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Effective utilization of azolla filiculoides for biodiesel generation using graphene oxide nano catalyst derived from agro-waste

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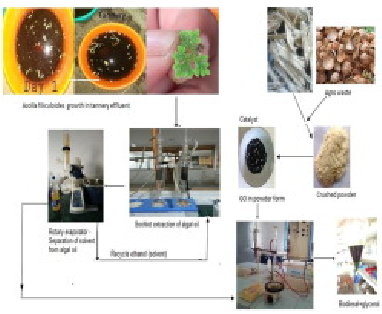
Abstract

A circular bioeconomy is concerned with environmental sustainability and waste valorization. Utilization of leftovers and trashes while elevating the value of biomass through the cascade is receiving greater attention in recent years. Biomass is expected to play a significant role in fixing global alternative fuel ambitions. Azolla, a type of macroalgae which grows very quickly, is employed to develop a self-sustaining Azolla biorefinery model. Tannery effluents are treated using the phytoremediation approach, and the algal oil extracted from the cultivated Azolla is employed to produce bio-diesel as an alternative energy source. Biodiesel is produced via the transesterification technique. N_2 sorption isotherms, scanning electron microscopy (SEM), FT-IR, and X-ray diffraction studies are used to evaluate the catalyst. The IR spectral analysis with the absorption bands corresponding to alkyl and ester stretching and bending modes of vibrations confirm biodiesel production. The reaction mechanism involved in the conversion process is proposed, and the process parameters such as the reaction temperature, oil-to-methanol molar ratio, and catalyst quantity are optimized. The results show that a catalyst loading of 2% (by weight) and a molar ratio of 1:9 produce a high biodiesel yield with GO as the catalyst at temperatures between 60 and 65 °C. Its ability to catalyze allowed for numerous cycles of repetitive use. The results show that employing GO as a catalyst to trans esterify Azolla oil to biodiesel is cost-effective and reliable.

Graphical abstract



Introduction

One of the most important aspects of economic progress is energy. As per the Global Energy Perspectives 2022, the global primary energy consumption is expected to triple by 2050 as the standard of living is growing. Renewable sources for energy is expected to become the new baseload, accounting for 50% of the power mix by 2030 and 85% by 2050. Fossil fuels are non-renewable resources on the verge of depletion and are in crisis. Because of the environmental impact of fossil fuels, the development of renewable liquid biodiesel has received a lot of interest as a possible replacement for petroleum-based fuels [1]. More studies are available for converting fossil fuels to bioethanol [2]. Liquid biodiesel is renewable and sustainable, similar to other renewable energy sources such as solar and wind. Biodiesel is the best alternative fuel for diesel engines [3]. In contrast, fossil fuels are not only non-renewable, but they also have other environmental negative impacts. Greenhouse gases such as CO and CO_2 are released during their burning. When ethanol is burnt, it produces CO_2. It is, nonetheless, considered carbon neutral [4]. This is because non-ethanol biomass feedstock absorbs CO_2. This indicates that burning biofuels does not contribute to greenhouse gas emissions. The conversion of residue of agrowaste to a valuable product is a budding opportunity for all researchers [5]. Azolla filiculoides is the only member of the genus and family Azollaceae in Africa and Asia. It's a scale-like freshwater fern with green to crimson fronds in bright light and winter [6]. It's especially widespread in on-farm dams and other still water bodies [7].

The plants are small and floating, yet they grow in vast mats and are often numerous. It has ready to use symbiotic cyanobacteria to fix nitrogen from the air. It can survive in water temperatures of 25–30°C, which is ideal for growth. Looking at the trichomes on the side of the leaves is the only way to tell this species apart from *Azolla filiculoides*. This species, previously known as *Azolla Caroliniana*, comprises *Azolla filiculoides* plants [8]. The common term “mosquito fern” comes from the belief that no mosquito can penetrate the fern's coating to lay its egg in water. It is widely grown as a commercial biofertilizer in southern and eastern Asia [9], [10]. It is appreciated for its nitrogen-fixing ability, which improves crop yield and minimizes the risk of using artificial fertilizers. They have a symbiotic connection with the cyanobacterium Anabaena Azollae, which fixes nitrogen in the atmosphere and provides vital nutrients to the plant [11]. The plant has been termed a “super-plant” because of its ability to colonize freshwater environments and develop rapidly, doubling its biomass every-two to three days. In reaction to various stimuli, such as strong sunshine and heat, most species show increased levels of deoxyanthocyanins [12]. Normal plants cannot survive in salinity, and even conditioned creatures die in salinity levels exceeding 5.5%.

Biomass may be a feasible alternative to fossil fuels as a natural feedstock for developing a sustainable pathway [13]. Energy and minerals from biomass/waste are critical to the bio-long-term economy's viability [14], [15]. Biomass is an honest feedstock for anaerobic digestion, and bio-mass devoid of oil can richly supply carbohydrates and proteins, allowing for value addition in various sectors [16]. Acidogenesis transforms many substrates into volatile fatty acids and green bio-hydrogen, including biomass and biodegradable organic wastes [17]. In this paper, a self-sustaining closed-loop model is developed with Azolla growing at the centre of the bio-refinery to holistically evaluate the production/conversion of the resulting biomass to value-added bio-based products [18].

