İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ENHANCEMENT OF ANAEROBIC SLUDGE STABILIZATION EFFICIENCY BY ULTRASONIC DISINTEGRATION

M.Sc. Thesis by
Ezgi KURDOĞLU

Department : Environmental Engineering

Programme : Environmental Sciences and Engineering

JANUARY 2011

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ENHANCEMENT OF ANAEROBIC SLUDGE STABILIZATION EFFICIENCY BY ULTRASONIC DISINTEGRATION

M.Sc. Thesis by
Ezgi KURDOĞLU
(501081715)

Date of submission : 20 December 2010
Date of defence examination: 26 January 2011

Supervisor (Chairman) : Prof. Dr. Rüya Taşlı TORAMAN (ITU)
Members of the Examining Committee : Prof. Dr. Emine Ubay ÇOKGÖR (ITU)
Prof. Dr. Ayşen ERDİNÇLER (BU)

JANUARY 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ULTRASONİK DEZENTEGRASYON İLE ANAEROBİK ÇAMUR STABİLİZASYON VERİMİNİN İYİLEŞTİRİLMESİ

YÜKSEK LİSANS TEZİ
Ezgi KURDOĞLU
(501081715)

Tezin Enstitüye Verildiği Tarih : 20 Aralık 2010
Tezin Savunulduğu Tarih : 26 Ocak 2011

Tez Danışmanı : Prof. Dr. Rüya Taşlı TORAMAN (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. Emine Ubay ÇOKGÖR (İTÜ)
Prof. Dr. Ayşen ERDİNÇLER (BÜ)

OCAK 2011

Canım Aileme ve Sevdiklerime,

FOREWORD

I would like to express my deepest gratitude to my supervisor, Prof. Dr. Rüya Taşlı Toraman for guiding and providing me with an excellent atmosphere for doing research. Her encouragement, confidence and suggestions helped me very much in accomplishing my thesis.

Then I would like to thank Assistant Professor Nevin Yağcı for her advice during the whole period of my thesis.

I would also like to thank, Assistant Professor Mahmut Altınbaş for his interest in our project and help during the anaerobic digestion tests.

I would like to thank, Associate Professor Süleyman Övez for his help on light microscopic images.

I owe a great deal to all my friends. I would especially like to thank my friends who were always willing to help in the laboratory. It would have been a lonely lab without them.

Special thank goes to a special person, Scott Heim; for his kindly supports during the whole thesis.

Final and the most important thanks go to my family members for their love and support, especially my mother Şenay Kurdoğlu and my father Hüseyin Kurdoğlu. They were always there cheering me up and stood by me through the good times and bad. Without them, I would not have finished the degree. And thanks to my little lovely nephew, Şana who always tired to sabotage my thesis.

January 2011

Ezgi Kurdoğlu

Environmental Engineer

TABLE OF CONTENTS

Page

FOREWORD ..... **vii**
TABLE OF CONTENTS ..... **ix**
ABBREVIATIONS ..... **xiii**
LIST OF TABLES ..... **xv**
LIST OF FIGURES ..... **xvii**
SUMMARY ..... **xxiii**
ÖZET ..... **xxv**
1. INTRODUCTION **1**
1.1 Objective and Scope 3
2. SLUDGE PROBLEM AND STABILIZATION APPLICATIONS **5**
2.1 An Overview to Sludge Problem 5
2.1.1 Sludge production 6
2.2 Sludge Treatment and Disposal Options 8
2.3 Sludge Stabilization 13
2.3.1 Alkaline stabilization 13
2.3.2 Composting 14
2.3.3 Aerobic sludge stabilization 14
2.3.4 Anaerobic stabilization 15
3. SLUDGE DISINTEGRATION PROCESS IN WASTEWATER TREATMENT PLANTS **23**
3.1 Sludge Disintegration 23
3.1.1 Floc destruction and cell disintegration 24
3.1.2 Release of soluble substances and small particles 27
3.1.3 Biochemical reactions 29
3.2 Sludge Disintegration Methods 30
3.2.1 Mechanical pre-treatments 31
3.2.1.1 High pressurized homogenizer 31
3.2.1.2 The lysate centrifuge thickener 34
3.2.1.3 Impact grinding 36
3.2.1.4 High performance pulse technique 37
3.2.1.5 Freezing and thawing 38
3.2.1.6 Gamma irradiation 42
3.2.1.7 Stirred ball mill 44
3.2.1.8 Ultrasound pretreatment 46
3.2.2 Chemical pre-treatments 58
3.2.2.1 Alkaline hydrolysis 58
3.2.2.2 Fenton process 60
3.2.2.3 Ozone pretreatment 61
3.2.3 Thermal pretreatment 67
3.2.3.1 Thermal hydrolysis 67
3.2.4 Biological pretreatment 76

4. MATERIAL AND METHODS 79
4.1 Plans of Experiments 79
4.1.1 Application of disintegration methods 79
4.1.1.1 Thermal disintegration 80
4.1.1.2 Thermo-chemical disintegration 80
4.1.1.3 Ultrasound disintegration 81
4.1.2 Anaerobic digestion tests 83
4.2 Experimental Equipments 91
4.2.1 Ultrasound homogenizer 91
4.2.2 Centrifuge equipment 92
4.2.3 Gas chromatography (GC) 93
4.3 Analytical Methods 93
4.4 Disintegration Degree (DD) 97
4.5 Alkaline Hydrolysis 97
4.6 Measurement Methods of Biogas Production and Composition 97
5. RESULTS AND DISCUSSIONS 99
5.1 Application of Disintegration Methods 99
5.1.1 Thermal disintegration 99
5.1.2 Thermo-chemical disintegration 102
5.1.3 Ultrasonic disintegration 110
5.1.3.1 Particle size analysis before and after ultraonic disintegration 127
5.1.3.2 Light microscopic images 128
5.1.4 Selection of disintegration method 130
5.2 Effect of Disintegration on Anaerobic Digestion Efficiency at F/M ratios of 1 and 0.5 130
5.2.1 Experimental results of RUN I with different ratios of disintegrated and untreated sludge 130
5.2.1.1 Biogas productions in RUN I 133
5.2.1.2 Sludge reduction in RUN I 139
5.2.1.3 Biochemical methane potential (BMP) in RUN I 142
5.2.2 The experimental results of RUN II with different percentages of centrifuged disintegrated sludge content 148
5.2.2.1 Biogas production in RUN II 150
5.2.2.2 Sludge reduction in RUN II 152
5.2.2.3 Biochemical methane potentiol (BMP) in RUN II 153
5.3 Disintegration Effects on Anaerobic Digestion Efficiency at F/M ratios of 5, 2, 1 and 0.5 156
5.3.1 The experimental results of RUN I (Second experiments) 158
5.3.1.1 The experimental results of RUN I for F/M 0.5 158
5.3.1.2 The experimental results of RUN I for F/M 1 159
5.3.1.3 The experimental results of RUN I for F/M 2 161
5.3.1.4 The experimental results of RUN I for F/M 5 163
5.3.1.5 Effect of ultrasonic disintegration on biochemical methane potential (BMP) 165
5.3.2 The experimental results of RUN II 168
5.4 Economic Efficiency 174
5.4.1 Cost analysis 177
5.4.2 Case study 178
6. CONCLUSION 181
REFERENCES 185

CURRICULUM VITAE 199

ABBREVIATIONS

BMP : Biochemical Methane Potential
BNR : Biological Nutrient Removal
COD : Chemical Oxygen Demand
CODc : Chemical Oxygen Demand after centrifuge
CODf : Chemical Oxygen Demand, filtered after centrifuge
DD_{COD} : Disintegration Degree
DOC : Dissolved Organic Carbon
DS : Dry Solids
EH : Enzymic Hydrolysis
ES : Excess Sludge
FSV : Floating Sludge Volume
FTS : Frozen/ Thawed System
FVS : Filterable Volatile Solids
KOI : Kimyasal Oksijen İhtiyacı
ODS : Organic Dry Solids
O&M : Operational and Maintenance
PS : Primary Sludge
RAS : Return Activated Sludge
RS : Raw Sludge
S_i : Soluble Inerts
SAS : Surplus Activated Sludge
SCOD : Soluble Chemical Oxygen Demand
SRT : Solid Retention Time
TCOD : Total Chemical Oxygen Demand
TDH : Thermal Disintegration Hydrolysis
TOC : Total Organic Carbon
TS : Total Solids
TSS : Total Suspended Solids
TVS : Total Volatile Solids
UAKM : Uçucu Askıda Katı Madde
UH : Ultrasonic Homogenizer
UKM : Uçucu Katı Madde
VFA : Volatile Fatty Acid
VS : Volatile Solids
VSS : Volatile Suspended Solids
WAS : Waste Activated Sludge
WWTP : Wastewater Treatment Plant
X_{ch} : Particulate Carbon-Hydrates
X_i : Particulate Inerts
X_{li} : Particulate Lipids
X_p : Decay Products
X_{pr} : Particulate Proteins

LIST OF TABLES

Page

Table 2.1: Typical composition of untreated sludge and digested biosolids. (Metcalf&Eddy, 2003) 7
Table 2.2: Moisture and organic content of sludges (Miklas, 2006)..... 8
Table 2.3: Treatment options for sludge (Miklas, 2006). 9
Table 2.4: Gas production from primary and activated sludge (Brown et al., 2003) 21
Table 3.1: Concentrations of organic components in the supernatant of excess sludge (1% SS) 28
Table 3.2: Characteristics of raw (RS) and frozen/thawed sewage sludge (FTS) supplied to RS and FTS systems. 40
Table 3.3: Terminology and the units of ultrasound systems 50
Table 3.4: Effects of ultrasound pre-treatment (at 31 kHz) and subsequent digestion time on anaerobic volatile solids degradation (VSdeg) of waste activated sludge and biogas production. (Neis et al., 2008)..... 53
Table 3.5: Biogas production enhacement, methane content and biodegradability percentage, at the end of the test (24 days) (Bougrier et al., 2006)..... 64
Table 3.6: Literature data on the efficiency of sludge solubilization. 65
Table 3.7: Full-scale application of ozonation for sludge treatment. 66
Table 3.8: Overview of some thermal pre-treatment studies. 74
Table 3.9: Impact of thermal pretreatments on primary sludge and waste activated sludge mesophilic anaerobic digestion..... 75
Table 4.1: Sludge characterization that thermal disintegration process applied to... 79
Table 4.2: Sludge characterization that ultrasound disintegration process applied to 80
Table 4.3: Thermal disintegration process applied at three different temperature for three different time 80
Table 4.4: Thermo-chemical disintegration process applied to the WAS at three different temperature and three different pH for 5 different time intervals 81
Table 4.5: Ultrasound disintegration process applied to the WAS of three different volume at three different amplitude for 5 different time intervals. 82
Table 4.6: Anaerobic digesters setup for RUN I 84
Table 4.7: Volume uses of serum bottles 85
Table 4.8: Time intervals of CODc, CODf, VS and TS parameters analysis of contol and disintegrated sludge 86
Table 4.9: Anaerobic digester setup for RUN II. 87
Table 4.10: Volatile solid concentrations of seed and return sludge 88
Table 4.11: Volume uses of serum bottles 89
Table 4.12: The composition of the anaerobic reactors influents 90
Table 5.1: Disintegration degrees of thermally disintegrated RAS 101
Table 5.2: VSS reductions at different temperatures 102
Table 5.3: Calculation of specific energies applied to the sludge in Stage I..... 113

Table 5.4: Disintegration degrees of ultrasonically disintegrated sludge in Stage I113
Table 5.5: Characterization of the return activated sludge..... 115
Table 5.6: The characterization of return activated sludge after chemical disintegration..... 116
Table 5.7: Calculation of specific energies that applied to the sludge in Stage II .. 120
Table 5.8: Disintegration degrees of ultrasonically disintegrated sludge in Stage II 121
Table 5.9: Characterization of the sludge types 131
Table 5.10: Sludge and seed volume calculations for RUN I (FM =1)..... 132
Table 5.11: Sludge and seed volume calculations for RUN I (FM =0.5)..... 132
Table 5.12: Reduction in CODf and VS values for all configurations of digesters at different F/Ms 140
Table 5.13: CODf and VS reduction during the digestion of digesters at different F/Ms 141
Table 5.14: Methane percentages (%) of control and disintegrated sludge at different percentages by the time at F/M 1. 143
Table 5.15: Methane percentages (%) of control and disintegrated sludge at different percentages by the time at F/M 0.5. 143
Table 5.16: VS(g) values of sludge added to the reactors for F/M 1 and F/M 0.5.. 145
Table 5.17: Sludge and seed volume calculations for RUN II (FM =1) 149
Table 5.18: Sludge and seed volume calculations for RUN II (FM = 0.5) 149
Table 5.19: Reduction in CODf and VS values for all configurations of digesters at different F/M ratios. 154
Table 5.20: Methane percentages (%) of disintegrated sludge and centrifuged sludge at different percentages by the time at F/M 1. 155
Table 5.21: Methane percentages (%) of disintegrated sludge and centrifuged sludge at different percentages by the time at F/M 0.5. 155
Table 5.22: Sludge and seed volume calculations for different F/M ratios for RUN I (Second Experiments)..... 157
Table 5.23: Methane percentages (%) of control and disintegrated sludge at different percentages by the time at four different F/M ratios..... 167
Table 5.24: Sludge and seed volume calculations of sludge mixed with supernatant after centrifuge at different percentages for different F/M ratios for RUN II (Second Experiments)..... 169
Table 5.25: Methane percentages (%) of disintegrated sludge and supernatant discarded sludge at different percentages at different F/M ratios..... 173
Table 5.26: Summary table for cost analysis 178
Table 5.27: Summary table for cost analysis of case study..... 179

LIST OF FIGURES

Page

Figure 2.1 : Degradation steps of anaerobic digestion process (United Tech, 2003). 16
Figure 2.2 : Schematic representation of the course of anaerobic methane generation from complex organic substances showing scanning electron micrographs of individual microorganisms involved. 18
Figure 3.1 : Model of sludge disintegration by ultrasound with increasing energy inputs according to Lehne *et al.* (2001) 23
Figure 3.2 : Disintegration points in the wastewater or sludge treatment chain (Minervini, 2008) 24
Figure 3.3 : Influence of disintegration on particle size and degree of disintegration in principle 25
Figure 3.4 : Floating sludge volume (FSV) in an anaerobic batch digester (Müller, 2000b) 27
Figure 3.5 : High pressure homogenizer (1) 32
Figure 3.6 : High pressure homogenizer (2) 32
Figure 3.7 : Gas production after 14 days of anaerobic digestion 33
Figure 3.8 : Schematic of a lysate-thickening centrifuge (modified from Otte-Witte et al., 2000) 34
Figure 3.9 : Impact grinding unit 37
Figure 3.10 : The biogas yields obtained from RS (raw sludge) and FTS (frozen/thawed) systems. 41
Figure 3.11 : The biogas composition observed in RS and FTS systems. 42
Figure 3.12 : Gamma Detector 43
Figure 3.13 : COD-fractionation of composite solids Xc of WAS with and without ball milling pre-treatment. 44
Figure 3.14 : Full scale ball milling installation. 45
Figure 3.15 : Stirred Ball Mill 45
Figure 3.16 : The growth and critical size of cavitation bubbles. 47
Figure 3.17 : Ultrasonic frequency that cavitation occurs. 48
Figure 3.18 : Ultrasound systems 49
Figure 3.19 : SCOD release at different energy inputs and TS contents, (Khanal et al., 2006c) 51
Figure 3.20 : Biogas production during anaerobic fermentation of untreated and sonicated waste activated sludge. 53
Figure 3.21 : The changes in VS destruction and Biogas production by ultrasound pretreatment. 54
Figure 3.22 : Effects of varios alkaline agents on COD solubilization 58
Figure 3.23 : Effects of alkaline pretreatment on solubilization 60
Figure 3.24 : Process schematic of the ozonation system (modified from Sievers et al., 2004) 62

Figure 3.25 : COD and TS solubilisation after various pre-treatments (mean of three measurements ± S.D.). 64
Figure 3.26 : COD-fractionation of composite solids Xc of WAS with and without TDH pre treatment (carbo-hydrates Xch, proteins Xpr, lipids Xli, decay products Xp, particulate inerts Xi, soluble inerts Si). 68
Figure 3.27 : The influence of the thermal treated sludges inoculum on biogas production (M. Dohanyos et al., 2000). 71
Figure 3.28 : Biogas production (ml/g Organic Dry Solid (ODS)) after 20 days for the different treatment temperature. 72
Figure 3.29 : Values obtained for % increment FVS/TVS ratio after thermal treatment of secondary sludge (dots) under different conditions of time and temperature and polynomial fit to the experimental points (surface). 73
Figure 3.30 : SCOD removal for digesters fed with sonicated and unsonicated sludge at different SRTs (Khanal et al., 2006b). 73
Figure 4.1 : Serum bottles used in BMP test. 88
Figure 4.2 : Ultrasonic equipment 91
Figure 4.3 : Picture of ultrasound machine 91
Figure 4.4 : Centrifuge device 92
Figure 4.5 : Helium gas purged to the reactor. 92
Figure 4.6 : Gas chromatography and the batch reactor 93
Figure 5.1 : CODc concentrations after thermal disintegration for three different temperatureand three different time intervals. 100
Figure 5.2 : CODf concentrations after thermal disintegrationfor three different temperature and three different time intervals. 100
Figure 5.3 : VSS/TSS rates of disintegrated sludge at different temperatures for different time intervals. 102
Figure 5.4 : CODc concentrations of thermochemically disintegrated sludge at 80^0C, at different pH values for different time intervals. 103
Figure 5.5 : CODc concentrations of thermochemically disintegrated sludge at 100^0C, at different pH values for different time intervals. 104
Figure 5.6 : CODc concentrations of thermochemically disintegrated sludge at 120^0C, at different pH values for different time intervals. 104
Figure 5.7 : CODf concentrations of thermochemically disintegrated sludge at 80^0C, at different pH values for different time intervals. 105
Figure 5.8 : CODf concentrations of thermochemically disintegrated sludge at 100^0C, at different pH values for different time intervals. 106
F**igure 5.9 :** CODf concentrations of thermochemically disintegrated sludge at 120^0C, at different pH values for different time intervals. 106
Figure 5.10 : Disintegration degree of disintegrated sludge at 80^oC for different pH values and different time intervals 107
Figure 5.11 : VSS reduction rates at 80^oC and at different pH values for different time intervals 108
Figure 5.12 : Disintegration degree of disintegrated sludge at 100^oC for different pH values and different time intervals 108
Figure 5.13 : VSS reduction rates at 100^oC and at different pH values for different time intervals 109
Figure 5.14 : Disintegration degree of disintegrated sludge at 120^oC for different pH values and different time intervals 109

Figure 5.15 : VSS reduction rates at 120^{o}C and at different pH values for different time intervals 110
Figure 5.16 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times. 111
Figure 5.17 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times. 112
Figure 5.18 : Relation between the specific energy change and the disintegration degree 114
Figure 5.19 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 40 % amplitude at different volumes for different sonication times. 116
Figure 5.20 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 40% amplitude at different volumes for different sonication times. 117
Figure 5.21 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times. 117
Figure 5.22 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60% amplitude at different volumes for different sonication times. 118
Figure 5.23 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 80% amplitude at different volumes for different sonication times. 119
Figure 5.24 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 80% amplitude at different volumes for different sonication times. 119
Figure 5.25 : Disintegration degrees of disintegrated sludge depending on the sonication time at 40% amplitude for three different volumes. 122
Figure 5.26 : Disintegration degrees of disintegrated sludge depending on the sonication time at 60% amplitude for three different volumes. 122
Figure 5.27 : Disintegration degrees of disintegrated sludge depending on the sonication time at 80% amplitude for three different volumes. 123
Figure 5.28 : Effect of sonication time on VSS/TSS values of disintegrated sludge at 40% amplitude for three different volumes. 124
Figure 5.29 : Effect of sonication time on VSS/TSS values of disintegrated sludge at 60% amplitude for three different volumes. 124
Figure 5.30 : Effect of sonication time onVSS/TSS values of disintegrated sludge at 80% amplitude for three different volumes. 125
Figure 5.31 : The changes of disintegration degrees with specific energy 126
Figure 5.32 : Particle size distribution of return activated sludge before disintegration process. 127
Figure 5.33 : Particle size distribution of return activated sludge after disintegration process applied. 128
Figure 5.34 : Microscopic images with 40X objective of A) Untreated B) Ultrasonically treated Sludge 129
Figure 5.35 : Microscopic images with 20X objective of A) Untreated B) Ultrasonically treated Sludge 129

Figure 5.36 : Microscopic images with 10X objective of A) Untreated B) Ultrasonically treated Sludge..... 130
Figure 5.37 : Total biogas production of disintegrated sludge and untreated sludge for F/M 1..... 133
Figure 5.38 : Total biogas production of sludge disintegrated at different percentages for F/M 1..... 134
Figure 5.39 : Total biogas production of disintegrated sludge and untreated sludge for F/M 0.5..... 135
Figure 5.40 : Total biogas production of sludge disintegrated at different percentages for F/M 0.5..... 136
Figure 5.41 : Total biogas amount of control sludge at different F/M ratio. 136
Figure 5.42 : Total biogas amount of disintegrated sludge at different F/M ratio.. 137
Figure 5.43 : Total biogas amount of 50% disintegrated sludge at different F/M ratios. 138
Figure 5.44 : Change in normalized mL CH_4/gVS $_{added}$ with respect to time of anaerobic digestion for F/M 1 145
Figure 5.45 : Change in normalized mL CH_4/gVS $_{added}$ with respect to time of anaerobic digestion for F/M 0.5. 146
Figure 5.46 : Comparison mL CH_4/gVS $_{added}$ with respect to time of anaerobic digestion for disintegrated sludge at different F/M ratios 147
Figure 5.47 : Total biogas amount produced during the anaerobic digestion period for different percentages of discarded supernatant at F/M 1. 150
Figure 5.48 : Total biogas amount produced during the anaerobic digestion period for different percentages of discarded supernatantat FM 0.5. 151
Figure 5.49 : Comparison of 10% of discarded supernatant values for different F/M ratios 151
Figure 5.50 : Comparison of 50% of discarded supernatant values for different F/M ratios 152
Figure 5.51 : Total biogas production of disintegrated sludge and untreated sludge for F/M 0.5..... 158
Figure 5.52 : Biogas production of control and disintegrated sludge at different percentages for F/M 0.5..... 159
Figure 5.53 : Total biogas production of disintegrated sludge and untreated sludge for F/M 1..... 159
Figure 5.54 : Biogas production of control and disintegrated sludge at different percentages for F/M 1..... 160
Figure 5.55 : Total Biogas production of disintegrated sludge and untreated sludge for F/M 2..... 161
Figure 5.56 : Biogas production by time at F/M 2 for control and disintegrated sludge at different percentages 162
Figure 5.57 : Total biogas production of disintegrated sludge and untreated sludge for F/M 5..... 163
Figure 5.58 : Biogas production by time at F/M 5 for control and disintegrated sludge at different percentages 163
Figure 5.59 : Biogas amount of control sludge at different F/M ratios..... 164
Figure 5.60 : Biogas amount of disintegrated sludge at different F/M ratios 165
Figure 5.61 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 0.5. 170
Figure 5.62 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 1. 170

Figure 5.63 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 2. 171
Figure 5.64 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 5. 171
Figure 5.65 : Comparison of biogas amount of 50% supernatant discarded sludge for different F/M ratios 172
Figure 5.66 : Energy balance 176

ENHANCEMENT OF ANAEROBIC SLUDGE STABILIZATION EFFICIENCY BY ULTRASONIC DISINTEGRATION

SUMMARY

In recent years, as a result of increasing of demand of wastewater treatment, amount of treatment sludges to be handled also increases. Sludge increase causes very serious problems which need to be solved.

