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Efficient algal lipid extraction via photocatalysis and its conversion to biofuel

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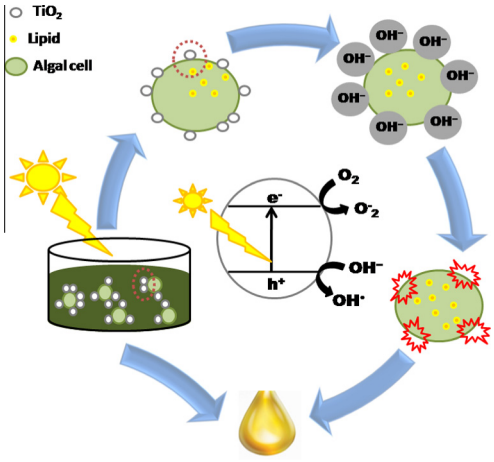
HIGHLIGHTS

- We report an efficient photocatalytic process for algal cell disruption leading to lipid release and thereby fuel generation.
- The method eradicates dewatering and drying steps required for conventional sustainable algal fuel production.
- This technique being economical, yields 52% of algal oil, on par with the existing pilot scale techniques.

GRAPHICAL ABSTRACT

Nanostructured semiconductor materials were used for photocatalytic algal cell membrane destruction leading to renewable algal oil production.



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ABSTRACT

Microalgae play an important role in energy production to solve the major energy crisis. The present study demonstrates an efficient and environmental friendly route for bio-oil extraction from wet *Nannochloropsis oculata* algal biomass through photocatalysis. The method uses abundant solar energy and catalytic amount of titanium dioxide photocatalyst for the rupturing of wet algal cells and reduces most of the cost by avoiding dewatering and drying, for algal oil production. The various spectroscopy and microscopy techniques used show destruction of algal cell membrane by the photocatalyst, with a release of 52.2% lipid yield. The obtained lipid by photocatalysis on esterification yields biofuel which is in complete agreement with results obtained from conventional techniques. Algal oil is converted to biofuel through acid catalyzed transesterification. Bio-oil and biofuel samples were analyzed by ATR-IR, NMR and GCMS. The physicochemical characterization of photocatalyst was carried out by

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Lipid
Transesterification

UV–Visible spectroscopy, XRD, EDS, BET and electron microscopy studies. The results suggest that the nanoparticles are efficient catalysts for rupturing the rigid micro algal cell membrane in an aqueous environment, using sunlight and hence prove to be a potential economic method for large scale bio-oil extraction.

1. Introduction

Steep increase in industrialization and human population are the two important concerns to add to the energy crisis and the world's economy has relied profoundly on fossil fuels as an energy source [1]. Liquid fuels derived from gas, coal or unconventional oil sources perhaps able to influence the input problem of diminishing oil supplies, but inevitably intensify the output problem of green house gas (GHG) emissions [2]. The International Energy Agency (IEA) has reported that world's primary energy need is projected to grow by 55% between 2005 and 2030 and on an average annual rate of 1.8% per year [3]. The existing renewable fuel and biofuel are censured for putting pressure on the global food markets, impacting water quality through extreme fertilizer use and driving undesired land-use causing deforestation. As a result, renewable energy and biofuel have drawn increasing interest, but they need to be produced in a sustainable manner in order to contribute to the reduction of fossil energy use and GHG emissions without adverse effects on biodiversity and food supply [4]. Such concerns have highlighted interest in developing advanced biofuels from more favorable feedstock such as algae [5–8] which overcome land use as well as food security issues due to their fast growth rate, flexible habitat preferences, superior productivity per cultured area, carbon sequestration, biodegradability and non toxicity, additionally the required global land mass essential to satisfy fossil fuel consumption can be reduced considerably [5,9–11]. The research has also proved that lipid content in microalgae is higher in contrast to terrestrial plants such as palm, rapeseed, soybeans or jatropha [12,13]. *Nannochloropsis oculata* (*N. oculata*) is one of the important marine microalgae which belongs to the genus Nannochloropsis and are considered as an emerging model to study algal biology, because of (a) their high growth rate (b) the availability of tools for genetic manipulation [14], and (c) their ability to accumulate large amounts of oil [15,16] (31–68% by dry weight) that makes them a promising candidate for biofuel production. Composition of *N. oculata* determined through proximate and ultimate analysis as reported by Rizzo et al. Proximate analysis is reported to have 6.0–7.0% of moisture and 13.2–26.4% of ash content. Ash content indicates the presence of inorganics in microalgae. The biomass exhibits C, H, N, O, S and P content with a slightly higher content of nitrogen. This implies that the residue may produce NO_x, chlorine oxides and SO_2 emissions but with a lesser quantity, which does not practically contribute to acid rain and destruction of the ozone layer, CO_2 emission of oil can be fixed by photosynthetic process of algae cultivation [17,18] (see Table 1).