A circular loop design with a step-by-step cascading technique has been investigated by combining several processes in a defined sequence. The study's overall objective is to construct a self-determining biomass-based refinery that will become a viable alternative to fossil-fuel refineries which emphasized added novelty in this research.

The phytoremediation activity of Azolla, where the wastewater is remediated and integrated with diverse bioprocesses, thereby making it a carrier, has been previously examined and published [19]. This study uses the biomass grown in tannery wastewater to develop a value-added bio-based product as a sustainable resource [20], [21], [22]. Furthermore, its biomass is utilized for making biodiesel and other fuels. The interconnection of this process in closed loop results in the most efficient use of the resource (biomass) and the production of a variety of bio-based products of commercial value [23]. The developed Azolla self-sustaining closed-loop system has a significant beneficial environmental impact [24], [25]. Compared with microalgae, which requires electricity, Azolla production and harvesting are considered cost-effective. Soxhlet extraction, which is commonly used and relatively inexpensive, is used to extract algal oil using ethanol. Acid catalyzed methylation of the extracted oil (FAMEs) transforms fatty acids

(FA), monoglycerides (MG), diglycerides (DG), and triglycerides (TG) into fatty acid methyl esters [26]. The transesterification process involves the interaction of a complex fatty acid or triglyceride molecule, where the removal of glycerin neutralizes the free fatty acids and produces an alcohol ester [27]. Using nanocatalysts with particular physical, chemical, and morphological features enable nanoscience and technology to boost biodiesel synthesis yield [28]. Epoxy, carboxylic, and hydroxyl groups are among the oxygen-rich functional groups that cover graphene oxide (GO). It is encouraging that solid GO catalysts for converting lipids can be made with simple separation and minimal corrosion. Safety evaluation is a crucial necessity that is inextricably linked to the formation of new technologies which would benefit the entire scientific needs. In order to assess the possible effects of graphene-based materials (GBMs) on both human health and the environment, researchers has expended a lot of time and energy. Furthermore, reduced size and improved surface area can produce more atoms/ molecules such that it could be exposed onto the surface compared to inner structure of the material. Perhaps, the quantity of atoms/molecules existing at the particle surface can determine the catalyst reactivity as well as biological efficiency which may result in unexpected toxicities. Hence, extreme care is maintained with respect to volume/surface area of GO nanocatalyst. The present work focuses on the kinetic studies of the algal biomass waste valorization into a renewable biofuel in the presence of a heterogeneous GO catalyst.

Section snippets

Materials and methods

Glasswares were acid washed before cleansing with a detergent solution and distilled water [29], [30]. The glasswares were dried for 20 min in a hot air oven. *Azolla filiculoides* algae were collected from the Aduthurai Rice Research Institute, Tamil Nadu. The solvents and reagents were of AR grade and were of high purity.…

Results and discussion

Since the yield of the oil content was higher, solvent extraction was chosen [36]. The last trace of oil couldn't be recovered using mechanical methods. The leftover cake included a lot of oil [37]. The extraction is performed several times using a syphon and the condenser by refluxing the ethanol. Refluxing was started after complete condensation of the vapour formed. The yield of the generated oil was calculated using the formula given below in Eq. (1).
$Oil\ Yield\ (in\,\%) = \frac{W_{oe}}{W_{cs}} X100$where Woe is the ...

Conclusion

The experimental results suggest that a 6.84 m^2/g GO nanocatalyst with a pore volume of 0.1118 cm^3/g, and a mean pore diameter of 8.8954 nm has outstanding catalytic activity and stability as a catalyst with a long lifetime. Under ideal process conditions of 1:9 oil to methanol molar ratio, 2.5 wt% GO nanocatalyst, 60–65 °C reaction temperature, and 120 min reaction time, the yield of Azolla oil transesterification approached 92%. The synthesized catalyst also outperformed the homogeneous…

CRediT authorship contribution statement

S. Sathish: Project administration, Conceptualization, Formal analysis, Software, Methodology, Validation, Writing - original draft, Writing - review & editing. **S. Supriya:** Conceptualization, Formal analysis, Software, Methodology, Validation, Writing – original draft, Writing - review & editing. **P. Andal:** Conceptualization, Formal analysis, Software, Methodology, Validation, Writing - original draft, Writing - review & editing. **D. Prabu:** Conceptualization, Formal analysis, Software,…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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> *Citation Excerpt :*
>
> …A. filiculoides belongs to the Salviniaceace family (Dohaei et al., 2020) while L. minor on the other side belongs to Lemnaceae family (Ifayefunmi et al., 2021). Both plants have the ability to grow fast (Sathish et al., 2022) with high growth rate of 0.5 day−1 and doubling biomass time of 2 days (Chakrabarti et al., 2018; Dohaei et al., 2020). The experiment was performed in the laboratory at a temperature range from 21–27 °C at Universiti Kebangsaan Malaysia.…

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