In wastewater treatment systems, anaerobic digestion of excess sludge is a common method which is applied to decrease pathogen microorganism concentration, amount of organic matter of sludge and produce energy as biogas.

As a result of anaerobic digestion, biogas is generated as an end product and energy source. Anaerobic digestion is a slow process, if the complete stabilization of the organic matters can not be achieved due to incomplete degradation, the amount of biogas produced is very limited.

Recently, "sludge disintegration" has been implemented as a new method to accelerate anaerobic digestion process and increase the stabilization degree.

Disintegration process can be described as breaking-up the sludge flocks and disrupting cell membranes of microorganisms so to force release of intracellular contents into the bulk liquid in a soluble form. After application of disintegration process the concentration of organic matter content in sludge can be decreased to the lowest level which allows obtaining lower sludge volume and more stable sludge. Degradation of organic matter in high levels provides more biogas production compared to the classic anaerobic sludge stabilization process.

The aim of this study is to increase the efficiency of anaerobic sludge stabilization and produced biogas amount by implementing ultrasound sludge disintegration prior to the anaerobic sludge digestion. Various disintegration methods are applied to the return activated sludge which is taken from Return Activated Sludge (RAS) line of Paşaköy Biological WWTP. The characterization of disintegrated sludge and its supernatant were determined by COD and VSS measurements.

The RAS samples treated with the Sonix probe are placed inside a 50, 100 and 250 ml beaker. By varying the sonication time between 1and 60 minute, at 40%, 60% and 80 % amplitude are used to treat the RAS samples. For the anaerobic digestion tests ultrasound disintegration under the conditions of 100 mL of volume, 80% amplitude and 30 minutes of duration is selected.

The effect of ultrasound pretreatment before anaerobic digestion has been studied for F/M ratios of 0.5 and 1, and five different percentages of treated sludge mixed with un-treated sludge (RUN I) in the first experiments. Different percentages of centrifuged disintegrated sludge are subjected to anaerobic digesters by discarding some part of the supernatant to represent the possible effect of returned supernatant

to the beginning of the system. The discarded supernatant amounts are in the range of 10 % to 50 % (RUN II).

In the first part of the experimental study, the return sludge is ultrasonically pre-treated for 30 minutes with a specific energy of 40700 kW.s/kg.DS. The mesophilic digester is operated with SRTs of 27 days and the amount of biogas production of disintegrated sludge increases **17%** compared to un-treated sludge at F/M 1, while the biogas production increase is **40%** at F/M 0.5 at the end of the anaerobic digestion period.

VS reduction percentages of un-treated (control) sludge and disintegrated sludge were **5%** and **19%** respectively at F/M 1, while the VS reduction increased from **24%** (untreated sludge) **to 34%** at F/M 0.5 during the anaerobic digestion period. Similarly,VS reduction of disintegrated sludge and reactor mixed at 50 % of discarded centrifuged sludge supernatant were **19% and 41%** respectively at F/M 1, while **23%** and **30%** at F/M 0.5 indicating that as the F/M ratio increases the difference in VS reduction also increases.

As a result, the methane volume per amount of VS added was **149 mL** CH_4/gVS_{added} for disintegrated reactor, while **21 mL** CH_4/gVS_{added} for control reactor at the end of the 28 days anaerobic digestion period for F/M 1. The methane volume per amount of VSS added was **186 mL**CH_4/gVS_{added} for disintegrated reactor at the end of the 27 days anaerobic digestion period for F/M 0.5. Decreasing the F/M ratio from 1 to 0.5 for disintegrated sludge, causes **25%** increase in terms of ml CH_4/gVS_{added}.

In the second part of experiments, anaerobic digestion tests are duplicated for F/M 0.5 and 1 and four different F/M ratios of 0.5, 1, 2 and 5, and five different percentages of treated sludge mixed with un-treated sludge has been studied. The percentages of treated sludge subjected to anaerobic digestion were varied from 0%, 25%, 50%, 75% and 100 (RUN I).

Different percentages of centrifuged disintegrated sludge are also subjected to anaerobic digesters by discarding some part of the supernatant in the range of 10 % to 50 % (RUN II).The return sludge is ultrasonically pre-treated for 30 minutes with a specific energy of 151387 kW.s/kg.DS. The mesophilic digester is operated with SRTs of 27 days. The ultrasonic pretreatment enhanced the subsequent anaerobic digestibility resulting better removal of TS and VS.

In the second experiments, total biogas amount at the end of the anaerobic digestion increased from 50 mL to 57 mL by disintegration of sludge resulting in **14%** increase for F/M 2, while 43 mL to 53 mL resulting in **23%** increase for F/M 1. Consequently, the amount of biogas production of disintegrated sludge was increased around **40%** by increasing F/M from 0.5 to 5.

Similarly, by increasing F/M from 0.5 to 5, the amount of methane gas of disintegrated sludge increases from 24 mL to 40 mL resulting in **67%** increase. Therefore, the results also imply that higher F/M ratios should be applied to get higher gas productions from the anaerobic digestion applications.

ULTRASONiK DEZENTEGRASYON İLE ANAEROBiK ÇAMUR STABİLİZASYON VERİMİNİN İYİLEŞTİRİLMESİ

ÖZET

Günümüzde atıksu arıtımı ihtiyacının giderek artmasıyla birlikte çamur oluşumu da artmakta ve arıtma çamurları giderek önem kazanan ve çözüm bekleyen önemli problemlerden biri olarak karşımıza çıkmaktadır.

Atıksu arıtma tesislerinde, arıtma işlemleri sonucunda oluşan arıtma çamurlarının anaerobik yöntemlerle çürütülmesi patojen mikroorganizma konsantrasyonunun, atık bünyesindeki organik madde içeriğinin azaltılması ve biyogaz eldesiyle enerji üretimi amacıyla yaygın olarak kullanılan bir yöntemdir.

Anaerobik çürütme uygulamasının derecesine bağlı olarak son ürün olan ve enerji kaynağı olarak nitelenen biyogaz elde edilmektedir. Anaerobik çürütme prosesinin oldukça yavaş bir süreç olması ve çürütme sonrasında organik maddelerin tümüyle parçalanamaması nedeniyle tam stabilizasyonun sağlanamaması ve elde edilen biyogaz miktarının az olması araştırmacıları anaerobik çürütmeyi hızlandıracak ve stabilizasyon derecesini artırmayı sağlayacak yeni yöntemler geliştirmeye yöneltmiş ve çamur ön arıtımı amacıyla kullanılan bir yöntem olarak çamur dezentegrasyonu geliştirilmiştir.

Dezentegrasyon işleminde, çamura uygulanan gerilmeler sayesinde çamur flok yapısı bozulmakta, mikroorganizma hücre duvarları parçalanmakta, hücre içeriğindeki organik çamur bileşenleri sıvı faza geçmektedir. Dezentegrasyon sonucunda, çamur katılarının organik madde içeriği en aza inmekte, dolayısıyla daha düşük miktarda ve daha stabil bir çamur eldesi mümkün olmaktadır. Organik maddenin yüksek derecede parçalanması klasik anaerobik çürüme işlemine göre daha fazla biyogaz üretimine olanak sağlamaktadır.

Bu çalışmanın amacı arıtma çamurlarına stabilizasyon öncesi dezentegrasyon işlemi uygulayarak stabilizasyon veriminin ve oluşacak biogaz miktarının arttırılmasıdır. Paşaköy biyolojik atıksu arıtma tesisi geridevir hattından alınan çamurda çeşitli dezentegrasyon işlemleri uygulanmıştır. KOİ, UAKM ve benzeri parametrelere bakılarak Çamur ve süpernetantın karakteri belirlenmiştir.

Geri devir hattından alınan çamur örnekleri 50, 100 ve 250 mL 'lik hacimlere ultrasonic prop yerleştirilerek dezentegrasyon işlemi uygulanmıştır. Ultrasonik dezentegrasyon işlemi 1 ile 60 dakika arasında sonikasyon süreleri ve %40, %60 ve %80 amplitütte uygulanmıştır. Anaerobik çürütme testleri için 100 mL hacimde, %80 amplitütte 30 dakikalık sonikasyon süreli ultrasonik dezentegrasyon yöntemi seçilmiştir.

Anaerobik çürütme testleri etkrar edilmiştir. İlk deneylerde anaerobik çürütme öncesi uygulanan ultrasonik dezentegrasyon yönteminin etkisini incelemek amacıyla dezentegre edilmiş çamur iki farklı F/M oranı için (0,5 ve 1), dezentegre edilmemiş çamurla 5 farklı yüzdede karıştırılmıştır (RUN I). Santrifüj sonrası çamur üst fazının

sistemin başına geri devrettirilmesi durumunda olası etkisini görmek amacıyla, üst fazı değişik yüzdelerde (%10 -%50) santrifüşlenmiş çamur anaerobik çürütme işlemine sokulmuştur (RUN II).

Deneysel çalışmanın ilk kısmında, geri devir çamuruna 40700 kW.s/kg.KM spesifik enerji uygulanarak 30 dakika süreyle ultrasonik dezentegrasyon işlemi uygulanmıştır. Mezofilik çürütücüler 27 gün süreyle işletilmi**l**tir ve stabilizasyon işlemi sonunda, F/M 1 oranı için, toplam gaz üretimi dezentegre olmamış çamura kıyasla dezentegre olmuş çamurda **% 17** artmıştır. Bu artış yüzdesi F/M 0,5 oranı için **% 40**'dır.

F/M 1 için, dezentegre olmamış ve dezentegre olmuş çamurun, uçucu katı madde azalma oranı **%5** ve **%19** iken, F/M 0,5 için, dezentegre olmamış ve dezentegre olmuş çamurun, uçucu katı madde azalma oranı % 24 ve %34'dir. Benzer olarak F/M 1 için, dezentegre olmuş ve % 50 santrifüj sonrası geridevrettirilmiş çamurun, uçucu katı madde azalma oranı **%19** ve **%41** iken, F/M 0,5 için, dezentegre olmuş ve % 50 santrifüj sonrası geridevrettirilmiş çamurun, uçucu katı madde azalma oranı **%23** ve **%30**'dur. Uçucu katı madde azalma oranındaki fark F/M oranı arttıkça artar.

Sonuç olarak F/M 1 için, 28 günlük anaerobik stabilizasyon prosesi sonunda, eklenen UKM başına oluşan metan miktarı dezentegre olmuş çamurda **149 mL** CH_4/gUKM iken kontrol reaktöründe bu miktar **21 mL** CH_4/gUKM'dir. F/M 0,5 için, 27 günlük anaerobik stabilizasyon prosesi sonunda, eklenen UKM başına oluşan metan miktarı dezentegre olmuş çamurda **186 mL** CH_4/gUKM'dir. F/M oranının 1 den 0,5 'e düşürülmesiyle, eklenen UKM başına oluşan metan miktarı dezentegre olmuş çamur için **%25** yükselmiştir.

İkinci deneylerde 4 faklı F/M (0,5, 1, 2 ve 5) oranı için dezentegre edilmiş çamur, dezentegre edilmemiş çamurla 5 farklı yüzdede karıştırılmıştır. Dezentegre olmamış çamura dezentegre olmuş çamur, %0, %25, %50 ve %75 oranlarında karıştırılmıştır (RUN I).

Santrifüj sonrası çamur üst fazının sistemin başına geri devrettirilmesi durumunda olası etkisini görmek amacıyla, üst fazı değişik yüzdelerde (%10 -%50) santrifüşlenmiş çamur anaerobik çürütme işlemine sokulmuştur (RUN II). Geri devir çamuru 30 dakika süreyle 151387 kW.s/kg.KM spesifik enerji harcanarak ultrasonik dezentegrasyon işlemi uygulanmıştır. Mesofilik reaktörler 27 gün(SRT) süreyle işletilmiştir. Ultrasonik dezentegrasyon işlemi anaerobik çürütme verimini iyileştirmiş ve KM ve UKM giderimini arttırmıştır.

İkinci deneylerde, anaerobik çürütme öncesi uygulanan dezentegrasyon işlemi anaerobik stabilizasyon prosesi sonunda, F/M 2 için, oluşan toplam gaz miktarını 50 mL'den 57 mL'ye yülseltmiş ve **%14** 'lük bir artışa neden olmuştur. F/M 1 için ise 43 mL'den 53 mL'ye artmasına, **%23**'lük bir artışa neden olmuştur. Sonuç olarak F/M oranının 0,5'den 5'e yükseltilmesi ile oluşan biogaz miktarı **%40** civarında artmıştır.

Benzer şekilde, anaerobik çamur çürütme işlemi sonunda dezentegre olmuş çamur için F/M oranının 0,5 den 5'e çıkarılmasıyla, oluşan metan gazı miktarı 24mL 'den 40 mL'ye yükseldiği ve **%67** artışa neden olduğu görülmüştür. Buna bağlı olarak anaerobik çamur çürütme işleminde daha yüksek F/M oranlarında çalışıldığında daha yüksek miktarlarda gaz elde edilebileceği sonucu çıkmaktadır.

1. INTRODUCTION

The treatment and disposal of sludge has become very important issue because of the increasing sludge production from wastewater treatment plants. Large volumes of putrescible organic sludge with high water contents are produced from primary and secondary sedimentation tanks and their dewatering and ultimate disposal may account for as much as 40 per cent of the cost of treatment. Volumes of sludge from water treatment operations are much lower and their relatively inert nature means that disposal is normally less of a problem

The current legal constraints, the rising costs and public sensitivity towards the various ways of sewage sludge disposal have provided considerable impetus to explore and develop strategies and technologies for the minimization of sludge production and pretreatment processes. Similarly the reduction of the organic matter content of the sludge is very important because, sludges with a high organic matter content constitute hazard due to their low stability feature.

In order to enable a sustainable and environmentally safe reuse, SAS must undergo several post-treatments to reduce its water content, its fermentation propensity and the presence of pathogens. A typical, complete posttreatment chain consists of: thickening; stabilisation; conditioning; dewatering; drying; storage; transportation and final reuse (Fytili and Zabaniotou, 2008). One of the most common stabilisation processes is anaerobic stabilization.

An anaerobic stabilization of particulate organics is considered to be a sequence of four steps: hydrolysis, acidogenesis, acedogenesis and methanogenesis. Among the these, biological hydrolysis of the particulate organics has been considered to be a rate limiting step (Tiehm et al., 2001). Municipal wastewater sludge, particularly waste activated sludge (WAS), is more difficult to digest than primary solids due to a rate-limiting cell lysis step. The cell wall and the membrane of prokaryotes are composed of complex organic materials such as peptidoglycan, teichoic acids, and complex polysaccharides, which are not readily biodegradable.Various mechanical,

ultrasonic, chemical, and thermal methods have been proposed to accelerate the hydrolysis of the sludge particles in anaerobic digestion.

Food to microorganism (F/M) ratio is the ratio of substrate amount as waste activated sludge to the inoculum amount as anaerobic digested sludge added to the reactor. It is an important digester parameter in terms of volatile solids loading performance of the system (Pranshanth et al., 2006). A high F/M ratio indicates higher organic loading (per unit amount of anaerobic microorganisms) to the digester whereas low F/M ratio shows that the loading is small.

Even though waste activated sludge is rich in nutrients, the bioavailability of its nutrients is very low. Various pretreatment processes have the ability to increase the solubility of the organic matter included in waste activated sludge. There are lots of researches reported the positive influence of sludge pretreatment on the enhancement of its biodegradability.

The use of the disintegration process as a sludge pretreatment method is a novel technique. The disintegration of waste activated sludge can be described as the destruction of sludge by external forces. These forces can be enumerated as physical, chemical, or biological forces. The disintegration process results in a lot of changes of sludge characteristics and these changes can be grouped in three main categories; destruction of floc structures and distruption of cells , release of soluble substances and fine particles and biochemical processes. During the disintegration walls of the cell structure are broken. This releases the intra-cellular material into the liquid. The released COD is available for subsequent anaerobic digestion and can increase biogas yield during digestion.

There are various applications of disintegration process such as mechanical, chemical, thermal and biological disintegration. Most common disintegration methods that applied to the sludge are ultrasonic disintegration as mechanical; thermal disintegration as thermal and alkaline disintegration as chemical disintegration.

Through the employment of a disintegration method before anaerobic digestion, the sludge production could be decreased and the anaerobic digestion rate and the biodegradability of sludge could be developed. So a high degree of stabilization and an enhancement of biogas production could also be achieved.

1.1 Objective and Scope

The aim of this study is to evaluate the effect of the ultrasonic disintegration as a pretreatment method on anaerobic digestion efficiency at different F/M ratios. In this context, a general overview to the sludge problem, sludge treatment & disposal options and the detailed information about sludge stabilization is given in second chapter. The mechanisms and aims of disintegration which is a pretreatment of anaerobic sludge treatment process are summarized and the methods are explained in third chapter. This study is based on laboratory scale experimental research and the materials and methods used during this research is described in fourth chapter. The results of the experiments are given in fifth chapter.

2. SLUDGE PROBLEM AND STABILIZATION APPLICATIONS

2.1 An Overview to Sludge Problem

One of the major problems facing the industrialized world today is to resolve environmental contamination and identify efficient treatments. Over the past two centuries wastewater treatment has developed from a non-existent field into a huge industry that has helped improve quality of life throughout the world. Wastewater treatment has developed from simple, small systems into huge treatment plants that receive millions of gallons of wastewater a day. The first systems were essentially septic tanks and lagoons, often utilizing anaerobic microorganisms to achieve treatment objectives (McCarty, 2001), whereas the current systems utilize a variety of microorganisms to achieve stringent discharge limits. One factor that has remained constant since the beginning of wastewater treatment is the generation of sludge or biosolids.

For sustainable development, recycling and use of wastes are the preferred options rather than incineration or landfilling, but with sewage sludge this is not simple because of perceptions over contaminants, pathogens and its fecal origin. For the foreseeable future, therefore, treatment plants will continue to function as 'sludge factories' with unceasing and unstoppable output.

Sewage sludge will also remain a product the quality of which is not strictly controllable, which may have no secure long-term outlet and which usually entails processing, transport and disposal costs of about half the total cost of operating the sewage works (Hall J., 1999).

Conventional municipal sewage treatment plants utilise mechanical and biological processes to treat wastewater. Activated sludge has been the most widely used biological material for industrial wastewater treatment. It facilitates the transformation of dissolved organicpollutants from wastewater into biomass, and these are finally converted into carbon dioxide and water by microorganisms.

The main by-product of municipal wastewater treatment of waste activated sludge (WAS) has been increasing worldwide as a result of an increase in the amount of wastewater being treated. The excess sludge contains high fractions of volatile solids (VS) and retain large amounts of water (>95% by weight), resulting in extremely large volumes of residual solids produced, and therefore, significant disposal costs. (Pérez-Elvira et al., 2006) which has been estimated to be 50–60% of the total expense of wastewater treatment plant (Egemen et. al., 2001).

2.1.1 Sludge production

Within the traditional wastewater treatment plant (WWTP) there are two locations where sludge is generated: primary clarification and waste biomass from the activated sludge system/biological process. The sludge that is generated at these two locations is significantly different: those from the primary clarifier are typically readily degradable, whereas those from the biological process are more resistant to degradation.

Primary sludge

Sludge from primary settling tanks can be readily digested under suitable conditions of operation. Compared to secondary sludge, primary sludge contains more fat and proteins and less carbonhydrate (Sykes, 2003) and that is why the gas yield of primary sludge is higher than that of secondary sludge, but on the other hand the methane content of the gas generated from primary sludge is lower than that of secondary sludge. Primary sludge is easily digestible compared to activated sludge.

Secondary sludge

Activated sludge comes from the secondary treatment. The excess sludge is called waste activated sludge and is a result of overproduction of microorganisms in the active sludge process. It is light and fluffy and composed of microorganisms flocculated organic matter (Liu and Liptak, 1999). The organisms are primarily bacteria and protozoa, but also rotifers and filamentous bacteria. Activated sludge is more difficult to digest than primary sludge.

Filamentous bacteria are a normal part of the activated sludge microflora (Bitton, 1999). If the process is run suboptimally the filamentous bacteria can increase in numbers and cause foaming of the active sludge process. A high number of

filamentous bacteria in the waste activated sludge can also cause foaming of anaerobic digesters. Common species are Nocardia spp and Microthrix parvicella.

The settled thickened sludge at the bottom of the clarifier is in part recycled back into the aeration tank (the return activated sludge, RAS), while the remaining part must be removed from the system (the waste or surplus activated sludge, WAS or SAS). SAS removal is needed to keep the process in steady and optimal operational conditions, with a constant ratio between the amount of organic substrate and biomass present in the system (Tchobanoglous et al., 2003)

Digested sludge

After anaerobic digestion of primary and activated sludge, the residual product is digested sludge. The digested sludge is reduced in mass, less odorous, and safer in the aspect of pathogens (Bitton, 1999) and more easily dewatered than the primary and activated sludges (Liu and Liptak, 1999).

Typical composition of untreated sludge and digested biosolids is shown in Table 2.1.

Table 2.1: Typical composition of untreated sludge and digested biosolids. (Metcalf&Eddy, 2003)

Item	Untreated Primary Sludge		Digested Primary Sludge		Untreated Activated Sludge
	Range	Typical	Range	Typical	Range
Total dry solids (TS),%	5-9	6	2-5	4	0.8-1.2
Volatile solids (% of TS)	60-80	65	30-60	40	59-88
Grease and fats (% of TS): Ether soluble	6-30	-	5-20	18	-
Ether extract	7-35	-	-	-	5-12
Protein (% of TS)	20-30	25	15-20	18	32-41
Nitrogen (N, % of TS)	1.5-4	2.5	1.6-3	3.0	2.4-5.0
Phosphorus (P_2O_5, % of TS)	0.8-2.8	1.6	1.5-4.0	2.5	2.8-11
pH	5.0-8.0	6.0	6.5-7.5	7.0	6.5-8.0
Alkalinity (mg/L as CaCO3)	500-1500	600	2500-3500	3000	580-1100
Organic acids (mg/L as HAc)	200-2000	500	100-600	200	1100-1700
Energy content, Kj/kg TSS	23,000-29,000	25,000	9000-14,000	12,000	19,000-23,000

The most important characteristics of sludges are their organic and moisture contents. A high organic content in an unstabilised sludge indicates that the sludge will continue to degrade, and is therefore likely to present health, odour and rodent problems. Table 2.2 summarises the typical moisture and organic content ranges of several sludges.

Table 2.2: Moisture and organic content of sludges (Miklas, 2006).

Sludge Type	Moisture Content (% by weight)	Organic Content (% dry weight)
Primary	93-97	48-80
Activated	98-99.5	65-75
Digested	96-99	30-60

The treatment and disposal of these sludge is often a significant portion of WWTPs' expenses. Since the early twentieth century anaerobic digestion has been the preferred method for stabilizing the sludge generated during treatment of wastewater (McCarty 2001).

2.2 Sludge Treatment and Disposal Options

The main objectives of sludge treatment and disposal are as follows:

• Stabilisation of the organic matter contained in the sludge;

• Reduction in the volume of sludge for disposal by removing some of the water;

• Destruction of pathogens;

• Collection of by-products, which may be used or sold to off-set some of the

costs of sludge treatment;

• Disposal of the sludge in a safe and aesthetically acceptable manner. (Miklas, 2006).

