

A Sugarcane-Bagasse-Based Adsorbent Employed for Mitigating Eutrophication Threats and Producing Biodiesel Simultaneously

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Keywords: reusability, harvest, biodiesel, Adsorption, sugarcane bagasse, eutrophication

Abstract:

Eutrophication is an inevitable phenomenon, and it has recently become an unabated threat. As a positive, the thriving microalgal biomass in eutrophic water is conventionally perceived to be loaded with myriad valuable biochemical compounds. Therefore, a sugarcane-bagasse-based adsorbent was proposed in this study to harvest the microalgal biomass for producing biodiesel. By activating the sugarcane-bagasse-based adsorbent with 1.5 M of H₂SO₄, a highest adsorption capacity of 108.9 ± 0.3 mg/g was attained. This was fundamentally due to the surface potential of the 1.5 M H₂SO₄ acid-modified sugarcane-bagasse-based adsorbent possessing the lowest surface positivity value as calculated from its point of zero charge. The adsorption capacity was then improved to 192.9 ± 0.1 mg/g by stepwise optimizing the adsorbent size to 6.7–8.0 mm, adsorption medium pH to 2–4, and adsorbent dosage to 0.4 g per 100 mL of adsorption medium. This resulted in 91.5% microalgae removal efficiency. Excellent-quality biodiesel was also obtained as reflected by the fatty acid methyl ester (FAME) profile, showing the dominant species of C₁₆–C₁₈ encompassing 71% of the overall FAMEs. The sustainability of harvesting microalgal biomass via an adsorption-enhanced flocculation processes was also evidenced by the potentiality to reuse the spent acid-modified adsorbent.

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Article

A Sugarcane-Bagasse-Based Adsorbent Employed for Mitigating Eutrophication Threats and Producing Biodiesel Simultaneously

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Abstract: Eutrophication is an inevitable phenomenon, and it has recently become an unabated threat. As a positive, the thriving microalgal biomass in eutrophic water is conventionally perceived to be loaded with myriad valuable biochemical compounds. Therefore, a sugarcane-bagasse-based adsorbent was proposed in this study to harvest the microalgal biomass for producing biodiesel. By activating the sugarcane-bagasse-based adsorbent with 1.5 M of H₂SO₄, a highest adsorption capacity of 108.9 ± 0.3 mg/g was attained. This was fundamentally due to the surface potential of the 1.5 M H₂SO₄ acid-modified sugarcane-bagasse-based adsorbent possessing the lowest surface positivity value as calculated from its point of zero charge. The adsorption capacity was then improved to 192.9 ± 0.1 mg/g by stepwise optimizing the adsorbent size to 6.7–8.0 mm, adsorption medium pH to 2–4, and adsorbent dosage to 0.4 g per 100 mL of adsorption medium. This resulted in 91.5% microalgae removal efficiency. Excellent-quality biodiesel was also obtained as reflected by the fatty acid methyl ester (FAME) profile, showing the dominant species of C16–C18 encompassing 71% of the overall FAMEs. The sustainability of harvesting microalgal biomass via an adsorption-enhanced flocculation processes was also evidenced by the potentiality to reuse the spent acid-modified adsorbent.

Keywords: eutrophication; sugarcane bagasse; adsorption; harvest; biodiesel; reusability

1. Introduction

“Eutrophication is the enrichment of water with nutrient salts that causes structural changes to the ecosystem, namely, the increase in production of microalgae and aquatic plants, depletion of fish species, general deterioration of water quality and other effects that reduce and preclude use”. This is one of the definitions given to the eutrophic process by the Organization for Economic Cooperation and Development [1,2]. Eutrophication is a serious environmental threat since it gives rise to deterioration of water quality, and it is also one of the major impediments in achieving the quality objectives established by the Water Framework Directive in the EU as well as those in other countries [3]. Intrinsically, all water resources are subjected to a natural and slow eutrophication process. However, in recent years, the eutrophication threat has undergone very rapid progression due to the presence of various human activities, particularly the farming of cash crops in agriculture. When the eutrophication threat becomes intense, undesirable effects and environmental imbalances arise. The two most acute phenomena to stem from eutrophication are hypoxia in the deep parts of lakes (or lack of oxygen) and microalgal blooms that may produce harmful toxins. Both occurrences can plausibly bring severe devastation to the aquatic life living in the afflicted water bodies [4–8].

