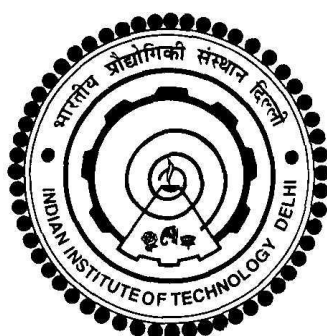


**DEVELOPMENT OF ALGAL BIOFILM REACTOR FOR
WASTEWATER TREATMENT INTEGRATED WITH
HYDROPYROLYSIS FOR A SUSTAINABLE BIOREFINERY**

POONAM CHOUDHARY



**CENTRE FOR RURAL DEVELOPMENT & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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by

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CENTRE FOR RURAL DEVELOPMENT & TECHNOLOGY

submitted

in fulfillment of the requirements of degree of Doctor of Philosophy

to the



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CERTIFICATE

This is to certify that the thesis entitled “**Development of algal biofilm reactor for wastewater treatment integrated with hydrolysis for a sustainable biorefinery**”, being submitted by **Ms. Poonam Choudhary** to the Indian Institute of Technology Delhi for the award of “**Doctor of Philosophy**” is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge the results contained in this thesis have not been submitted in part or full to any other university or institute for award of any degree or diploma.

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ABSTRACT

The present study attempted to address major limitations hindering feasibility of algal biofuels by developing an algal biorefinery process involving cost-effective cultivation, *in situ* harvesting and efficient biomass conversion with balanced energy and nutrient recovery. To begin with, preliminary screening of fourteen algae in standard medium (BG11), followed by secondary screening of selected species under diverse wastewaters was done. *Chroococcus* sp.1 and *Scenedesmus* dominated consortium (PA1) was found to be suitable for biomass production and treatment of low strength grey water while consortium PA6 (*Chlorella* and *Phormidium*) with highest biomass concentration (1.5-2.2 g L⁻¹) as well as nutrient removal efficiency (80-95%) was outstanding performer for difficult high strength wastewaters viz livestock wastewater (LSW) and anaerobically digested slurry (ADS). LSW and ADS were the most favorable media for algal growth and can efficiently reduce the algae cultivation cost by replacing expensive nutrient medium.

In order to overcome the limitations of low cell density and subsequent biomass harvesting of suspended culture, the next attempt was targeted to design a cultivation system with *in situ* harvesting. Two inclined algal biofilm reactors (ABR), fiber sheet based lab scale (L-ABR) and bamboo based (B-ABR) were made with all waste, locally available and recyclable materials (except pumps). They were further tested to identify suitable attachment material and optimum biomass harvest frequency. Among five biofilm support materials, non-woven spun bond fabric (70 GSM) was selected as suitable choice for biofilm attachment material based on its attachment efficiency, durability, global availability and cost. With highest biomass productivity (2.18 g m⁻²d⁻¹) as well as biofilm thickness (332.28 μm), 6 day biomass harvest frequency was optimized. Further, the performance of pilot scale algal biofilm reactor (P-ABR) was evaluated for six months and results showed a stable long term operation with biomass productivity varying from 16.8 g m⁻²d⁻¹ to 20 g m⁻²d⁻¹. Next study was focused on assessment of developed reactor to produce algal biomass and treat variable strength wastewater without any design modifications for specific wastewater. As compared to suspended cultivation, ABR resulted in high biomass potential as well as improved nutrient removal efficiency especially in high strength wastewaters like LSW and ADS and avoided the need for dilution or pretreatment of wastewater. The characterization of wastewater grown biomass indicated potential application for biomethane, livestock feed and bio fertilizers production.

Considering the high conversion efficiency to produce multiple products of varied application potential, hydrolysis (HyPy) was selected as appropriate route for bioconversion of ABR grown biomass. The effect of temperature and catalyst on yield and quality of hydrolysis products was investigated in detail, which indicated highest yield of biocrude (42%) at 200 °C using K₂CO₃ catalyst. A comparative assessment of the ZSM-5 and K₂CO₃ and their catalytic efficiencies in terms of yield and recovery showed that a combination of K₂CO₃ and moderate temperature could be the ideal choice for high biocrude yield while ZSM-5 with high temperature is suitable for high gas yield. Moreover, ZSM-5 catalysed reaction produced biocrude rich in organic acids at low temperature (150-200 °C) and hydrocarbons at higher temperature (250-300 °C). The major compounds identified in K₂CO₃ reaction were phenol (33%), benzaldehyde (22%) and acetophenone (11%) at (150-200 °C) and nitrogenous compounds like piperidinone (21%), pyrazine (23%), and pyrrole (10%) and hydrocarbons (25%) at higher temperatures (250-300 °C). On the basis of results the possible mechanism of hydrolysis catalysed by alkaline K₂CO₃ and acidic ZSM-5 was also elucidated. Further optimization studies using response surface methodology showed operational parameters : 230 °C (temperature), 27 kg cm⁻² (pressure), 20 min (reaction time) and 6 as W/B ratio as optimal conditions for the maximum biocrude yield (~ 45 %). In order to maximize the output from HyPy, co-products (aqueous and solids) were also assessed for recovery of nutrients as well as energy. Aqueous fraction being rich in amides, amines, alkaloids, sugars, organic acids and peptides, indicated potential source for recovery of nutraceutical compounds. The assessment of solids showed its suitability as biogas feedstock with improvement in biomethane yield from 106 to 200 mL gVS⁻¹. Finally, energetic feasibility of algal biofilm based three conversions routes, namely hydrolysis (HyPy), anaerobic digestion (AD) and coupling of the two (HyPy-AD) was compared. With highest net energy recovery (NER=2.3) and negative CO₂ emission value (-180 g), sequential biomass conversion by hydrolysis and anaerobic digestion (HyPy-AD) was found to be most appropriate conversion energetically and ecologically. Finally, an algal biorefinery based on present findings was suggested as a one stop shop for generation of fuels, chemicals and value added products accompanied with wastewater treatment and recycling of CO₂.

