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Sargassum wightii, a marine alga is the source for the production of algal oil, bio-oil, and application in the dye wastewater treatment

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ABSTRACT

The utilization of algal biomass is a field that is fast reaching the lime light as their overflowing potentials are just being realized. The marine macroalga, *Sargassum wightii*, known for its photosynthetically efficient nature, has been considered as the main source of biomass. In this research, the algal biomass has been utilized for three different purposes (i) production of algal oil, (ii) production of bio-oil, and (iii) the oil-free algal biomass was used as a biosorbent in the treatment of dye wastewater. Optimal conditions of the influencing parameters such as the solvent systems, pre-treatment methods, optimum temperature, and time of exposure for the production of algal oil and bio-oil were studied. Once the oil extraction was completed, the remaining algal biomass acts as a solid waste. This waste was utilized as an effective biosorbent for the removal of methylene blue (MB) dye from the aqueous solution. The effect of operating parameters such as solution pH, biosorbent dose, initial dye concentration, time, and temperature on the removal of MB dye from the aqueous solution has been investigated. Biosorption kinetics, mechanism, isotherm, and thermodynamics of dye removal by the algal biomass were studied. Freundlich and pseudo-second-order models provide the best fit to the biosorption equilibrium and kinetic data, respectively. Biosorption of dye molecules onto the biomass was controlled by both particle and film diffusion. The thermodynamic study showed that the biosorption process was found to be an exothermic and spontaneous in nature.

Keywords: Algal oil; Biosorption; Bio-oil; Methylene blue dye; *Sargassum wightii*

1. Introduction

Algae are the fastest growing plants in the world and they are one of the most important sources of biomass. These algae can be grown anywhere from the sewage water to salty seawater which does not require any fertile land for their growth. They are the most photosynthetically efficient plants on the earth. These marine algae (i.e. seaweeds) are often used directly as a source of food or as protein supplement, but algae have also been considered as an emerging alternative for the conventional fuels. For decades, algae have been used to make a variety of products from nutraceuticals to pigments to organic fertilizers. The oil which is extracted from the algae can act as a substitute as well as a blend to the existing conventional fuel. Biodiesel, bio-oil, ethanol, methane, hydrogen,

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and bio-gasoline are some of the products which are recovered from the algae and the biomass can be used as a feedstock for the combustion process.

Macroalgal bloom is another major environmental problem which causes changes in the bio-geochemical cycles of C, N, P, and S [1]. The utilization of this biomass is not only beneficial to the society but it also helps to keep the algal bloom in check. The algal species, *Sargassum wightii*, a kind of brown seaweed which is distributed throughout the tropical and temperate sea waters. The required environmental conditions for the growth of algae are the presence of sea/brackish waters and sufficient sunlight to drive photosynthesis. The process of obtaining the thallus of this species is greatly simplified as they are located at the relatively shallow parts of the ocean and on coral reefs [2].

One of the most important advantages of using the algal biomass is that it contains natural oils, proteins, and carbohydrates. Many species of algae can produce oils comprising up to 35% or more of their dry weight and the so produced oil is very similar in structure to the oil derived from plants and vegetables such as soya, palm, and rapeseed [3]. The oil and fats are derived from the algae which are generally composed of triglycerides. Based on the available property, it can be converted to a variety of high-value commodity products, primarily bio-fuels such as biodiesel, through the transesterification process. This biodiesel has the viscosity close to that of petrodiesel. Also this biodiesel is biodegradable, renewable, and non-toxic in nature which proves to be a promising alternative substitute for the fossil diesel [4]. It virtually emits no sulfur, aromatics, or particulates, and is thus a safer alternative to petroleum diesel. Unlike in the production of crop-oil, where 80% of the cost stems from the cost of the crops, the alga is obtained much more economically [5].

Recently, the burning of an enormous amount of fossil fuel has increased the CO_2 level in the atmosphere, causing global warming. Marine biomass such as macroalgae is a renewable resources, which on combustion has no impact on the CO_2 balance in the atmosphere, because, the CO_2 emitted by the burning of biomass is offset by the CO_2 fixed by photosynthesis [6]. Therefore, replacing the fossil fuel with the biomass can contribute to the mitigation of global warming by reducing the CO_2 emission from the burning of fossil fuels. Marine algal biomass can be used to produce benign biofuel. Since they are primarily composed of polysaccharides and which can be converted to fuel such as bio-oil [7–9] or bio-alcohol [10,11]. However, the availability of the oil crops for the production of bio-fuel is limited. Hence, the algae can be act as a source. Bio-oil is the fuel obtained by the thermochemical decomposition of algal biomass. The produced bio-oil has the potential to be upgraded into diesel and gasoline range compounds that are of high demand. It is a dark brown liquid that has a higher heating value. It is a complex mixture of alcohols, acids, aldehydes, ketones, esters, sugars, furans, phenols, and other aromatics. It finds application in boilers, engines, turbines, etc.

Once the oil was extracted from the marine algae, the algal biomass was acting as a waste and which was ready for the disposal. Instead of disposing this waste into the environment, this waste may be utilized as a biosorbent for the removal of methylene blue (MB) dye from the aqueous solution. The wastewater from the dyeing and finishing processes in the textile industries are one of the major sources of wastewater production because these techniques require a large amount of water for their successful operations [12]. MB dye is a cationic dye which was used for the dying of silk, cotton, and wood materials [13]. The synthetic and toxic nature of the dye molecules which causes several harmful effects such as eye burns, gastritis, diarrhea, anemia, hypertension, vomiting, fever, and dizziness to the human beings and other living organisms. Therefore, it is a compulsion that the wastewater containing MB dye must be treated before letting out in to the environment.

Besides the conventional treatment of dye wastewater using chemical coagulation, membrane filtration, ion exchange, trickling filter, activated sludge process, and the like; adsorption proves to be a very important and effective method in the removal of the dye. This is due to its simple operational principle, easy, effective, and efficient methodologies and its insensitivity towards toxic substances. Generally, activated carbon was used as the adsorbent for the treatment of dye containing wastewater due to its high-adsorbing capabilities and suitable atmospheric properties. However, its usage was restricted because of its high initial and regenerative costs. Therefore as an alternative, low-cost algal are considered as biosorbents for dye removal, these include certain *Saccharomyces cerevisiae* [14], *Pasapalum notatum* [15], *Cupressus sempervirens* cones [16], *Feronia acidissima* [17], the brown alga *Cystoseira barbatula* Kutzing [18], dead *Streptomyces rimosus* [19], dead fungus *Aspergillus niger* [20], *Posidonia oceanica* (L.) fibres [21], *Caulerpa racemosa var. cylidracea* [22], algal waste [23], alga *Sargassum muticum* seaweed [24], activated sludge biomass [25], etc.

The main objective of the present research was to extract the oil from algal biomass, to produce bio-oil, and to utilize the used algal biomass for the treatment

of wastewater which contains dye molecules. The parameters which influence the production of algal oil and bio-oil such as solvent systems, pre-treatment methods, optimum temperature, and the time of exposure were investigated. The used algal biomass was utilized as an effective biosorbent for the removal of MB dye molecules from the aqueous solution. The parameters which affect the biosorption process such as solution pH, biosorbent dose, contact time, initial MB dye concentration, and temperature were investigated on the removal of MB dye molecules by the algal biomass. The different biosorption models such as kinetics, mechanism, isotherms, and thermodynamics were investigated at optimum conditions for the maximum removal of MB dye molecules.

2. Experimental

2.1. Materials

The organic solvents of analytical grade (extra pure 99%) were purchased from Merck limited, Mumbai, India.

2.2. Collection of algal sample

The algal biomass of the species, *S. wightii*, was collected by handpicking from the infra littoral fringe zone of Mandapam, Rameshwaram, South Coast (Gulf of Mannar), Tamil Nadu, India (Geo Coordinates: Latitude—9.27, Longitude—79.13). The whole parts of the well-matured plants (dark brown in color) were collected which included, the holdfast base, cylindrical and glabrous stem, and leaves. The collected seaweeds were well cleaned with sea water to remove all extraneous matter such as epiphytes, adhering sand particles, and unwanted impurities. Then the samples were preserved in plastic bags containing sea water mixed with formaldehyde (10% w/w) before sealed tightly, labeled, and transported to the laboratory. For further processing in the laboratory, the holdfasts from all the plants were removed by scalping with a sharp sterile knife.