Unfortunately, the recycling of by-products see is an 'ideal scenario' rarely achieved in practice, except in the case of methane gas, which is produced in anaerobic digestion. The methane is often collected and used as a fuel to provide heat for

controlling the temperature of the digesting sludge and, occasionally, for driving dual fuel engines, which may be used to generate power for the treatment plant. The production of a compost and the use of sludges for agricultural purposes can be viewed as waste recycling.

The most commonly used method of sludge stabilisation is anaerobic digestion. Digested sludges are suitable for direct disposal, or they can be further treated, and subsequently handled without odour or hygiene problems.

Treatment options for sludge is shown in Table 2.3.

Table 2.3: Treatment options for sludge (Miklas, 2006).

Thickening	Stabilisation	Dewatering
Gravity	Anaerobic digestion	Drying beds
Flotation	Aerobic digestion	Filter press
Centrifuge	Lagooning	Centrifuge
Elutriation	Heat treatment	Vacum filter; belt press and lagooning
Constructed	Constructed wetland	Constructed wetland

The handling of sewage sludge is one of the most significant challenges in wastewater management (Metcalf and Eddy, 1991). Disposal options fall into five main categories:

- Landfill,
- Disposal to agricultural land,
- Disposal to sea,
- Incineration,
- Other processes

Other processes include sacrificial land use, forestry, land reclamation, use as building materials and as feed stuff. These other processes currently utilize a very small percentage of the total volume of sludge produced.

Digested sludges are often further treated and dewatered in drying beds or in lagoons. Mechanical dewatering further reduces sludge volumes, and is a necessity for incineration. Ultimate disposal of any residue or sludge is to land or sea, though some national and international guidelines have stopped these options. Spreading sludge on agricultural land was the least preferable option from an environmental point of view. Energy was required for transportation, spreading and pasteurisation of the sludge, whereas the other three options enabled energy recovery. Spreading also caused release of nutrients and acidifying substances and transferred the content of heavy metals in the sludge to agricultural soil. The economic assessment showed that agricultural application had the lowest cost of the options, whereas co-incineration had the highest cost.

EU is revising the Directive 86/278 . The third draft of a new Directive on land application considerably reduces the limit values for heavy metals, proposes new values for organic micropollutants and distinguishes between advanced or conventional treatments for sludge, making it more difficult to use sewage biosolids in agriculture (Spinosa,2001).

One of the other disposal methods is incineration which is a high cost/high technology option and is currently only likely to be cost-effective for large cities. It does not have a high level of public acceptability due to concerns over gas emissions and gaining consent to construct new incinerators is often difficult.(Hall J., 1999). Incineration is in effect only a means of sludge minimization; it is not a means of complete disposal since 30% of the dry solids remain as an ash. The ash is classified as hazardous waste due to its content of heavy metals, and so incurs further expense for its disposal in special landfill sites. However, there are opportunities for utilizing, such as for construction materials, and when sludge is used as a fuel in cement production, the ash becomes an integral part of the product.

Landfill disposal of sludge has been the most widely used and lowest cost method of sludge disposal in Europe, 35–45% of the sludge in Europe is disposed of in this manner. It is now widely accepted that landfill disposal of organic wastes, such as sludge, is not a sustainable option due to concern over gas and leachate emissions and the need to conserve landfill void for those wastes that cannot be reused or recovered. National measures vary but include limits on organic matter, taxes on reactive wastes and carbon taxes, and the separation of municipal solid wastes.

Land filling is restricted from the European Commission Landfill Directive and the use of biosolids on land is limited by national and local guidelines, based on the EC "Use of Sludge on Agricultural and Land Directive (1986). Therefore, it is now widely recognized as being an unsustainable outlet due to concerns over pollution, loss of recyclable materials and loss of void for those wastes which cannot be recycled (Hall J., 1999). Hence, deposition of sludge and its components will not be accepted in the future. This point to direct use of sludge on land as the most sustainable alternative. Therefore, the current legal constraints, the rising costs and public sensitivity of sewage sludge disposal necessitate development strategies for reduction and minimization of excess sludge production (Pérez-Elvira et al., 2006). In the UK, agricultural recycling of sludge saves farmers over £8 million in fertilizer replacement value. This is in line with the Government's vision for sustainable waste management and the widely held view that agricultural recycling of sludge is the Best Practical Environmental Option in most circumstances. Europe's Sixth Community Environment Action Program includes the sustainable use of natural resources and management of wastes (Decision No 1600/2002/EC) and it prompted a revision to Directive 86/278/EEC on the protection of the environment with measures aimed to achieve the long-term goal of 75% recycling of urban sludge to land in the whole of the EU.

The EU Directive on hazardous wastes (91/689/EEC) and its amendment (94/31/EEC) categories wastes as either hazardous or non-hazardous, which then affects how it may be disposed of. It categories wastewater sludges in the European Waste Catalogue (EWC) under the general code 19-08. Sludge from industrial wastewater (EWC code No. 19-08-04) and domestic wastewater treatment (19-08-05) are not included in the list of hazardous wastes. However, some types of water and wastewater treatment sludges are classified as hazardous (e.g. 19-08-03: Fat and oil mixtures from oil separators; 19-08-06: Saturated or used ion-exchange resins; 19-08-07: Solutions and sludges from the regeneration of ionexchangers). Where sludges contain metals or metal compounds, making them unsuitable for use in agriculture, or contain listed toxic substances, then these sludges are automatically classified as hazardous and cannot then be mixed with other nonhazardous wastes.

Disposal of sludge generated in wastewater treatment plants has become an important problem in Turkey. High amounts of sludge is produced in industrial and

domestic wastewater treatment plants but on the other hand the available areas for sludge disposal are getting diminished, therefore it is necessary to reduce the amount of sludge so that the hazardous waste sites and/or landfills last for a longer period of time. It is also important to reduce the organic content of the sludge. According to Turkish regulation "Control of Hazardous Wastes" treatment sludge that have a DOC concentration in the eluent above 50 mg/L or a TOC concentration of 50000 mg/kg are defined as hazardous waste and they can only be disposed to hazardous waste sites or they can be incinerated. In order to be able to use treatment sludge beneficially, the organic carbon content of the sludge must be decreased below these limit values. Beneficial use of treatment sludge carries a great importance because; the amount of area for sludge disposal is reduced through these beneficial uses.

One option is reducing sludge production in the wastewater treatment instead of post-treating the sludge produced. The instruments for reducing the generation of excess sludge acting on the wastewater treatment process, without changing the composition of sewage, can be of different kind: (Tilche A. et al., 1992)

1. To use the biochemical energy contained in the wastewater for conversion processes that need energy (denitrification, P removal) and not only for carbon oxidation;

2. To apply waste water treatment processes that are characterized by low biomass growth;

3. To apply long sludge age systems (extended aeration, membrane bioreactors, biofilm processes);

4. To manage the activated sludge food chain, stimulating the balanced growth of bacterial predators (with the warning of not grazing the slow growers, like nitrifies);

5. To enhance biological sludge stabilization (pre-treatments, termophilic anaerobic digestion, etc.).

Sludge disposal has become an important problem and the most appropriate solution to this problem is the reduction of sludge production in wastewater treatment plants (Bougrier et al., 2006). The achievement of this reduction can be obtained through several pretreatment methods.

2.3 Sludge Stabilization

Sludge stabilization processes are the key to reliable performance of any wastewater treatment plant. These processes treat the sludges generated in the main treatment process, converting them to a stable product for ultimate disposal or use and include both volatile solid destruction and biomass stabilization. Volatile solid destruction is needed in order to reduce the volume of sludge requiring ultimate disposal, while the biomass stabilization process limits pathogens and provides a less odorous product, reducing the potential to impact negatively on human and biotic health. Traditionally, both processes have been considered together, in such a way that, when volatile solid destruction is achieved, the biomass is considered stabilized.

The digestion stability and its efficiency can vary depending upon the mode of operation, waste type, digestion design, digestion temperature, and other factors. The longer a substrate is kept under proper reaction conditions the more complete its degradation will become. But the reaction rate will decrease with increasing residence time. The disadvantage of a longer retention time is the increasing reactor size needed for a given amount of substrate to be treated. A shorter retention time will lead to a higher production rate per reactor volume unit, but a lower overall degradation. These two effects have to be balanced in the design of the full scale reactor (Nava, 2007).

The principal methods used for stabilization of sludge are;

- Alkaline Stabilization (usually with lime)
- Composting
- Aerobic Stabilization
- Anaerobic Stabilization

2.3.1 Alkaline stabilization

A method to eliminate nuisance conditions in sludge is through the use of alkaline material to render the sludge unsuitable for the survival of microorganisms. In the lime stabilization process, lime is added to untreated sludge in sufficient quantity to raise the pH to 12 or higher. The high pH creates an environment that halts or substantially retards the microbial reactions that can otherwise lead to odor production and vector attraction. The sludge will not putrefy, create odors, or pose a

health hazard so long as the pH maintained at this level. The process can also inactivate virus, bacteria, and other microorganisms present.

A disadvantage is that the product mass is increased by the addition of alkaline material.

2.3.2 Composting

Composting is an aerobic bacterial decomposition process to stabilise organic wastes and produce humus (compost). Compost contains nutrients and organic carbon that are excellent soil conditioners. Composting takes place naturally on a forest floor where organic materials (leaf litter, animal wastes) are converted to more stable organic materials (humus) and the nutrients are released and made available for plant uptake. The process is slow on a forest floor, but can be accelerated under optimum conditions.

The optimum conditions for composting are a moisture content of about 50 %, a carbon to nitrogen ratio of about 25 to 30, and temperature of 55 ^{o}C. Because wastewater sludge is rich in nutrients, its carbon to nitrogen ratio is low (5 to 10). It is also high in moisture. Addition of dry sawdust, which is very high in carbon to nitrogen ratio (500) can adjust both the moisture and carbon to nitrogen ratio.

2.3.3 Aerobic sludge stabilization

Aerobic stabilization is the biological conversion of organic matter in the presence of air (or oxygen), usually in an open-top tank. Aerobic sludge stabilization is the less costly solution for municipal treatment plants below 50 000 pe (population equivalent) compared to the anaerobic stabilization of the sludge (Nowak, 2006). According to the European Urban Waste Water Treatment Directive (91/271/EEC), it is expected to construct additional wastewater treatment plants in the near future. Since the majority of these treatment plants will be of average size, the preferred sludge digestion systems will be primarily aerobic (Sanchez et al., 2006). Aerobic stabilization requires less investment and less maintenance compared to the anaerobic stabilization (Nowak, 2006). In order to use stabilized sludge for different purposes (i.e., agricultural application and land filling) it is required to know both the sludge properties and the degree of stability achieved. The volatile solids are a common indicator of the amount of organic matter content in the sludge. The amount

of achieved volatile solids destruction in a sludge stabilization process can be used to measure sludge stabilization performance.

Advantages of aerobic stabilization as compared to anaerobic stabilization

Advantages of aerobic stabilization as compared to anaerobic stabilization are;

1) Volatile solids reduction in a well-operated aerobic digester is approximately equal to that obtained anaerobically
2) Lower BOD concentrations in supernetant liquor
3) Production of an odorless, humuslike, biologically stable end product
4) Recovery of more of the basic fertilizer values in the sludge
5) Operation is relatively easy
6) Lower capital cost
7) Suitibility for digesting nutrient-rich biosolids.

Disadvantages of aerobic stabilization

Disadvantages of aerobic stabilization are:

1) High power cost is associated with supplying the required oxygen
2) Digested biosolids produced have poorer mechanical dewatering characteristics
3) The process is affected significantly by temperature, location, tank geometry, concentration of feed solids, type of mixing/aeration device, and type of tank material.
4) Useful byproduct such as methane is nor recovered.

2.3.4 Anaerobic stabilization

The most widespread stabilization process in municipal wastewater treatment plants is anaerobic digestion. The biological conversion of organic matter by fermentation in a heated reactor to produce methane gas and carbondioxide. Fermentation occurs in the absence of oxygen. The major applications of anaerobic digestion are in the stabilization of concentrated sludges produced from the treatment of municipal and industrial wastewater. (Metcalf&Eddy, 2003).

Anaerobic stabilization process is considered to follow four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. (Machnicka et al., 2005). Anaerobic digestion is a multi-step process carried out by a mixed culture of different groups of microorganisms. The process consists of four main steps which are carried out by at least three groups of microorganisms: acidogenic bacteria, acetogenic bacteria and methanogenic bacteria (Ecke and Lagerkvist, 2000; De Mes et al., 2003).

Degradation steps of anaerobic digestion process is shown in Figure 2.1.

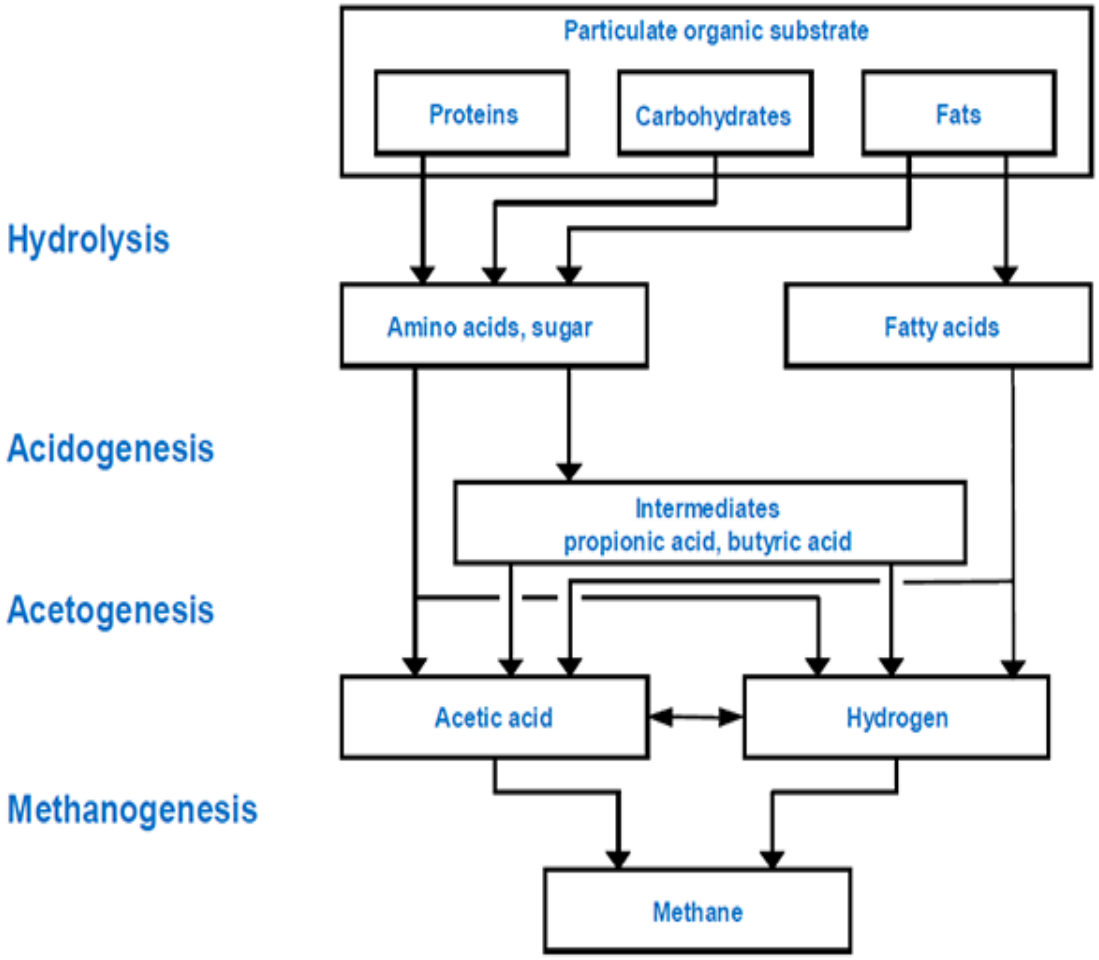

Figure 2.1 : Degradation steps of anaerobic digestion process (United Tech, 2003).

Hydrolysis

During hydrolysis, the first stage, bacteria transform the particulate organic substrate into liquefied monomers and polymers i.e. proteins, carbohydrates and fats are transformed to amino acids, monosaccharides and fatty acids respectively.

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \quad \textbf{(2.1)}$$

Equation represents a typical hydrolysis reaction where biowaste is broken down into glucose (Ostrem, 2004).

In hydrolysis the anaerobes break the sludge floc into smaller, more readily degraded particles. The floc is difficult to break apart because it contains biopolymers (proteins, polysaccharides, lipids) and fatty acids which act as a glue holding it together; these compounds are typically composed of long-chain structures which are difficult to break apart (Hogan et al. 2004). Once the flocs have been hydrolyzed to smaller particles the subsequent steps in the digestion process are free to be carried out by their respective anaerobes. Because of the long duration of the hydrolysis step there has been significant interest over the past several decades in developing methods to accelerate it from a process that requires days to complete to one that is achieved in hours or even minutes.

Due to the rate limiting step of biological sludge hydrolysis, the anaerobic degradation is a slow process. Therefore, long residence times in the fermenters and large fermenter volumes are required (Neis U. et al., 2000).

Acidogenesis

In the second stage, acidogenic bacteria transform the products of the first reaction into short chain volatile acids, ketones, alcohols, hydrogen and carbon dioxide. The principal acidogenesis stage products are propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), acetic acid (CH_3COOH), formic acid ($HCOOH$), lactic acid ($C_3H_6O_3$), ethanol (C_2H_5OH) and methanol (CH_3OH), among other.

From these products, the hydrogen, carbon dioxide and acetic acid will skip the third stage, acetogenesis, and be utilized directly by the methanogenic bacteria in the final stage (Figure 2.2).

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \quad \textbf{(2.2)}$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \quad \textbf{(2.3)}$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \quad \textbf{(2.4)}$$

Equations represent three typical acidogenesis reactions where glucose is converted to ethanol, propionate and acetic acid, respectively (Bilitewski et al., 1997).

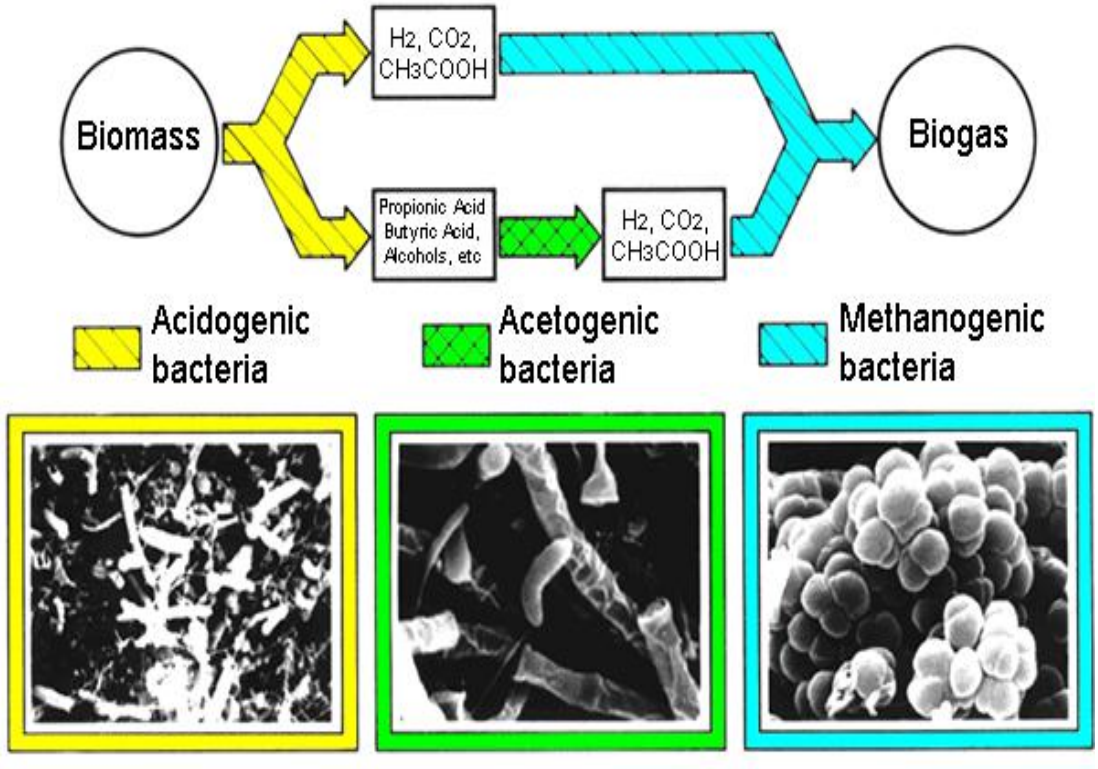

Figure 2.2 : Schematic representation of the course of anaerobic methane generation from complex organic substances showing scanning electron micrographs of individual microorganisms involved.

Acetogenesis

The third stage is acetogenesis. In this stage, the rest of the acidogenesis products, i.e. the propionic acid, butyric acid and alcohols are transformed into hydrogen, carbon dioxide and acetic acid by acetogenic bacteria. Hydrogen plays an important role in this process, as the reaction will only occur if the hydrogen partial pressure is low enough to thermodynamically allow the conversion of all the acids. As a consequence accumulation of organic acids will occur and the pH in the process will finally decrease, which will inhibit the methanogens even more. In the worst case, the whole anaerobic degradation process will stop (Jarvis, 2004).

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2 \quad \textbf{(2.5)}$$

This equation represents the conversion of propionate to acetate, only achievable at low hydrogen pressure.

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad \textbf{(2.6)}$$

$$CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 2H_2 + H^+ \quad \textbf{(2.7)}$$

Glucose and ethanol among others are also converted to acetate during the third stage of anaerobic fermentation (Ostrem, 2004).

Methanogenesis

The last stage is called methanogenesis. During this stage, methane is produced by bacteria called methanogens. These bacteria can produce methane in different ways. One group is called the hydrogenotrophic methanogens and converts hydrogen gas and carbon dioxide to methane. The other group is called the acetotrophic methanogens and splits acetate to methane and carbon dioxide (Gerardi, 2003).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \textbf{(2.8)}$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \quad \textbf{(2.9)}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad \textbf{(2.10)}$$

In general, the methanogens are a very sensitive group of microorganisms. They are sensitive to low pH levels, heavy metals, organic pollutants, ammonia and even small amounts of oxygen. The methanogens grow very slowly and in order to avoid wash out of these organisms the hydraulic retention time must not be to short (Jarvis, 2004). To avoid disturbances and obtain optimal degradation efficiency, as well as biogas production, conditions allowing all microorganisms to grow must be fulfilled (Jarvis, 2004).

Due to the rate limiting step of biological sludge hydrolysis the anaerobic degradation is a slow process and large fermenters are necessary (Eastman and Ferguson, 1981). During this phase, particulate organics become solubilized and as such, they can serve as a substrate and an energy source for the anaerobic bacteria, responsible for the process. It may be assumed, that the increased surface of the sludge flocs particles (due to their decomposition) might also enhance the rate of hydrolysis. Therefore, any technology that can stimulate higher hydrolysis rates might also intensify both VFA production and methane digestion, since these processes are coupled. And VFAs is an important consideration for good performance of a digester. That is, it is necessary to investigate the optimum conditions and efficiencies of digesters by examining VFAs.

Typical digestion times are 20 and more days. The degree of degradation of organic matter varies between 25% and 60%. (Neis, 2000).

Low biogas yield from excess activated sludge is caused by the low biodegradability of the cell walls and of the extracellular biopolymers formed in activated sludge. The enhancement of the biodegradability of particular substrate is mainly based on a better accessibility of the substrate for enzymes (Tilche A. et al., 1992).