Malaysia and Indonesia are growing countries with steadily improving economies due to huge contributions from many agricultural sectors such as palm oil, rice and paddies, sugarcane, and other planted cash crops. Although oil palm is a major cash crop that can promote the gross domestic product (GDP), another rising cash crop in Malaysia and Indonesia is sugarcane, with total productions of 28.1 and 28.0 million metric tons, respectively, in years 2016/17 [9–12]. This gives rise to gigantic levels of agricultural waste from the juice crushing process, i.e., sugarcane bagasse which is usually left to decay on the fields. The accumulated sugarcane bagasse waste without proper management will potentially lead to the spreading of diseases that adversely affect humans, animals, and the environment. Of late, a fraction of this bagasse has been used as fuels in sugar factories, and some raw materials have been exploited in pulp and paper making. Sugarcane bagasse is a type of lignocellulosic biomass that generally consists of cellulose (50%), hemicellulose (25%), and lignin (25%) [13]. The hemicelluloses are made up of C5 and C6 sugar, while lignin comprises about one-fourth of the lignocellulose biomass. These biological polymers have hydroxyl and/or phenolic functional groups that can be chemically activated to produce materials with new properties. Accordingly, the carboxylic and hydroxyl groups can improve the capacity of adsorption via ion exchange and complexation processes. Owing to its low ash content (approximately 2.4%), sugarcane bagasse can offer many advantages when compared with other crop residues such as rice straw and wheat straw, which have about 17.5% and 11.0% ash contents, respectively [14]. In addition, sugarcane bagasse is a porous material with a relatively high fixed carbon content. Considering these advantages, sugarcane bagasse has been among the preferred waste materials chosen to be used as an adsorbent by many researchers previously to resolve issues associated with water pollution via adsorption processes [5,8,9,15,16].

Nevertheless, the application of adsorption processes to concentrate planktonic microalgal cells and subsequently flocculate and separate them from a liquid medium has been documented little of late. Accordingly, the potential use of a fabricated sugarcane-bagasse-based adsorbent to mitigate the eutrophication phenomenon served as the prime objective of this comprehensive study. The adsorptive operating conditions were initially optimized to spur the removal of microalgal biomass via adsorption-enhanced flocculation processes from the eutrophic water. In tandem with this study, the fundamental rationale describing the attachment of microalgal cells onto the surface of the fabricated sugarcane-bagasse-based adsorbent was also unveiled. Since microalgal biomass is conventionally lauded for containing myriad valuable biochemical compounds, the harvested sugarcane-bagasse-based adsorbent loaded with microalgal biomass was subsequently exploited for biodiesel production. The plausible reusability of the spent sugarcane-bagasse-based adsorbent was lastly assessed to confirm the sustainability of the fabricated sugarcane-bagasse-based adsorbent in mitigating the eutrophication threat.

2. Materials and Methods

2.1. Fabrication of Acid-Modified Sugarcane-Bagasse-Based Adsorbents

The residual sugarcane bagasse generated after juice crushing was used as a precursor in fabricating various acid-modified sugarcane-bagasse-based adsorbents. Residual sugarcane bagasse was initially amassed from the local market and cut into pieces of about 3–4 cm each. The pieces of bagasse were then boiled and washed thoroughly to remove the entrapped sugar. The wet sugar-free bagasse was later air-dried to partially remove the water content before drying to constant weight at 102–105 °C in an oven. The dried sugarcane bagasse was pulverized using a 0.5 mm blade grinder and subsequently activated using various H₂SO₄ acid concentrations: 0.1, 0.5, 1.0, 1.5, 2.0, and 2.5 M. This was achieved by individually introducing 15 g of pulverized sugarcane bagasse into 1 L of each of the H₂SO₄ acid concentrations. Each mixture was finally stirred for 24 h and washed with distilled water until a neutral pH was attained in discarded washing water prior to once again drying to constant weight at 102–105 °C in an oven. All the fabricated acid-modified sugarcane-bagasse-based adsorbents were separately kept in a desiccator ready for use.

2.2. Determination of Adsorbent Point of Zero Charge

Points of zero charge (pH_{PZC}) were initially measured from each of the fabricated acid-modified sugarcane-bagasse-based adsorbents. The pH_{PZC} is determined as the adsorption medium pH that causes the surface charge density of the adsorbent to become zero. The pH_{PZC} values of all the acid-modified sugarcane-bagasse-based adsorbents were measured following the solid addition method as described by Ofomaja and Naidoo [17] with modifications. Briefly, to a series of 100 mL Erlenmeyer flasks, 45 mL of KNO₃ solution with a concentration of 0.01 M was added to every flask. The pH in each flask was then individually adjusted from pH 2 to 9 and filled up to 50 mL using a similar KNO₃ solution. The initial pH values of all flasks were accurately recorded, and 0.1 g of specific acid-modified sugarcane-bagasse-based adsorbent was administered into each flask. All flasks were securely capped and agitated manually and sporadically for the next 2 days, allowing the charges to equilibrate before recording the final pH values from each flask. Subsequently, the differences between the initial and final pH values (Δ pH) of each flask were plotted against the respective initial pH values. The pH_{PZC} of the adsorbent was finally determined from the point of intersection of the resulting curve at Δ pH = 0. Later, these procedures were repeated using other acid-modified sugarcane-bagasse-based adsorbents to determine their respective pH_{PZC} values.

2.3. Characteristics of Eutrophic Water

A water sample was collected from a eutrophic body at a site which receives discharged streams from the aquacultural activities in the vicinity (Figure 1). The in situ measurements indicated a pH of 3.8 ± 0.3 , temperature of 31.6 ± 1.7 °C, and dissolved oxygen concentration of 0.1 ± 0.1 mg/L. The sample was instantly transported to the laboratory, and ex situ determination of the microalgal biomass concentration was immediately executed via gravimetric analysis. The eutrophic water was found to be loaded with 0.86 ± 0.2 g/L of microalgal biomass. The remaining sample was stored in the cold room upon reaching the laboratory at 2.0 ± 1.5 °C to minimize biological and chemical changes after isolating the sample from the eutrophic body. A predetermined volume of eutrophic water was later siphoned from the homogenized stock sample in the cold room and allowed to reach ambient temperature prior to use in the experiments outlined hereafter.



