

**CHEMICAL AND BIOLOGICAL TREATMENT OF WASTEWATER  
FROM  
N, N'-DINITROSOPENTAMETHYLENETETRAMINE  
MANUFACTURING INDUSTRIES**

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JANUARY 2019**

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**CHEMICAL AND BIOLOGICAL TREATMENT OF WASTEWATER  
FROM  
N, N'-DINITROSOPENTAMETHYLENETETRAMINE  
MANUFACTURING INDUSTRIES**

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**JANUARY 2019**

# Certificate

This is to certify that the thesis entitled “**Chemical and Biological Treatment of Wastewater from N, N’- Dinitrosopentamethylenetetramine Manufacturing Industries**” which is being submitted by **Mandeep Kumar** in fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** to the Indian Institute of Technology; Delhi, India is a record of bonafide research work carried out by him under my supervision and guidance. The thesis fulfils the requirements relating to the nature and standard of work prescribed for the award of Doctor of Philosophy degree. To the best of my knowledge, the research work incorporated in this thesis has not been submitted to any other University or Institute for the award of any other degree or diploma.

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## Acknowledgements

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The work described in this thesis was mostly performed at the Environmental Engineering Laboratory of Indian Institute of Technology, Delhi. A journey is easier when you travel together. Interdependence is certainly more valuable than independence. This thesis is the result of seven years of work whereby I have been accompanied and supported by many people. It is a pleasant aspect that I have now the opportunity to express my gratitude for all of them.

My mind is filled with memories of those who helped me in this venture and have a place in my heart. First of all, I take this opportunity to express my recondite sense of gratitude and indebtedness to the supervisor of my thesis, **Dr. A. K. Mittal**. A true friend, philosopher and guide, his constant and continuous encouragement has been the source of inspiration throughout my research of work. I am really glad that I have come to get know **Dr. Mittal** in my life.

I would like to express my sincere thanks to **Dr. A. K. Nema** and **Dr. Gazalla Habib** the coordinators of Environmental Engineering and management group in the Department of Civil Engineering, IIT, Delhi for providing me all facilities in the Environmental Laboratory for smooth completion of my research work. I acknowledge my deep sense of gratitude to all the members of my doctoral scrutiny committee, **Dr. B. Alappat, Dr. T. R. Sreekrishnan, Dr. K. C. Iyer** and also to the other faculty members for their valuable support, suggestions and encouragement.

I am exceptionally thankful to Dr. Sanjay Gupta, Mr. Vikram, Mr. Rajveer Gupta and Mr Ishwar Singh for their pain taking efforts in experimental set-up as well as their continuous encouragement during my stay in this institute. Without them, reactor set-up as well and analytical tests would have been much more difficult and time consuming.

I would remiss if I did not acknowledge the help and entertainment provided by M. Tech students, junior and senior research scholars. They always had time for me and a few things to say if I was willing to listen.

Management support and constant encouragement from my friends played a great part in the completion of my research work. I am profoundly grateful to all my friends Mr. Pravin Mutiyar, Miss. Vijya Singh, Mr. Santosh Kolte, Mr. Jai Prakash, Mr. Burni and Mr. Gorve, for their constant help in various stages and also for making my stay enjoyable throughout the research period.

I thank Govt. of Himachal Pradesh Irrigation and Public Health Department, giving me the opportunity to pursue the Doctorate of Philosophy at Department of Civil Engineering, Indian Institute of Technology Delhi.

Last but not least, the successful completion of this research work is attributed to the dedicated support of my mother, my wife and children, who have been a major source of motivation and strength during my endeavour.

Mandeep Kumar

## Abstract

The present study focuses on developing a cost effective option of integrated chemical and biological treatment of wastewater from N, N'- Dinitrosopentamethylenetetramine manufacturing industry and using hexamine (HMT) as a constituent of their product which has come up at Baddi in district Solan, of the state of Himachal Pradesh, India. Hexamine is a raw material for this industry. The industrial plant produces nearly 15,000 L/d the wastewater. COD of effluent from this industrial process is 14,000-19,500 mg/L.