सार

वर्तमान अध्ययन में एक शैवाल बायोरेफ़ाइनरी प्रक्रिया विकसित करके शैवाल द्वारा जैव ईंधन की व्यवहार्यता में बाधा रखने के लिए प्रमुख सीमाओं को हल करने का प्रयास किया, जिसमें स्थिर ऊर्जा और पोषक तत्व वसूली के साथ स्वस्थानी कटाई और कुशल बायोमास रूपांतरण शामिल हैं। आरंभ करने के लिए, मानक माध्यम (बीजी 11) में चौदह शैवाल की प्रारंभिक स्क्रीनिंग, विभिन्न उपनिवेशों के तहत चयनित प्रजातियों की माध्यमिक स्क्रीनिंग के बाद किया गया था। चैरोकोकस एसपीए 1 और स्केंडेसमस वर्चुअल कंसोर्टियम (पीए 1) बायोमास उत्पादन और कम ताकत वाले भूरे रंग के पानी के लिए उपयुक्त साबित हुआ जबकि कंसोर्टियम पीए 6 (क्लोरेला और फोर्मिडियम) में उच्च बायोमास एकाग्रता (1.5-2.2 ग्राम एल -1) के साथ ही साथ पोषक तत्व हटाने की दक्षता (80-95%) मुश्किल उच्च शक्ति अपशिष्ट जल के लिए उत्कृष्ट कार्यकर्ता थी, जैसे पशुधन अपशिष्ट जल (एलएसडब्ल्यू) और एनारोबिक रूप से पचाने वाली घोल (एडीएस)। एलएसडब्लू और एडीएस अलग विकास के लिए सबसे अनुकूल मीडिया थे और महंगी पोषक माध्यम की जगह के द्वारा शैवाल खेती की लागत को कुशलता से कम कर सकते हैं।

कम सेल घनत्व की सीमाओं और निलंबित संस्कृति के बाद के बायोमास संचयन की सीमाओं पर काबू पाने के लिए, अगले प्रयास को एक स्वस्थानी कटाई के साथ एक खेती प्रणाली तैयार करने का लक्ष्य रखा गया। दो झुका हुआ अल्वल बायोफ़िल्म रिएक्टर (एबीआर), फाइबर शीट आधारित लैब स्केल (एल-एबीआर) और बांस आधारित (बी-एबीआर) सभी अपशिष्ट, स्थानीय रूप से उपलब्ध और रीसाइक्लेबल सामग्री (पंपों को छोड़कर) के साथ बनाया गया था। उन्हें उपयुक्त लगाव सामग्री और इष्टतम बायोमास फसल की आवृत्ति की पहचान करने के लिए आगे परीक्षण किया गया। पाँच बायोफ़िल्म समर्थन सामग्री में, गैर-बुना काता बंधन कपड़ा (70 जीएसएम) को इसके लगाव दक्षता, स्थायित्व, वैश्विक उपलब्धता और लागत के आधार पर बायोफ़िल्म लगाव सामग्री के लिए उपयुक्त विकल्प के रूप में चुना गया था। उच्चतम बायोमास उत्पादकता (2.18 ग्राम एम -2 डी -1) के साथ ही साथ बायोफ़िल्म मोटाई (332.28 माइक्रोन), 6 दिन की बायोमास फसल आवृत्ति अनुकूलित थी। इसके अलावा, पायलट स्केल अल्वल बायोफ़िल्म रिएक्टर (पी-एबीआर) का प्रदर्शन छह महीने के लिए मूल्यांकन किया गया था और परिणामों से बायोमास उत्पादकता के साथ एक स्थिर दीर्घकालिक संचालन दिखाया गया है जो कि 16.8 ग्राम-2 डी -1 से 20 ग्राम-2 डी -1 अगले अध्ययन में विकसित किए गए रिएक्टर के मूल्यांकन पर ध्यान केंद्रित किया गया था ताकि जैविक गैस का उत्पादन किया जा सके और विशिष्ट अपशिष्ट जल के लिए किसी भी डिजाइन संशोधनों के बिना चर शक्ति अपशिष्ट जल का इलाज किया जा सके। निलंबित खेती की तुलना में, एबीआर के परिणामस्वरूप उच्च बायोमास क्षमता और बेहतर पोषक तत्व हटाने की दक्षता विशेष रूप से एलएसडब्लू और एडीएस जैसे उच्च शक्ति अपशिष्ट जल में हुई और अपशिष्ट जल के कमजोर पड़ने या प्रीटैराइटमेंट की आवश्यकता से बचने के लिए। अपशिष्ट जल के बायोमास के लक्षण वर्णन में बायोमेथेन, पशुधन और जैव उर्वरक उत्पादन के लिए संभावित अनुप्रयोगों का संकेत दिया गया है।