Figure 1. Eutrophic body which currently receives discharged streams from the aquacultural activities in the vicinity.

2.4. Setups for Eutrophic Water Treatment

Six 150 mL Erlenmeyer flasks were each initially filled with 100 mL of the eutrophic water sample. The sample was homogenized via vigorous shaking before the predetermined volume was transferred into each Erlenmeyer flask. A quantity of 0.5 g of acid-modified sugarcane-bagasse-based adsorbent with respective H_2SO_4 concentrations of 0.1, 0.5, 1.0, 1.5, 2.0, and 2.5 M was individually administered into each of the Erlenmeyer flasks containing a eutrophic water sample. All the mixtures were immediately adjusted to pH 3, and sufficient agitation was provided for each flask to prevent the settlement of adsorbents to the bases of all flasks. Sampling of microalgal biomasses present in the eutrophic water over time from each flask was executed to determine the residual microalgal biomass concentrations as well as for the time course studies. Samplings were also performed to determine the adsorption efficiencies (Equation (1)) and capacities (Equation (2)) of each acid-modified sugarcane-bagasse-based adsorbent loaded into each flask at equilibria as confirmed from the time course studies.

$$\text{Adsorption efficiency} = \frac{[\text{Initial microalgal biomass}] - [\text{Microalgal biomass at any time}]}{[\text{Initial microalgal biomass}]} \times 100\% \quad (1)$$

$$\text{Adsorption capacity} = \frac{\text{Weight of adsorbed microalgal biomass}}{\text{Weight of adsorbent}} \quad (2)$$

The best acid-modified sugarcane-bagasse-based adsorbent was then selected and sieved into four different sizes, namely, <4.0 mm, 5.6–6.7 mm, 6.7–8.0 mm, and >8.0 mm. A quantity of 0.5 g of each size of adsorbent was individually administered into the Erlenmeyer flasks containing the eutrophic water sample. Similar procedures to those described above were later executed in selecting the best size of acid-modified sugarcane-bagasse-based adsorbent. Afterward, stepwise optimization of the pH of the adsorption media and the adsorbent dosage were also performed to enhance the adsorptive removal of microalgal biomass from the eutrophic water. The studied ranges of the pH of adsorption media and adsorbent dosage were from pH 2 to 10 and 0.1 to 0.7 g in 100 mL of adsorption medium, respectively.

2.5. Microalgal Lipid Extraction and Transesterification into Fatty Acid Methyl Esters (FAMES) of Biodiesel

Lipid extraction from the adsorbed microalgal biomass was accomplished following the procedures described by Bligh and Dyer [18] with modifications. Initially, the microalgal biomass adsorbed onto

acid-modified sugarcane-bagasse-based adsorbent was harvested from the adsorption medium using a sieving net and dried to constant weight at 102–105 °C in an oven. The dried microalgal biomass, together with the adsorbent, was doused with water mixed with chloroform: methanol (1:2 *v/v*) at a ratio of 1.6:6.0 *v/v*. The mixture was immediately sonicated for 30 min at 40 kHz and 40 °C. For further separating the free lipids into the chloroform layer after sonication, an approximately 20% chloroform: water (1:1 *v/v*) solution by volume with respect to the total volume of the sonicated sample was added and mixed well manually. Centrifugation for 20 min at 5600 rpm was then employed to separate the sample solution into three layers, namely, a lipid and chloroform mixture (bottom layer), residual microalgal biomass adsorbed onto the spent sugarcane-bagasse-based adsorbent (middle layer), and a methanol and water mixture (top layer). The bottom layer was then collected by suction, and 8% chloroform by volume with respect to the total volume of the sample was added to the remaining mixture, mixed well manually, and centrifuged again to recover the residual lipids. The amassed volume of the lipid and chloroform mixture from both consecutive separation processes was lastly dried under compressed air blow to constant weight prior to the lipid yield determination (Equation (3)).

$$\text{Lipid yield} = \frac{\text{Weight of extracted lipid from adsorbed microalgal biomass}}{\text{Weight of adsorbed microalgal biomass onto adsorbent} - \text{Weight of initial adsorbent}} \times 100\% \quad (3)$$

The extracted lipids from the adsorbed microalgal biomass were subsequently transesterified into FAMES of biodiesel following the procedures as described by Mohd-Sahib and Lim [19]. Briefly, a vortex mixer at 2000 rpm was initially employed to homogenize about 10–15 mg of extracted lipid, 1 mL of chloroform, and 2 mL of KOH in methanol (1.5 mg/mL). The sample was then capped well and transesterified for 3 h at a temperature of 60 °C. The temperature was maintained by placing the sample in a water bath until the transesterification process was completed. The FAMES mixture of the biodiesel produced was later purified by repeatedly washing with 5 mL of distilled water followed by separation using a separating funnel until a neutral pH was measured from the aqueous phase. Next, the chloroform layer loaded with FAMES was dried under compressed air blow to constant weight. The FAMES mixture was finally injected into a gas chromatograph to analyze the individual FAME composition forming the biodiesel. The FAME profile obtained determines the quality of the biodiesel derived from the harvested microalgal biomass from eutrophic water. The details of the operating conditions of the employed Shimadzu brand gas chromatograph (Model GC-2010 plus) equipped with a flame ionization detector (GC-FID) can be acquired from Mohd-Sahib and Lim [19]. Ultimately, the individual FAME composition was calculated as follows:

$$\text{Composition of specific FAME species} = \frac{A_S}{A_{ISTD}} \times \frac{C_{ISTD} \times V_{ISTD}}{m} \times 100\% \quad (4)$$

where A_S = Peak area of specific FAME species;

A_{ISTD} = Peak area of internal standard;

C_{ISTD} = Concentration of internal standard;

V_{ISTD} = Volume of internal standard;

m = Mass of sample.