Chemical treatment with Fenton's reagent (prepared by mixing  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ (30%) in molar ratio of 1:5) could remove only 38.8% COD. Higher doses were required to bring down the COD further. Feasibility of treating wastewater was also examined using biological treatment with aerobic batch reactors supplemented with various types of co-substrate like glucose, sucrose, cow dung extract and fruit waste extract. Kinetics of biodegradation in batch reactors with various co-substrates to wastewater ratio ranged from 0.67 to 4.0 was investigated. COD removal was up-to 92.6% in aerobic batch reactor for co-substrate (glucose and sucrose) to wastewater ratio as 4.0. Effects of nitrate, pH, dissolved oxygen, turbidity and COD were also investigated. Degradation of wastewater was better at higher dilution and co-substrate to wastewater ratio.

Other co-substrates as cow dung extract and apple fruit waste extract have been investigated for different co-substrate to wastewater ratio ranging from 0.67 to 4.0 with initial COD as 5000 mg/L. Studies with initial COD 1000, 2000, 3000, 4000 and 5000 mg/L having cow dung extract to wastewater ratio as 0.67 and 4.0 has also been investigated. These experiments were conducted for 144 h. The reactors having less initial COD shows higher COD removal in shorter

duration of time as compared to the higher initial COD reactors taking more time. Experiment with initial COD 1000, 2000, 3000, 4000 and 5000 mg/L and apple fruit waste extract to wastewater ratio as 0.67 and 4.0 were also investigated.

Experiments using anaerobic process (UASBR) with various compositions of wastewater and co-substrate (cow dung extract and apple fruit waste extract) have also been investigated. OLR, HRT, temperature and flow rate were maintained in the laboratory set-up. Reactor took longer time to get acclimatized with wastewater. Continuous UASB reactor was started with sucrose as starter. Various parameters like alkalinity, pH, COD removal, nitrate, turbidity,  $\text{NH}_4\text{-N}$ , TKN, sulphate, sulphide, methane generation and temperature were measured. Improved degradation was observed with higher wastewater content in the wastewater composition using a co-substrate in anaerobic process.

A decrease in alkalinity decreased the COD removal efficiency of the reactor. Decrease in alkalinity is directly related to the reduction in bicarbonate addition, which affects the cost of the treatment. Formation of granulation depended on the type of feed. Treatment of 100% industrial wastewater without any co-substrate has also been studied. COD removal ranged between 52.8 - 93.3% with average removal as 72.9% for 100% industrial wastewater in UASB reactor. Removal efficiency was affected by an increase in  $\text{NH}_4\text{-N}$  in the influent. High nitrogen content (700-800 mg/L as ammonia-N) in industrial wastewater inhibits biodegradation and hydrolysis of hexamine (HMT) and DNPT.

Industrial wastewater has been analyzed for formaldehyde using spectrophotometer and hexamine using HPLC. Both these constituents were removed during treatment.

Treatment by aerobic process and anaerobic process has been compared. Anaerobic process avoids the external stirring and aeration, which reduces the energy cost of the process. As the aeration and mixing is essential part of aerobic process. Also better degradation was observed in higher wastewater content in anaerobic process as compared in the aerobic process. In anaerobic process, treatment cost reduces due to low consumption of co-substrate. Production of less sludge also makes the anaerobic process cost effective as compared to the aerobic process. However, ammonia-N remains in the anaerobically treated wastewater.

## सार

वर्तमान अध्ययन एन, एन'- Dintrosopentamethylenetetramine निर्माण उद्योग से अपशिष्ट जल के एकीकृत रासायनिक और जैविक उपचार का एक प्रभावी विकल्प विकसित करने पर केंद्रित है और हेक्सामाइन (एचएमटी) का उपयोग अपने उत्पाद के एक घटक के रूप में करते हैं जो जिला सोलन के बद्दी, हिमाचल प्रदेश राज्य, भारत में आया है। हेक्सामाइन इस उद्योग के लिए एक कच्चा माल है। औद्योगिक संयंत्र लगभग 15,000 L / d अपशिष्ट जल का उत्पादन करता है। इस औद्योगिक प्रक्रिया से प्रवाह की सीओडी 14,000-19,500 मिलीग्राम / एल है।