2.3. Preparation of algal biomass

The collected seaweeds were then thoroughly washed with tap water followed by rinsing with distilled water. Washed seaweeds were laid out evenly and dried at room temperature in shade. Once the biomass was dry enough, they were ground in order to reduce the particle size. This powdered biomass was then subjected to two different processes.

2.4. Sequence strategy for the extraction of algal oil

The extraction of oil from *S. wightii* was performed on the following sequence: (a) pre-treatment to destruct the algal cells, (b) mixing of pre-treated algal biomass with solvent mixture, (c) extraction using soxhlet apparatus, and (d) separation of oil and solvent mixture by a simple distillation setup.

2.4.1. Pre-treatment methods

The pre-treatment was mainly carried out with the aim of disrupting the algal cell walls in order to increase the efficiency and yield of the extraction process. For the microwave pre-treatment, the algae and the solvent were taken in the ratio 1:3 and were subjected to a radiation of frequency 2.5 GHz for duration of 10 min. Similarly for ultrasonication, the algae and the solvent were taken in the same ratio as above and were subjected to ultrasonication frequency of 20 kHz, bath type system for about 30 min. After the pre-treatment, the algal biomass was separated from the solvent using filtration technique. The retentate was used for the extraction process.

2.4.2. Solvent systems

After the destruction of algal cells using pre-treatment methods, different solvent systems were used for the extraction of oil such as n-hexane, chloroform: methanol (3:1), n-hexane:ether (1:1), and chloroform: methanol (2:1). During the selection of solvent study, the solvent-to-solid ratio was maintained as 6:1.

2.4.3. Extraction of algal oil

The extraction was carried out in a soxhlet apparatus which was used for extracting fatty material with a volatile solvent. Fifty grams of the powdered pre-treated algal biomass was taken in a thimble and placed in a vertical glass cylindrical extraction tube that has both a siphon tube and a vapor tube which was fitted at its upper end to a reflux condenser and its lower end to a round-bottomed flask where the solvent mixture was taken. The solvent may be distilled from the flask into the condenser from where it flows back into the cylindrical tube and siphons over into the flask to be distilled again. This was considered to be one cycle. Similarly cycles follow, and the setup was undisturbed for about 12 h.

2.4.4. Separation of oil from solvent

Once the extraction process was completed, the packed thimble was removed from the apparatus and

its contents are dried and stored for future use. The solvent-oil mixture left behind in the round-bottom flask was taken and subjected to distillation process. During the distillation process, the solvent mixture was separated from the extracted oil. The recovered solvent was stored and the algal oil was filtered and weighed.

2.5. Characterization of algal oil

The extracted oil was subjected to gas chromatography–mass spectroscopy (GC–MS) analysis in order to identify its composition. The instrument used for GC/MS was JEOL GC MATEII for which the inlet temperature was maintained at 220˚C and the oven temperature at 50–250˚C with the rise of 10˚C per min. The ion chamber temperature was maintained at 250˚C and the voltage used was of 70 eV. The column specifications of the instrument used were of HP 5 Ms and which used-high pure helium as a carrier gas. The flow rate of the carrier gas was maintained at 1 ml/min. The detector used to analyze was Photo Multiplier Tube (PMT).

2.6. Production of bio-oil

Ten grams of the freshly powdered algal biomass was neatly packed in a simple silica crucible. The packed silica crucible was placed in a furnace which was closed on one side while the volatile gases were collected and condensed from the other end. The incondensable gases were allowed to escape. The temperature maintained in the furnace was of the order 700˚C. The sample was at this temperature for 30 min. After 30 min, the furnace was switched off and the setup was allowed to cool nicely such that it can be handled. The condensed gases were also isolated and stored. The crucible containing the bio-char was then carefully removed from the interior of the furnace. This bio-char was washed with acetone in order to remove all that was soluble. The furnace itself was then washed with a little of acetone to remove all the soluble substances adhering to the interior surface and then this acetone was allowed to evaporate. The condensed gases in addition to the soluble substances (isolated with the help of acetone) form the bio-oil.

2.7. Algal biomass as biosorbent in wastewater treatment

The solid waste that resulted during the production of algal oil and bio-oil has the potential to replace the commercially available activated carbon and this can act as an effective biosorbent in the treatment of dye wastewater. Thus, they provide with an advantage of complete utilization of the biomass.

2.7.1. Preparation of biosorbent

The oil-stripped algal biomass was retrieved from the soxhlet apparatus and which was first washed and rinsed with distilled water. Then it was dried completely using a hot air oven. This dried biomass was ground once again in order to further reduce its size. Thus, the powdered algal biomass was used as a biosorbent for the removal of MB dye from the aqueous solution.

2.7.2. Preparation of MB dye solution

MB dye [CI: 52015, molecular formula: ($C_{16}H_{18}N_3SCl{\cdot}3H_2O$) molecular weight: 373.9, λ_{max} = 664 nm] was procured from E. Merck (India). A stock solution of MB dye (500 mg/L) was prepared by dissolving 0.5 g of MB dye powder in 1 L of double-distilled water. The stock solution was diluted with double-distilled water to obtain the working solutions of desired concentrations (100–500 mg/L).

2.7.3. Batch biosorption experiments

Batch biosorption of MB dye onto the biosorbent was investigated in aqueous solutions under the various operating conditions, namely pH (2–10), adsorbent dose (0.1–0.8 g), contact time (2–60 min), initial MB dye concentration (100–500 mg/L), and temperature (30–60˚C). Batch adsorption equilibrium studies were carried out in Erlenmeyer conical flasks at room temperature. MB dye solutions (100 mL each) with increase in concentration from 100 to 500 mg/L were shaken in a shaker (180 rad min^{-1}, Orbital incubation shaker, Royal Testing Equipment, Chennai, India) with an optimum adsorbent dosage and at optimum pH. Once the system was attained the equilibrium condition, the mixture was centrifuged to separate the adsorbent and supernatant liquid. The concentration of MB dye in the supernatant was analyzed using the UV–vis spectrophotometer (UV-670, USA). All the experimental studies were carried out in duplicates. The percentage of MB dye removal was calculated using the following equation:

$$\% \text{ MB dye removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (1)$$

where C_o and C_e are the initial and final or equilibrium concentration of MB dye solution (mg/L), respectively.

For biosorption kinetic studies, the biosorption process was carried out at optimum conditions, based on the effect of operating variables on the removal of MB dye from the aqueous solution. The residual MB dye concentration in the solution was measured at known time intervals using UV–vis spectrophotometer. The amount of MB dye adsorbed at time t, q_t (mg/g), was estimated by the following equation:

$$q_t = \frac{(C_o - C_t)\,V}{m} \tag{2}$$

where C_t is the concentration of MB dye solution at any time t (mg/L), V is the volume of the MB dye solution (L), and m is the mass of the biosorbent (g).

For biosorption isotherm studies, the adsorption process was carried out at equilibrium and at optimum conditions. The residual MB dye concentration in the solution was measured using UV–vis spectrophotometer. The amount of MB dye adsorbed at equilibrium time, q_e (mg/g), was estimated by the following equation:

$$q_e = \frac{(C_o - C_e)\,V}{m} \tag{3}$$

where C_e is the concentration of MB dye solution at equilibrium condition (mg/L).

For biosorption thermodynamic studies, the adsorption process was carried out at different temperatures and at optimum conditions. The residual MB dye concentration in the solution was measured using UV–vis spectrophotometer. The removal of MB dye molecules was calculated using the Eq. (1).

3. Results and discussion

3.1. Determination of algal oil yield

The yield of the oil extracted was calculated using the following equation [26]:

$$\text{Oil extraction yield } (\%) = \frac{\text{Weightofoil}}{\text{Weight of biomass taken}} \times 100 \tag{4}$$

3.2. Solvent optimization

The selection of solvent system plays an important role in the extraction of oil from the algal biomass. The solvent selected for extraction should have a good extraction capacity i.e. the ability to penetrate the biomass and extract the lipid contents present in the biomass. Different solvent systems such as n-hexane, chloroform:methanol (2:1), n-hexane:diethylether (1:1), and chloroform:methanol (3:1) were used for extraction. The oil extraction yield using different solvents was shown in Table 1. The highest yield of oil extraction (2.1%) was obtained when chloroform:methanol (2:1) was used as the solvent system, whereas the yield decreased (1.8%) when using chloroform:methanol (3:1). n-hexane and hexane:ether (1:1) solvents resulted in the yield of 1.2 and 0.6%, respectively.