Biogas can be used for heat production, co-generation of electricity and heat or be upgraded to motor vehicle fuel. Generation of heat and/or electricity in a gas boiler, gas engine, gas turbine or fuel cell system can be accomplished with the methane content normally reached in a digester (55–75 % (de Mes et al., 2003)). For use as motor vehicle fuel the methane content has to be increased to at least 96–97 %. Biogas of vehicle fuel quality has the same methane concentration as natural gas and can be co-distributed in a natural gas network.

Anaerobes are very sensitive to environmental conditions like pH, temperature, and the presence of toxins. One of the most important one is temperature.

Anaerobic fermentation significantly reduces the total mass of wastes, generates solid or liquid fertilizer and yields energy. It can be maintained at

- psychrophilic (12-16 °C, e.g. in landfills, swamps or sediments),
- mesophilic (35-37 °C, e.g. in the rumen and in anaerobic digester)
- thermophilic conditions (55-60 °C; e.g. in anaerobic digesters or geothermally heated ecosystems).

A thermophilic digestion process can sustain a higher organic loading compared to a mesophilic digestion. But the thermophilic process produces a gas with a lower methane concentration (Ecke and Lagerkvist, 2000) and is more sensitive to toxicants (Bitton, 1999). Also thermophilic anaerobic fermentation reduces the process stability and reduces dewatering properties of the fermented sludge and the requirement for large amounts of energy for heating, whereas the thermal destruction of pathogenic bacteria at elevated temperatures is considered a big advantage (Winter, J. And Temper, U., 1987).

Anaerobic sludge digestion can occur in the mesophilic range which is more usual, or in the thermophilic range, which is less common. It is important that the

temperature remains constant. Degradation of volatile suspended solids in the conventional mesophilic anaerobic process is about 40% at retention times between 30 an 40 days (Gene, 1986).

According to the sludge type that wastewater treatment plants generate, the amount of gas produced in anaerobic stabilization changes. Table 2.4 shows values of gas production from primary sludge and activated sludge.

Table 2.4: Gas production from primary and activated sludge (Brown et al., 2003)

Reference	Gas Production (mL/g VS)	
	Primary Sludge	Activated Sludge
Sato et al., 2001	612	380
Speece, 2001	362	281
Ritman and McCarty, 2000	375	275

Advantages of anaerobic stabilization

Anaerobic digestion offers significant advantages like;

- Less energy required
- Less biological sludge produced
- Lower nutrient demand
- Methane production: Providing potential energy source with possible revenue both from sale of the energy, and benefit from government tax, and (Kyoto agreement) CDM etc. payments arising from renewable fuels/non-fossil fuel incentives
- Methane production: Anaerobic digestion contributes to reducing greenhouse gases by reducing demand for fossil fuels
- Smaller reactor volume required
- Biomass acclimatization allows most organic compounds to be transformed
- Rapid response to substrate addition after long periods without feeding

- End product can be potentially saleable products biogas, soil conditioner and a liquid fertilizer.
- Process more effectively provides sanitization/removal of diseases.

Disadvantages of anaerobic treatment

Anaerobic digestion offers significant disadvantages like;

- Longer start-up time to develop necessary biomass inventory
- May require alkalinity and/or specific ion addition
- May require further treatment with an aerobic treatment process to meet discharge requirements
- Biological nitrogen and phosphorus removal is not possible
- Much more sensitive to the adverse effect of lower temperatures on reaction rates
- May need heating (often by utilization of process gas) to achieve adequate reaction rates
- May be more less stable after 'toxic shock'(eg after upsets due to toxic substances in the feed)
- Increased potential for production of odors and corrosive gases.
- Hazards arise from explosion. (In the EU, such additional Health & Safety Regulations as the ATEX Directive, and possibly also Gas Institute Regulations will require various compliance measures to be applied for AD.)
- Anaerobic treatment is not effective for treatment of methanogenic landfill leachate, it may (rarely) be efficacious for the early stage leachate production period while the waste is still acetogenic.

3. SLUDGE DISINTEGRATION PROCESS IN WASTEWATER TREATMENT PLANTS

3.1 Sludge Disintegration

The aim of such pretreatment is to rupture the cell wall and membrane to the release the intra and extra cellular matter into the aqueous phase for subsequent degradation, and this process is called sludge disintegration.

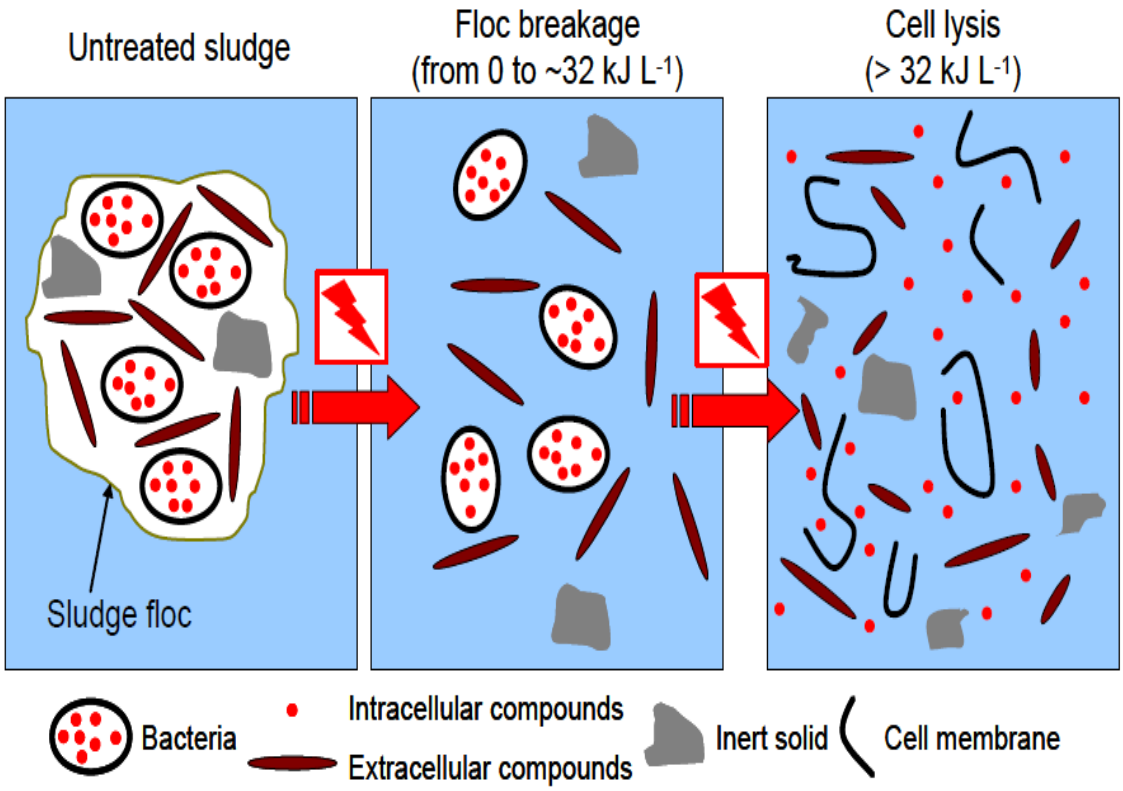

Figure 3.1 : Model of sludge disintegration by ultrasound with increasing energy inputs according to Lehne *et al.* (2001)

Sludge disintegration process can be implemented at a number of locations in the wastewater treatment plants. The current large-scale applications of sludge disintegration specifically concern the treatment of secondary sludge before sludge digestion, because the application has a number of positive effects combined

with a high effectiveness (Müler, 2004) An integration of a disintegration device into a sludge treatment process can be seen in Figure 3.2.

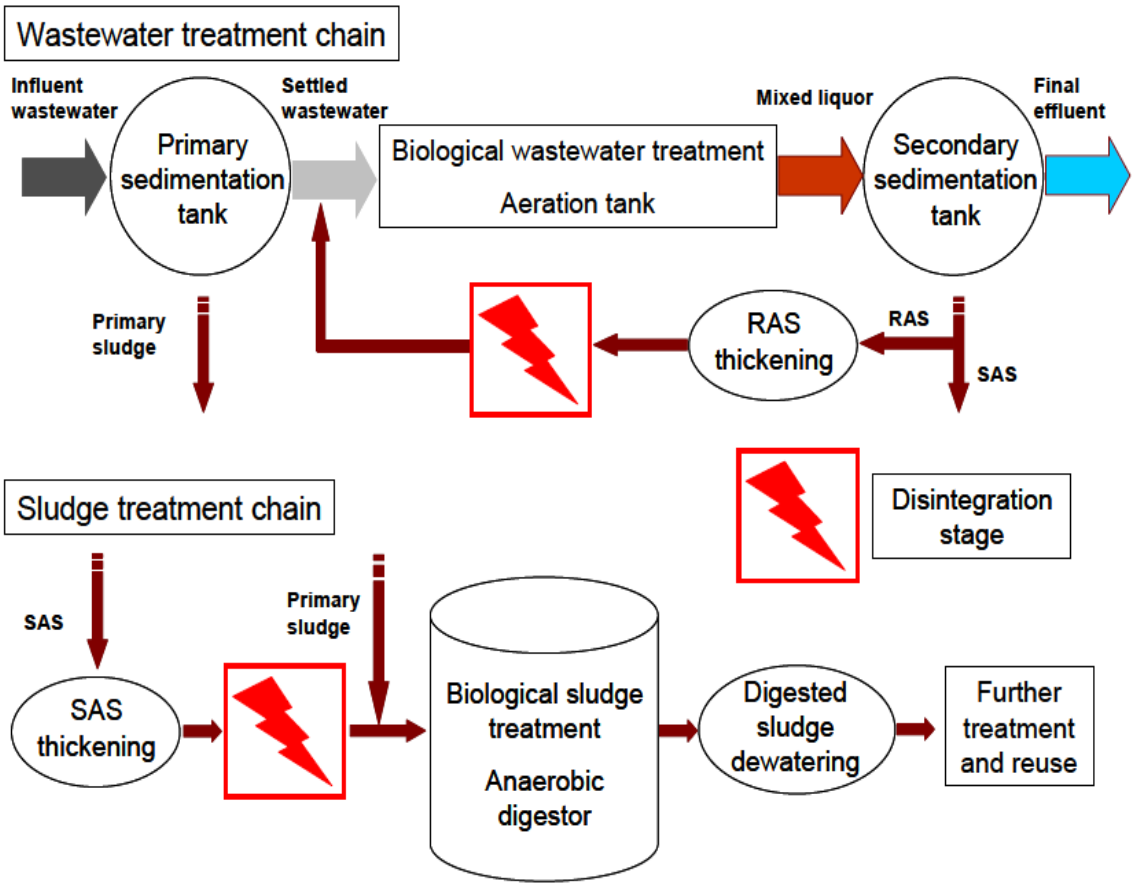

Figure 3.2 : Disintegration points in the wastewater or sludge treatment chain (Minervini, 2008)

The disintegration of waste activated sludge can be described as the destruction of sludge by external forces. These forces can be enumerated as physical, chemical, or biological forces. The disintegration process results in a lot of changes of sludge characteristics and these changes can be grouped in three main categories (Müller et al., 2004).

- Destruction of floc structures and distruption of cells
- Release of soluble substances and fine particles
- Biochemical processes

3.1.1 Floc destruction and cell disintegration

The stress that is applied during the disintegration causes the destruction of floc structures within the sludge and/or leads to the break-up of micro-organisms. If the

energy input is increased, the first result is a drastic decrease in particle size within the sludge (Figure 3.3). The destruction of floc structures is the main reason for this behavior. The disruption of microorganisms is not as easily determined by the analysis of particle size because disrupted cell walls and the original cells are of similar size (Müller et al., 2004).

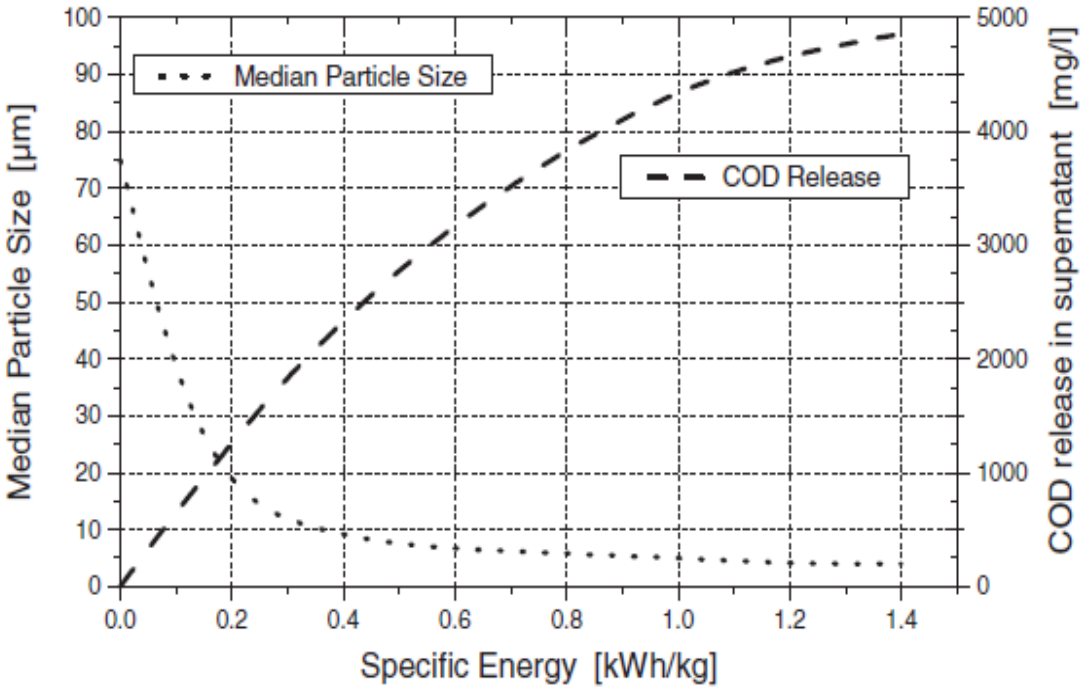

Figure 3.3 : Influence of disintegration on particle size and degree of disintegration in principle

Floc destruction and cell disruption can change sludge properties as follows:

Hydrolysis

Disintegrated micro-organisms are much more easily hydrolyzed than undisrupted ones. The reduction in particle size generally allows an easier hydrolysis of solids within the sludge due to larger surface areas in relation to the particle volumes. The result is an accelerated and enhanced degradation of the organic fraction of the solid phase.

Disinfection

Disintegration process affect all microorganisms. Higher organisms are disrupted easiest because of their size and gram-positive bacteria are the most difficult

organisms to be disrupted due to their strong cell wall. Depending upon the treatment a partial up to a complete disinfection of the sludge is possible since pathogenic micro-organisms are also disintegrated.

Thermal treatment is known as a suitable technique to deactivate micro-organisms in wastewater and in sludge. All of the pre-treatment methods discussed herein at least partially disinfect the sludge. An increase in energy input leads to a further reduction of pathogenic micro-organisms. The best results are obtained by thermal treatment.

Settling and dewatering

A large amount of organic solid material is transferred into the liquid phase in case of a strong disintegration The residual solid sludge particles of the sludge contain a higher percentage of inorganic substance. The result is a higher content of dry substance after dewatering (Müller, 2003). On the other hand in case of a less intense disintegration combined with a partial disruption of floc structures the results in settling of a well sedimenting sludge are worse. But the settling properties of filamentous sludges (bulking sludge) can be improved due to the destruction of voluminous floc structures.

Flocculation

The reduction of particle size and therefore the increase of the specific surface causes a higher amount of surface charges that need to be neutralized when the sludge is conditioned. Consequently, disintegrated sludges use more flocculant.

Bulking and foaming

The aim is to prevent foam problems in the aeration tank and in the digester, as well as the prevention of bulking sludge loss in the final clarification. This can be achieved by disintegrating the voluminous flocs of foaming and bulking sludge to a size of sludge flocs of normal shape thus improving their settling properties. By breaking up the filament structure of the voluminous flocs the supporting structure of filamentous organisms can be removed, gas bubbles are released, and the smaller fragments of the floc are able to settle and can be compacted better (Müller,2000c).

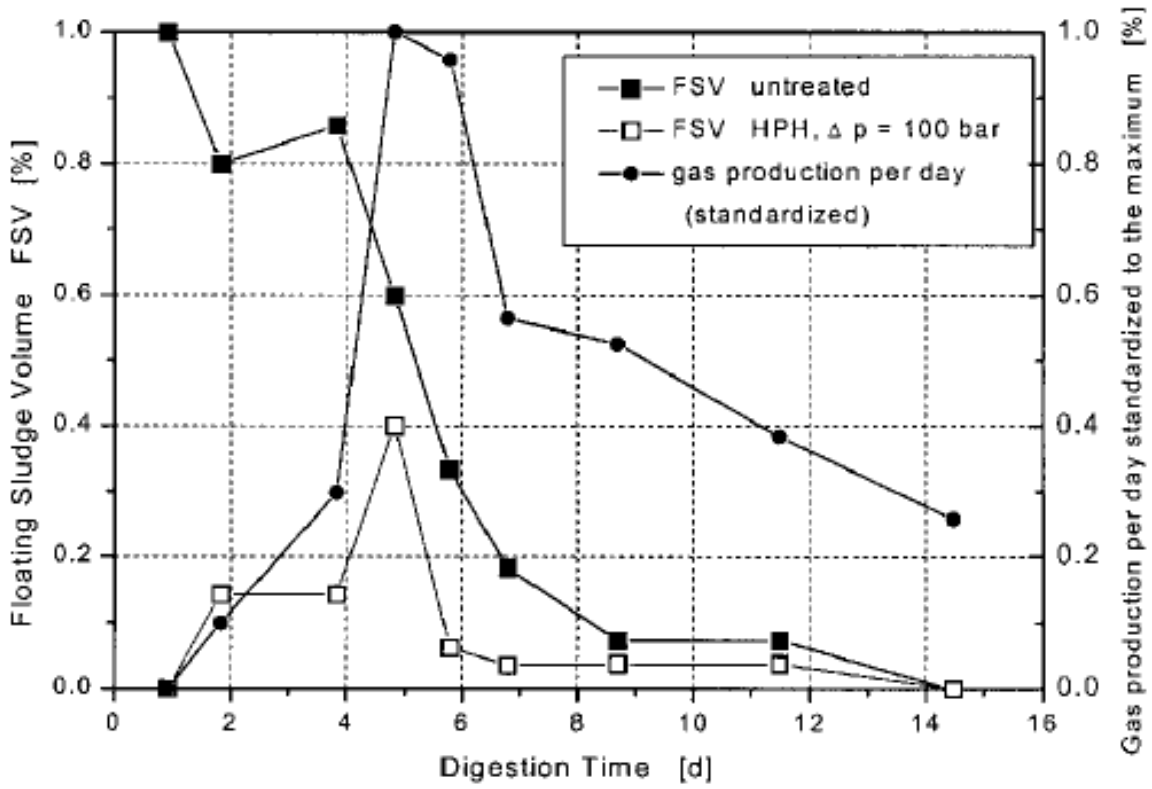

Figure 3.4 : Floating sludge volume (FSV) in an anaerobic batch digester (Müller**,** 2000b)

Results of batch-experiments (Müller, 2000) which are shown in Figure 3.4 showed that, after just one day of degradation both the waste activated sludge and the seeding anaerobic sludge were floating (FSV=100%). The disintegrated sludge starts with no foaming at all (FSV=0%). After five days of digestion the FSV rises up to 40%, because of the high gas production during that period.

3.1.2 Release of soluble substances and small particles

The result of floc destruction and cell disruption is the release of organic sludge components into the liquid phase. These components are either in dissolved phase or can be liqufied. Particle size or colloidal components may still be present within the solution because they cannot be separated from the liquid phase. Their minute particle size and only a slight difference in density of particle and surrounding water are the cause. But the components are easily biodegradable on the other hand. Since they are already liquefied or offer a large surface in comparison to their volume, the hydrolyzing process is simple.

The influence of the released amounts of carbon, nitrogen and phosphorus compounds on sludge characteristics are:

Degradation

Carbon compounds are easily accessible and can be digested much faster in later biological processes than sludge in a particular phase. The results are shorter degradation times and higher degrees of degradation during the aerobic and anaerobic stabilization.

The most appropriate type of sludge for disintegration is excess sludge because of the disintegration process is based on cell disruption. Through the disintegration process the biodegradability of excess sludge is enhanced and significant increase in methane and biogas production can be attained after the anaerobic digestion of disintegrated sludge. But these significant developments can only be obtained at high energy inputs. On the other hand there is only slight increase in the biodegradability of primary sludge because it does not cantain bacteria (Müller, 2000a).

Carbon source

Easily accessible compounds can further be used for carbon limited process steps within the wastewater treatment such as denitrification or the biologically enhanced phosphorus elimination.

Müller et al. (2000), showed that applying anaerobic digestion to the disintegrated sludge can increase the content of Kjeldahl-Nitrogen in the supernatant that caused by the extended degradation, which resulted in solution of nitrogen from the degredaded biomass.

Concentrations of organic components in the supernatant of excess sludge are shown in Table 3.1.

Table 3.1: Concentrations of organic components in the supernatant of excess sludge (1% SS)

	Untreated sample (mg/L)	Disintegrated sample (mg/L)	Factor
VSS	150-300	3000-5500	10-20
COD	50-200	1000-3000	5-20
Kjeldahl-Nitrogen	30-100	150-400	2-5
Phosphate PO_4–P	10-40	50-170	3-4

Return-Flow pollution

The wastewater has to be cleaned from released nitrogen and phosphorus compounds before leaving the treatment plant. If this happens by returning the water into the WAS-process, additional capacities have to be taken into account.

Recycling

A separate treatment and recycling is possible as well, e.g. through ammonia stripping or phosphor crystallization. Disintegration within the sludge pre-treatment has advantages in combination with selective recycling processes due to the increased nitrogen and phosphorus concentrations.

3.1.3 Biochemical reactions

During or immediately after the disintegration, biochemical reactions may appear. The influence of these reactions on the degradability of the sludge is contrary:

• Continuing formation or release of easily degradable compounds

• Formation of hardly degradable compounds (Müller et al., 2004).

The formation of problematically biodegradable, humic-like reaction products if sludges are disintegrated at higher temperatures can be explained by the "Maillard reaction". At lower temperature ranges this effect is less strong, but it is suspected that problematically biodegradable compounds are produced in any thermal disintegration process.

Many times proven is the transformation of problematic compounds to easily degradable compounds by partial oxidation. This effect has been found especially in the treatment of industrial wastewaters, but it is not fully verified in sludge treatment through ozone or other oxidation partners. The formation of hardly degradable compounds was found as well and degradation processes only performed well after an adaptation of the micro-organisms (Scheminski *et al*., 1999).

Biochemical reactions following the disintegration that is catalyzed by released enzymes are seen controversially by experts. While some authors see great potential, others have not been able to prove any kind of effect (ATV, 2003).

Potential benefits which have been claimed for pretreatment stages are:

- Improved pathogen kill

- More uniform end product
- Improved solids reduction
- Improved residuals stability
- Increase biogas yield and hence energy production
- Increase degradation of difficult compounds such as organics and pharmaceutical residues;
- More rapid digestion – short residence times in digesters
- Reduced foaming
- Provision of cell components for recycling into the treatment process ie carbon to improve denitrification
- Solubilisation of cell bound N and P to permit recovery and reuse Improve settleability of bulking sludges

Potential disadvantages of pretreatment include:

- Increased cost
- Increased process complexity
- Creation of recalcitrant components
- Additional odour
- Increased organic compounds (COD) in sludge liquor
- Impaired dewaterability requiring greater polymer use

Pretreatment methods may be used individually or in combination to deliver optimal results for a number of objectives.