2.6. Assessment of the Reusability of Spent Sugarcane-Bagasse-Based Adsorbent

Upon lipid extraction, the spent sugarcane-bagasse-based adsorbent or lipid-exhausted sugarcane-bagasse-based adsorbent was dried to constant weight at 102–105 °C in an oven. The dry adsorbent was then administered into 100 mL of fresh eutrophic water sample, and the optimum operational conditions to remove microalgal biomass from the adsorption medium were employed according to the first cycle, termed Cycle-1. Cycle-2 was allowed to continue until the equilibrium was attained as confirmed from the time course measurement of the residual microalgal biomass concentration. To that end, the adsorption efficiency and capacity were recorded following Equations (1) and (2), respectively. The harvested microalgal biomass adsorbed onto spent

sugarcane-bagasse-based adsorbent was subsequently subjected to lipid extraction again, followed by drying of the lipid-exhausted sugarcane-bagasse-based adsorbent to constant weight at 102–105 °C. The dry adsorbent was later reused to remove microalgal biomass from fresh eutrophic water samples in Cycle-3 to Cycle-5.

3. Results and Discussion

3.1. Enhancement of Microalgal Biomass Adsorption from Eutrophic Water

The potential of various acid-modified sugarcane-bagasse-based adsorbents for removing microalgal biomass via adsorption-enhanced flocculation is presented in Table 1. In essence, the fresh negatively charged microalgal cells are hypothesized to be electrostatically attracted to the positively charged supporting materials. The acid-modified treatment mode was employed in this study in order to economically intensify the positive surface potential of the sugarcane-bagasse-based adsorbents. Increasing the H₂SO₄ acid concentration during the treatment of sugarcane-bagasse-based adsorbents progressively increased the separation of the microalgal biomass from the liquid medium, reaching the highest adsorption efficiency of 89.6% while using 1.5 M of H₂SO₄ to acid-modify the sugarcane-bagasse-based adsorbent. The adsorption efficiency and capacity were observed to gradually decrease thereafter when concentrations of H₂SO₄ higher than 1.5 M were employed to treat the sugarcane-bagasse-based adsorbents. Many studies have associated the reduction of adsorption with increasing acid concentration employed for treating adsorbents to the destruction of adsorbent structures [20,21]. Instead of agreeing with this typical rationale, the surface potentials of all fabricated acid-modified sugarcane-bagasse-based adsorbents were measured and exploited to elucidate the adsorption phenomena observed in this study. The positivity value of each adsorbent calculated by subtracting the pH of the adsorption medium from their pHPZC is demonstrated in Figure 2. A mirror image trend against either the adsorption efficiency or capacity (Table 1) was obtained for the positivity values of increasingly H₂SO₄ acid-modified sugarcane-bagasse-based adsorbents. In this regard, the 1.5 M H₂SO₄ acid-modified sugarcane-bagasse-based adsorbent presented the lowest positivity value, attracting more negatively charged microalgal cells to adsorb onto the adsorbent surfaces. On the flipside, the higher positivity values of the surface potentials of other acid-modified sugarcane-bagasse-based adsorbents would attract more counter ions from the adsorption medium, forming a layer of negatively charged counter ions. This layer would shield the microalgal cells from interacting with the acid-modified sugarcane-bagasse-based adsorbents, indirectly preventing the adsorption-enhanced flocculation processes. In the case of putting the 1.5 M H₂SO₄ acid-modified sugarcane-bagasse-based adsorbent to use, the formation of this counter ions layer was inconspicuous, thereby permitting the adsorption of greater microalgal biomass than the other fabricated adsorbents.

Table 1. The performance of various acid-modified sugarcane-bagasse-based adsorbents in removing microalgal biomass from eutrophic water.