In general, there are four key processes involved in algal biofuel production: microalgae cultivation, harvesting, cell wall disruption (lipid extraction) and transesterification of the lipid oil to fatty acid methyl esters (FAMEs). The conversion of algal biomass to biofuel is not efficient using the available technology [19]. Most of the conventional methods like solvent extraction, supercritical fluid extraction, microwave [20], ultrasonic assisted extraction, bead-beating, press/expeller, pyrolysis needs dry algal biomass, high temperature, long time or high energy inputs [21] for the extraction of lipid. But to get a gallon of dry algal biomass, 1000 gallons of dewatering is necessary, in addition to that physical or chemical pre treatment required for cell degradation to effectively remove lipids [22,23]. Extraction using aqueous algal solution without these steps is hence worthwhile to investigate and can equally address the problem of huge costs involved in biofuel extraction, opening a scope for new area of research to make it sustainable towards large scale production [24]. To overcome the above limitation a novel efficient photocatalysis method was designed to use the wet algal solution directly for oil extraction, excluding dewatering and drying.

Photocatalysis is an exponentially growing research field in nanoscience in the past decades, which utilizes nanometer scale photocatalyst and light for the chemical reaction. Titanium dioxide (TiO_2) is the most widely investigated photocatalyst due to its high photo-activity, low cost, low toxicity, good chemical and thermal stability [25], hence used in degradation of toxic chemical, bacterial disinfection, hydrogen generation and solar cells, etc. When TiO_2 absorbs light of wavelength smaller than its band gap energy, electron/hole (e^-/h^+) pair (exciton) will be generated and migrate to the surface of the semiconductor where reactive oxygen species (ROS) can be generated. These ROS are extremely powerful oxidants used in various applications like lysis of bacteria cell membrane and degradation of organic substances [26].

$$\left.\begin{aligned} &TiO_2 + h\nu \rightarrow e^- + h^+ \\ &h^+ + {}^-OH \rightarrow \cdot OH \\ &O_2 + e^- \rightarrow O_2^{-\cdot} \end{aligned}\right\} \quad (1)$$

Literature results show that nanomaterials inhibit the growth of algae cells and are toxic to algae [27,28]. Metzler et al. reported that Al_2O_3, SiO_2 and TiO_2 engineered nanoparticles are toxic to *Pseudokirchneriella subcapitata* (*P. subcapitata*) [29]. Some researchers also stated that nano-TiO_2 aggregates might entrap algal cells contributing to the toxic effects [30]. The present research article for the first time demonstrates the cell membrane disruption technique for the extraction of lipid from aqueous algal solution of *N. oculata* through photocatalysis using titanium dioxide (TiO_2) nanoparticles and sunlight with a lipid yield of 52.218%. The destruction of algal cell by ·OH radicals generated by nano-titania in the presence of solar energy in aqueous medium without dewatering reduces the energy consumption for the lipid extraction and produces renewable biofuel.

2. Experimental materials and methods

2.1. Material

$TiCl_4$ (99.5% Loba chemie, Boisar, Tarapur) was used as titanium precursor for the preparation of TiO_2. A pure culture of *N. oculata*

Table 1
Ultimate analysis of *N. oculata*.

Ultimate analysis	C (wt% dry)	H (wt% dry)	N (wt% dry)	S (wt% dry)	O (wt% dry)	P (wt% dry)
	48.2–58	6.9–8	7.5–8.6	0.2–0.4	25.7–23.2	0.6