3.3. Pre-treatment methods optimization

The algal biomass was subjected to two pre-treatment methods such as ultrasonication and microwave method. The highest yield of oil extraction was obtained when the algal biomass was subjected to ultrasonication pre-treatment method. Ultrasonication was a powerful tool to accelerate many physical operations [27]. Microwave-assisted method resulted in a lower yield compared to that of ultrasonication because of the partial hydrolysis and pre-esterification of the oil that occurs. The different pre-treatment

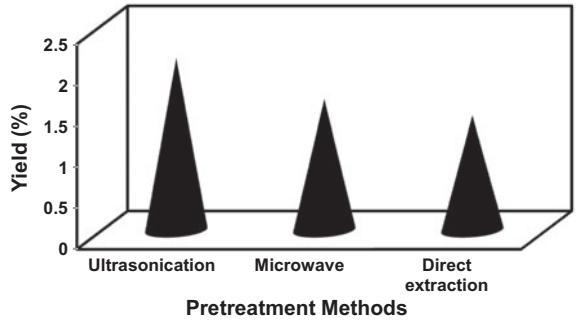

Fig. 1. Pre-treatment optimization.

Table 1
Solvent systems

S. No.	Solvent	Ratio	Oil extraction yield (%)
1	n-hexane	–	1.2
2	Chloroform: methanol	2:1	2.1
3	Chloroform: methanol	3:1	1.8
4	Hexane:ether	1:1	0.6

methods and their yields were presented in Fig. 1. The highest yield of oil using ultrasonication pre-treatment method was considered by SEM images of cell disruption structure of algal biomass was shown in Figs. 2(a) and 2(b). It can be seen that there is a distinct difference between the two images. The SEM image of the raw algal sample shows a continuous mass, whereas the SEM image of the ultrasonicated sample shows a disrupted structure indicating that this change had been formed during the ultrasonication process. The ultrasonication process breaks the continuity of the cell walls and this destruction ensures a greater chance for penetration of solvent into cellular materials and thereby improving release of cellular contents into the bulk medium. Hence, there is a higher yield in the extraction of the algal oil. Ultrasonication pre-treatment has many advantages such as reduced extraction time, reduced solvent consumption, increased yield, and high efficiency.

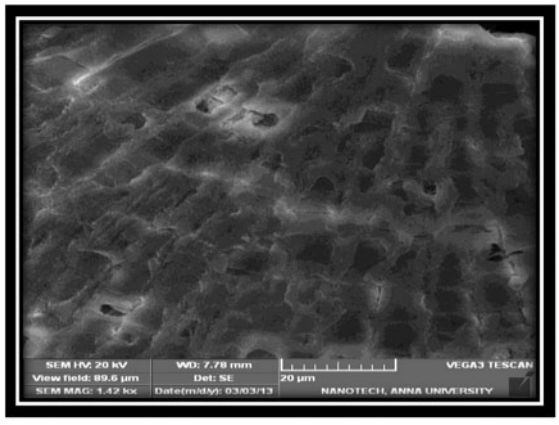

Fig. 2(a). SEM image of raw algal sample.

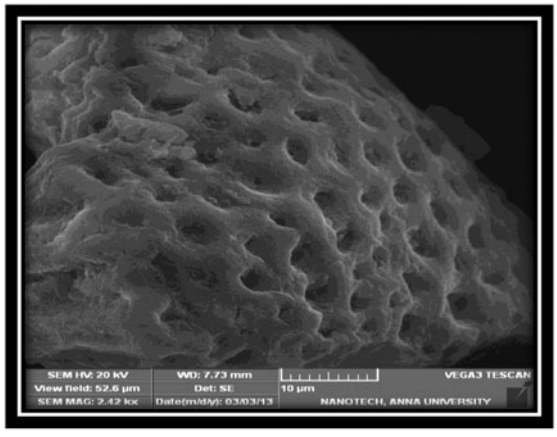

Fig. 2(b). Ultrasonicated algal sample.

3.4. Characterization of algal oil

Fatty acid composition of algal oil was analyzed using gas chromatography–mass spectrometry (GC–MS) analysis. The fatty acid profile was shown in Table 2. From the GC–MS analysis, the algal oil was found to contain 40.07% of saturated fatty acids, 48.44% of unsaturated fatty acids, and polyunsaturated fatty acids of about 11.36%. The nature of fatty acid was shown in Fig. 3. The GC image of the algal oil sample is shown in Figs. 4(a) and 4(b).

3.5. Determination of molecular weight of algal oil

The average molecular weight of the algal oil was calculated using the following equation [28]:

$$\text{Molecular weight of oil} = 3 \times \sum (MW_i * \%\, m_i) + 38 \quad (5)$$

The molecular weight of the algal oil was calculated using the above equation was found to be of 882.05 g/mol.

Table 2
Fatty acid profile

Fatty acid	Carbon atoms	Relative (%)
Palmitic acid	C16:0	21.75
Hexadecanedioic acid	C16:0	5.52
Elaidic acid, Ozonide	C18:0	12.8
Palmitoleic acid	C16:1	3.94
Oleic acid	C18:1	27.17
16-Octadecenoic acid	C18:1	17.33
Linoleic acid	C18:2	3.76
Pyrulic acid	C17:3	3.2
Octadecatrienoic acid	C18:3	2.6
Eicosatrienoic acid	C20:3	1.8

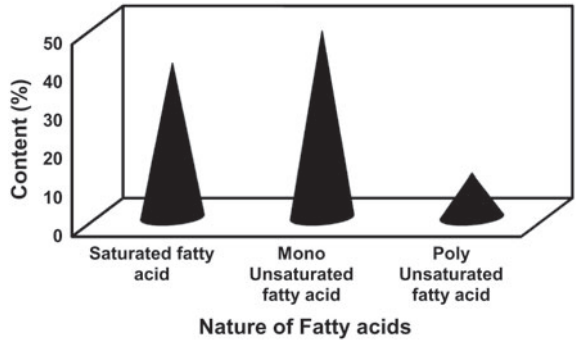

Fig. 3. Fatty acid profile of *S. wightii*.