Concentration of H ₂ SO ₄ Used for Adsorbent Modification (M)	0.1	0.5	1.0	1.5	2.0	2.5
Adsorption efficiency (%)	88.0 ± 0.5	88.6 ± 0.3	89.4 ± 0.8	89.6 ± 0.9	86.6 ± 0.1	85.9 ± 0.1
Adsorption capacity (mg/g)	106.9 ± 0.4	107.6 ± 0.3	108.5 ± 0.3	108.9 ± 0.3	105.0 ± 0.3	104.3 ± 0.4

To examine adsorbent sizes, the 1.5 M H₂SO₄ acid-modified sugarcane-bagasse-based adsorbent was sieved into four different sizes, namely, <4.0 mm, 5.6–6.7 mm, 6.7–8.0 mm, and >8.0 mm. The residual biomass concentrations of microalgae along with the adsorption time and the consequential adsorption capacities from the use of each adsorbent size are shown in Figure 3. Although the adsorption capacities attained by the adsorbent sizes of 6.7–8.0 and >8.0 mm were comparable, the use of 6.7–8.0 mm sized adsorbent could achieve a faster adsorption-enhanced flocculation equilibrium than the >8.0 mm sized adsorbent—specifically, 0.0576 and 0.0522 g/L h, respectively. As the targeted adsorbate in

this study was a suspended microalgal biomass having a size range of 20–50 μm rather than the dissolved adsorbate, a large adsorbent size offered more macropores for accommodating microalgal cells. For comparison with dissolved adsorbate, the powdered form of adsorbents is generally preferred due to the presence of more micropores and mesopores capable of capturing the targeted dissolved adsorbate [22,23]. However, continuous increase of adsorbent size, especially beyond 8.0 mm, would culminate in the reduction of external surface area, impoverishing the frequency of contact between the adsorbent and microalgal cells. Therefore, acid-modified sugarcane-bagasse-based adsorbent with a size range of 6.7–8.0 mm was regarded as the best size for adsorption-enhanced flocculation of microalgal biomass; its adsorption capacity increased to 143.6 ± 1.7 mg/g, as compared with only 108.9 ± 0.3 mg/g using the unsieved adsorbent (Table 1). Besides this, the flocculated microalgal biomass adsorbed onto this size range of adsorbent could also be easily harvested from the liquid medium via a simple sieving net.

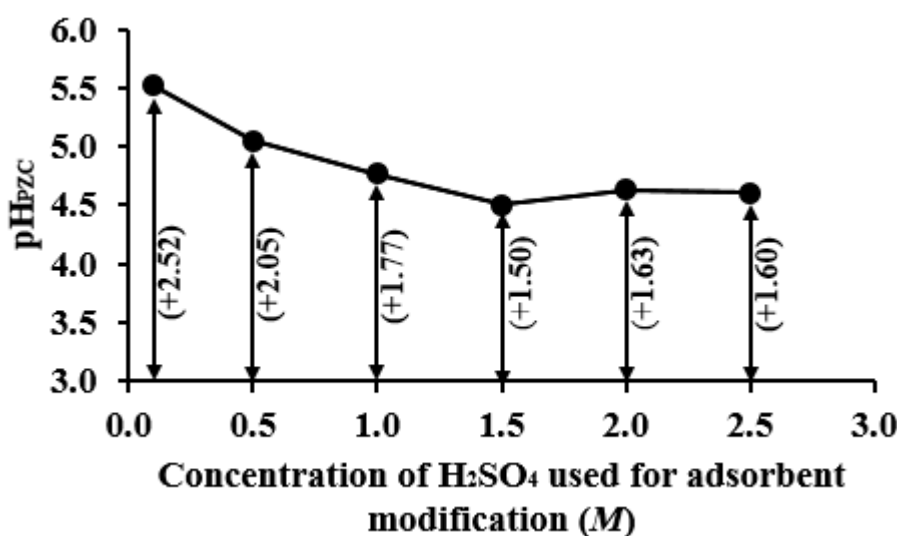


Figure 2. The point of zero charge (pH_{PZC}) values of various acid-modified sugarcane-bagasse-based adsorbents. The values in parentheses indicate the positivity of pH_{PZC} subtracted by pH 3, i.e., the pH of the adsorption medium.

The adsorption capacities were maintained in a range of 143.0–148.0 mg/g when the adsorption-enhanced flocculation processes were performed in adsorption media with pH values between 2 and 4. Increasing the pH of the adsorption medium to 6 caused a decrease in the adsorption capacity to 127 ± 4.3 mg/g. The adsorption capacities were noticed to plummet to merely 119.9 ± 0.5 and 104.3 ± 3.3 mg/g when the pH was shifted to basic in the adsorption media, namely, at pH values of 8 and 10, respectively. As the 1.5 M H_2SO_4 acid-modified sugarcane-bagasse-based adsorbent possessed a pH_{PZC} value of 4.50 (Figure 2), increasing pH value of the adsorption medium above 4.50 would gradually increase the adsorbent surface potential negativity. Since microalgal cells are negatively charged, repulsion between the adsorbent and adsorbate arising from charge similarity would debilitate the adsorption-enhanced flocculation processes of the microalgal biomass. In acidic adsorption media, adsorption efficiencies of more than 80% could be easily attained at pH values between 2 and 4. Indeed, the pH value of the eutrophic water of 3.8 ± 0.3 also fell within this pH range, therefore safely circumventing the necessity to pretreat the eutrophic water through pH adjustment prior to adsorption-enhanced flocculation processes.