3.2 Sludge Disintegration Methods

*****Mechanical Pre-treatments

- High pressure homogenizers
- The Lysat-centrifugal technique
- Impact grinding

- High Performance Pulse Technique
- Gamma Irradiation
- Freezing and thawing
- Stirred ball mill
- Ultrasound treatment

*Chemical Pre-treatments

- Acid or alkaline hydrolysis
- Ozone
- Fenton

*Thermal Pre-treatment

- Thermal hydrolysis

*****Biological Pre-treatment

3.2.1 Mechanical pre-treatments

3.2.1.1 High pressurized homogenizer

High pressure homogenizers consist of a multistep high-pressure pump and a homogenizing valve. The pump compress the sludge with pressures of several hundreds of bar. When the sludge passes through the homogenizing valve, the pressure drop drastically and high turbulence, shear forces and acceleration occur. As a result of that cavitation bubbles are created in the sludge particles. The cavitation bubbles formed implode and induce temperatures of several hundred degrees of Celsius. In the high pressurized homogenization unit disintegration takes place through cavitation created by sudden pressure release (Müller, 2000b).

The operating parameters which affect the cell breaking efficiency of high-pressure homogenizers are as follows:

- Operating Pressure
- Process Temperature
- Number of passes

- Valve/Orifice design
- Flow rate of the sample

There are certain variables to be considered while designing a homogenizer. They are:

- type of homogenizing valve/orifice
- operating pressure
- stages of disruption
- viscosity of the sample
- temperature
- type of the surfactant

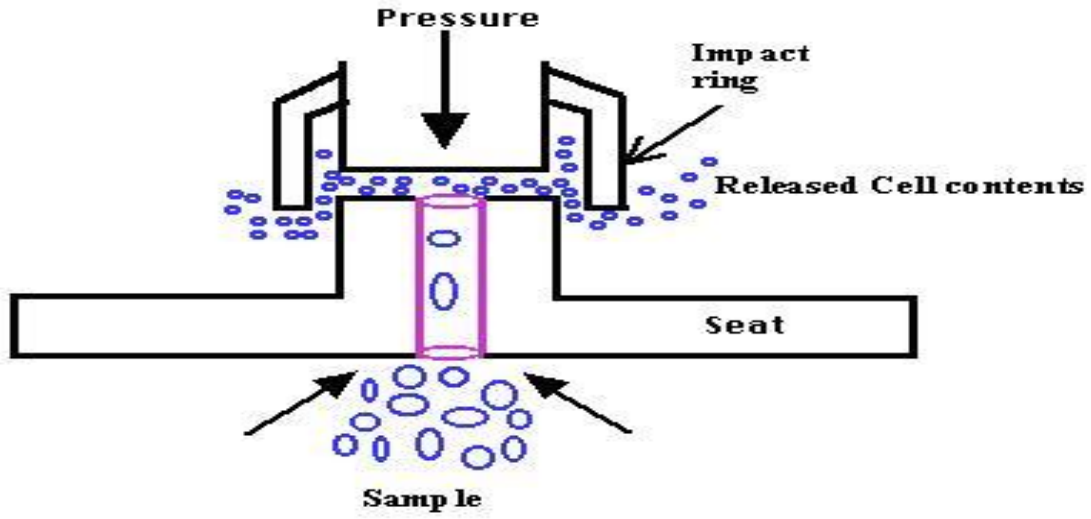

Figure 3.5 : High pressure homogenizer (1)

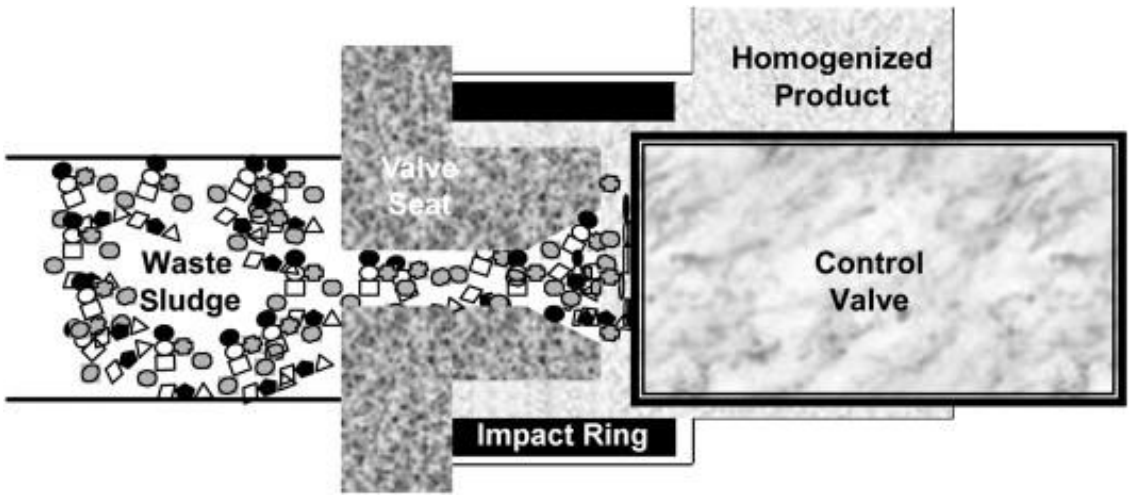

Figure 3.6 : High pressure homogenizer (2)

Advantages of high pressure homogenizers are:

*Easy to implement in WWTP

*No odor generation

*Better dewaterability of the final sludge

Disadvantages of high pressure homogenizers are:

*Low reduction of pathogens

*High tensions and erosion in the pump and homogenizing valve

*Clogging problems caused by coarse and fibrous particles.

In the study of Machnicka et al., High Pressurized Homogenizer is used for disintegration of sludge. Mechanical disintegration was executed with a high pressure pump (100bar) which recirculated sludge, from a 25 liter container, through a 1.2 mm nozzle. To force 25 liter of sludge through the nozzle 3 minutes were required. The disintegration process is applied for different durations such as 15, 30 and 60 minutes. The achieved recirculation rate was 5, 10 and 20. Waste activated sludge taken from the full scale treatment plant was added to samples of disintegrated sludge or foam and mixed. This mixture was digested in 2,5 liters glass bottles at constant temperature of 30 ^{o}C. Disintegrated activated sludge constituted 20% in volume, and foam 20 and 40 % in volume. During 14 days of digestion the amount of produced biogas was daily monitored (Figure 3.7).

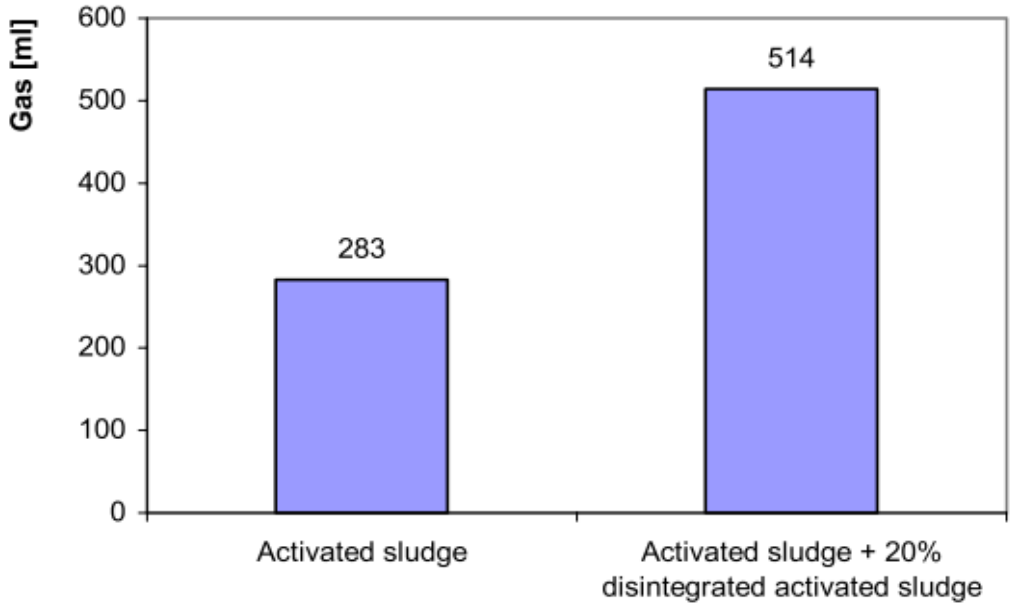

Figure 3.7 : Gas production after 14 days of anaerobic digestion

The results of addition of 20 % in volume of activated sludge on the effects of sludge anaerobic digestion is shown in Figure 3.7, the biogas production was almost doubled. After 14 days of anaerobic digestion the gas production of untreated waste activated sludge was 283 mL, where as the biogas production of the sample with added disintegrated sludge (20 %) was 514 mL.

3.2.1.2 The lysate centrifuge thickener

The use of altered centrifuges (Figure 3.8) to enhance cell lyses and to produce centrate which is rich in cellular degradation products has been suggested as a means of improving the performance of anaerobic digestion (Doha´nyos et al., 1997, 2004; Otte-Witte et al., 2000). The special adaptive modification to a centrifuge for extracting lysate is the addition of an impact gear or a ring allowing for the continued cellular disruption after the sludge has been thickened. The disintegrating gear is mounted at the end of the flow of thickened sludge and does not influence the centrate quality (Dohányos et al., 1997).

The method is capable of producing a 10–15% degree of disintegration (Müller et al., 2004), while also being capable of handling high volume flow rates. Energy consumption is dependent on the centrifuge output and, for high capacity centrifuges, is almost negligible (Zábranská et al., 2000). The addition of aerobic cell lysate with WAS thickened to 6% has been shown to increase anaerobic digestion performance as indicated by increased biogas production by as much as 86% (Doha´nyos et al., 1997).

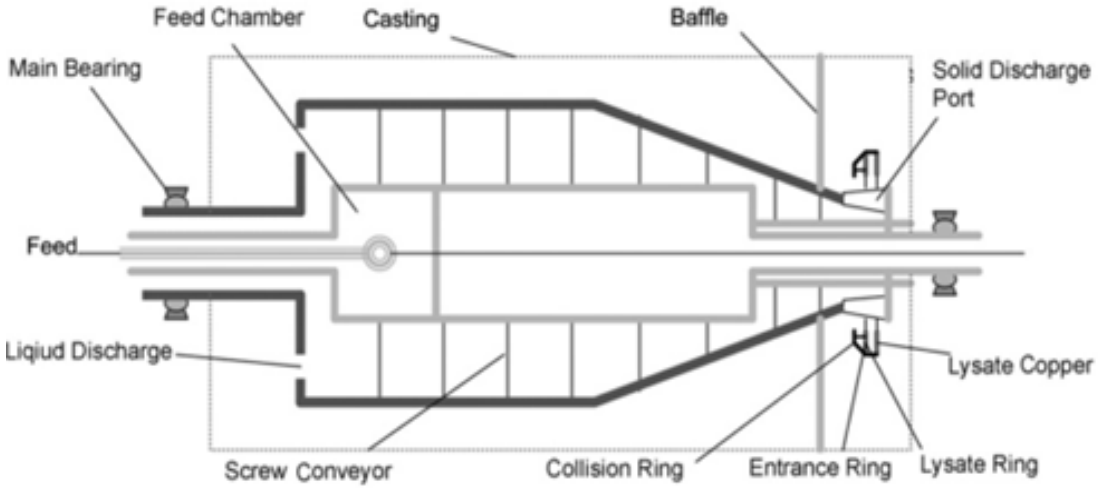

Figure 3.8 : Schematic of a lysate-thickening centrifuge (modified from Otte-Witte et al., 2000)

The extent of increase in methane production was found to depend on WWT plant operating parameters such as;

- Sludge age
- The content of organic material in mixed raw sludge
- Type of organic material in mixed raw sludge,
- The hydraulic retention time in digesters (Za´branska´ et al., 2000, 2005).

The higher effect of disintegration is achieved with a lower WAS age, shorter retention time in digesters, and with a higher anaerobic microorganism activity in the digesting sludge (Doha´nyos et al., 1997).

Advantages of the lysat-centrifugal technique are:

*Pathogen kill
*Enhancement of biogas production in anaerobic digestion
*Decrease in sludge viscosity
*Shorter retention time
*Enhancement of sludge settleability (no bulking problems)
*No odour generation

Disadvantages of the lysat-centrifugal technique are:

*The cellular disintegration is not effective

The primary benefit described by the developers of this process is the pathogen kill; however, a further benefit is the enhancement of biogas production in anaerobic digestion. During laboratory trials, a 10% improvement in biogas production was found (Mayhew et al., 2003).

One of the benefit obtained from using a thickening centrifuge is a considerable decrease in sludge viscosity. The limit for pumping of thickened excess sludge is typically around 6% TS. Greater thickening causes problems with clogging especially when pumping over longer distances. Disintegration enabled the excess activated sludge to be thickened to 9–11% TS, thereby reducing the volume of the input sludge, increasing the retention time of organic matter in the digester and decreasing the energy demand for digester heating. Hence, in addition to increased energy production from enhanced biogas output, energy demands in other component stages of the treatment process were reduced (Zábranská et al 2006).

The first full-scale lysate thickening centrifuge was installed at a WWT plant in Prague, Czech Republic. Another installation can be found in Liberec, Czech Republic, which resulted in a 26% increase in biogas production (Doha´nyos et al., 2004). Recently, Za´branska´ et al., (2006) reported long-term monitoring results from three full-scale installations of lysate thickening centrifuges. Biogas yield was increased by between 15 and 26% and the organic matter in the (mesophilic) digested sludge significantly decreased to 48–49%.

The technology has patents worldwide and its major licensee is VTA Engineering, Germany. The use of microbial enzymes for the enhancement of degradation of WAS is the basis for another process called the Enzymic Hydrolysis (EH) Process (Mayhew et al., 2002, 2003).

The EH stage, which has a retention time of 2 days, involves the use of a holding chamber where the WAS is kept at 42 1C (Mayhew et al., 2003). The process has been implemented at a municipal treatment plant in the UK. Another study adding prepared enzyme solutions to a pre-hydrolyzation contact chamber with an HRT of 4h increased the methane production of subsequent anaerobic digesters by 60% during pilot-scale trials (Davidsson et al., 2007).

3.2.1.3 Impact grinding

Impact grinding unit consist of two rotors revolve in opposite direction in a grinding chamber. It generates pressure differences which diminishes the particle size. The flocs are disrupted, but the cells are not disintegrated (Cartmell et al., 2004; Peltola et al., 2004).

Advantages of impact grinding are:

*No odour generation

*Enhances sludge settleability(no bulking problems)

Disadvantages of impact grinding are:

*The cellular disintegration is not effective

Figure 3.9 : Impact grinding unit

An impact grinding as a pre-treatment option was found to have beneficial effects on treatability of the studied wastes (sewage sludge, SS). In case of SS, the impact grinding resulted in effective disintegration of sludge flocks which in turn may help foaming problems during the following digestion.

Peltola et al., (2004, pp. 2,129 – 2,132) showed that impact grinding can increase the soluble chemical oxygen demand (COD) content of the organic fraction by approximately 2.5 times. This increased COD indicated partial disintegration of microbial floc of the organic fraction tough no increase in biogas production was observed, the onset of methane production began sooner. The breakdown of cell walls as a result of impact grinding could also improve the anaerobic digestion of dairy manure.

3.2.1.4 High performance pulse technique

The High Performance Pulse Technique is an electro-hydraulic method. The sludge is treated by high voltage of up to 10 kV. So a sudden disruption and release of organic substances takes place. The pulse period is only 10 milliseconds, inducing shockwaves in the sludge which lead to disintegration.

Advantages of high performance pulse technique are:

*No odour generation

*Erosion in the electrodes

Disadvantages of high performance pulse technique are:

*Low research and development

*High energy input

According to the Müller (2000c), the results obtained in large scale investigations using the HPP techniques have shown that significant improvement of the degradation process can only be obtained at higher energy input.

3.2.1.5 Freezing and thawing

By freezing and thawing activated sludge, the floc structure will be irreversibly changed into a more compact form, the bound water content will be reduced, and therefore the sludge dewatering characteristics can be significantly improved (Chu et al. 1999).

Advantages of freezing and thawing are:

*Beter dewaterability of the final sludge

Disadvantages of freezing and thawing are:

*High energy consumption (unless the freezing is natural)

The literature review by Pérez-Elvira et al. (2006), shows that the influence of sludge pre-treatment technology preceding its anaerobic digestion on the enhanced biogas production, sludge removal efficiency and pathogen reduction was so far investigated regarding different methods, although the freezing/thawin technique was examined only with reference to the dewatering ability (Reed et al., 1986; Martel, 1989; Chu et al., 1997; Örmeci and Vesilind, 2001). Its involvement in anaerobic digestion seems to be counter-productive due to high energy consumption. This does not apply to some countries that have specific climate conditions, or that have access to natural or artificial ice – thereby allowing freezing without additional operational costs. The practical aspects of this process and its effect on the anaerobic stabilization of sewage sludge should be examined. If the production of biogas could be increased,

the whole process would become more cost-effective despite environmental restrictions.

Only a few studies regarding sludge pre-treatment via freezing/thawing in the enhancement of its anaerobic digesting efficiency were found; furthermore, they concern merely waste-activated sludge (Wang et al., 1995). Reports relating to the evaluation of the effects of such pre condition technique on the chemical composition of mixed sewage sludge (which consists of primary sludge and waste-activated sludge) were not found. Similarly, its influence on anaerobic digestion process and biogas production was not investigated. Considering a specific character of the primary and waste-activated sludge and taking into account that mixed sludge is a typical digester feed in the full-scale systems, these issues are worth researching.

In the present studies, the influence of freezing/thawing disintegration on the change in characteristics of mixed sewage sludge was evaluated. Moreover, its effect on anaerobic digestion was analyzed based on changes in bioreactor operational conditions, enhanced biogas production and the quality of the digester supernatant. The freezing/thawing technique followed by the mixed sludge anaerobic digestion was evaluated on the basis of the global mass balance calculations and the question of whether freezing/thawing disintegration could be considered as a pre-treatment method or as the first stage of the “double-phase digestion”.

Table 3.2: Characteristics of raw (RS) and frozen/thawed sewage sludge (FTS) supplied to RS and FTS systems.

Parameter	Unit	Value	Raw sludge (influent to RS reactor)	Frozen/thawed sludge (influent to FTS reactor)
pH	–	Average	6.39	5.82
		Upper/Lower 95% mean	6.46/6.32	5.87/5.77
Alkalinity	mg/L	Average	1100	1400
		Upper/Lower 95% mean	1157/1043	1470/1330
COD	mg/L	Average	43,844	38,566
		Upper/Lower 95% mean	45,531/42157	42,586/34,546
SCOD	mg/L	Average	3190	6756
		Upper/Lower 95% mean	3411/2969	7638/5874
VFA	mg/L	Average	1757	3755
		Upper/Lower 95% mean	1804/1710	3845/3665
TS	g/kg	Average	41.0	34.4
		Upper/Lower 95% mean	42.3/39.7	35.5/33.3
VS	g/kg	Average	31.4	26.1
		Upper/Lower 95% mean	32.3/30.5	26.9/25.3

The average biogas yields attained during investigations (Montusiewicz et al., 2010) are shown in Figure 3.10. The biogas production per kg of VS removed, which was calculated in the RS system and amounted to 0.86 m^3/kg VS, was in compliance with the range of 0.75–1.12 m^3/kg VS that was suggested by Tchobanoglous et al. (2003), as an adequate yield from sewage sludge anaerobic digestion. A comparison of such values in both systems showed that the biogas yield obtained from the frozen/thawed sludge exceeded approximately 1.5 times the value achieved from the raw sludge and

reached 1.31 m^3/kg of volatile solids removed. A similar tendency was observed with regard to the biogas yields based on the removed TS and COD. The increased values were achieved in the FTS system despite a lower solids loading rate and a minor concentration of VS. The possible explanation is that the solubilisation of organic matter resulted from sludge disintegration and this was confirmed by both the high concentrations of SCOD and VFA. An increased content of the solutes regarded as the substrate, being more available and easy to convert for microorganisms, resulted in an improved biogas yield.

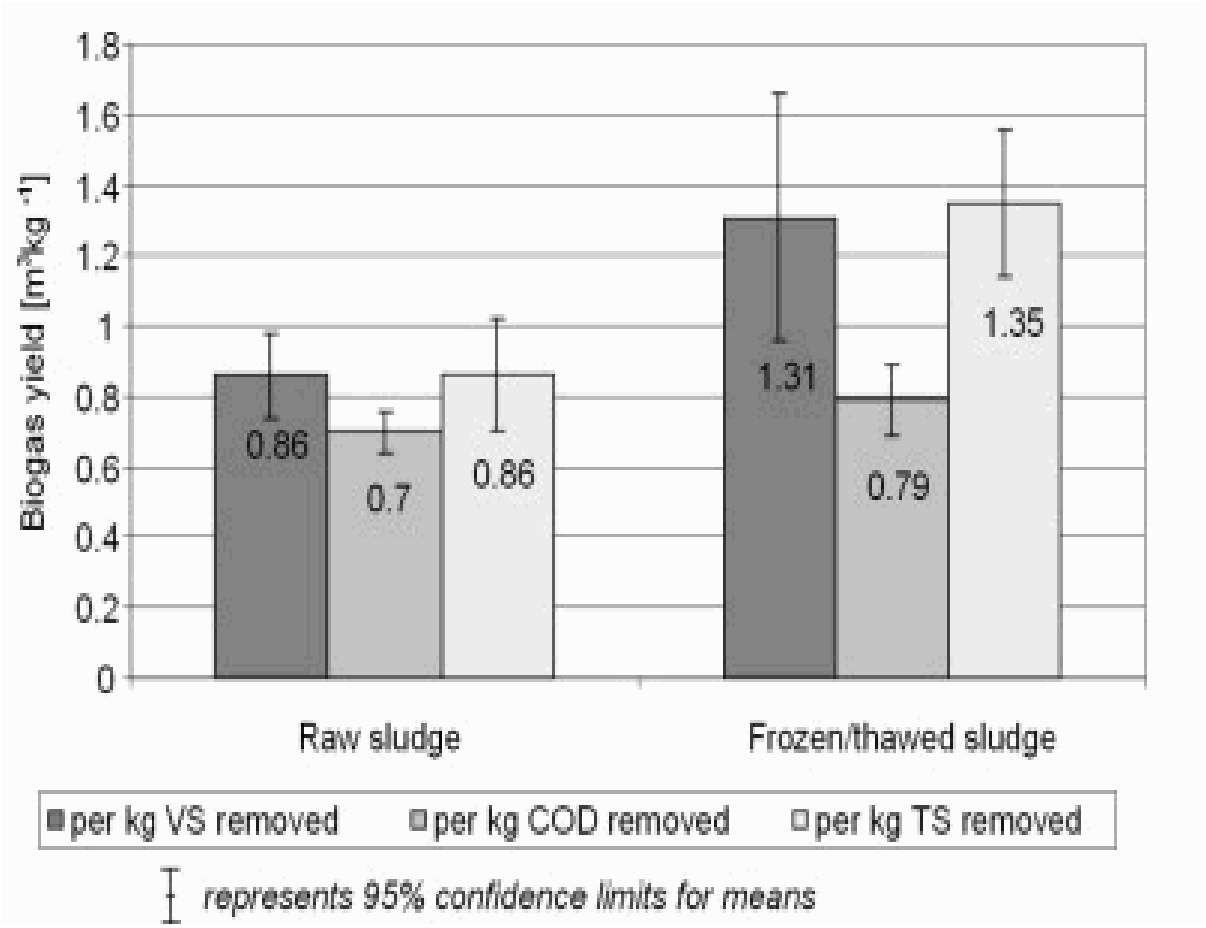

Figure 3.10 : The biogas yields obtained from RS (raw sludge) and FTS (frozen/thawed) systems.

