THIN FILM ADVANCED OXIDATION MEDIATED PRETREATMENT FOR COST EFFICIENT BIOFUEL PRODUCTION AND SLUDGE MANAGEMENT

A THESIS

Submitted by

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in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

FACULTY OF CIVIL ENGINEERING

ANNA UNIVERSITY

CHENNAI 600 025

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CENTRE FOR RESEARCH

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CERTIFICATE

This is to certify that all corrections and suggestions pointed out by the Indian /Foreign Examiner(s) are incorporated in the Thesis titled " Thin film advanced oxidation mediated pretreatment for cost efficient biofuel production and sludge management " submitted by Mr./Ms. Godvin Sharmila.V

J. Rajesh
Signature of the Supervisor

Place : Tirunelveli

Date : 4/11/2019

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Proceedings of the Ph.D. Viva-Voce Examination of Mr./Ms.Godvin Sharmila.V held at 11:00 AM on 04.11.2019 in Conference Hall Anna University Regional Campus Tirunelveli 627007

The Ph.D. Viva-Voce Examination of Mr./Ms.Godvin Sharmila.V (Reg. No. 16241897103) on his/her Ph.D. Thesis Entitled " Thin film advanced oxidation mediated pretreatment for cost efficient biofuel production and sludge management " was conducted on **04.11.2019** at 11:00 AM in the Conference Hall Anna University Regional Campus Tirunelveli 627007.

The following Members of the Oral Examination Board were present:

1.	Dr. P Sivagurunathan,Research Officer,Department of Bioenergy Research,Indian Oil Corporation Limited,R and D Center Faridabad Haryana - 121 007 India	Indian Examiner
2.	Dr. P Sivashanmugam,Professor,Department of Chemical Engineering,National Institute of Technology,Tiruchirappalli - 620 015	Subject Expert
3.	Dr. Rajesh Banu.J,Assistant Professor, Department of Civil Engineering, Regional Center of Anna University,Tirunelveli	Supervisor

The research scholar, Mr./Ms. Godvin Sharmila.V presented the salient features of his/her Ph.D. work. This was followed by questions from the board members. The questions raised by the Foreign and Indian Examiners were also put to the scholar. The scholar answered the questions to the full satisfaction of the board members.

The corrections suggested by the Indian/Foreign examiner have been carried out and incorporated in the Thesis before the Oral examination.

Based on the scholars research work, his/her presentation and also the clarifications and answers by the scholar to the questions, the board recommends that Mr./Ms.Godvin Sharmila.V be awarded Ph.D. degree in the **Faculty of Civil Engineering**.

4/11/2019

Indian Examiner

Dr. P. Sivagurunathan
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4/11/2019

Subject Expert

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CERTIFICATE

The research work embodied in the present Thesis entitled **"THIN FILM ADVANCED OXIDATION MEDIATED PRETREATMENT FOR COST EFFICIENT BIOFUEL PRODUCTION AND SLUDGE MANAGEMENT"** has been carried out in the Department of Civil Engineering, Anna University Regional Campus, Tirunelveli. The work reported herein is original and does not form part of any other thesis or dissertation on the basis of which a degree or award was conferred on an earlier occasion or to any other scholar.

I understand the University's policy on plagiarism and declare that the thesis and publications are my own work, except where specifically acknowledged and has not been copied from other sources or been previously submitted for award or assessment.

GODVIN SHARMILA V
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ABSTRACT

Proper management of the huge amount of waste activated sludge (WAS) generated during the conventional treatment of dairy wastewater is nowadays a major environmental issue. Recently, intensive efforts have been made for the development of innovative technologies to treat sludge resourcefully. Proper treatment and disposal of sludge is a substantial task around the biosphere. To address this issue, the chemo mediated EPS (Extracellular Polymeric Substances) extraction was utilized to enhance pretreatment for anaerobic digestion is investigated in this sludge treatment technique.

Anaerobic treatment of sludge is an utmost extensively used method which has a benefit of methane generation and sludge reduction. The degradation of complex macrobiotic substances in WAS is restricted during the hydrolysis step. Various pretreatment process such as physical mechanical, chemical and biological are adopted to overcome hydrolysis, the rate-limiting step of biomethanation. The complex extracellular polymeric substances (EPS) existences in biomass hinder hydrolysis of the substrate. Exclusion of EPS followed by pretreatment improves substrate hydrolysis. AOP (Advanced Oxidation Process) is an emerging method and currently, its usage in EPS extraction is attracting the attention of researchers. It has an advantage of least energy input, eco-friendly process without pollution, and non-toxic by-products.

The present exploration provides the outcomes of the process such as photocatalyst immobilization (TiO_2 and ZnO), de-aggregation, immobilized photocatalyst pretreatment and bacterial pretreatment of WAS achieved during lab-scale analysis. The dairy waste activated sludge sample was collected from the Aavin dairy industry, Madurai, India. (13°6′35.172″ N, 80°9′530856″ E).

In the first phase, an attempt has been made to pretreat the de-aggregated sludge through thin layer immobilized titanium dioxide (TiO_2) as photocatalyst under solar irradiation. The de-aggregation of sludge was carried out by 0.05 g/g SS sodium citrate aiming to facilitate more surface area for subsequent TiO_2 mediated pretreatment. The proposed mode of pretreatment was investigated by varying TiO_2 dosage and time. The maximum COD solubilization of 18.34% was obtained in the optimum 0.4 g/L of TiO_2 dosage and exposure time of 40 min. Anaerobic assay of pretreated samples confirms the role of de-aggregation in methane yield was found to be higher in de-aggregated (0.158 g COD/g COD) than the pretreated sludge (0.102 g COD/g COD). Moreover, the proposed method (net cost for control - net cost for de-aggregation) saves sludge management cost of about 89.47% with 53.5% of suspended solids (SS) reduction.

In the second phase, sodium citrate induced exopolymer extraction on the photocatalytic thin film (TiO_2) pretreatment efficiency of waste activated sludge (WAS) was carried out. The optimized dosage of sodium citrate of 0.05 g/g SS was utilized to remove the exopolymer. The exopolymer removal of 94.2% promotes better disintegration. Then, TiO_2 was immobilized through DC spluttering method followed by the annealing process. This TiO_2 thin film efficiently extricates the intracellular components of de-aggregated sludge at 60 min increasing the solubilization to 19.33%. As a result, the de-aggregated sludge sample yields high methane generation of 0.168 g COD/g COD which was comparatively higher than the other (pretreated sludge without exopolymer removal - 0.112 g COD/g COD and raw sludge without treatment - 0.075 g COD/g COD). The methane generated during sodium citrate induced TiO_2 thin film pretreated sludge was 340 kWh during energy balance. In the cost analysis, it gives net cost of -1614 ₹/ton of sludge. In addition, the proposed method also accounts 54.6% of solid reduction.