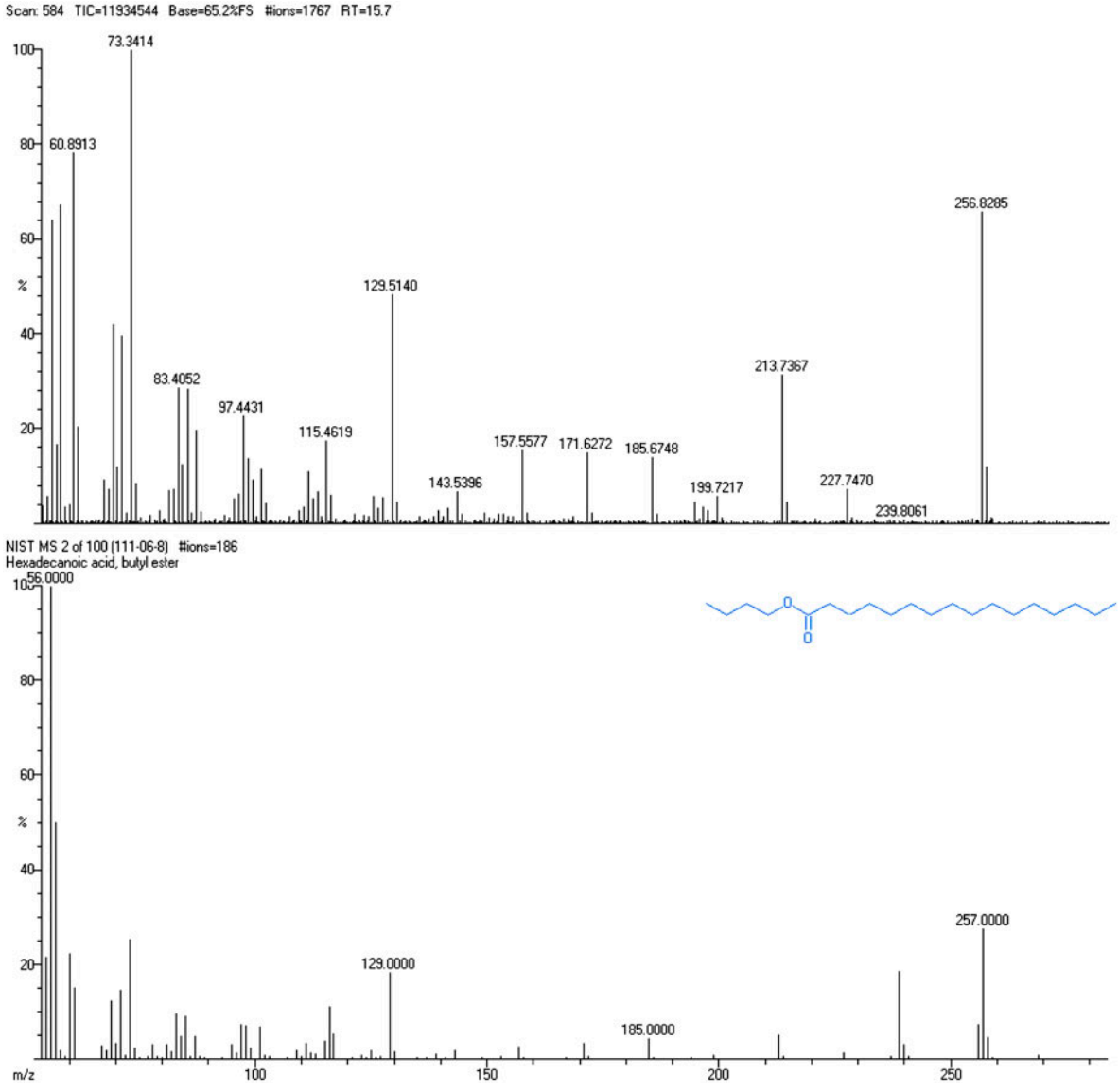

Fig. 4(a). GC of algal oil—palmitic acid.

3.6. Thermogravimetric analysis of algal biomass

From the figures of TGA and DTG shown in Fig. 5 and Fig. 6, respectively, it was observed that the loss in the weight of the biomass occurs in three distinct stages during its thermochemical decomposition process [29]. During the first stage (i.e. from 30 to 200°C), the water in the cells and the external water bounded to the surface by surface tension were lost. Stage II occurs from 200 to 352°C. This stage was called as devolatilization stage during which the compound was thermochemically decomposed. In this stage, the volatile compounds were gradually released from the biomass and hence, resulted in the major weight loss. Stage III which occurs from 352 to 640°C the major weight loss was due to slow decomposition of the remaining residue from stage II. This results in the formation of a loose and highly-porous residue known as the bio-char.

3.7. Bio-oil yield

The Eq. (4) was used to estimate the yield of bio-oil and the value was found to be of 25%.

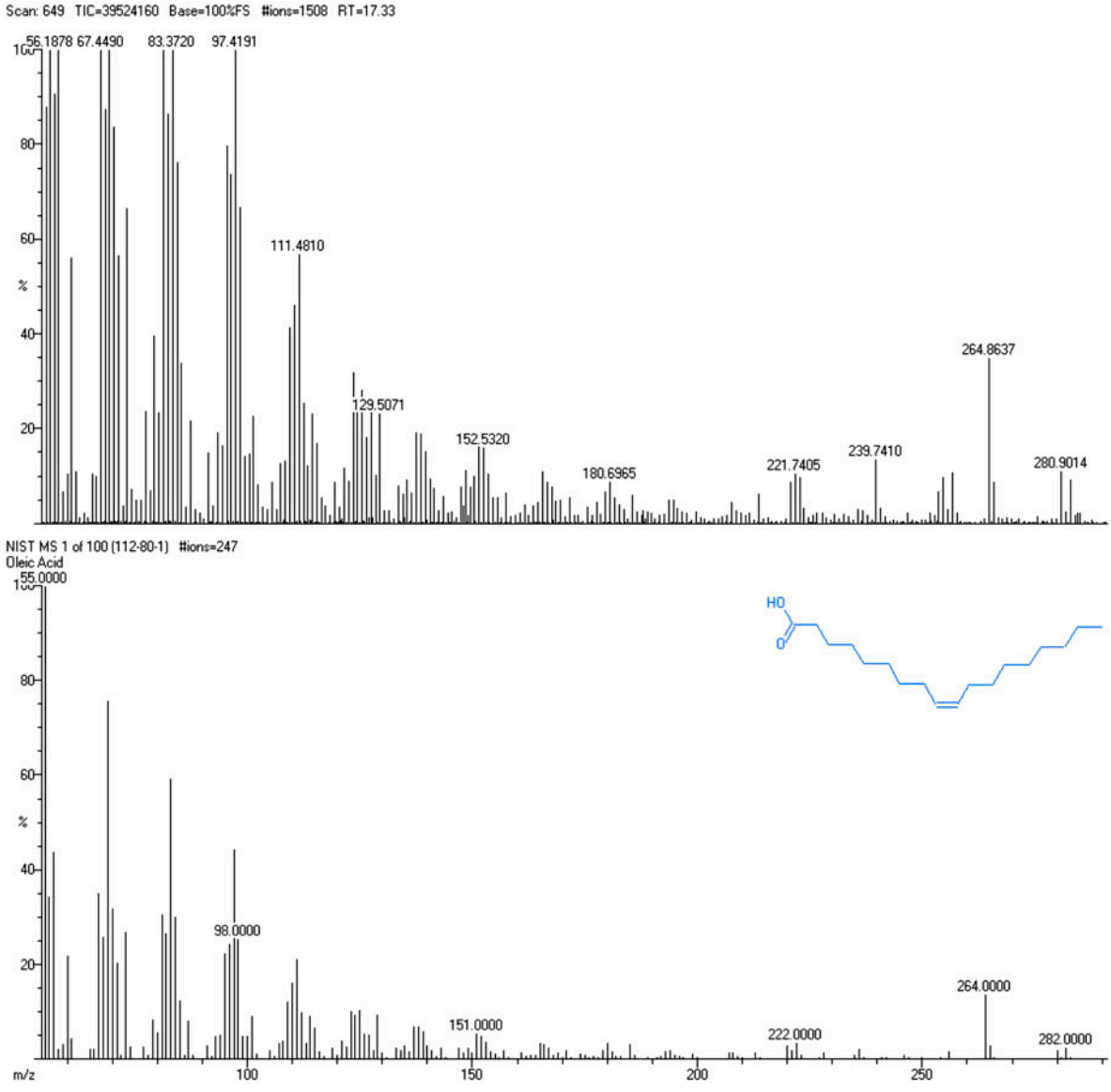

Fig. 4(b). GC of algal oil—oleic acid.

3.8. Characterization of bio-oil

The bio-oil obtained from the thermochemical decomposition of algal biomass was given for GC–MS analysis. The different compounds were present in the bio-oil are as follows: 4-hexenoic acid, 2-amino-6-hydroxy-4-methyl, heptamethylene diacetate, cyclohexanone, 2–((dimethyl amino)methyl), 9-hexadecenoic acid, 9-octadecenyl ester, 2,2,5-trimethylcyclohexane 1,4-diol, 9,12,15–octadecatrienoic acid, 2–((trimethylsilyl)oxy–1– (trimethylsilyloxy)methyl)ethyl ester (Z,Z,Z), 2-ethoxycarbonyl-3-methyl-4-azafluorenone-2-flourenylimine, 1,2,3,4—cyclopentane trol, and piperidine, 2,3-dimethyl. The GC image of one of the compound of the bio-oil was shown in Fig. 7.

3.9. Batch biosorption experiments

3.9.1. Characterization of biomass

It was observed from the Figs. 8(a) and 8(b), there is a significant difference between the two SEM images of the biomass. The SEM Image of the raw algal biomass sample i.e. before adsorption shows a highly porous surface whereas the SEM image of the sample after adsorption of MB dye shows that the

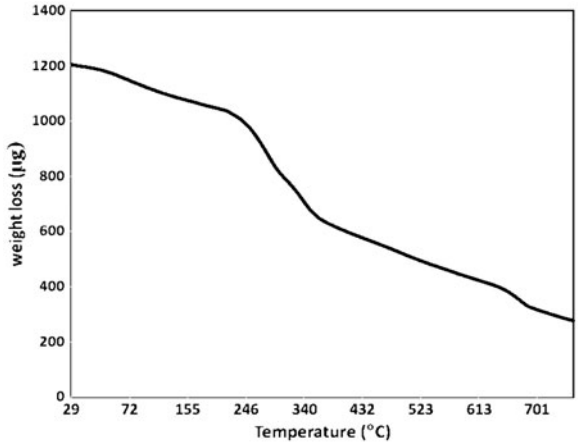

Fig. 5. TGA of biomass.