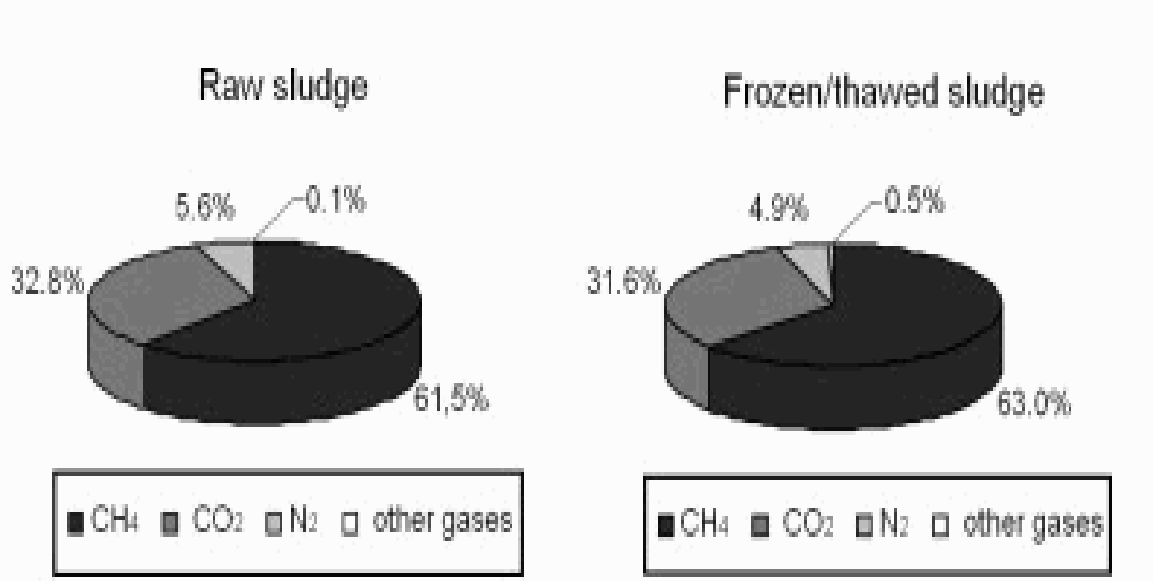

Figure 3.11 : The biogas composition observed in RS and FTS systems.

During experiments, a comparable biogas composition in both reactors was observed (Figure 3.11). The average methane content was 61.5% and 63.0%, respectively, in the system fed with raw and frozen/thawed sludge; an average difference of only 1.5% was obtained. These results indicated that disintegration of mixed (primary and waste) sewage sludge via freezing/thawing influenced the share of biogas components to a minor extent.

3.2.1.6 Gamma irradiation

Gamma irradiation has been studied mainly for its pasteurization effect (Etzel et al. 1969; Yeager and O'Brien 1983) Also; gamma irradiation is known to release soluble carbohydrate from activated sludge (Mustapha and Foster 1985). The technology of irradiation – pasteurization liberates the soluble existing in the sludge. It has been shown toquickly, efficiently and reliably deal with potential health hazard materials in sewage sludge.

Irradiation of sludge can be carried out with cobalt-60 source, which emits gamma rays. These rays penetrate and pass through the sludge, inactivating microorganisms and decomposing various organic compounds without leaving in any residual radioactivity or making the sludge radioactive. The finished product "clean sludge" can be utilized as an organic, sanitary fertilizer/soil conditioner or use as animal feed.

Figure 3.12: Gamma Detector

Advantages of gamma irradiation are ;

*On drying, it could be powdered easily and does not have bad odour

*Increase the mobility of Pb, Cu and Zn in soil (Campanella et al., 1989)

*Gamma rays can remove a wide variety of organic contaminants and disinfect the sludge of harmful microorganisms (Borerely et el., 1998).

Disadvantages of gamma irradiation are;

*No significant improvements in terms of biogas volumes.

The effects of γ-irradiation pretreatment on anaerobic digestibility of sewage sludge were investigated in China. Parameters like solid components, soluble components, and biogas production of anaerobic digestion experiment for sewage sludge were measured. The values of these parameters were compared before and after γ-irradiation pretreatment. Total solid (TS), volatile solid (VS), suspended solid (SS), volatile suspended solid (VSS), and average floc size of samples decreased after γ-irradiation treatment. Besides, floc size distribution of sewage sludge shifted from 80–100 μm to 0–40 μm after γ-irradiation treatment at the doses from 0 to 30 kGy, which indicated the disintegration of sewage sludge. Moreover, microbe cells of sewage sludge were ruptured by γ-irradiation treatment, which resulted in the release

of cytoplasm and increase of soluble chemical oxygen demand (SCOD). Both sludge disintegration and microbe cells rupture enhanced the subsequent anaerobic digestion process, which was demonstrated by the increase of accumulated biogas production. Compared with digesters fed with none irradiated sludge, the accumulated biogas production increased 44, 98, and 178 mL for digesters fed sludge irradiated at 2.48, 6.51, and 11.24 kGy, respectively. The results indicated that γ-irradiation pretreatment could effectively enhance anaerobic digestibility of sewage sludge, and correspondingly, could accelerate hydrolysis process, shorten sludge retention time of sludge anaerobic digestion process.

3.2.1.7 Stirred ball mill

Stirred ball mill consist of a cylindrical grinding chamber which is almost completely filled with grinding beads. A rotor forces the beads into a rotational movement. The microorganisms are disintegrated between the beads by shear and pressure forces.

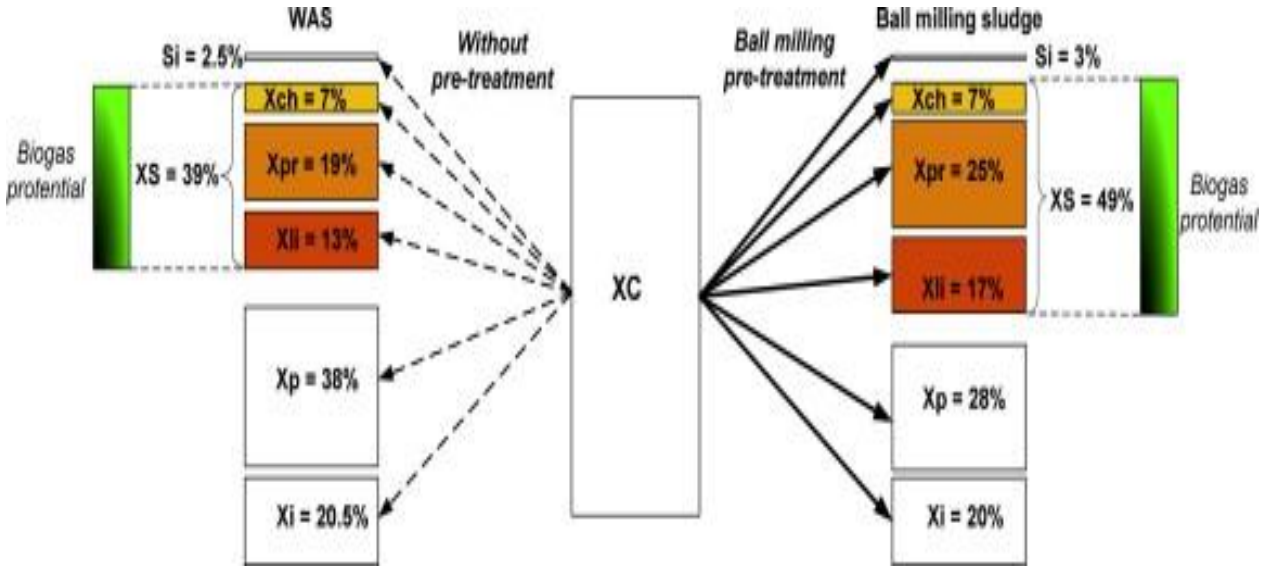

Figure 3.13 : COD-fractionation of composite solids Xc of WAS with and without ball milling pre-treatment.

Figure 3.14 : Full scale ball milling installation.

Figure 3.15 : Stirred ball mill

Full-scale studies have been done in Germany. The result at one German WWTP showed a high rate of disintegration for the stirred ball mill, approximately 23 % (Müller et al., 2004). The energy input in this study was approximately 21 kWh/m3 WAS. At another German WWTP, the biogas production and the degree of degradation increased by approximately 20 % (Winter, 2002). However, in both studies, the disintegration method was considered to be cost effective only if the waste sludge disposal costs are high.

Advantages of stirred mills are:

*Reliability of operation

*No odour generation

Disadvantages of stirred mills are:

*Huge erosion in the grinding chamber

*High energy friction losses

*Clogging problems

*The degree of the disintegration sludge is lower compared to other techniques.

3.2.1.8 Ultrasound pretreatment

Ultrasound is defined as sound with a frequency beyond the upper limit of human hearing. The normal range of hearing is between 16 Hz and about 18 kHz and ultrasound is generally considered as any sound with a frequency greater than 20 kHz (Ince et al., 2001).

In practice, three ranges of frequencies are reported (Ince et al., 2001):

- High frequency, or diagnostic ultrasound (2–10 MHz)
- Medium frequency ultrasound (300–1000 kHz)
- Low frequency or conventional power ultrasound (16–100 kHz).

Ultrasonic disintegration is a common used method for breaking up of microbial cells and for the withdrawal of intracellular material (Harrison, 1991). Ultrasound waves influence a liquid in which, they cause periodical compression (Positive pressures) and rarefaction (negative pressures) of the media.

Micro bubbles occur above a certain intensity threshold in rarefaction due to the negative pressure.

These micro bubbles also known as cavitation bubbles, essentially containing vaporized liquid and gas that was previously dissolved in the liquid. As the wave fronts propagate, microbubbles oscillate under the influence of positive pressure. Cavitation bubbles first grow in size until reach adequate bubble size within a few microseconds and then violently collapse when they reach its critical size is shown in the Figure 3.16.

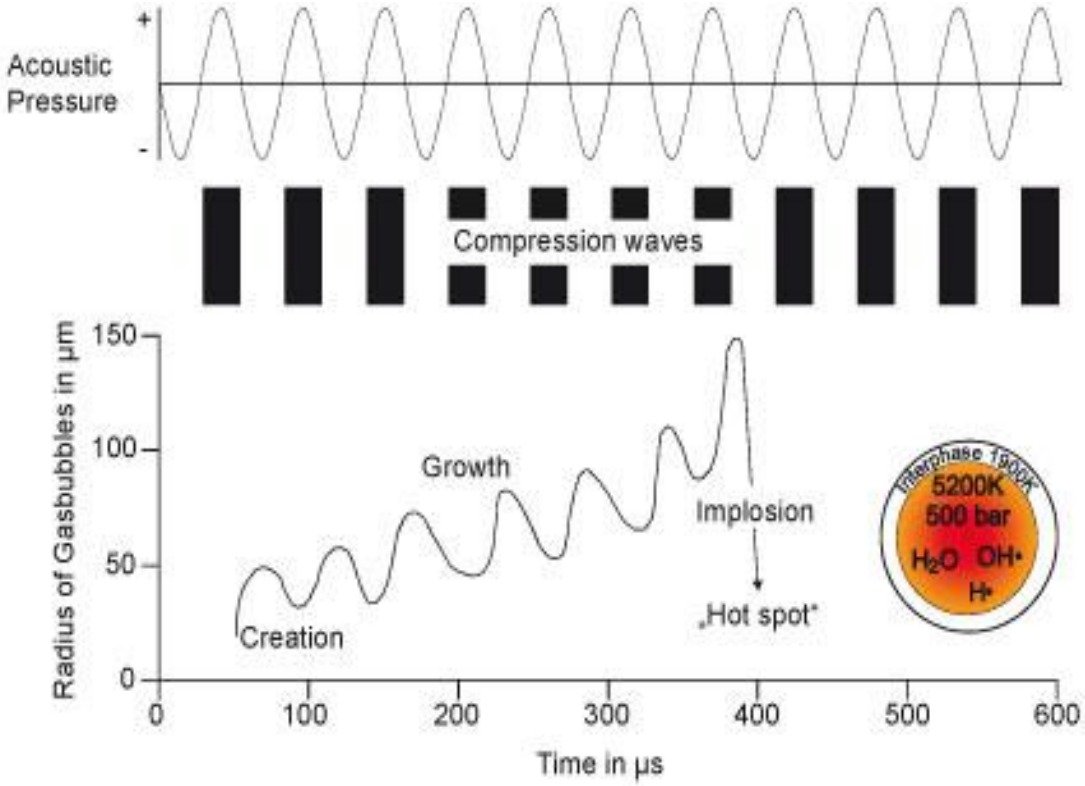

Figure 3.16 : The growth and critical size of cavitation bubbles.

In the following compression phase these bubbles implode under extreme conditions in micro scale (cavitation). This generates pressures of over 500 bar and enormous shear forces at temperatures of up to 5,200 Kelvin. These processes tear up the walls of organic cells, bacteria, fungi etc

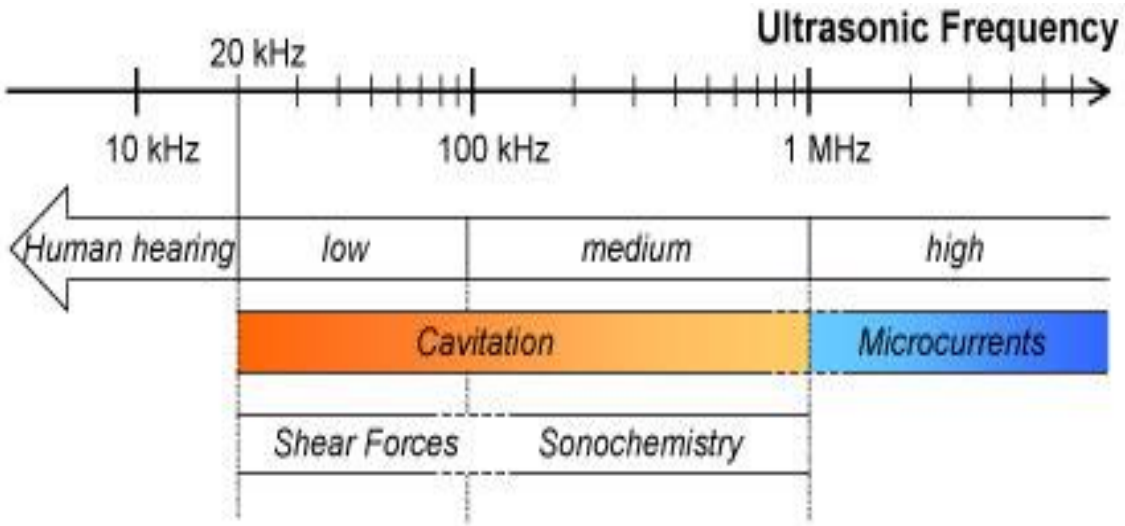

Figure 3.17 : Ultrasonic frequency that cavitation occurs.

In the lower frequency range (20 kHz to 100 kHz) big cavitation bubbles are generated which excite extremely high shear forces and strong effects.In the middle frequency range (100 kHz to 1 MHz) the bubbles are smaller but the cavitation is more effective, generating radical sono-chemical reactions in the water. Sonicating such a liquid with a frequency of over 1 MHz, the liquid begins to flow on molecular level.

There are four paths, which are shown as following, responsible for the ultrasonic activated sludge disintegration:

- Hydro-mechanical shear forces;
- Oxidizing effect of •OH, •H, •N and •O produced under the ultrasonic radiation;
- Thermal decomposition of volatile hydrophobic substances in the sludge;
- Increase of temperature during ultrasonic activated sludge disintegration (Wang et. al., 2005).

Ultrasound can provide the driving force for a wide range of chemical and industrial processing. Its potential stems from three main types of actions: mechanical, chemical and thermal effects, related to the formation and collapse of bubbles (cavitation) in the liquid to which the ultrasound is applied (Neis and Tiehm, 1999). The specific effects that can be observed when cavitation is generated are summarized below (Portenlänger, 1999; Neis et al., 2001):

- Mechanical action: generation of shear stress and forces, jets and shock waves resulting in rapid mass transfer, particle size reduction and cell destruction
- Chemical action: radical reactions due to the generation of hydrogen atoms and hydroxyl radicals which can trigger subsequent chemical transformation of (organic) substances
- Thermal action: generation of high temperature with breakdown of volatile hydrophobic substances within the imploding bubbles.

Ultrasound systems

There are three basic methods of applying acoustic power to liquids in general and sludge in particular:

- Probe systems
- Tube reactors
- Bath reactors.

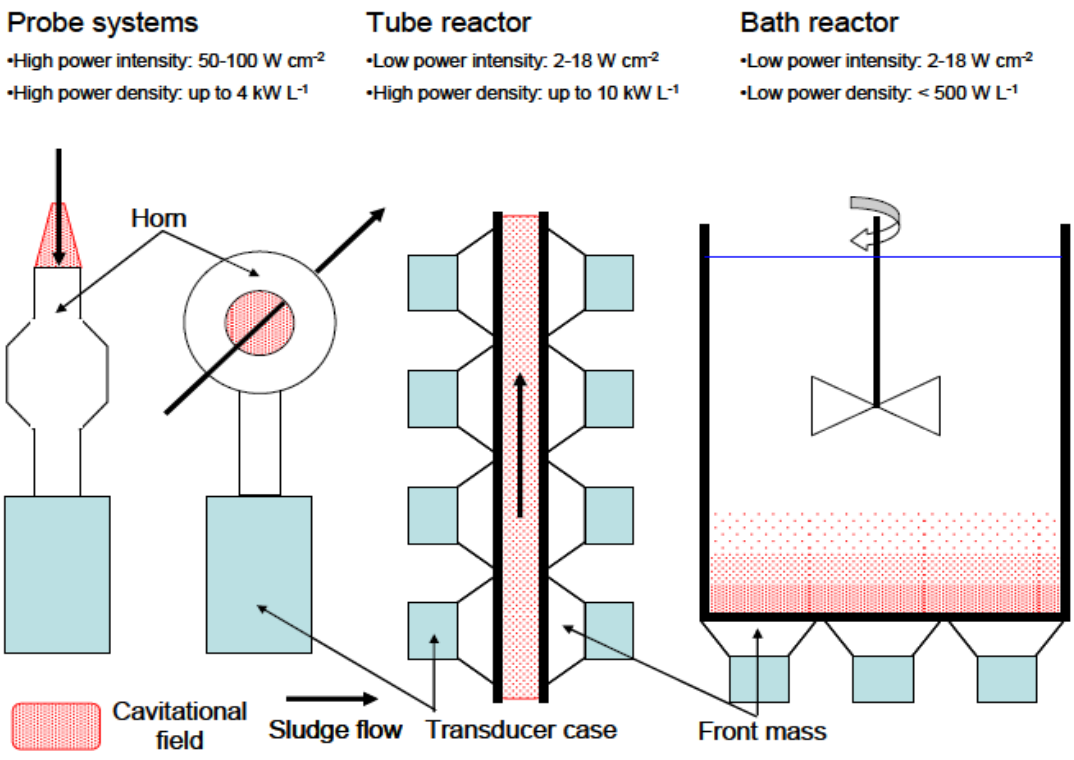

Figure 3.18 : Ultrasound systems

Probe systems

Probe systems are usually used for laboratory research and in the environmental field. Most of full-scale applications of ultrasound are equipped with these systems to enhance anaerobic digestion by sludge disintegration, as described by Kurth (2002), Panter (2002), Purcell (2002), Winter (2002), Enpure (2008), Wolff (2007).

There is a single powerful transducer in probe systems which couples energy into a chemical reaction by means of a horn or velocity transformer. The power input per transducer in sludge disintegration processes is generally between 1 and 6 kW (Enpure, 2005; Ultrawaves, 2008a), up to 16 kW (Hielscher, 2005). The horn focuses the energy into the radiating surfaces immersed in the liquid sample. The motion of the radiating surfaces creates the sound waves that propagate through the liquid, generating microbubbles and causing cavitation.

Operational parameters

Ultrasound systems are really sensitive to operational parameters, that can't be controlled without a good knowledge of physical and chemical phenomena (Ince et al., 2001). A reliable description of the sound field would be accomplished by a local energy density formulation which includes the distribution of sound energy in the liquid volume and takes into account the reactor geometry (Horst and Hoffmann, 1999). In practice, the ultrasound power input is quantified by calorimetric or, even more directly, by electrical measurements. The most common parameters used are defined in Table 3.3.

Table 3.3: Terminology and the units of ultrasound systems

Terminology	Definition	Units
Ultrasonic Intensity	Power supplied per horn or transducer area	W/ cm^2
Ultrasonic Density	Power supplied per sample volume	W/mL
Ultrasonic Dose	Energy supplied per sample volume	W-s/ mL
Spesific Ultrasonic Dose (SUD)	Power supplied for an exposure time per unit volume and mass of sample	W-s/kg-solids

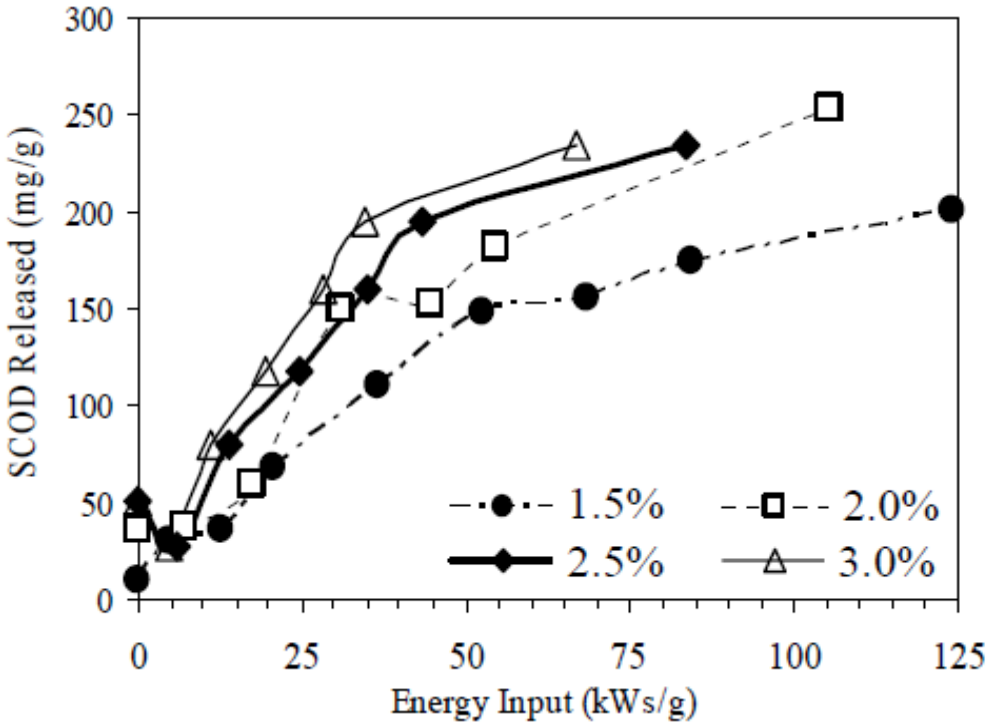

Figure 3.19 : SCOD release at different energy inputs and TS contents (Khanal et al., 2006c)

Dewil et al., (2006), conducted a thorough study to evaluate the effect of TS contents on SCOD release at different specific energy inputs. The results are presented in Figure 3.19.