फेंटन के अभिकर्मक के साथ रासायनिक उपचार (1: 5 के molar अनुपात में  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  और  $\text{H}_2\text{O}_2$  (30%) को मिलाकर तैयार किया गया) केवल 38.8% COD निकाल सकता है। सीओडी को और नीचे लाने के लिए उच्च खुराक की आवश्यकता थी। अपशिष्ट जल के उपचार की व्यवहार्यता का भी परीक्षण किया गया जिसमें एरोबिक बैच रिएक्टरों के साथ जैविक उपचार का उपयोग करके ग्लूकोज, सुक्रोज, गाय के गोबर के अर्क और फलों के अपशिष्ट के निष्कासन के विभिन्न प्रकारों को शामिल किया गया। बैच रिएक्टरों में बायोडिग्रेडेशन के कैनेटीक्स को 0.67 से 4.0 तक अपशिष्ट जल अनुपात में विभिन्न सह-सब्सट्रेट के साथ जांच की गई थी। COD निष्कासन अप-टू-92.6% एरोबिक बैच रिएक्टर में सह-सब्सट्रेट (ग्लूकोज और सुक्रोज) के लिए अपशिष्ट जल अनुपात 4.0 के रूप में था। नाइट्रेट, पीएच, भंग ऑक्सीजन, टर्बिडिटी और सीओडी के प्रभावों की भी जांच की गई। अपशिष्ट जल का अधिशेष उच्चतर कमजोर पड़ने और अपशिष्ट पदार्थ के अनुपात में सह-सब्सट्रेट में बेहतर था।

गाय के गोबर के अर्क और सेब के फलों के अपशिष्ट के अर्क के रूप में अन्य सह-सब्सट्रेटों की जांच अलग सह-सब्सट्रेट के लिए किया गया है जो 0.67 से 4.0 तक प्रारंभिक सीओडी के साथ 5000 मिलीग्राम / एल के

रूप में होता है। प्रारंभिक सीओडी 1000, 2000, 3000, 4000 और 5000 मिलीग्राम / एल वाले गोबर के अपशिष्ट को 0.67 और 4.0 के रूप में अपशिष्ट निकालने के साथ अध्ययन में भी जांच की गई है। ये प्रयोग 144 घंटे के लिए किए गए थे। कम प्रारंभिक सीओडी वाले रिएक्टर कम समय में सीओडी को हटाने में अधिक प्रारंभिक सीओडी रिएक्टरों की तुलना में अधिक समय लेते हैं। प्रारंभिक सीओडी 1000, 2000, 3000, 4000 और 5000 मिलीग्राम / एल और सेब फल अपशिष्ट निकालने के साथ अपशिष्ट जल अनुपात 0.67 और 4.0 के रूप में प्रयोग की भी जांच की गई।

अपशिष्ट जल और सह-सब्सट्रेट (गाय के गोबर के अर्क और सेब के फलों के अपशिष्ट निकालने) की विभिन्न रचनाओं के साथ अवायवीय प्रक्रिया (यूएसबीआर) का उपयोग करने वाले प्रयोगों की भी जांच की गई है। प्रयोगशाला सेट-अप में ओएलआर, एचआरटी, तापमान और प्रवाह दर को बनाए रखा गया था। रिएक्टर को अपशिष्ट जल से जमने में अधिक समय लगता था। सतत यूएसबी रिएक्टर को स्टार्टर के रूप में सुक्रोज के साथ शुरू किया गया था। क्षारीयता, पीएच, सीओडी हटाने, नाइट्रेट, टर्बिडिटी,  $\text{NH}_4\text{-N}$ , TKN, सल्फेट, सल्फाइड, मीथेन पीढ़ी और तापमान जैसे विभिन्न मापदंडों को मापा गया। अवायवीय प्रक्रिया में सह-सब्सट्रेट का उपयोग करके अपशिष्ट जल संरचना में उच्च अपशिष्ट पदार्थ के साथ बेहतर गिरावट देखी गई।

क्षारीयता में कमी से रिएक्टर की सीओडी हटाने की क्षमता कम हो गई। क्षारीयता में कमी का सीधा संबंध बाइकार्बोनेट में कमी से है, जो उपचार की लागत को प्रभावित करता है। दाने के निर्माण फ़ीड के प्रकार पर निर्भर करता है। बिना किसी सह-सब्सट्रेट के 100% औद्योगिक अपशिष्ट जल के उपचार का भी अध्ययन किया गया है। UASB रिएक्टर में 100% औद्योगिक अपशिष्ट जल के लिए 72.9% के रूप में औसत हटाने के साथ सीओडी 52.8 - 93.3% हटाने के बीच था। निष्कासन दक्षता एनएच 4-एन में वृद्धि से प्रभावित हुई।