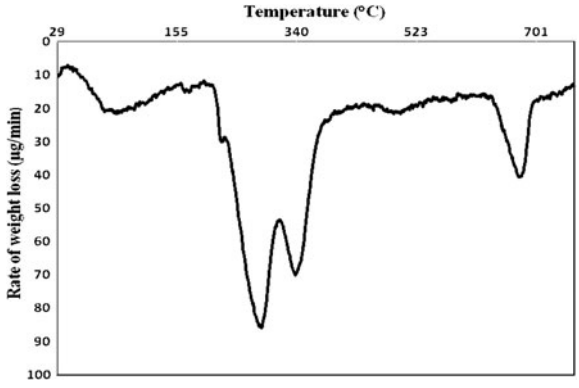

Fig. 6. DTG analysis.

pores are clogged. From this, it was observed that the MB dye molecules were adsorbed on the surface of the algal biomass thus, proving that *S. wightii*, marine algal biomass can act as an excellent biosorbent for the adsorption of MB dye.

3.9.2. Optimization of operating parameters on MB dye biosorption

The solution pH is an important operating factor in the adsorption process. The percentage removal of MB dye by algal biomass over the pH range 2.0–10 was studied and the results are shown in Fig. 9(a). From the Fig. 9(a), it was inferred that the removal of MB dye was increased with an increase in solution pH till pH 8.0. Maximum removal of MB dye was observed at the optimum pH of 8. For further experimental studies, the initial solution pH was maintained at 8.0. At lower pH, there is relative competence between the MB dye (cationic) and the hydronium ions for the adsorbent sites. At higher pH, the negatively charged biosorbent sites increase, which in turn enhances the adsorption of positively charged MB dye.

The effect of adsorbent dose on the removal of MB dye was illustrated in Fig. 9(b). The results showed that the optimum biosorbent dose was chosen as 0.5 g for further experimental studies. It can be seen that the removal of MB dye gradually increases with increase in biosorbent dose, loading up to 0.5 g. The maximum removal of MB dye was attained at 0.5 g/100 mL. However, the removal of MB dye becomes nearly constant above the optimized biosorbent dosage value which was due to the reduction in the concentration gradient between MB dye solution and the adsorbent surface.

Another important operating parameter in the adsorption process was contact time. Fig. 9(c) illustrates the effect of contact time on the removal of MB dye. It can be seen from the Fig. 9(c) that the removal of dye was increased with increase in contact time and the equilibrium was attained at 10 min, after which it remained constant. Therefore, the optimum contact time was fixed as 10 min for further experimental studies.

The effect of initial MB dye concentration (100–500 mg/L) on MB dye removal was shown in Fig. 9(d). It was observed from the Fig. 9(d) that there is a gradual decrease in the removal of MB dye as the MB dye concentration increases from 100 to 500 mg/L. This was due to the fact that at lower initial MB concentration, only less number of dye molecules is available and it was easily removed by the biosorbent. But at higher initial MB dye concentration, the large number of MB dye molecules is available for biosorption and it was not possible to remove all these molecules, since there are only limited active sites available for biosorption.

The effect of temperature on the biosorption of MB dye onto the algal biomass was studied and the Fig. 9(e) clearly showed that there was a decrease in the removal of dye as there was an increase in the temperature. This was because of exothermic effect of the biosorption process. Thus, lower the temperature higher was the removal of MB dye molecules. As there is a maximum removal of MB dye molecules at atmospheric temperature (30˚C) itself, there was no need to operate at temperatures further below it. Therefore, the optimized temperature for the experimental studies was fixed at 30˚C.

3.9.3. Biosorption kinetics

The obtained kinetic data from the effect of contact time between the dye solution and biosorbent were utilized to test the adsorption kinetic models such as

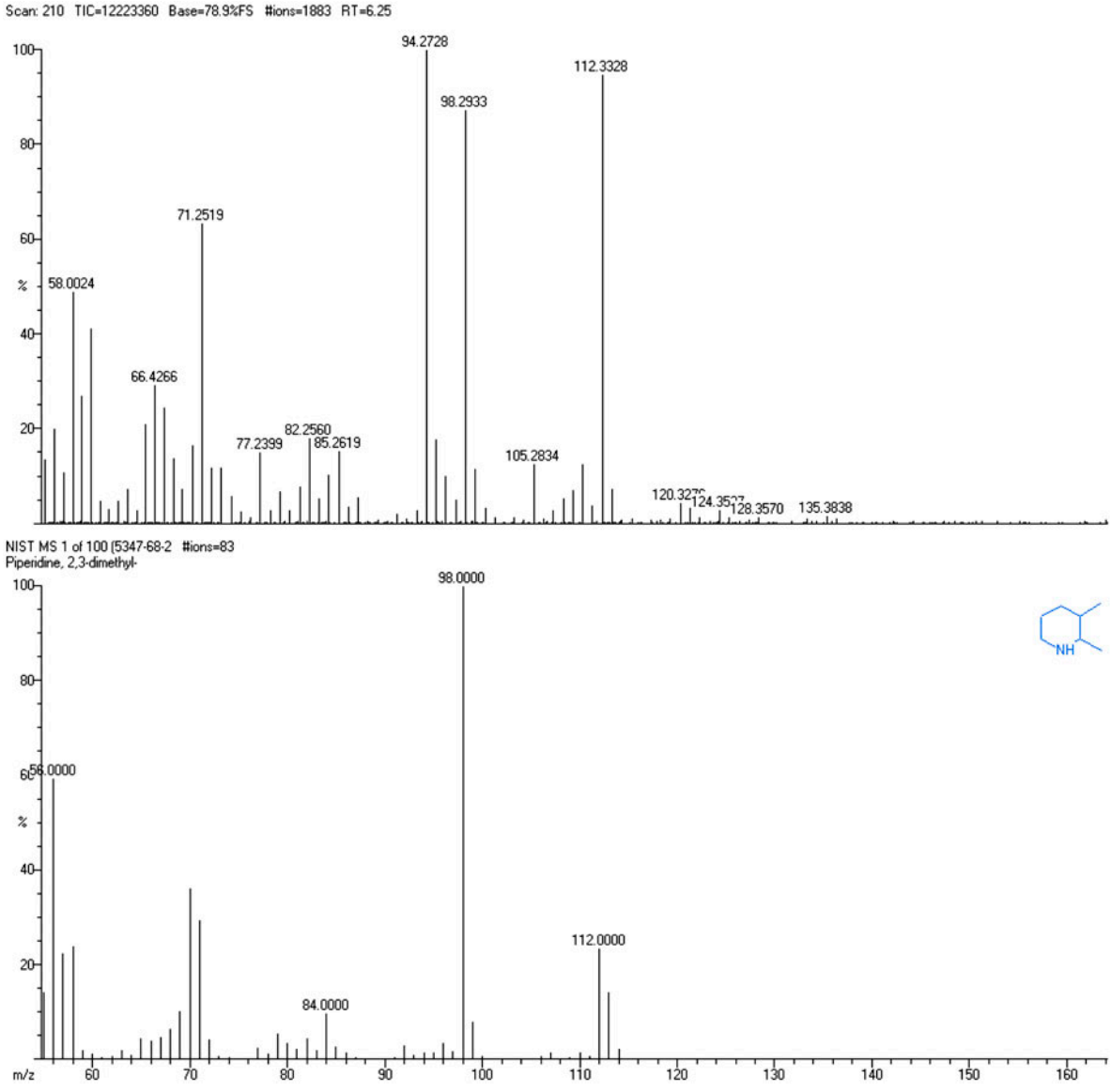

Fig. 7. GC image of Bio-oil—Piperidine, 2,3 dimethyl.

pseudo-first-order [30] and pseudo-second-order [31]. The results of the kinetic studies are shown in Fig. 10(a) and (b). The linear form of Lagergren pseudo-first-order kinetic model is given by following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\, t \tag{6}$$

and the linear form of pseudo-second-order kinetic model is given by following equation:

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} t \tag{7}$$

where q_e is the biosorption capacity at equilibrium (mg/g), q_t is the biosorption capacity at time t (mg g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}), t is the time (min), k_2 is the pseudo-second-order rate constant (g/mg·min), and $h = k_2 q_e{}^2$ is the initial biosorption rate (mg g^{-1} min^{-1}). Using the slope and intercepts obtained from the Fig. 10(a) and (b), the various parameters such as kinetic parameters, equilibrium biosorption capacity, and the coefficient of

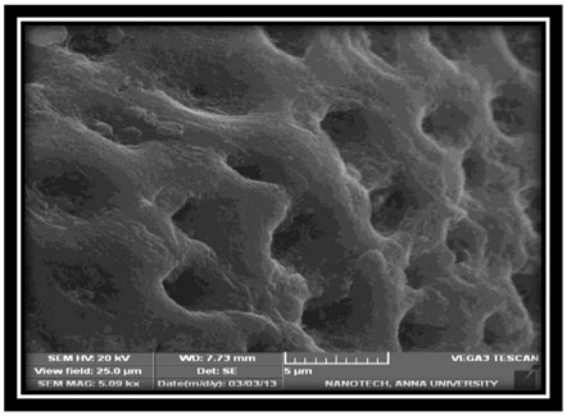

Fig. 8(a). Before adsorption.