Advantages of ultrasonic technologies are;

- Average payback period of the installed plants is below two years; this is mainly due to the high cost of recycling of sludge. (the main influences on payback time would consist of local legislation, treatment type, land availability, electricity price and views on renewable energy)
- Improves degradation of organic material (30-45%)
- Increases yield in digester biogas (30-45%); the increase in biogas production could produce as much as 240 million m3 of gas or 480 GWh/yr of "green" electricity.
- Reduces sludge solids content (5-25%)
- Increases dry solids with dewatering with or without prior digestion (5-10%)
- Reduces polymer and other flocculant use (15-45%)
- Minimizes sludge cake quantity (25-40%)
- Eliminates sludge bulking

- Less sludge, improved sludge stabilization, and enhanced dewaterability result in an improved C/N ratio for denitrification. (Bartholomew,R., 2002)

Disadvantages of ultrasonic homogenizers are:

- Erosion in the sonotrode.
- Negative energy balance due to the high energy consumption of the equipment.

Tiehm et al., 1997 showed that applying ultrasound (3.6kW, 31 kHz, 64 s) to sludge disintegration can release the organic substances into the sludge, so that the soluble chemical oxygen demand (SCOD) in the supernatant increases from 630 to 2270 mg/L. Moreover, the digestion time reduces from 22 days to 8 days. Neis et al., 2000, used a pilot- scale plant consisting of a 3.6 kW ultrasound reactor and five stirred tank fermenters. The average waste activated sludge (WAS) retention time is 16 days. The dry solids (DS) content of the thickened WAS varied between 0.7 and 2.6 % and the volatile solids (VS) concentration was 78 %.

The pilotscale reactor was developed for operation at a low frequency of 31 kHz. Two control fermenters were operated with untreated sludge at sludge residence times (SRT) of 16 and 8 days. Three fermenters were fed with ultrasonically treated sludge at SRT of 16, 8 and 4 days. The enhanced degradation rates resulted in a significant increase of biogas production (Figure 3.20). Specific biogas yields ranged between 520 and 730 L/kg VS degraded. The methane concentration of the biogas varied between 67 to 72 %.

Table 3.4: Effects of ultrasound pre-treatment (at 31 kHz) and subsequent digestion time on anaerobic volatile solids degradation (VSdeg) of waste activated sludge and biogas production (Neis et al., 2008).

WAS	HRT(d)	Degradation rate (gVS_{deg}/ (m^3 digester volume *d))	Degree of degradation (%)	Biogas production rate (m^3/ m^3 digester volume *d)
Untreated	16	257	32.3	0.19
Disintegrated	16	335	42.4	0.21
Untreated	8	430	27.0	0.31
Disintegrated	8	603	38.1	0.36
Disintegrated	4	1011	32.0	0.52

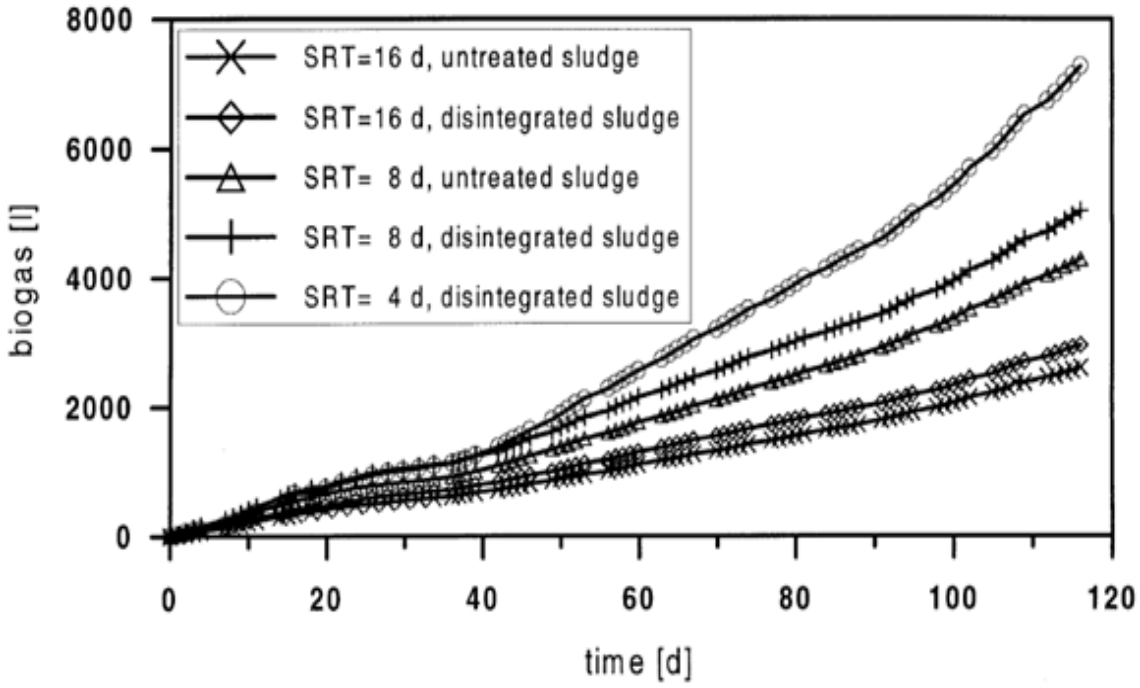

Figure 3.20 : Biogas production during anaerobic fermentation of untreated and sonicated waste activated sludge.

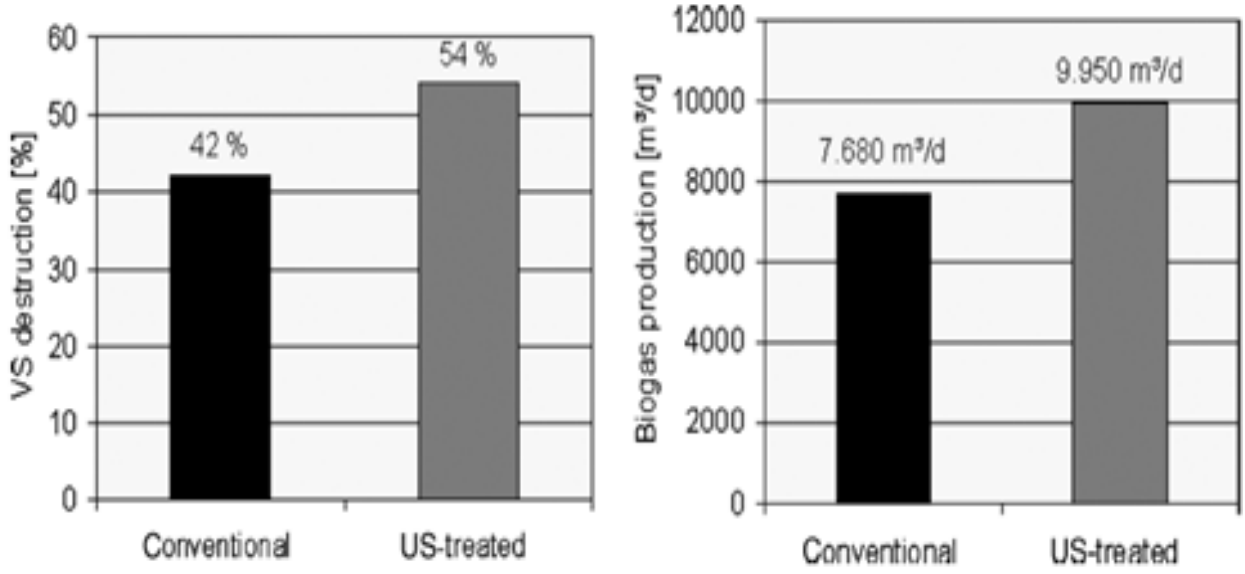

Figure 3.21 : The changes in VS destruction and Biogas production by ultrasound pretreatment.

An increase of VS destruction and biogas production was apparent at the Bamberg WWTP after ultrasound had been installed. As compared to the conventional digestion, VS destruction increased by 28% and biogas production increased by nearly 30% in the digester fed with ultrasound treated sludge (Figure 3.21).

Süd Treatment Works in Germany anaerobically digests a waste stream consisting of 100% secondary sludge. Since operation of the ultrasound plant began in May 2000, the digesters have experienced an average of 50% improvement in volatile solids destruction. This has resulted in a 45% increase in biogas production.

Xie et al., 2009, studied with municipal wastewater treatment sludge, was disposed by the anaerobic sludge with/without ultrasonic treatment. The result showed that the COD removal efficiency increased 3.60% after ultrasonic treatment and the effluent COD was about 30% lower than that of the control.

Braguglia et al., (2006), investigated the kinetics of anaerobic degradation of the original and sonicated sludge. Sonication was reported to increase the reaction rate, as indicated by the increase in hydrolysis constant values from 30% to 80%. The low ultrasound energy input (6000 kJ/kg solids) in their experiments showed that the digestibility of the secondary sludge can be greatly improved just by reducing the floc size as opposed to completely destroying bacterial cells.

Muller et al., (2005), used mesophilic reactors (38 L with 15-day retention times) to determine the impact of ultrasonic pretreatment and its point of application on

treatment performance. Various scenarios were evaluated; including pretreatment of WAS before entering the anaerobic reactor and that of the anaerobic sludge recycling within the anaerobic digesters. Results showed only a small difference for the two cases. However, a correlation was found to exist between gas production and energy applied. The authors elaborated further that, upon scale-up, one should expect the recycle sonication system to outperform a WAS pretreatment system. This would come as the majority of solids in the recycle line are refractory compounds which would be specifically disintegrated by sonication. Contrary to this, the pretreatment of WAS exposes both the readily degradable substrate as well as the refractory compounds, thus requiring more energy. The researchers were able to improve gas production by 17%, with a 6.2% increase in total solids destruction. This enhanced degradation coincided with an increase in nitrogen in the liquid phase, suggesting that the protein component of the sludge flocs had been degraded.

Not all studies confirmed an enhancement of VS reduction and higher biogas production with ultrasound pretreatment. Sandino et al., (2005), reported an insignificant increase in VS destruction based on a 7-month pilot trial using 18-L mesophilic digesters. It was mentioned, however, that the WAS had become somewhat septic. Pretreatment by sonication only resulted in a faster rate of reaction but the VS reduction endpoint remained the same. This finding suggests that smaller anaerobic reactors could be designed with sonication pretreatment, while achieving the same rate of VS reduction and gas production.

There have been a number of full-scale trials to demonstrate the effectiveness of sonication pretreatment. Xie et al., (2005), reported on a trial at a municipal treatment facility in Singapore that uses egg-shaped anaerobic digesters to treat its primary and secondary sludges. Two full-scale digesters (4500 m^3 volume), an experimental and a control digester, were used for the trial. The sludge flow rate was 200 m^3/d. The experimental line was fed sludge which had passed through an ultrasound chamber, while the reference line received sludge without pretreatment. The ultrasound facility consisted of a 20 kHz generator and a stack of five donut-shaped horns which produced a central holding capacity of 3.5 L. The exposure time to sonication was estimated to be 3.5 s. The solids retention time (SRT) in the digesters was approximately 30 days. Over a 6-month data collection period, the experimental system consistently produced a minimum of 200 m^3/d more gas than

the reference system. Marginal decrease in total suspended solids (TSS) and volatile suspended solids (VSS) was reported after sonication. The authors postulated that there would be a net energy gain of 3.6 times if only WAS was treated.

Other full-scale trials include the one in Avonmouth, UK, where one of the six mesophilic digesters (2700 m^3, 12 day HRT) received WAS pretreated with Sonix technology (Hogan et al., 2004). Primary sludge, which is relatively easy to digest, remained untreated. Sonication pretreatment of the WAS resulted in three times more sludge being assimilated in the anaerobic digester with a 20–30% increase in gas production. A similar 5-month trial was performed at the WWTP in Orange County, US, with a 50% increase in gas production (Hogan et al., 2004).

Wolff et al., (2007) considered the ultrasound treatment technique for EAS to be cost effective even though the disposal costs in the actual case were low. The payback time for the equipment was calculated to be approximately three years. The energy input was 0.044 kWh/kg TS. Since the volatile solid degree of degradation increased from 34 % to 45 %, the improvement in digester performance was 32 %.

Table 3.5: Literature view about the results of ultrasonic disintegration method on anaerobic digestion

Substrate	Treatment Conditions	Anaerobic Digestion Conditions	Results	References
Mixed Sludge	31 kHz 3.6 kW, 64 s	Continuous, HRT: 22days 37 ^{o}C	Increase of VS removal from 45.8* to 50.3 % (+9 %)	(Tiehm et al., 1997)
Mixed Sludge (25 g TS/L)	9 kHz 200 W, 30 min.	Batch, 11 days 36 ^{o}C	Increase of CH_4 production from 210* to 345 ml/g VS_{in} (+64 %)	(Wang et al., 1999)
Activated Sludge (SRT: 16 days)	41 kHz 150 min.	Semi-continuous, HRT: 8days 37^{o}C	Increase of VS removal from 21.5* to 33.7 % (+36 %)	(Tiehm et al., 2001)
Activated Sludge (9.38 g TS/L)	20 kHz 0.33 W/mL 20 min.	Batch, 1OO days 35 ^{o}C	Increase of CH_4 production from 143* to 292 g/kg TS_{in} (+104 %)	(Chu et al., 2002)
Sewage Sludge (54 g TS/L)	20 kHz 200 W, 30 min.	Batch, 33 days 37 ^{o}C	Increase of biogas production (+138 %)	(Onyeche et al., 2002)
Mixed Sludge	20 kHz 180 W, 60 s	Batch, 28 days 35 ^{o}C	Increase of biogas production (+24%)	(Bien et al., 2004)
Activated Sludge (27 g TS/L)	20 kHz, 7,000 and 15,000 kJ.kg/TS	Batch, 16 days 35 ^{o}C	Increase of biogas production (+40 %)	(Bougrier et al., 2005)
Activated Sludge	5,000 kJ.kg/TS	Semi-continuous, HRT: 20 days	Increase of biogas production (+36 %)	(Braguglia et al., 2008)
Activated Sludge (17.1 g TS/L)	20 kHz 108,000 J.kg/TS	Batch, 50 days 37 ^{o}C	Increase of biogas production (+84 %)	(Salsabil et al., 2009)
Activated Sludge (2.14 % TS)	20 kHz 9690 kJ.kg/TS	Batch, 35 days 36 ^{o}C	Increase of biogas production (+44 %)	(Erden and Filibeli, 2009)
Activated Sludge	30 kWh/m^3 sludge	Batch	Increase of biogas production (+42 %)	(Perez-Elvira et al., 2009)
Activated Sludge	30 kWh/m^3 sludge	Continuous, HRT: 20 days	Increase of biogas production (+37 %)	
Activated Sludge	Sonication of 25 % of WAS	WWTP 330,000 PE	Increase of biogas production (+30 %)	(Neis et al., 2008)
Mixed Sludge (1.5 % VSS)	20 kHz 13.7 W/cm^2 1.5s	5000 m^3 egg-shape digester HRT: 22.5 days, 29-33 ^{o}C	Increase of biogas production (+45 %)	(Xie et al., 2007)

3.2.2 Chemical pre-treatments

3.2.2.1 Alkaline hydrolysis

Alkaline pretreatment is a commonly examined pretreatment method which is very effective in terms of solubilizing extracellular polymers (Neyens et al., 2003). Alkali ambient conditions allow the improvement of hydrolysis and the conversion of lipids, proteins and hydrocarbons into more simple and soluble molecules such as aliphatic acids, polysaccharide and amino acids (Everett, 1973).

For the chemical pretreatment, various alkaline agents were used such as NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$.

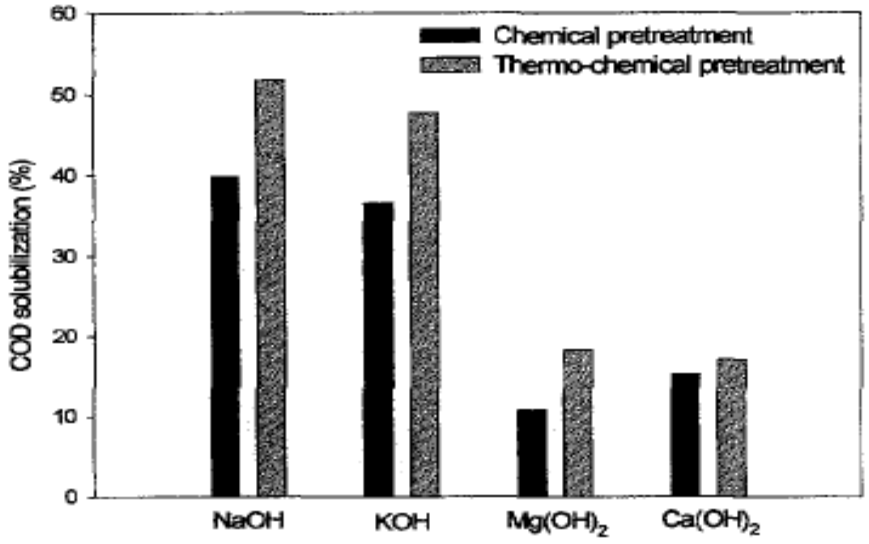

Figure 3.22 : Effects of varios alkaline agents on COD solubilization.

Alkaline pretreatments were performed at pH 12 with various alkaline agents NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$. At ambient temperature, the COD solubilization values after NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$ addition at final concentrations ranging from 0 to 21 *g/l* were 39.8%, 36.6%, 10.8% and 15.3%, respectively. Similarly, following treatment at 121°C for 30 rain, NaOH addition resulted in 51.8% COD solubilization with the other values being 47.8, 18.3 and 17.1, respectively. COD solubilization levels are shown in Figure 3.22 (Kim et al., 2003).

Sodium hydroxide can solubilize municipal waste activated sludge efficiently at ambient temperature even at low dosages.

Alkaline pretreatment has been also used to solubilize various substrates such as lignocellulosic materials or WAS. Lin *et al.* showed that COD and volatile solids (VS) reduction, gas production and dewaterability were enhanced when WAS was pretreated with NaOH.

Lin et al., (1997), pretreated waste activated sludge using different amounts of sodium hydroxide (20 – 40 meq/l). They observed that the COD removal rates of anaerobic reactors fed with sludge pretreated with sodium hydroxide were 46 – 52 % while it was 38 % for the anaerobic reactor fed with untreated sludge. Moreover they noted that sludge pretreatment supplied 30 – 163 % increase in the biogas production rate during anaerobic biodegradation.

Tanaka et al., (1997), investigated a chemical pretreatment before anaerobic digestion. In the chemical pretreatment NaOH was added to combined WAS. It was found that VSS solubilisation increased as the alkali dose increase up to 0.6 g NaOH / g VSS, and became constant around 15 % above the dose of 0.6 g NaOH / g VSS (1h. Contact time). The methane production of the sebsequent anaerobic digestion increased about 50 % over the control at the dose of 1.0 g NaOH / g VSS.

Woodard and Wukasch (1994), conducted a laboratory-scale study for the improvement of a hydrolysis, thickening and filtration technology to develop the efficency of stabilization of the waste activated sludge. Remarkable solubilization like 50 – 60 % of waste activated sludge suspended solids was reached at room temperature, in a short hydrolysis time. Rajan et al., (1989), demonstrated that at a low level alkaline pretreatment of waste activated sludge with NaOH, degree of solubilization can be increased to 46 %.

Advantages of alkaline hydrolysis are:

- Low energetic requirements.
- Very good dewaterability of the final sludge.

Disadvantages of alkaline hydrolysis are:

- Modification of the sludge composition.
- Possible damage to the bacteria responsible for the microbiologic activities.
- Bad odour generation.
- Corrosion and fouling of the equipment.

- Higher COD in the final effluent due to the presence of non-biodegradable substances.

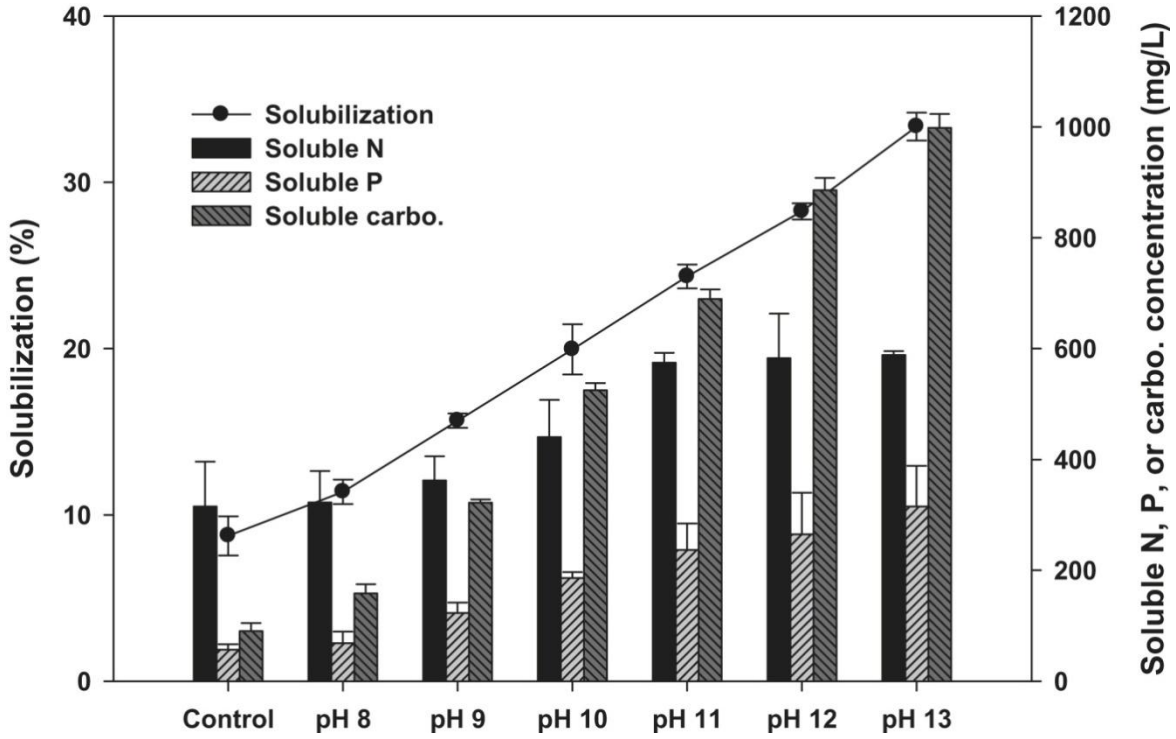

Figure 3.23 : Effects of alkaline pretreatment on solubilization

As shown in Figure 3.23, alkaline pretreatment showed a positive effect on the solubilization (SCOD/TCOD) of sewage sludge. The solubilization proportionally increased from 11.4% at pH 8 to 33.4% at pH 13 in alkaline pretreatment (Kim et al., 2010).

3.2.2.2 Fenton process

Fenton oxidation process and ozone treatment are widely used in experimental studies. In Fenton oxidation process, organic substances react with hydrogen peroxide in the presence of inexpensive ferrous sulfate to reduce toxicity and organic load. The oxidation mechanism by Fentons reagent is due to the reactive OH generated in an acidic solution by the catalytic decomposition of hydrogen peroxide. Although the Fenton reaction has been widely studied, there is no agreement on the ratio $[H_2O_2]/[Fe^{2+}]$ that gives the best results. The same occurs with H_2O_2/UV reactions, where an excess of H_2O_2 can act as a hydroxyl scavenger instead of a HO source and which in addition interferes with the determination of the chemical oxygen demand (COD) (Kaynak, G.E. and Filibeli, A. 2007; Schrank et al., 2005).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^* + OH^- \quad \textbf{(3.1)}$$

Erden and Filibeli (2009), investigated the effects of fenton process on anaerobic sludge bioprocessing. They applied a ratio of 0.067 g Fe (II) / g H_2O_2 and 60 g H_2O_2 / kg dried solids for the pretreatment of biological sludge samples preceding anaerobic digestion. They compared single stage thermophilic anaerobic digestion with two-stage anaerobic digestion (mesophilic digestion prior to thermophilic digestion). They obtained higher solid reduction and higher methane production with the fenton processed sludge for each experiment. According to their results, thermophilic sludge digestion supplied the highest reduction in the sludge solids. At the end of the 30 days operation of thermophilic reactors, dried solids and volatile solids contents of the control reactor were 14.4 and 20.5 %, respectively while those of the reactor fed with fenton processed sludge were 28.2 and 26.8 %. Altough the second stage digestion under mesophilic conditions did not induce an extra improvement in solidmreduction, it provided more methane production. They reported that at the end of the 30 days operation time, fenton pretreatment provided 1.4 and 1.2 times higher methane productions in single stage of digestion and second stage of digestion.