औद्योगिक अपशिष्ट जल में उच्च नाइट्रोजन सामग्री (700-800 मिलीग्राम / एल अमोनिया-एन के रूप में) हेक्सामाइन (एचएमटी) और डीएनपीटी के बायोडिग्रेडेशन और हाइड्रोलिसिस को रोकता है।

एचपीएलसी का उपयोग करते हुए स्पेक्ट्रोफोटोमीटर और हेक्सामाइन का उपयोग करके फॉर्मलाडेहाइड के लिए औद्योगिक अपशिष्ट जल का विश्लेषण किया गया है। इन दोनों घटकों को उपचार के दौरान हटा दिया गया था।

एरोबिक प्रक्रिया और एनारोबिक प्रक्रिया द्वारा उपचार की तुलना की गई है। एनारोबिक प्रक्रिया बाहरी सरगर्मी और वातन से बचाती है, जो प्रक्रिया की ऊर्जा लागत को कम करती है। वातन और मिश्रण के रूप में एरोबिक प्रक्रिया का आवश्यक हिस्सा है। एरोबिक प्रक्रिया की तुलना में अवायवीय प्रक्रिया में उच्च अपशिष्ट पदार्थों में बेहतर गिरावट देखी गई। अवायवीय प्रक्रिया में, सह-सब्सट्रेट की कम खपत के कारण उपचार लागत कम हो जाती है। एरोबिक प्रक्रिया की तुलना में कम कीचड़ का उत्पादन भी अवायवीय प्रक्रिया को प्रभावी बनाता है। हालांकि, अमोनिया-एन अनैरोबिक रूप से उपचारित अपशिष्ट जल में रहता है।

# Contents

Sr. No.	Title	Page No.
	<b>Acknowledgements</b>	i-ii
	<b>Abstract</b>	iii-v
	<b>Contents</b>	vi-xii
	<b>List of figures</b>	xiii-xix
	<b>List of tables</b>	xx-xxi
	<b>Nomenclature</b>	xxii-xxiv
<b>Chapter 1.0</b>	<b>Introduction</b>	1-4
<b>Chapter 2.0</b>	<b>Literature Review</b>	5-26
2.1	Toxicity	5-6
2.1.1	Toxicity of dinitrosopentamethylenetetramine (DNPT)	6-7
2.1.2	Toxicity of hexamethylenetetramine (HMT)	7-8
2.1.2.1	Chronic toxic effects of hexamine on humans	8
2.1.2.2	Acute toxic effects of hexamine on humans	8
2.1.2.3	Applications of hexamine	8-9
2.1.3	Toxicity of formaldehyde	10-11
2.2	Manufacturing process of dinitrosopentamethylenetetramine as used in the industry	11-12
2.2.1	Generation of wastewater in DNPT manufacturing industry	12
2.3	Methods for the treatment of DNPT wastewater	12-13
2.3.1	Advanced Oxidation Processes	13-14

---

2.3.1.1	Fenton's reagent	15-17
2.3.2	Biological methods	17
2.3.2.1	Aerobic biodegradation of HMT	18-19
2.3.2.2	Aerobic biodegradation of formaldehyde	20-21
2.3.3	Anaerobic treatment	21-22
2.3.3.1	Anaerobic degradation of HMT	22-23
2.3.3.2	Anaerobic degradation of formaldehyde	23-24
2.3.3.2.1	Toxicity of formaldehyde during anaerobic treatment	25
2.4	Applicability of different processes to treat hexamine, formaldehyde and DNPT	25-26
<b>Chapter 3.0</b>	<b>Objective and Scope of the Thesis</b>	27-28
3.1	Objective	27-28
<b>Chapter 4.0</b>	<b>Chemical Treatment: Advanced Oxidation Process</b>	29-37
4.1	Introduction	29-30
4.2	Dinitrosopentamethylenetetramine	30
4.3	Physical properties of dinitrosopentamethylenetetramine	30-31
4.4	Hexamethylenetetramine	32
4.5	Physical properties of hexamethylenetetramine	32-33
4.6	Material and methods	33
4.6.1	Industrial plant under study	33
4.6.2	Characteristics of the industrial wastewater under study	34
4.6.3	Preparation of Fenton's reagent	35
4.7	Treatment in batch process	35