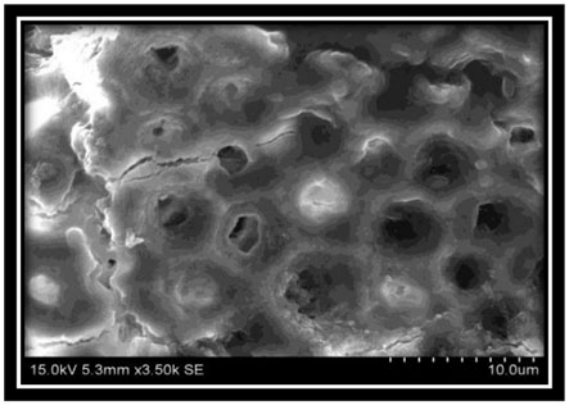

Fig. 8(b). After adsorption.

determination values (R^2) were estimated and are clearly listed in Table 3. It was noticed from Table 3 that the coefficient of determination values (R^2) for the pseudo-second-order kinetic model was found to be higher. This indicates that the biosorption of MB dye onto the algal biomass was well described using pseudo-second-order kinetic model. Also the calculated biosorption capacity (q_e,cal) values from the pseudo-second-order kinetic model are very close to the experimentally obtained equilibrium biosorption capacity (q_e,exp) values. Thus, it was further confirmed that the biosorption of MB dye followed the pseudo-second-order kinetic model.

These two kinetic models were insufficient to explain the biosorption mechanism and the rate-limiting steps in the biosorption process. This has been sufficiently explained with the help of Weber and Morris intraparticle diffusion model [32], Boyd kinetic plot [33], and shrinking core model (SCM) [34–36]. Film diffusion or particle diffusion or both are the usual characteristics that are described for a solid–liquid adsorption process. The following are the three consecutive steps that take place during the biosorption of MB dye onto the algal biosorbent surface:

(1) Transport of MB dye molecules from the bulk solution to the external surface of the biosorbent (film diffusion or external diffusion).
(2) Transport of MB dye molecules into the pores of the algal biomass, excluding the small amount of biosorption occurring at the external surface of the biosorbent (particle diffusion or internal diffusion).
(3) Biosorption of the MB dye molecules on the interior surface of the biomass (biosorption).

The biosorption mechanism was identified by fitting the biosorption kinetic data into an intraparticle diffusion equation, Boyd kinetic equation, and SCM equation. The data fitting to the different model results are clearly shown in Fig. 11(a)–(c). The Weber and Morris intraparticle diffusion is represented by the following equation:

$$q_t = k_p t^{1/2} + C \tag{8}$$

where q_t is the biosorption capacity at time t (mg g^{-1}), k_p is the intraparticle diffusion rate constant (mg g^{-1} min$^{0.5}$), t is the time (min), and C is the intercept. If the linear plot of q_t vs. $t^{1/2}$ passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, in the present scenario, the linear plot does not pass through the origin, indicating that there is some degree of boundary layer control and this further confirm that the intraparticle diffusion is not the only rate-limiting step, and that biosorption can also be the rate-limiting step or both may be operating simultaneously. The two linear portions that were observed in the intraparticle diffusion plot (Fig. 11(a)) indicates that the biosorption of MB dye onto algal biomass proceeds by surface biosorption and intraparticle diffusion. The first linear portion of the plot indicates a boundary layer effect and the second portion of the linear plot indicates the intraparticle diffusion. Table 4 lists all the estimated parameters, constants, and R^2 values.

The biosorption kinetic data were tested with the Boyd kinetic plot to predict the actual slowest step in the biosorption of MB dye onto the algal biomass and the results obtained were presented in Fig. 11(b). The Boyd kinetic model is given by following equation:

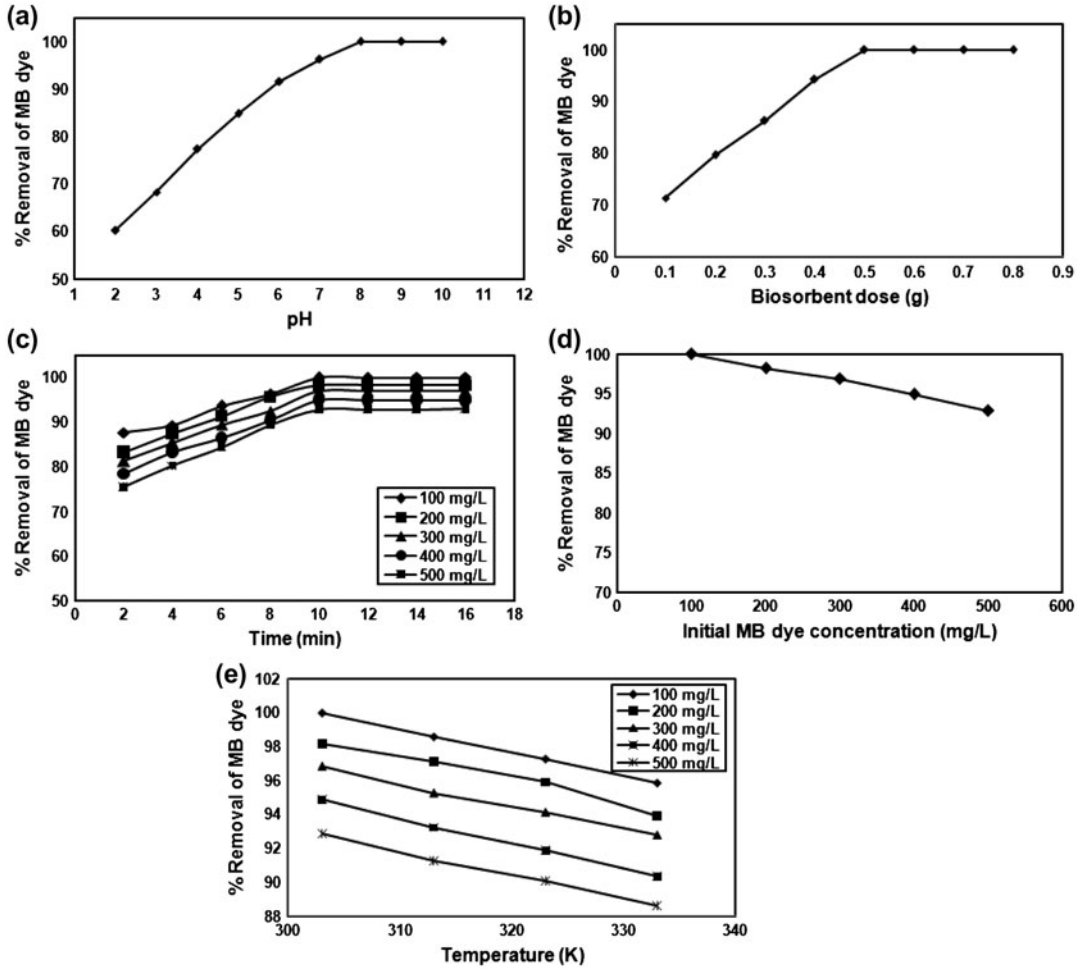

Fig. 9. Effect of operating parameters on MB dye adsorption.

$$\frac{q_t}{q_e} = F = 1 - \frac{6}{\pi^2}\exp(-Bt) \tag{9}$$

The Eq. (9) can be rearranged into the following form:

$$Bt = -0.4977 - \ln(1 - F) \tag{10}$$

where q_e is the equilibrium biosorption capacity (mg/g), q_t is the biosorption capacity at time t (mg/g), F is the fraction of MB dye molecule biosorbed at any time t, and Bt is a mathematical function of F.

