the adsorbents](image)

4. Conclusions

The chemical modification on sugarcane bagasse-derived adsorbents has shown positive effects on the adsorption of microalgae biomass. Since the surface charge of microalgae is negative, chemical modification with acid seems relevant. Next, the most suitable acid concentrations for the modification was 1.5M with adsorption capacity of 66% and explained using pH_{PZC} experiments. Higher concentration may have destructive effect on the modification of adsorbents. Meanwhile the surface morphology of the adsorbents after adsorption occurred can be viewed under SEM. The adsorbents with bigger sizes showed high adsorption capacity compared to the smaller size.

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