---

---

4.7.1	Wastewater treatment using Fenton's reagent	35-37
<b>Chapter 5.0</b>	<b>Aerobic Biological Treatment</b>	<b>38-86</b>
5.1	Introduction	38-39
5.2	Material and methods	40
5.2.1	Microbial biomass to seed aerobic batch reactors	40
5.2.2	Seed acclimatization	40
5.2.3	Wastewater (WW)	41
5.2.4	Co-substrate	41
5.3	Aerobic batch reactors with glucose as co-substrate	41-42
5.4	Aerobic batch reactors with sucrose as co-substrate	42-43
5.5	Cow dung extract (CDE)	43
5.5.1	Aerobic batch reactors with cow dung extract as co-substrate	44
5.6	Fruit waste extract (FWE)	45
5.6.1	Aerobic batch reactors with fruit waste extract (FWE) as co-substrate	45-46
5.7	Characteristics of the industrial wastewater (WW), cow dung extract (CDE) and fruit waste extract (FWE)	46-47
5.8	Analysis and quantification of HMT using HPLC	47-48
5.8.1	Quantification of samples	48
5.9	Performance of aerobic batch reactors	48
5.9.1	Glucose as co-substrate	48-50
5.9.2	Sucrose as co-substrate	50-51
5.9.3	Cow dung extract as co-substrate	52

---

---

5.9.3.1	Nitrification in W(20:80) and W(60:40) with CDE co-substrate	53-54
5.9.3.2	Aerobic batch reactor integrated with chemical treatment	54-55
5.10	Studies with varying initial strength of wastewater (COD: 1000, 2000, 3000, 4000 and 5000 mg/L)	56
5.10.1	Cow dung extract as co-substrate using substrate to co-substrate ratio as 20:80	56-58
5.10.1.1	Nitrification in W(20:80) with CDE co-substrate	58-59
5.10.1.2	Cow dung extract as co-substrate using substrate to co-substrate ratio as 60:40:	59-61
5.10.1.3	Nitrification in W(60:40) with CDE co-substrate	61-62
5.10.1.4	Effect of initial co-substrate, WW concentration and co-substrate to WW ratio on degradation	63
5.10.2	Batch reactors with fruit waste extract (FWE) as co-substrate	64
5.10.2.1	Effect of WW to FWE co-substrate ratio	64
5.10.2.2	Nitrification in FWE reactors	65
5.10.2.3	Effect of initial strength of wastewater using FWE as co-substrate	65-66
5.10.2.4	Nitrification in W(20:80) reactors with FWE as co-substrate	67
5.10.2.5	Studies on batch reactors having substrate to FWE co-substrate as 60:40	67-69

---

---

5.10.2.6	Nitrification in W(60:40) reactors having FWE as co-substrate	69-70
5.10.2.7	COD removal in reactors of different initial COD concentration for co-substrate (WW: FWE-20:80, total reaction time 144 h and WW: FWE-60:40, total reaction time 192 h)	70-71
5.11	Fate of Hexamine during wastewater treatment	71-81
5.12	Statistical analysis of data obtained from batch aerobic reactors	82-83
5.12.1	Statistical analysis of CDE and industrial wastewater in 20:80 experiments	83
5.12.2	Statistical analysis of FWE and industrial wastewater in 20:80 experiments	83-84
5.12.3	Statistical analysis of CDE and industrial wastewater in 60:40 experiments	84-85
5.12.4	Statistical analysis of FWE and industrial wastewater in 60:40 experiments	85-86
<b>Chapter 6.0</b>	<b>Anaerobic Biological Treatment</b>	<b>87-126</b>
6.1	Introduction	87
6.2	Materials and methods	88
6.2.1	Experimental set-up of pilot scale UASB reactor	88
6.2.2	Operation of the UASB Reactor	88-92
6.2.3	Seed sludge	92
6.2.4	pH	92

---

---

6.2.5	Alkalinity	93
6.2.6	Chemical Oxygen Demand	93
6.2.7	Average settling velocity	93-94
6.2.8	Gas measurement	94
6.2.9	Feed inlet	95
6.2.10	Specific methanogenic activity of sludge	95-97
6.2.11	Analysis of formaldehyde	98
6.2.11.1	Standard Curve for formaldehyde	99
6.3	Performance of the UASB reactor using different co-substrates	100
6.3.1	Start-up of UASB reactor	100-101
6.3.2	COD variation and removal efficiency in UASB	101-103
6.3.3	Variation of volatile fatty acid formation	103-104
6.3.4	Alkalinity and pH variation	105-107
6.3.5	Effect of co-substrate on degradation and methane generation	107-111
6.3.6	Granules formation	111-112
6.3.7	Average settling velocity	112
6.3.8	Aerobic and anaerobic degradation comparison	113
6.3.9	Temperature variation	114
6.3.10	Effect of bicarbonate alkalinity on removal efficiency	114-116
6.3.11	Sulphate variation	116-117
6.3.12	Specific methanogenic activity	117-119
6.4	Effect of 100% industrial wastewater $W_{(100:0)D}$ without any co-substrate on treatment process	119