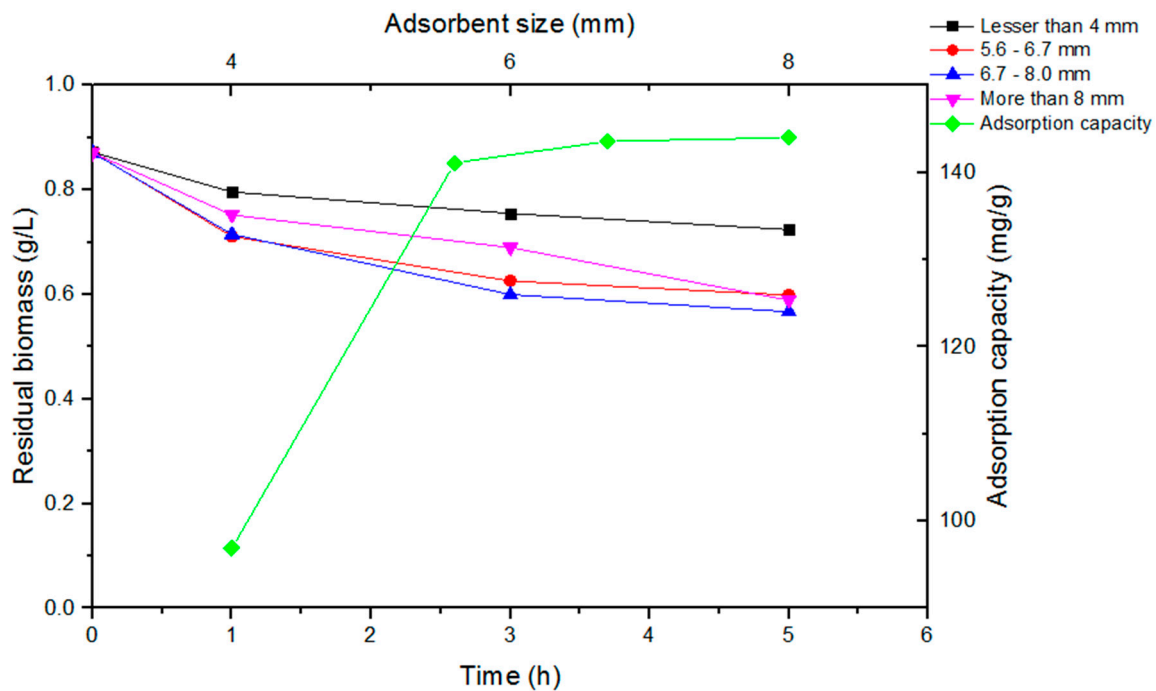


Figure 3. The time courses of residual biomass concentrations of microalgae adsorbed onto various sizes of acid-modified sugarcane-bagasse-based adsorbent and the consequent adsorption capacities from the use of each adsorbent size.

Increased amounts of adsorbent in terms of grams per 100 mL of adsorption medium increased the adsorption capacity, as revealed in Figure 4. At an adsorbent dosage of 0.1 g/100 mL, all the macropore active sites were swiftly occupied by microalgal cells, as demonstrated by the rapid attainment of adsorption-enhanced flocculation equilibrium during the early time course study. The insufficient active sites were later offset by the increasing adsorbent dosage, reaching a maximum adsorption capacity of 192.9 ± 0.1 mg/g when 0.4 g of adsorbent was introduced into 100 mL of adsorption medium, equivalent to an adsorption efficiency of 91.5%. Further increment of adsorbent dosages beyond 0.4 g/100 mL gave rise to the presence of increasing numbers of free active sites, thereby reducing the adsorption capacities. Increasing the adsorbent dosage from 0.4 to 0.7 g/100 mL slightly prompted more microalgal biomass to adsorb onto the adsorbent, steadily increasing the adsorption efficiency from 91.5% to 94.9%, respectively. This negligible rise in adsorption efficiency was due to the presence of excessive free active sites available to capture more microalgal cells from the diluted adsorption medium. As the percentage point increase was only about 3% (from 91.5% to 94.9%) but required a 75% increase in adsorbent dosage (from 0.4 to 0.7 g/100 mL), the 0.4 g/100 mL adsorbent dosage was considered ideal for executing adsorption-enhanced flocculation processes for the remediation of eutrophic water.

In summary, 1.5 M H_2SO_4 acid-modified sugarcane-bagasse-based adsorbent with a size range of 6.7–8.0 mm was employed to spur the separation of microalgal biomass from eutrophic water via adsorption-enhanced flocculation processes. The adsorption capacities achieved from sequential studies were 108.9 ± 0.3 and 143.6 ± 1.7 mg/g, respectively. Subsequently, the adsorption capacity was maintained in the range of 143.0–148.0 mg/g when adsorption-enhanced flocculation processes were carried out in adsorption media with pH values between 2 and 4. Finally, the adsorption capacity was further improved to 192.9 ± 0.1 mg/g when an adsorbent dosage of 0.4 g was introduced into 100 mL of adsorption medium. A high adsorption efficiency of microalgae of 91.5% and low residual biomass concentration of microalgae of 0.064 g/L in the adsorption medium were attained.

