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Optimization and kinetic studies on algal oil extraction from marine macroalgae *Ulva lactuca*

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ABSTRACT

In this present investigation, kinetic studies on oil extraction were performed in marine macroalgae *Ulva lactuca*. The algal biomass was characterized by scanning electron microscopy and Fourier Transform-Infra Red Spectroscopy. Six different pre-treatment methods were carried out to evaluate the best method for maximum oil extraction. Optimization of extraction parameters were performed and high oil yield was obtained at 5% moisture content, 0.12 mm particle size, 500 rpm stirrer speed, 55 °C temperature, 140 min time and solvent-to-solid ratio as 6:1 with 1% diethyl-ether and 10% methylene chloride in n-hexane solvent mixture. After optimization, 10.88% (g/g) of oil extraction yield was achieved from 30 g of algal biomass. The rate constant was obtained for the first order kinetic study by differential method. The activation energy (Ea) was calculated as 63.031 kJ/mol. From the results obtained in the investigation, *U. lactuca* biomass was proved to be a suitable source for the biodiesel production.

1. Introduction

Biodiesel seems to be a viable choice, but the most significant drawback is the cost of crop oils, that accounts for 80% of total operating cost, used for the biodiesel production (Demirbas, 2007). Biodiesel is usually produced from oleaginous crops such as rapeseed, soybean, sunflower and palm (Gouveia and Oliveira, 2009). Moreover, the availability of the oil crops serve as the sources for the biodiesel production are limited (Chisti, 2008). Therefore, it is necessary to find new feedstock suitable for biodiesel production, which does not drain on the edible vegetable oil supply. One alternative to the conventional oil crop is the algae because they contain oil, suitable for esterification/transesterification reaction for the biodiesel production.

Biodiesel production from algae is widely considered as one of the most efficient methods. It appears to represent the recent renewable source of oil that could meet the global demand for transport fuels (Miao and Wu, 2006). The occurrence of algal blooms greatly disturbs the ecosystems by modifying food chains and faunal community structure. The accumulation of algal biomass relocating natural communities of sea grasses and higher plants (Taylor et al., 1995). Similarly, macroalgal blooms cause changes in the main biogeochemical cycles of C, N, P and S (Viaroli et al., 2001).

As a result of this problem there is much attention needed to clean up the macro algae biomass. Hence this biomass is utilized for the production of biodiesel.

Only less information is available for the production of biodiesel from marine macro algae and limited research work was observed for the extraction of oil from marine macro algae.

Extraction is one of the fundamental processing steps used for recovering oil from biomass for the production of biodiesel. Various methods are available for the extraction of algal oil, such as mechanical, enzymatic, chemical extraction through different organic solvents and supercritical extraction. Solvent extraction is a common and an efficient technique for oil extraction. Solvent extraction involves the transfer of a soluble fraction from a solid material to a liquid solvent. Commercial grade n-hexane was used as a solvent for the extraction of oil from biomass for many years (Amin et al., 2010).

Ulva lactuca is a thin flat green algae. The margin is ruffled and often torn. The membrane is thick, soft and translucent, and also grows without a stipe. This species in the Chlorophyta is formed of two layers of cells irregularly arranged.

In this investigation, oil extraction from *U. lactuca* was studied. The main aim of the study was to find the efficiency of algal oil extraction using 6 different extraction methods and 12 different solvent systems. Optimization study for extraction was established with various parameters, such as moisture content, particle size, stirrer speed, extraction temperature, extraction time and solvent-to-solid ratio to obtain maximum oil extraction. The rate constant and activation energy was determined using the first order rate kinetics for the extraction of oil from *U. lactuca* biomass.

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2. Methods

2.1. Materials

Organic solvents of analytical grade (Extra pure 99%) were purchased from Merck Ltd., Mumbai, India. They were reused after preliminary distillation.

2.2. Collection of algal sample

U. lactuca belongs to green algae chlorophyta family. *U. lactuca* was collected from Rameswaram, Mandapam, South coast (Gulf of Mannar), India. The macroalgae was collected by hand picking from the intertidal and sub tidal regions. Sample collection was carried out during low tide period.

2.3. Preparation of U. lactuca algal biomass

The collected algae was brought to laboratory and it was washed with fresh water followed by distilled water to separate potential contaminants such as adhering impurities, sand particles, epiphytes and animal castings. The samples were spread for shade drying. The dried biomass was grounded and particle size distribution was determined using a sieve analyzer as per ASTM standards.