---

---

6.4.1	COD variation for 100% industrial wastewater without co-substrate $W_{(100:0)D}$	119-120
6.4.2	Alkalinity variation for 100% industrial wastewater without co-substrate $W_{(100:0)D}$	120-121
6.4.3	Variation in VFA/alkalinity during the biodegradation of 100% industrial wastewater without any co-substrate $W_{(100:0)D}$	121-123
6.4.4	Effect of ammonia	123-125
6.5	Variation of formaldehyde with $W_{(90:10)}$ wastewater	125-126
<b>Chapter 7.0</b>	<b>Conclusions</b>	127-130
	<b>References</b>	131-141
<b>Biographical Profile of the Researcher</b>	<b>International Publications</b>	142

---

## List of Figures

Figure No.	Title	Page No.
4.1	Dinitrosopentamethylenetetramine-DNPT- $(\text{CH}_2)_5(\text{NO})_2 \text{N}_4$	30
4.2	Cage like Symmetric Tetrahedral Structure of Hexamethylenetetramine Molecule	32
4.3	Change in COD with reaction time at different doses of Fenton's reagent ( $R_{20}$ :20 mL/L, $R_{50}$ : 50 mL/L, and $R_{100}$ : 100 mL/L)	36
5.1	COD reduction in batch reactors of different (wastewater: glucose) ratio, contact time 96 h	49
5.2	Overall COD reduction in various batch reactors of different (wastewater: glucose) ratio, contact time 96 h	50
5.3	COD reduction in batch reactors of different (wastewater: sucrose) ratio, contact time 72 h	51
5.4	Overall COD reduction in various batch reactors of different wastewater co-substrate (sucrose) ratio, contact time 72 h.	51
5.5	Biodegradation in reactors of different (WW: CDE) ratio, contact time 144 h.	52
5.6	Nitrate and pH variation in reactors (WW: CDE), contact time 144 h.	53
5.7	COD removal and pH variation in reactor (co-substrate cow dung extract) W(20:80) in chemical treatment process after biodegradation.	55
5.8	COD removal in reactor (co-substrate cow dung extract) W(20:80) biologically and chemically.	55

---

5.9	COD removal kinetics in reactors of different initial COD (WW: CDE), contact time 264 h.	57
5.10	Overall COD reduction in reactors of different initial COD (WW: CDE), contact time 264 h.	57
5.11	Nitrate variation in reactors of initial COD (WW: CDE), contact time 264 h.	59
5.12	COD removal kinetics in reactors of different initial COD (WW: CDE), contact time 240 h.	59
5.13	Overall COD reduction in reactors of different initial COD (WW: CDE), contact time 240 h.	60
5.14	COD removal in reactors of varying initial COD concentration of different initial COD (WW: CDE-20:80) & (WW: CDE- 60:40).	61
5.15	Nitrate variation in reactors of different initial COD (WW: CDE), contact time 240 h.	62
5.16	COD removal comparison in reactors of varying initial COD concentration of different initial COD (WW: CDE-20:80) & (WW: CDE- 60:40)	63
5.17	COD removal in reactors W(20:80) and W(60:40) (co-substrate FWE), contact time 120 h.	64
5.18	Nitrate variation in reactors W(20:80) and W(60:40) (co-substrate FWE), contact time 120 h.	65
5.19	Biodegradation in reactors of different initial COD (WW: FWE-20:80), contact time 144 h.	66

---

---

5.20	Overall COD reduction in reactors of different initial COD (WW: FWE-20:80), contact time 144 h.	66
5.21	Nitrate variation in reactors of different initial COD (WW: FWE-20:80), contact time 96 h.	67
5.22	Variation of COD in reactors of different initial COD concentration (WW: FWE-60:40), contact time 192 h.	68
5.23	Overall COD reduction in reactors of different initial COD concentration (WW: FWE-60:40), contact time 192 h.	68
5.24	Variation of nitrate in reactors of different initial COD concentration (WW: FWE-60:40), contact time 192 h.	69
5.25	Biodegradation in reactors of varying initial COD concentration (WW: FWE-20:80, contact time 144 h and WW: FWE-60:40, contact time 192 h)	71
5.26	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(20:80) at 0 h.	74
5.27	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(20:80) at 24 h.	74
5.28	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(20:80) at 48 h.	75
5.29	HPLC Chromatograph for sample drawn from aerobic reactor containing	75