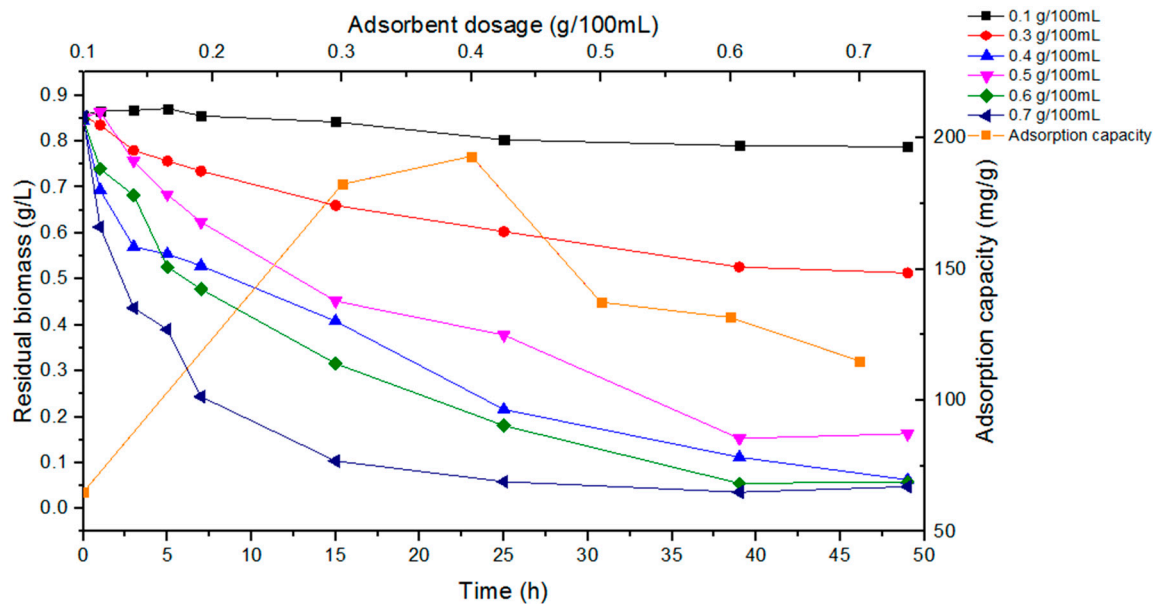


Figure 4. The time courses of residual biomass concentrations of microalgae adsorbed onto various dosages of acid-modified sugarcane-bagasse-based adsorbent and the consequent adsorption capacities from the use of each adsorbent dosage.

3.2. Biodiesel Derived from Harvested Microalgal Biomass

The microalgal biomass harvested from the eutrophic water was then sequentially subjected to extraction to obtain the lipid biocompounds and perform transesterification into a FAMES mixture of biodiesel. The lipid yield acquired from the extraction was 30.3 ± 0.0 wt %, which was very close to the lipid yield of the control microalgal biomass of 31.0 ± 0.2 wt %. The control microalgal biomass was harvested via the centrifugation of fresh eutrophic water. With a standard deviation value of merely 0.5%, the insignificant difference between the two lipid yields showed that the adsorption-enhanced flocculation processes employed to remove the microalgal biomass from the liquid medium did not have an obvious deleterious impact on the microalgal lipid content. Finally, the FAME profile obtained from the transesterification of extracted lipids is presented in Table 2. The FAMES are important components of biodiesel; thus, the quality of biodiesel can be concluded from the FAME profile study. There were 21 species of FAMES identified in the biodiesel derived from microalgal biomass adsorbed onto the sugarcane-bagasse-based adsorbent. Among the FAMES, C16 to C18 were the dominant species, making up approximately 71% of the overall FAMES mixture. These species are also naturally found in many oil-bearing crops, e.g., soybean, sunflower seed, cottonseed, and palm oil, which are suitable for use as biodiesel [24]. According to Song and Pei [25], feedstock suited for the production of biodiesel must contain palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3) acids, which were all found in the FAME profile of the microalgal biomass adsorbed onto the sugarcane-bagasse-based adsorbent. The saturation degrees of the FAMES mixture were calculated afterward and showed the mixture to contain 44.87% of saturated fatty acid (SFA), 32.55% of monounsaturated fatty acid (MUFA), and 22.58% of polyunsaturated fatty acid (PUFA). Biodiesel with higher levels of SFA will generally have a high cetane number and oxidative stability but poor low-temperature properties. The presence of MUFA species of palmitoleic (C16:1), oleic (C18:1), eicosenoate (C20:1), and erucate (C22:1) acids also essentially give rise to biodiesel with suitable oxidative stability, besides ameliorating cold flow [26]. The presence of high levels of PUFA, on the other hand, will offer excellent cold flow. However, this biodiesel type is easily oxidized [27]. The low degree of PUFA (<30%) and high degree of MUFA and SFA (>65%) as reported by Mohd-Sahib and Lim [19] were also attained in biodiesel derived from microalgal biomass adsorbed onto the sugarcane-bagasse-based adsorbent. According to Mohd-Sahib and Lim [19], this type of FAMES

mixture has great potential for the production of high-quality biodiesel with acceptable oxidative stability and cold flow properties.

Table 2. The fatty acid methyl ester (FAME) profile of biodiesel from microalgal biomass harvested via adsorption-enhanced flocculation processes.

