

**SLUDGE REDUCTION BY ADVANCED
OXIDATION – FENTON AND MODIFIED
FENTON PROCESSES THROUGH
DEFLOCCULATION USING CITRIC ACID**

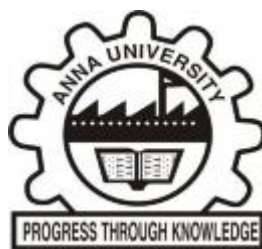
A THESIS

Submitted by

AMUDHA V

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY



FACULTY OF SCIENCE AND HUMANITIES

ANNA UNIVERSITY

CHENNAI 600 025

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CENTRE FOR RESEARCH
ANNA UNIVERSITY, CHENNAI-600 025



CERTIFICATE

This is to certify that all corrections and suggestions pointed out by the Indian /Foreign Examiner(s) are incorporated in the Thesis titled " SLUDGE REDUCTION BY ADVANCED OXIDATION - FENTON AND MODIFIED FENTON PROCESSES THROUGH DEFLOCCULATION USING CITRIC ACID " submitted by Mr./Ms. Amudha.V

J. Rajesh
Signature of the Supervisor

Place : *Tiruchelvi*

Date : *18/08/17*



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Proceedings of the Ph.D. Viva-Voce Examination of Mr./Ms. Amudha.V held at 11:00 AM on 18.08.2017 in Anna University Regional Campus Tirunelveli

The Ph.D. Viva-Voce Examination of Mr./Ms. Amudha.V (Reg. No. 1424789108) on his/her Ph.D. Thesis Entitled " SLUDGE REDUCTION BY ADVANCED OXIDATION - FENTON AND MODIFIED FENTON PROCESSES THROUGH DEFLOCCULATION USING CITRIC ACID " was conducted on 18.08.2017 at 11:00 AM in the Anna University Regional Campus Tirunelveli.

The following Members of the Oral Examination Board were present:

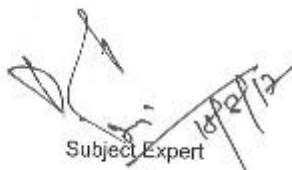

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|---|-----------------------|
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The research scholar, Mr./Ms. Amudha.V presented the salient features of his/her Ph.D. work. This was followed by questions from the board members. The questions raised 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 scholar's research work, his/her presentation and also the clarifications and answers by the scholar to the questions, the board recommends that Mr./Ms. Amudha.V be awarded Ph.D. degree in the **Faculty of Science and Humanities**.


 Indian Examiner
 (DR. S. T. RAMESH)


 Subject Expert
 Dr. M. Rajkumar

 Supervisor & Convenor
 (DR. J. RAJESH BANU)

ANNA UNIVERSITY**CHENNAI 600 025****CERTIFICATE**

The research work embodied in the present Thesis entitled “**SLUDGE REDUCTION BY ADVANCED OXIDATION – FENTON AND MODIFIED FENTON PROCESSES THROUGH DEFLOCCULATION USING CITRIC ACID**” has been carried out in the Department of Civil Engineering, Regional Centre of Anna University, 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.

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ABSTRACT

In recent years, generation of waste activated sludge (WAS) increased in huge quantity from urban waste water treatment plants. Now a days, municipal waste water treatment is mandatory, as it reduces the organic matter and pathogens, before it discharged to water sources. Disposal of excess sludge from the waste water treatment plants (WWTP) had become a serious environmental problem. Therefore sludge treatment is necessary before its final disposal. The fundamental problem faced by industries and municipal WWTP is treatment and disposal of sludge, which occupies as most expensive part of waste water treatment. Conventional activated sludge process is normally employed in many of the WWTPs due to their easy operation, high treatment efficiency and low operational cost. The major drawback of this method is production of excess sludge.

Advanced oxidation processes (AOPs) is one of the pioneering techniques for waste water treatment. Many researchers elaborated the methods based on AOPs of contaminants. The Fenton reaction has attracted greater attention due to its unique advantages such as eco-friendliness and minimization of the excess sludge. The organic polymers of Extracellular polymeric substances (EPS) are positioned about the cell surface. Flocculant characteristic of activated sludge is due to the presence of EPS, which are accountable for the formation of microbial colonies and protection of microbial cells from external factors. Thus, removal of EPS from sludge matrix can enhance biomass solubilization. There are only limited studies which explore deflocculation prior to treatment methods. However deflocculation prior to Fenton treatment has not been documented in literature so far. The present study focuses on investigating the efficiency of deflocculation in the subsequent treatment. Thus, in the present study, a novel

and new method is adopted to improve the efficiency of Fenton's treatment process through deflocculation of sludge.

The present study affords the consequences attained from laboratory scale experiments of deflocculation using citric acid and different sludge reduction methods such as Fenton and modified Fenton processes. The WAS was collected from municipal WWTP at Trivandrum, Kerala.

At first phase, effective deflocculation of sludge was studied in detail. Deflocculation is achieved by removing the divalent cations tightly holding the EPS with sludge using citric acid as a cation binding agent. Effective deflocculation with negligible cell cleavage was achieved at 0.06 g/g SS citric acid dosage.

At second phase, Fenton treatment for sludge reduction through the implication of a deflocculating agent citric acid was studied in detail. Fenton optimization studies using Response Surface Methodology (RSM) revealed that 0.5 g/g SS and 0.0055 g/g SS were the optimal dosages of H_2O_2 and Fe^{2+} for 30 minutes oxidation time. The addition of a cation binding agent set the pH value of sludge to 5 which did not affect Fenton efficiency. The results presented in this study shows the advantage of deflocculating the sludge as Chemical Oxygen Demand (COD), Suspended Solids (SS) and Volatile Suspended Solids (VSS) reduction were observed to be higher in the deflocculated (72%, 53% and 63%) than in the flocculated sludge (34%, 22% and 35%). Kinetic investigation of the treatment showed that the rate of the reaction was four times higher in deflocculated sludge than the flocculated. The methodology reported in this manuscript was successfully applied to a real case where the deflocculated mediated Fenton process reduced the sludge disposal cost in Indian rupees from 20250 to 4224 per ton of sludge.

At third phase, for the excess sludge reduction by modified Fenton process (MFP) using zero valent iron (ZVI, Fe^0) as a catalyst under the influence of sludge deflocculation was studied in detail. The optimization of operational parameters such as pH, initial dosages of Fe^0 and H_2O_2 , and time were performed elaborately for the MFP by RSM. The optimum conditions have been found as Fe^0 dosage of 0.006 g/g SS, H_2O_2 dosage of 0.5 g/g SS and pH value of 3.5 with 50 minutes oxidation time period. The benefit of deflocculation was evident from the study as deflocculated sludge undergoing MFP produced higher reduction percentage of COD, SS and VSS (76%, 52% and 65%) than the flocculated (38%, 25% and 39%). Kinetic analysis proves that the rate was four times higher in the deflocculated sludge. The unsolved ZVI can be separated easily from the reaction mixture using magnet to avoid iron contamination in the treated sludge at the end of the process. Cost analysis revealed that ZVI mediated Fenton process through deflocculation reduced the sludge disposal cost in Indian rupees from 20250 to 4275 per ton of sludge.

At last, the comparison of different treatment methods was made in terms of reduction percentage of COD, SS and VSS in its optimized condition. Economic applicability also compared for both the treatment methods in terms of solids removal efficiency. Based on the outcome of the present study, it was concluded that the deflocculation prior to the both Fenton and modified Fenton processes enhances the sludge reduction potential and zero valent iron is a potential substitute for the ferrous salt in the modified Fenton process.