---

---

	industrial wastewater and co-substrate fruit waste extract W(20:80) at 144 h.	
5.30	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(60:40) at 0 h.	75
5.31	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(60:40) at 24 h.	76
5.32	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(60:40) at 48 h.	76
5.33	HPLC Chromatograph for sample drawn from aerobic reactor containing industrial wastewater and co-substrate fruit waste extract W(60:40) at 144 h.	76
5.34	Hexamine reduction and COD reduction in aerobic reactors W(20:80) and W(60:40) with FWE as co-substrate of initial COD 5000 mg/L in aerobic process.	77
5.35	Box Plot for COD removal using wastewater W(20:80) and cow dung extract co-substrate.	83
5.36	Box plot for COD removal using wastewater W(20:80) and fruit waste extract co-substrate.	84
5.37	Box plot for COD removal using wastewater W(60:40) and cow dung extract co-substrate.	85

---

---

5.38	Box plot for COD removal using wastewater W(60:40) and fruit waste extract co-substrate.	86
6.1	A UASB reactor experimental set up for anaerobic process in the laboratory	90
6.2	Experimental set up for settling column analysis (settling velocity)	94
6.3	Feed inlet systems to the UASB reactor	95
6.4	Experimental set-up for specific methanogenic activity (SMA)	96
6.5	Standard curve for analyzing formaldehyde in the industrial wastewater.	99
6.6	Influent and effluent COD variation with different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	102
6.7	Overall and dissolved COD removal efficiency with different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	103
6.8	VFA variation during process of different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	104
6.9	pH variation during process of different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	105
6.10	Variation of alkalinity during the process of different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	106
6.11	Effect of co-substrate on biodegradation and methane generation during the process of different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	108

---

---

6.12	COD removal and CH <sub>4</sub> generation during the process of different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	110
6.13	Performance of the reactor during the process of different wastewaters mixture of industrial wastewater and co-substrate in different proportions.	111
6.14	Sludge wash out and COD removal during the process of different wastewaters mixture of industrial wastewater and FWE co-substrate in different proportions.	112
6.15	Performance of aerobic and anaerobic reactors with various wastewaters mixture of industrial wastewater and co-substrate in different proportions, initial COD 2000 mg/L.	113
6.16	Temperature variation with time during throughout operation of the experimental setup reactor.	114
6.17	Bicarbonate addition, alkalinity variation and COD removal for different wastewaters mixture of industrial wastewater and co-substrate in different proportions in COD units of initial COD 2000 mg/L and wastewater without co-substrate with initial COD 1200 mg/L.	116
6.18	Sulphate variation in influent and effluent for wastewater W <sub>(80:20)C</sub> of initial COD 2000 mg/L and W <sub>(100:0)</sub> of initial COD 1200 mg/L processed @ HRT 48 h.	117
6.19	COD/SO <sub>4</sub> <sup>2-</sup> ratio variation and COD removal for wastewater W <sub>(80:20)C</sub> of initial COD 2000 mg/L and W <sub>(100:0)D</sub> of initial COD 1200 mg/L @ HRT	118

---

---

	48 h.	
6.20	Influent-effluent COD and COD removal for wastewater without co-substrate $W_{(100:0)D}$ of initial COD 1000 mg/L processed @ HRT 48 h.	120
6.21	Alkalinity and pH variation for wastewater without co-substrate $W_{(100:0)D}$ of initial COD 1000 mg/L processed @ HRT 48 h.	121
6.22	Variation of VFA-Alkalinity ratio and COD removal for wastewater without co-substrate $W_{(100:0)D}$ of initial COD 1000 mg/L processed @ HRT 48 h.	122
6.23	VFA and pH variation for wastewater without co-substrate $W_{(100:0)D}$ of initial COD 1000 mg/L processed @ HRT 48 h.	123
6.24	$NH_4-N$ and TKN variation for wastewater without co-substrate $W_{(100:0)D}$ of initial COD 1000 mg/L processed @ HRT 48 h.	124
6.25	Variation of total COD and formaldehyde COD of influent and effluent of the reactor during the process of wastewater $W_{(90:10)}$ with CDE as co-substrate of initial COD 1000 mg/L @ HRT 48 h.	126