Carbon Number — FAME Species	Composition in Biodiesel (%)
C14:1 — M. myristoleate	0.78
C15:0 — M. pentadecenoate	0.97
C15:1 — M. cis—10—pentadecenoate	1.25
C16:0 — M. palmitate	13.76
C16:1 — M. palmitoleate	1.49
C17:1 — M. cis—10—heptadecanoate	2.88
C18:0 — M. stearate	22.08
C18:1 — cis M. oleate	7.14
C 18:1 — (E) — M. 9—octadecanoate	7.74
C18:2 — M. linoleate	8.39
C18:2 — M. linoleaidate	6.60
C18:3 — M. γ —linolenate	0.74
C20:1 — M. eicosenoate	7.04
C20:2 — M. cis—11,14—eicosadienoate	3.95
C20:3 — M. cis—11,14,17—eicosatrienoate	2.10
C21:0 — M. heneicosanoate	1.44
C22:0 — M. arachidate	0.35
C22:1 — M. erucate	4.23
C22:6 — M. cis—4,7,10,13,16,19—docosahexaer	0.80
C23:0 — M. tricosanoate	5.30
C24:0 — M. lignocerate	0.97

3.3. Potential Reusability of Spent Sugarcane-Bagasse-Based Adsorbent

From the point of view of sustainability, the potential to reuse spent sugarcane-bagasse-based adsorbent after the first cycle of removing microalgal biomass via adsorption-enhanced flocculation processes was evaluated. The performance results of spent sugarcane-bagasse-based adsorbent for five consecutive cycles of reuse are presented in Table 3. Cycle-1 represents the first use of virgin sugarcane-bagasse-based adsorbent upon fabrication to carry out adsorption-enhanced flocculation processes. After extracting the lipids from the microalgal biomass adsorbed onto sugarcane-bagasse-based adsorbent, the lipid-exhausted sugarcane-bagasse-based adsorbent was then used to carry out adsorption-enhanced flocculation processes again in Cycle-2, and these procedures were reiteratively repeated until Cycle-5. The adsorption efficiency diminished about 10% in Cycle-2 when compared to Cycle-1, though the adsorption capacity was still maintained above 100 mg/g. This could be undoubtedly rationalized by the presence of vacant and unexploited active sites left unoccupied after Cycle-1. When the same adsorbent was employed for the third time, parts of the loose cellulosic materials were noticed to inevitably detach from the sugarcane-bagasse-based adsorbent. Accordingly, the total weight of the lipid-exhausted sugarcane-bagasse-based adsorbent plunged about 20% to merely 0.33 g in Cycle-3. This could be due to continuous mechanical abrasion among the adsorbent solids, stemming from the agitation provided during the adsorption-enhanced flocculation and lipid extraction processes. As a result, the adsorption efficiency and capacity also dropped to lowest values of 38.2% and 59.8 mg/g, respectively, in this cycle. As the material structure of the remaining lipid-exhausted sugarcane-bagasse-based adsorbent was more firm and stable after Cycle-3, the adsorption efficiency was observed to improve to about 48% in Cycle-4, later plateauing in Cycle-5. As the total weight of the lipid-exhausted sugarcane-bagasse-based adsorbent did not differ much in Cycle-4 and Cycle-5, the adsorption capacities were measured in the range of approximately 70–80 mg/g in these two cycles.

Table 3. Performance of spent sugarcane-bagasse-based adsorbent for reiterative removal of microalgal biomass via adsorption-enhanced flocculation processes.

Reusability (Cycle)	Cycle-1	Cycle-2	Cycle-3	Cycle-4	Cycle-5
Adsorption efficiency (%)	91.5 ± 1.1	77.5 ± 1.3	38.2 ± 1.5	48.8 ± 8.3	44.7 ± 3.0
Adsorption capacity (mg/g)	192.9 ± 0.1	129.0 ± 4.0	59.8 ± 2.2	82.5 ± 0.1	70.3 ± 1.0
Lipid-exhausted adsorbent (g)	0.42 ± 0.00	0.4 ± 0.03	0.33 ± 0.03	0.32 ± 0.01	0.29 ± 0.01

4. Conclusions

Acid-modified sugarcane-bagasse-based adsorbent was successfully employed to remove microalgal biomass from eutrophic water via adsorption-enhanced flocculation processes. By activating the adsorbent with only 1.5 M of H₂SO₄, a microalgal biomass adsorption capacity of 108.9 ± 0.3 mg/g was achieved at equilibrium. This is due to 1.5 M H₂SO₄ acid-modified sugarcane-bagasse-based adsorbent having the lowest surface positivity value among the adsorbents tested, minimizing negative counter ion formation whilst maximizing the negatively charged microalgal cell interaction. In enhancing microalgal biomass separation from eutrophic water, the employment of a 6.7–8.0 mm adsorbent size resulted in an increase of the adsorption capacity to 143.6 ± 1.7 mg/g. Further optimizing the adsorbent dosage permitted the adsorption capacity to reach 192.9 ± 0.1 mg/g with a dosage of 0.4 g of acid-modified adsorbent in 100 mL of adsorption medium. This was equivalent to a 91.5% microalgae removal efficiency from eutrophic water. The harvested microalgal biomass also produced excellent-quality biodiesel, as manifested by the high levels of C16–C18 components (71%) in the FAME profile. The biodiesel quality was also proven by the low degree of PUFA (22.58%) and high degree of MUFA (32.55%) and SFA (44.87%). From the sustainability viewpoint, the spent acid-modified adsorbent also could be reused immediately after lipid extraction from the adsorbed microalgal biomass without the necessity to regenerate.

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