2.4. Characteristics of U. lactuca algal species

To gain further insight into the effect of the ultra sonic pre-treatment on the algal oil extraction, the microstructure of the algal biomass was analyzed with scanning electron microscopy (SEM, JEOL Ltd, Tokyo, Japan). The analysis was carried out for the algal biomass before and after treating with ultra sonication to identify the changes in the surface morphology. The presence of various functional groups in the algal biomass was analyzed using Fourier Transform Infra Red Spectroscopy (Spectrum RX1, US).

2.5. Sequence strategy for oil extraction from biomass

The extraction of oil from *U. lactuca* marine macro algal biomass was performed based on the following sequence: (a) pre-treatment was performed to destruct the algal cells with various methods to increase the efficiency of the extraction, (b) after destruction of algal cells and cell wall, the algal biomass was mixed along with solvent mixture placed in a temperature controlled extraction unit with a magnetic stirrer for agitation, (c) solvent systems were selected for oil extraction to increase the efficiency of oil extraction, (d) optimization study was carried out with various extraction parameters to achieve high oil yield, (e) the extraction parameters were optimized for the maximum oil extraction yield from algal biomass, and (f) kinetic study was carried out for the algal oil extraction from *U. lactuca* marine macro algae to determine the order of the reaction, reaction rate constant and activation energy for oil extraction.

2.6. Destruction of algal cells

Dry algal biomass of 30 g along with water (water to biomass ratio as 3:1) was taken into a 250 ml of conical flask. In order to compare the oil extraction yield with direct extraction using solvent, the following methods for destruction of algal cells were tested: (1) ultra sonication using ultra sonic probe at 24 kHz with constant temperature (50 °C ± 1) for 5 min, (2) heat treatment was performed using auto clave. The experimental conditions for autoclave method were maintained as temperature of 121 °C, pressure of 15 lbs and time duration of 5 min (Kasai et al., 2003), (3) deep freezing pre-treatment was carried out using deep freezer. The algal biomass sample was placed under freezing conditions at −20 °C, (4) microwave pre-treatment was conducted in the microwave oven for 5 min time duration at 100 °C, 500 W and 2455 MHz (Lee et al., 2010), (5) lyophilization was carried out at 4 °C under vacuum pressure (14 Pa) using lyophilizer and (6) bead-beater pre-treatment was performed with 1 mm glass beads at high speed of 1500 rpm. After pre-treatment, the algal biomass was separated from water by using filtration technique through filter paper. Then the algal biomass was dried in hot air oven to maintain specific moisture content (Kabutey et al., 2011). The different moisture content % (*MC*%) of the algal biomass obtained were calculated from Eq. (1) (Kabutey et al., 2011):

$$MC\ (\%) = \frac{M_i - M_f}{M_i} \times 100 \quad (1)$$

where M_i is weight of the sample in the initial state (g) and M_f is weight of the sample after drying (g).

The dried algal biomass with specific moisture content was allowed to mix with solvent mixture for the extraction of oil. After particular time of extraction, the slurry was transferred to a separating funnel to separate solvent–oil mixture and biomass. Solvent was separated from oil by distillation. All experiments were conducted with triplicate.

2.7. Solvent systems for oil extraction

After the destruction of algal cells by ultrasonication, 12 different solvent systems were used for oil extraction such as n-hexane, methyl tertbutyl ether, chloroform:methanol (1:1), n-hexane:ether (3:1), chloroform:methanol (2:1), 1% diethyl ether and 10% methylene chloride in n-hexane, chloroform:2 propanol (2:1), hexane:2 isopropanol (3:2), dichloromethane:methanol (1:1), dichloromethane:ethanol (1:1), acetone:dichloromethane (1:1) and hexane:ethyl alcohol (1:1). During the selection of solvent study, the solvent-to-solid ratio was maintained as 5:1 for the oil extraction from algal biomass.

2.8. Extraction experimental set up

Extraction set up mainly consists of a three necked round bottom flask (250 ml). The large neck in the middle of the flask was connected to a reflux condenser, a thermometer was placed in one of the two side necks and the third neck was used for taking samples during the extraction process. The flask was submerged in a temperature controlled water bath with magnetic stirrer.

2.9. Optimization of extraction parameters to enhance the oil yield

There are many factors influencing the oil extraction yield. The extraction parameters such as moisture content (2–6%), particle size (0.359–0.104 mm), stirrer speed (200–600 rpm), extraction temperature (35–65 °C), extraction time (20–160 min) and solvent-to-solid ratio (3:1–7:1) were optimized to increase the oil extraction yield.

2.10. Determination of oil extraction yield

Oil extraction yield was calculated with respect to time for different temperatures. The oil extraction yield (% w/w) was calculated using the following Eq. (2) (Gutierrez et al., 2008):

$$\text{Oil extraction yield}\ (\%) = \frac{\text{Weight of oil extracted (g)}}{\text{Weight of algal biomass (g)}} \times 100 \quad (2)$$