---

## List of Tables

Table No.	Title	Page No.
2.1	Various Advanced Oxidation Processes	14
4.1	Physical Properties of Dinitrosopentamethylenetetramine (DNPT)	31
4.2	Physical Properties of Hexamethylenetetramine (HMT)	32-33
4.3	Characteristics of the Industrial Wastewater (WW)	34
5.1	Constituents of Different Wastewater with Co-substrate Glucose Used in Various Reactors	42
5.2	Constituents of Different Wastewater with Co-substrate Sucrose Used in Various Reactors	43
5.3	Constituents of Wastewater and Co-substrate Cow Dung Extract Used in Various Reactors	44
5.4	Constituents of Batch Reactors Containing Industrial Wastewater and Fruit Waste Extract	46
5.5	Characteristics of the Wastewater (WW), Cow Dung Extract and Fruit Waste Extract (FWE)	47
5.6	Calculations Related to the Utilization of Nitrogen in Heterotrophic Cell Synthesis	54
5.7	Analysis of Wastewater W(20:80) and W(60:40) with Fruit Waste Extract Co-substrate in Aerobic Reactors for Hexamine Using HPLC	72
5.8	Various Results with Glucose, Sucrose and Cow Dung Extract Co-	79-81

---

	substrate Along-with Other Similar Work Done by Others	
6.1	Trace Elements Used in the Feed to UASB Reactor	91
6.2	Constituents of Synthetic Feed to UASB Reactor	91
6.3	Constituents of Different Wastewater Prepared with Actual Industrial Wastewater	92
6.4	Different Wastewater Processed to the Reactor with Flow Parameters	101

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## Nomenclature

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Abbreviation	detail
Ac	Acetic acid
AOP	Advanced Oxidation Process
APHA	American Public Health Association
BOD <sub>5</sub>	5 days Biological oxygen demand at 20°C
CAS	Chemical abstract service
CD	Cow dung
CDE	Cow dung extract
CO <sub>2</sub>	Carbon dioxide
COD	Chemical oxygen demand
CH <sub>4</sub>	Methane
DO	Dissolved oxygen
DNPT	Dinitrosopentamethylenetetramine
EF-Feox	Anodic electro-Fenton
FAS	Ferrous ammonium sulphate
FID	Flame ionization detector
FSR	Fenton sludge recycling
FWE	Fruit waste extract
GC	Gas Chromatograph
h	Hour
HCl	hydrochloric acid

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HCHO	Formaldehyde
H <sub>2</sub> O <sub>2</sub>	Hydrogen per-oxide
HMT	Hexamethylenetetramine
HMX	Cyclotetramcthylenetetranitramine
HPMC	Horticulture Produce Marketing Corporation
HRT	Hydraulic Retention Time
HS <sup>-</sup>	Hydrogen sulphide
KH <sub>2</sub> PO <sub>4</sub>	Potassium di-hydrogen phosphate
K <sub>2</sub> HPO <sub>4</sub>	Di-potassium phosphate
KMnO <sub>4</sub>	Potassium dichromate
LPD	Litres per day
LPM	Litres per minute
MLD	million litres per day
NaHOCl	Sodium hypochlorite
NaHCO <sub>3</sub>	Sodium bicarbonate
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Ammonium
NO <sub>3</sub> <sup>-</sup>	Nitrate
NO <sub>2</sub> <sup>-</sup>	Nitrite
O <sub>3</sub>	Ozone
OH*	Hydroxyl radical
OH-	Hydroxyl ion
OLR	Organic loading rate

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PVC	Polyvinylchloride
R	Reactor
RDX	Cyclotrimethylenetrinitramine
rpm	Rotation per minute
SMA	Specific methanogenic activity
SO <sub>4</sub> <sup>2-</sup>	Sulphate
SRB	Sulphate reducing bacteria
SS	Suspended solids
SRT	Solids retention time
T	Temperature °C
TCD	Thermal conductivity detector
TKN	Total Kjeldahl nitrogen
UASBR	Up-flow anaerobic sludge blanket reactor
UV	Ultraviolet
VFA	Volatile fatty acids
VSS	Volatile suspended solids
WW	Industrial Wastewater

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