If a linear plot that passes through the origin is obtained when Bt is drawn against time, then the actual slowest step is the particle diffusion in the process of biosorption of MB onto biomass. However, from Fig. 11(b) we can notice that the plots are linear but does not pass through the origin indicating that biosorption of MB dye may be controlled by film diffusion. The values of B estimated from the linear plot were used to obtain the effective diffusion coefficient, D_i (m^2/s) using the following Eq. (11) and the values are listed in Table 4:

$$B = \frac{\pi^2 D_i}{r^2} \tag{11}$$

where D_i is the effective diffusion coefficients of MB dye molecules in algae surface and r is the radius of the algal biomass particles.

Further, the analysis of the biosorption kinetic data was carried out using the SCM model and the results are shown in Fig. 11(c). The kinetic models have been developed to estimate the mass transfer characteristic parameters in the biosorption process. The overall biosorption rate of binding of MB dye molecules to the biosorbent (diffusion plus reaction) depends primarily on diffusivity. In case of a process controlled by

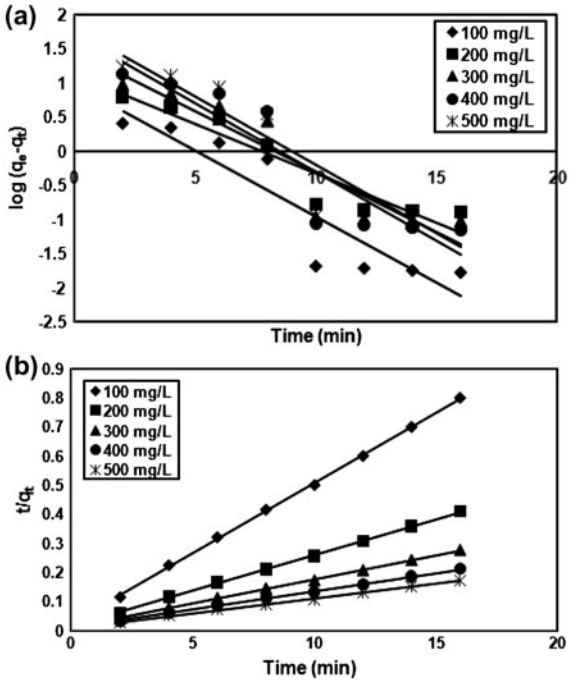

Fig. 10. Adsorption kinetics for the removal of MB dye by algal biomass.

diffusion of MB dye molecules through the liquid film (film diffusion control), the extent of the biosorption of MB dye onto the algal biomass, shown as a function of time will be given by the following equation:

$$X = \frac{3D}{\delta RC}\alpha \tag{12}$$

If the film diffusion is controlling in the biosorption of MB dye molecules onto algal biomass, a plot of X vs. α yields a straight-line relationship. If the process is controlled by diffusion through reacted shell (particle diffusion control), then the model can be represented by the following expression:

$$F(X) = 1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) = \frac{6D}{R^2 C^o}\alpha \tag{13}$$

In case of particle diffusion control, a plot of $F(X)$ vs. a gave a straight-line relationship (Fig. 11(c)) and the diffusivity of the MB dye molecules in algal biomass could be estimated from the slope of the plots of the Fig. 11(c). It is given in Eq. (13)

$$D = (\text{Slope})\frac{C^o R^2}{6} \tag{14}$$

where

$$X \text{ is the extent of reaction } = \frac{(C_o - C)}{(C_o - C_{eq})} \tag{15}$$

$$\alpha = \int_0^t C\,dt \tag{16}$$

where C_o is the initial MB dye concentration (mg/L), C^o is the average MB dye molecules binding site density of the algae (mg/L), C is the final MB dye concentration (mg/L), C_{eq} is the concentration of MB dye molecules at equilibrium (mg/L), D is the diffusion coefficient (m^2/s), and R is the radius of algae (m). From Fig. 11(c), it was found that the slope of the straight-line portion decreases with increase in the initial MB dye concentration and these results are shown in Table 4. Intraparticle diffusion proved to be a good fit.

3.9.4. Biosorption isotherms

The basic requirement in the designing of a biosorption system is the biosorption isotherms. The

Table 3
Estimated kinetic parameters for the adsorption of MB dye onto the algal biomass

Kinetic model	Parameters	Concentration of MB dye solution (mg/L)				
		100	200	300	400	500
Pseudo-first order kinetic equation	k_1 (min^{-1})	0.444	0.334	0.405	0.463	0.458
	$q_e$cal (mg/g)	9.397	13.304	28.379	50.234	60.954
	R^2	0.849	0.890	0.851	0.849	0.858
Pseudo-second order kinetic equation	k_2 (g/mg min)	0.092	0.044	0.0272	0.021	0.0157
	$q_e$cal (mg/g)	20.833	41.667	60.606	76.923	95.238
	h (mg/g min)	40	76.92	100	125	142.857
	$q_e$exp (mg/g)	20.012	39.435	58.204	75.988	92.444
	R^2	*0.999*	*0.999*	*0.999*	*0.999*	*0.999*

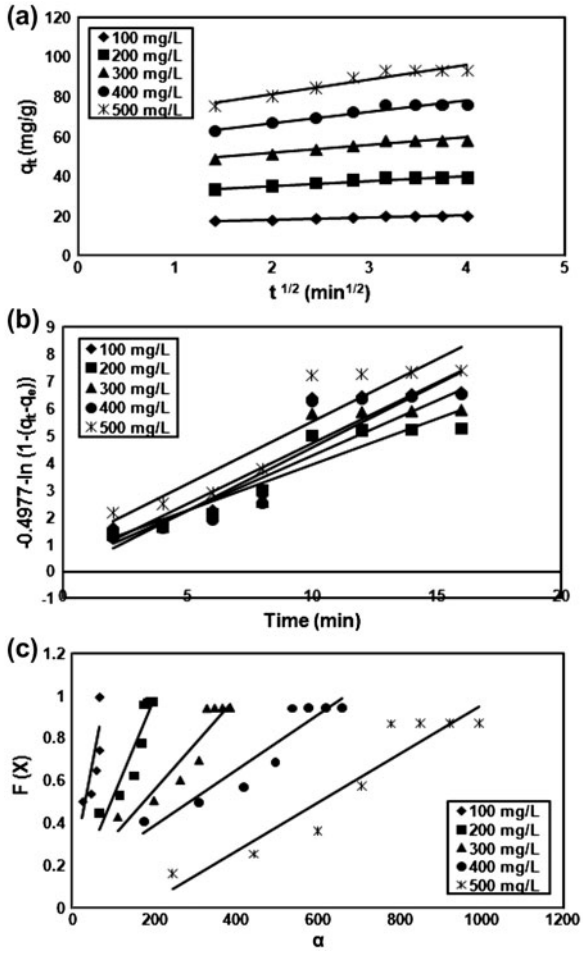

Fig. 11. Adsorption mechanism for the removal of MB dye by algal biomass.

distribution of MB dye molecules between the dye solution and the algal biomass is a measure of the position of equilibrium in the biosorption process. This can be expressed by one or more of a series of biosorption isotherm models such as Langmuir [37] and Freundlich [38] to know the types of biosorption process. The results are shown in Fig. 12. The non-linear Langmuir biosorption isotherm model is given by the following expression:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{17}$$

where q_e is the equilibrium biosorption capacity (mg/g), q_m is the maximum monolayer biosorption capacity (mg/g), K_L is the Langmuir constant related to the affinity of MB dye molecule to that of the algal biomass (L/mg), and C_e is the equilibrium concentration of MB dye solution (mg/L). The main characteristics of the Langmuir biosorption isotherm parameters can be used to predict the affinity between the MB dye molecule and the algal biomass using a separation factor "R_L" [39]. The separation factor from the Langmuir model is given as follows:

$$R_L = \frac{1}{1 + K_L C_o} \tag{18}$$

where K_L is the Langmuir constant (L/mg) and C_o is the initial MB dye concentration (mg/L). The R_L values provide important information about the nature of biosorption. The significance of the R_L values is given as follows: $R_L = 0$ (irreversible), $0 < R_L < 1$ (favorable), $R_L = 1$ (linear), and $R_L > 1$ (unfavorable). For this scenario, the R_L value was found to be 0.0679–0.0144 for the initial MB dye concentration of 100–500 mg/L. Since this value lies within the range of 0–1, it was indicated that the biosorption was favorable [40].