विविध अनुप्रयोग क्षमता के कई उत्पादों का उत्पादन करने के लिए उच्च रूपांतरण दक्षता को देखते हुए, हाइड्रोपोलिसिस (हाईपी) को एबीआर की बढ़ी हुई बायोमास के बायोकॉनवर्जन के लिए उचित मार्ग के रूप में चुना गया था। तापमान और उत्प्रेरक का प्रभाव और हाइड्रोपोलिसिस उत्पादों की गुणवत्ता पर विस्तार से जांच की गई, जिसने जैविक ईंधन (42%) का अधिकतम 200 डिग्री सेल्सियस K_2CO_3 उत्प्रेरक का उपयोग करते हुए संकेत दिया। उपज और वसूली के मामले में जेडएसएम -5 और के 2 सीओ 3 की तुलनात्मक आकलन और उनकी उत्प्रेरक क्षमता से पता चला है कि के 2 सीओ 3 और मध्यम तापमान का संयोजन उच्च जैविक ईंधन उत्पादन के लिए आदर्श विकल्प हो सकता है जबकि उच्च तापमान के साथ ZSM-5 उच्च गैस के लिए उपयुक्त है प्राप्ति। इसके अलावा, उच्च तापमान (250-300 डिग्री सेल्सियस) पर कम तापमान (150-200 डिग्री सेल्सियस) और हाइड्रोकार्बन पर कार्बनिक अम्लों में समृद्ध जैविक ईंधन उत्पन्न करने वाले ZSM-5 उत्प्रेरित प्रतिक्रिया। के 2 सीओ 3 प्रतिक्रिया में पहचान की गई प्रमुख यौगिकों में फिनोल (33%), बेंजाल्डीहाइड (22%) और एसीटोफेनोन (11%) (150-200 डिग्री सेल्सियस) और नाइटरोजेन यौगिकों जैसे पाइपरडाइनोन (21%), पैराजिना (23%), और उच्च तापमान (250-300 डिग्री सेल्सियस) में पायरोला (10%) और हाइड्रोकार्बन (25%) परिणामों के आधार पर क्षारयुक्त K_2CO_3 और अम्लीय ZSM-5 द्वारा उत्प्रेरित हाइड्रोपोलिसिस के संभव तंत्र को भी स्पष्ट किया गया था। प्रतिक्रिया की सतह पद्धति का उपयोग करते हुए आगे के अनुकूलन अध्ययनों में परिचालन मापदंडों का पता चला: 230 ° C (तापमान), 27 किलो सेमी-2 (दबाव), 20 मिनट (प्रतिक्रिया समय) और 6 डब्ल्यू / बी अनुपात के रूप में अधिकतम जैविक ईंधन (~ 45%) HyPy से उत्पादन को अधिकतम करने के लिए, पोषक तत्वों के साथ-साथ ऊर्जा की वसूली के लिए सह-उत्पादों (जलीय और ठोस) का भी मूल्यांकन किया गया। अक्सास अंश अमिडम, एमाइंस, एल्किलॉइड, शक्कर, कार्बनिक एसिड और पेप्टाइड्स में समृद्ध है, न्यूट्रेशनल यौगिकों की वसूली के लिए संभावित स्रोत का संकेत मिलता है। ठोस पदार्थों के मूल्यांकन में बायोगैस फीडस्टॉक के रूप में अपनी उपयुक्तता को दिखाया गया है जिससे बायोमेथेन पैदावार में सुधार 106 से 200 एमएल जीवीएस -1 होता है। एल्वैल बायोफिल्म के तीनों रूपांतरण मार्गों, अर्थात् हाइड्रोपोलिसिस (हायपी), एनेरोबिक पाचन (एडी) और युग्मन दो (HyPy-AD) तुलना की गई थी। उच्चतम शुद्ध ऊर्जा वसूली (एनईआर = 2.3) और नकारात्मक CO_2 उत्सर्जन मूल्य (-180 ग्राम) के साथ, हाइड्रोपोलिसिस और एनारोबिक पाचन (हायपी ईड) द्वारा अनुक्रमिक बायोमास रूपांतरण ऊर्जावान और पारिस्थितिक रूप से सबसे उपयुक्त रूपांतरण पाया गया था। अंत में, वर्तमान निष्कर्षों के आधार पर एक अल्ट्रा बायोरेफ़ाइनर का सुझाव दिया गया था कि ईंधन, रसायन और मूल्यवर्धित उत्पादों के उत्पादन के लिए एक स्टॉप शॉप के रूप में अपशिष्ट जल उपचार के साथ CO_2 के पुनर्चक्रण हो सकता है।

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