The non-linear form of Freundlich biosorption isotherm model is given by following expression:

$$q_e = K_F C_e^{1/n} \tag{19}$$

where K_F is the Freundlich constant [(mg/g)(L/mg)$^{(1/n)}$] related to the bonding energy and n is

Table 4
Estimated parameters for the adsorption mechanism of the MB dye onto the algal biomass

Conc. of MB dye in solution (mg/L)	Adsorption mechanism							
	Intraparticle diffusion model			Boyd kinetic model			SCM model	
	k_p (mg/g·min$^{1/2}$)	C	R^2	B	D_i (x 10^{-9} m^2/s)	R^2	D (x 10^{-9} m^2/s)	R^2
100	1.107	15.97	0.916	0.446	1.416	0.849	0.220	0.671
200	2.512	30.28	0.910	0.334	1.060	0.890	0.314	0.866
300	3.961	43.75	0.926	0.405	1.286	0.851	0.346	0.889
400	5.585	55.66	0.926	0.464	1.473	0.849	0.299	0.889
500	7.354	66.38	0.913	0.459	1.457	0.858	0.183	0.894

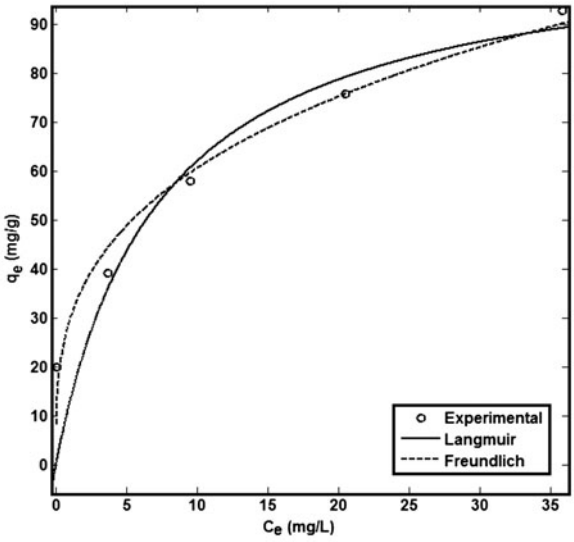

Fig. 12. Adsorption isotherm for the removal of MB dye by algal biomass.

a measure of the deviation from linearity of biosorption (g/L). The significance of n is follows: if $n = 1$ then biosorption is linear; if $n < 1$ then biosorption is a chemical process; and if $n > 1$ then biosorption is a physical process. The n value in Freundlich equation was found to be 3.219 for algal biomass. Since, n lies between 1 and 10, this indicates physical biosorption of MB dye molecules onto algal biomass [41].

The biosorption isotherm parameters, constants, and R^2 values were estimated from the Langmuir and Freundlich biosorption isotherm plots and are presented in Table 5. This shows that the maximum monolayer biosorption capacity was 107.5 mg/g. The results suggests that the Freundlich biosorption isotherm model is the best option among the Langmuir adsorption isotherm model to describe the biosorption behavior of MB dye molecules onto algal biomass based on its better R^2 values and also the error function values [sum of squared errors (SSE) and root mean squared errors (RMSE)]. The results indicated that the Freundlich biosorption isotherm model was valid for multilayer biosorption of MB dye onto a completely heterogeneous surface.

3.9.5. Biosorption thermodynamics

The thermodynamic parameters such as change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) of the biosorption of MB dye onto algal biomass can be estimated using the following expressions:

Table 5
Adsorption isotherm parameters for the adsorption of MB dye onto the algal biomass

Adsorption isotherm model	Parameters	Values	R^2
Langmuir	q_m (mg/g)	107.5	0.875
	K_L (L/mg)	0.1372	
	SSE	416.8	
	RMSE	11.79	
Freundlich	K_F ((mg/g) (L/mg)$^{(1/n)}$))	29.69	*0.9667*
	n (g/L)	3.219	
	SSE	110.8	
	RMSE	6.077	

$$\Delta G^\circ = -RT \ln\left(\frac{C_{Ae}}{C_e}\right) \tag{20}$$

$$\log\left(\frac{C_{Ae}}{C_e}\right) = \frac{\Delta S^\circ}{2.303\,R} - \frac{\Delta H^\circ}{2.303\,RT} \tag{21}$$

where K_c is the biosorption equilibrium constant, C_e is the concentration of MB dye at equilibrium (mg/L), C_{Ae} is the amount of MB dye biosorbed onto algal biomass per liter of solution at equilibrium (mg/L), R is the gas constant (8.314 J/mol K), and T is the temperature (K). The thermodynamic parameters were estimated from the Fig. 13 using the slope and intercept values, which are listed in Table 6. From Table 6, it can be seen that the negative values of ΔG° confirms the feasibility of the process of biosorption. Similarly, the negative values of ΔS° indicates that the biosorption process is driven by the randomness at the biosorbent–solution interface during adsorption and the negative values of ΔH° confirms that the process of biosorption of MB dye onto the algal biomass is an exothermic process.

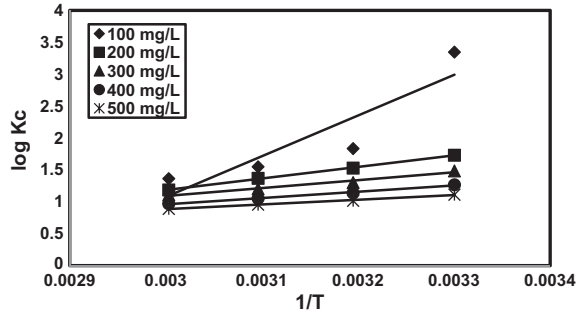

Fig. 13. Adsorption thermodynamics for the removal of MB dye by algal biomass.

Table 6
Thermodynamic parameters for the adsorption of MB dye molecules onto the algal biomass

Initial conc. of MB dye solution (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)			
			30℃	40℃	50℃	60℃
100	−122.006	−345.414	−19.412	−10.994	−9.579	−8.690
200	−34.656	−81.318	−10.038	−9.159	−8.463	−7.559
300	−23.704	−50.261	−8.609	−7.804	−7.447	−7.072
400	−18.938	−38.428	−7.352	−6.823	−6.509	−6.184
500	−14.081	−25.313	−6.451	−6.093	−5.910	−5.673

4. Conclusion

The present research concentrates in the complete utilization of the alga, *S. wightii*'s biomass in order to accomplish three distinct purposes in three different phases. In first phase: the lipid content present in the biomass was extracted using a soxhlet extractor that was run for 12 h. Best yield of oil (of 2.1%) was obtained when ultrasonication was the pre-treatment used followed by the extraction process with the solvent system of chloroform: methanol in the ratio 2:1. It was found that the extraction process was more efficient when the algal biomass was used in its dried and powdered form. The extracted oil when analyzed using GC–MS showed that the fatty acids, such as oleic acid (27.17%) and palmitic acid (21.75%) were found to be the major components. The molecular weight of the algal oil obtained was found to be 882.05 g/mol. The triglyceride content of *S. wightii* (collected in the month of January) was found to be 2.33% of its dried weight. In the second phase: the dried and powdered biomass (fresh algal biomass) when subjected to 500℃ for about 30 min underwent thermochemical decomposition process and resulted in the formation of bio-oil. Best yield of bio-oil obtained was 25% of the dried weight of the biomass. The so produced bio-oil was found to be a complex mixture of alcohols, ketones, aldehydes, fatty acids, esters, and nitrogen containing heterocyclic compounds. In the third phase: the oil-stripped biomass, which is a solid waste residue obtained in the first phase, was used as the biosorbent in the treatment of MB dye wastewater. The removal of dye from the aqueous solution by the algal biomass was investigated by varying the operating factors which influences biosorption process. The optimum conditions for the maximum removal of dye molecules were estimated. The maximum removal of MB dye was found to be of 99.955% at optimum conditions of solution: pH = 8.0; biosorbent dose = 0.5 g; contact time = 10 min; temperature = 30℃ for an initial MB dye concentration of 100 mg/L of 100 mL solution. Biosorption kinetic data followed the pseudo-second-order kinetic model. Biosorption of MB dye molecules by the algal biomass was controlled by both film and particle diffusion, which was explained by the intraparticle diffusion, Boyd kinetic, and SCM. Biosorption isotherm data were best explained by the Freundlich isotherm model, which indicates that the biosorption process may be of multilayer biosorption. The thermodynamic parameters indicate that the biosorption of MB dye molecules onto the algal biomass was found to be feasible, spontaneous, and exothermic in nature. The overall result of the present research showed that the algal biomass can be effectively utilized for the preparation of algal oil, bio-oil, and also the solid waste i.e. algal biomass, was successfully applied for the dye wastewater treatment.

Acknowledgment

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