3.2.2.3 Ozone pretreatment

Ozone is an unstable gas, that comes to existance through ignition of oxygen by electrical power. Ozone has a high density and its color is blue. Electrical field created under high voltage, increase the kinetic energy of free electrons, that leads collision of electrons resulting in the breakup of oxygen molecules and the formation of ozone molecules.

Ozone is a powerful oxidant and can oxidize a wide range of organic and inorganic compounds. Ozone has strong cell lytic activity, and can kill the microorganisms found in activated sludge and further oxidize the organic substances released from the cells (Cui and Jahng, 2004 and Saktaywin et al., 2005).

Oxidation of ozone takes place through direct ozone reactions and/or indirect reactions of secondary redicals like OH* radicals. Practically, direct and indirect oxidation reactions occur simultaneously, but one type of of these reactions occur dominantly related to some factors like;

- Temperature
- pH
- Properties of matter to be oxidized.

The process of sludge ozonation is generally described by the sequential decomposition reactions of floc disintegration, solubilization, and the subsequent oxidation of the released organics into carbon dioxide (mineralization) (Ahn et al., 2002 and Lee et al., 2005). Basically, it is supposed that one-oxygen atom of O_3 reacts with the oxidant. This means that 48 g of ozone can stoichiometrically decompose 16 g of COD (mineralization). However, the detected mineralization is generally lower than this value. Lee et al., (2005), reported that with 0.05 g O_3/g total suspended solid (TSS) ozone contact, raw sludge was significantly transformed and resulted in 8% mineralization, 22% solubilization and 70% residuals based on chemical oxygen demand (COD).

Process schematic of the ozonation system is shown in Figure 3.24.

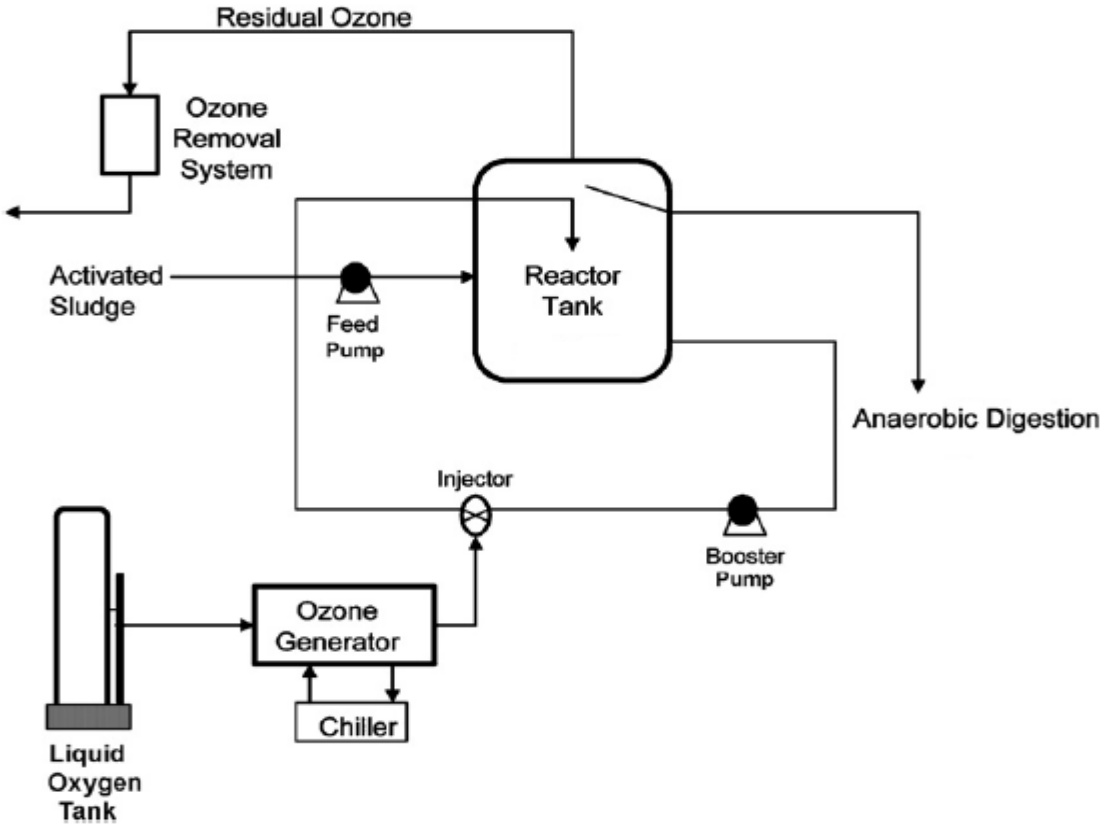

Figure 3.24 : Process schematic of the ozonation system (modified from Sievers et al., 2004)

For raw sludge, it was reported to take 24 days to produce 300 mL of biogas per gram of COD added, and around 15–18 days for ozonated sludge to produce the same amount of biogas at an ozone dose of 0.10–16 g O_3/g TS (Bougrier et al., 2006) (Figure 3.25).

According to Yeom et al., (2002), the ozonated sludgeat 0.1 g O_3/g TSS showed about 2–3 times greater biodegradation compared with the raw sludge in both aerobic and anaerobic conditions for 5 days. In aerobic conditions, the biodegradation of the ozonated sludge after 15 days was 45.4%, 63.0% and 77.1% at an ozone dose of 0.02, 0.05 and 0.1 g O_3/g TSS, respectively, compared with 36% degradation for raw sludge. With anaerobic digestion, biodegradation increased with ozone dose up to 0.2 g O_3/g TSS. However, further increases in ozone dose did not improve biodegradation. This was because ozone was also utilized to oxidize the biodegradable products produced initially and consequently ozone was not consumed to transform the remaining refractory organic matter.

In the studies of Bougrier et al., (2006), sludge was ozonized in batches in a bubble column. Ozone was generated from pure oxygen. Ozone concentrations in gas phase, before and after reaction with sludge, were measured, during the oxidation every 30 s. Gas flow rate was 1L/min, ozone inlet concentration was about 30 mg/L. Reactor volume was 1 L, sample volume was 0.3 L. The transferred ozone dose was 0.10 and 0.16 gO_3/g TS. The results for both conditions were relatively close (Table 3.6).

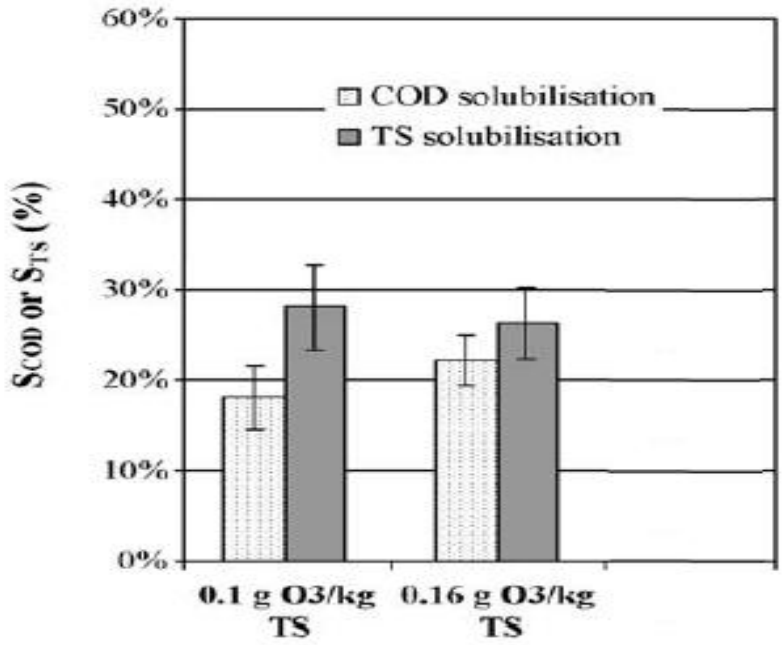

Figure 3.25 : COD and TS solubilisation after various pre-treatments (mean of three measurements ± S.D.).

Table 3.5: Biogas production enhacement, methane content and biodegradability percentage, at the end of the test (24 days) (Bougrier et al., 2006).

Treatment	Untreated	O_3	
		0.1 gO_3/gTS	0.16 gO_3/gTS
Biogas enhancement	1	1.08	1.25
Methane Content (%)	75	77	74
Methane Production	221	246	272
Biodegradability (%)	63	70	78

At the end of the experiments (24 days), volume of biogas produced through the application of ozonation with an ozone dose of 0.16 g O_3 / g TS was only 1.25 times higher than volume produced with untreated sludge, but according to the previous studies (Bougrier, 2005), the enhacement of biogas production expected to be around 2.58. this slight enhacement could be caused by inhibitory conditions (too much ozone remained in soluble phase), the formation of refractory compounds, a not well-adapted inoculum or ozone consumption by reduced compounds of the sludge (Bougrier et al., 2006).

Literature data on the efficiency of sludge solubilization is shown in Table 3.6.

Table 3.6: Literature data on the efficiency of sludge solubilization.

Initial TSS conc. (mg/L)	Volume (L)	Ozone conc. (mg/L)	Ozone dose (g O_3/g TSS)	Operation mode	Solubilization efficiency (%)	References
3790–4570	630	–	0.025–0.035	Continuous	20–30%	Manterola et al., 2008
1200–4000	2	20-90	0.03–0.04	Semi-batch	30	Saktaywin et al., 2005
–	6000	–	0.03–0.06	Semi-batch	9.2–13.3	Sievers et al., 2004
5000–5300	350	50	0.05	Semi-batch	30	Lee et al., 2005
18900	1	30	0.1–0.16	Semi-batch	20–25	Bougrier et al., 2006
8000–12000	1000	150	0.1	Semi-batch	45	Park et al., 2003
			0.2		55	
			0.5		66	
–	2		0.57–1.09	Semi-batch	50–56	Mines et al., 2008
2850	2.1	50	1.2	Semi-batch	58.9	Cui and Jahng, 2004

Because of the well-known potential and performance of sludge ozonation in reducing the amount of sludge for disposal, full-scale plants using sludge ozonation are increasing. Table 3.7 shows the various full-scale applications of sludge ozonation for sludge reduction, where 40–100% of sludge reduction was achieved as a result of these applications.

Table 3.7: Full-scale application of ozonation for sludge treatment.

Capacity	Wastewater type	Ozonation	Period	Sludge reduction (%)	Source
Anaerobic digestion with ozonation					
Digestion tank: 1125 m^3	Sewage	24 kg O_3/d Ozonated sludge: 22–44 m^3/d	2 years	70	Yasui et al., 2005
Feed sludge: 25 m^3/d 17,000 p.e.	Municipal	V = 6 m^3, 1 kg O_3/h, 0.030.06 g O_3/g TSS		55.5	[Winter, 2002] and [Sievers et al., 2004]
Aerobic digestion with ozonation					
12000 p.e. Digestion tank: 400 m^3	Municipal	V = 3.7 m^3, 0.01–0.014 g O_3/g TS	9 months	78	Caffaz et al., 2005

Advantages of ozone pre-treatment are:

- Decreased viscosity, improved settleablity and reduced odors (Bougrier et al., 2007a);
- Yield reduction in activated sludge systems (Kamiya and Hirotsuji 1998; Lee et al., 2005; Sakai et al., 1997);
- Potential carbon source for denitrification with equivalent energy to glucose (Ahn et al., 2002; Lee et al., 2005; Sakai et al., 1997; Yeom et al., 2002; Zhao et al., 2007);
- Increased mineralization of organic material (Bougrier et al., 2007a).

Disadvantages of ozone pre-treatment are:

- Increased inert and colloidal COD due to the disintegration of sludge flocs and cells which often increases the non-biodegradable COD in the plant effluent due to recycling of dewatering centrate to the biological process or the use of ozone treatment on the RAS line (Boehler and Siegrist 2006);
- Decreased dewaterability, increased sludge volume index (SVI) and capillary suction time (CST) of digested sludge because of smaller particles (Ahn et al. 2002, Bougrier et al., 2006a; Bougrier et al., 2007a; Carballa et al., 2007);
- Decreased pH due to formation of carboxylic acid from organic material and consumption of alkalinity by the oxidation or organic material (Bougrier et al., 2007a);
- When used to minimize yield, phosphorus removal is reduced because one of the primary removal mechanisms is sludge wasting (Sakai et al., 1997);
- Ozone generation is an energy intensive process and requires significant capital investment in machinery (Panda and Mathews 2008);
- Mass transfer kinetics need to be optimized to the sludge characteristics (Lee et al., 2005; Panda and Mathews 2008).

3.2.3 Thermal pretreatment

3.2.3.1 Thermal hydrolysis

Thermal pre-treatment is a disintegration technique which has been installed in many wastewater treatment plants (WWTPs) (Kepp et al., 2000). The input of thermal energy is mostly realised by heat exchangers or by application of steam to the sludge. Excess heat obtained within the wastewater treatment plant can be used, thus reducing the costs significantly. While the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected against the enzymatic hydrolysis by the cell wall. Thermal pre-treatment destroys the cell walls and makes the proteins accessible for biological degradation. The wastewater purification process transfers the organic substances of the inlet into cell substance, which contains a lot of protein. The more the sludge is pre-stabilised aerobically or anaerobically, the higher the

content of proteins in the sludge and the higher the resulting increase in gas caused by the thermal pre-treatment.

Thermal disintegration process impacts mainly biomass and decay products (matching measured ammonia release) whereas particulate inerts Xi already contained in the raw wastewater are hardly converted (Figure 3.26).

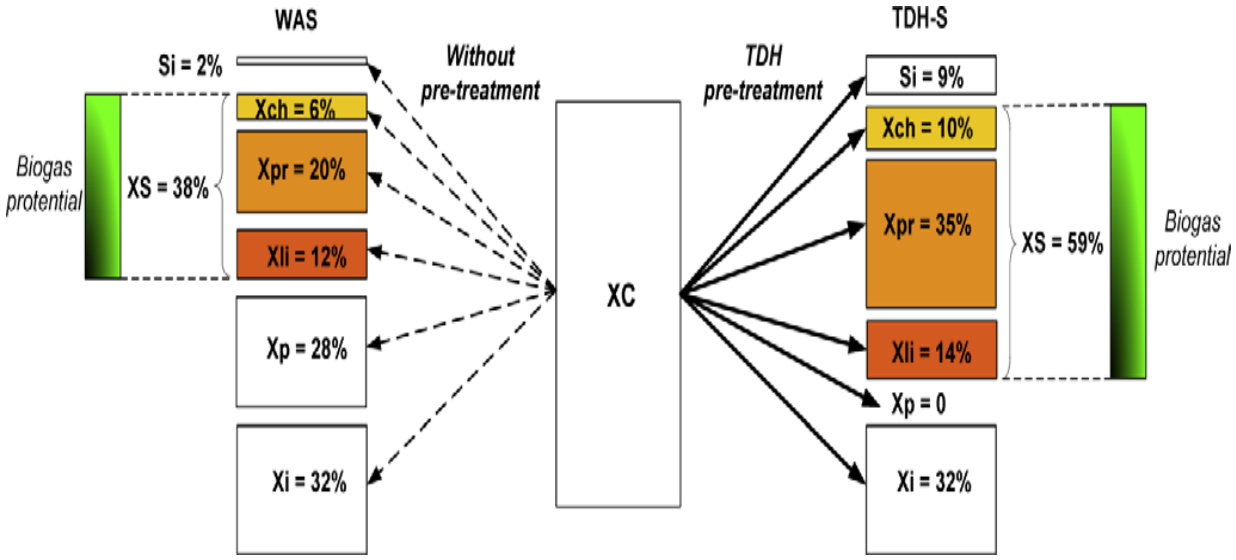

Figure 3.26 : COD-fractionation of composite solids Xc of WAS with and without TDH pre treatment (carbo-hydrates Xch, proteins Xpr, lipids Xli, decay products Xp, particulate inerts Xi, soluble inerts Si).

Thermal pretreatment of waste activated sludge was examined in many researches. These researches involve thermal pretreatment in the:

- Moderate temperature range of 60 – 100 ^{o}C (Hiraoka, 1984; Li and Noike, 1992)
- Medium temperature range of 100 – 175 ^{o}C (Haug et al., 1978)
- High temperature range of 175 – 225 ^{o}C.

Optimal conditions of thermal pre-treatment are generally reported to be 160–180◦C for 30–60 min (Haug et al., 1978; Tanaka et al., 1997; Bougrier et al., 2006) However, treatment time is often mentioned to have a very low influence, and Dohanyos et al., proposed a very fast thermal treatment lasting only 1 minute. The impact of thermal treatments (160–180◦C) on mesophilic anaerobic digestion is highly variable according to the authors. In the extremes, Haug et al., found no increase of methane production during continuous anaerobic digestion of primary sludge with a 15-day sludge retention time. Li and Noike showed 100% enhancement

of methane production during continuous anaerobic digestion of waste-activated sludge with a 5-day sludge retention time. In fact, as thermal pre treatments allow accelerating sludge anaerobic digestion, their impact on continuous anaerobic processes is higher for lower sludge retention times. Moreover, Haug et al., applied thermal pretreatment to different types of sludge. They found that thermal pretreatment impact was higher on waste-activated sludge (62% increase of methane production) than on a mixture of waste activated and primary sludge (14% increase of methane production) and on primary sludge (no increase of methane production). It is thus more interesting to apply thermal treatment on waste-activated sludge than on primary sludge. However, no published works provide the comparison of thermal pre-treatment results on the biodegradability enhancement of different waste-activated sludge samples (Carrere et al., 2008).

Advantages of thermal hydrolysis are:

- The improvement of filterability and disintegration of the sludge and the improvement of digestibility and dewaterability (Barr et al., 2008; Bougrier et al., 2008; Fernandez-Polanco et al., 2008);
- A final product that meets Class A standards for land application;
- The high temperatures ensure the destruction of foam causing organisms that can cause issues in digesters (Barr et al., 2008);
- Digester size can be significantly reduced because of the reduced residence time that is achieved by the acceleration of the hydrolysis phase and the ability to feed a sludge with a higher TS concentration (Barr et al., 2008);
- The system is typically a net energy producer because of the increased biogas quantity and quality that can be used to heat the boilers and generate power that exceeds the requirements of the THP system (Barr et al., 2008).

Disadvantages of thermal hydrolysis are:

- As was mentioned previously, there are higher concentrations of recalcitrant compounds that are difficult to remove and are recycled to the main biological process in the dewatering supernatant;

- The supernatant also contains high concentrations of nutrients that will affect the operation of the activated sludge system especially in plants where nutrient removal is a high priority;
- Due to the reduced particle size there have been issues with dewatering, especially using centrifuges, so Cambi typically utilizes belt filter presses for final dewatering (Barr et al., 2008);
- Depending on the influent wastewater stream, there can be issues with the heat exchangers clogging as happened at the installation in Dublin, Ireland because it was receiving wastewater with high fiber content from a pulp mill but the issue was solved by recycling digested sludge to the heat exchangers which raised the pH (Pickworth et al., 2006).

Higher degradation efficiency is associated with higher biogas production and a lower content of volatile solids in the digested sludge which represents a smaller output of stabilized sludge with better dewatering properties (Zabranska et al., 2006). Kepp et al. (2000) implemented a full scale thermal pre-hydrolysis at the WWTP in Hamar, Norway, to pre-treat mixed raw-sludge with a temperature range of 165–180 ^{o}C. Although digester volume for pre-treated sludge was smaller than for conventional digestion (1500 m^3 and 3500 m^3, respectively), the energy yield from biogas production increased from 678 kW (conventional digestion) to 1000 kW by thermal pre-treatment when the digester feed was 6–9 tons dissolved solids per day. Thermal pre-treatment is supposed to reduce also the hardly degradable materials (Elliott and Mahmood, 2007), therefore it improves the overall removal efficiency of organics in the digestion process.

The influence of the portion of thermal treated sludge in the inoculum on the biogas production from the same amount of substrate (Excess Sludge (ES) + Primary Sludge (PS)) is presented in Figure 3.27.

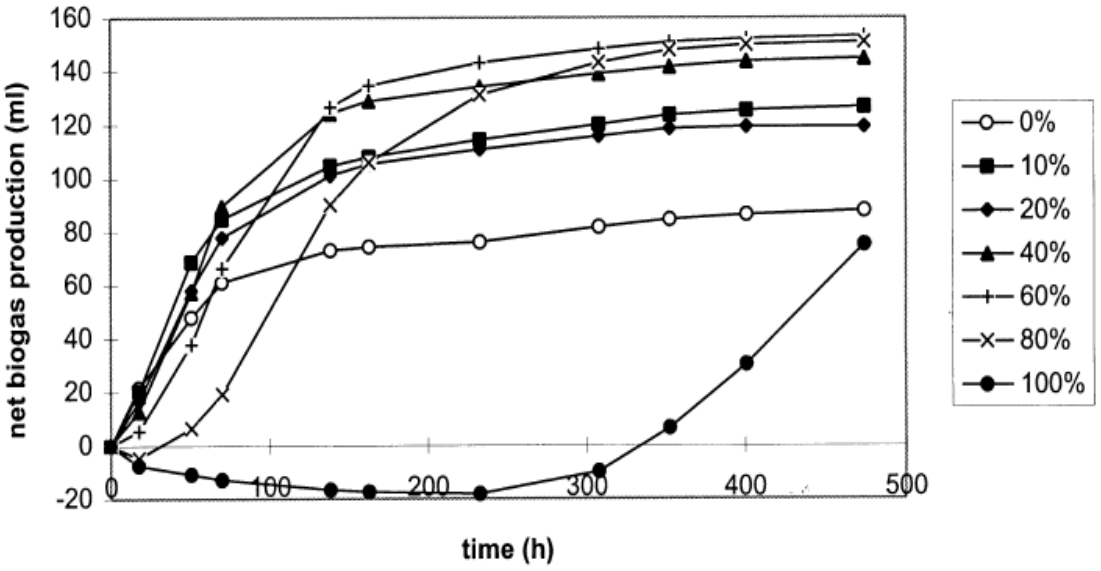

Figure 3.27 : The influence of the thermal treated sludges inoculum on biogas production (M. Dohanyos et al., 2000).

The results show that the thermal treatment causes a deterioration of the treated sludge activity, but it can be regenerated even in the case of 100% of the treated sludge used as inoculum. The presence of 80 and 60% of the thermal treated sludge in the inoculum causes only a slight inhibition of biogas production at the beginning of the test. However, the total biogas production is higher when compared with the untreated digested sludge due to a higher amount of better degradable soluble COD. The optimal mixture of the thermal treated and digested sludge for efficient substrate degradation seems to be about 40% and 60% respectively (M. Dohanyos et al., 2000).

Biogas production (mL/g Organic Dry Solid (ODS)) after 20 days for the different treatment temperature is shown in Figure 3.28.

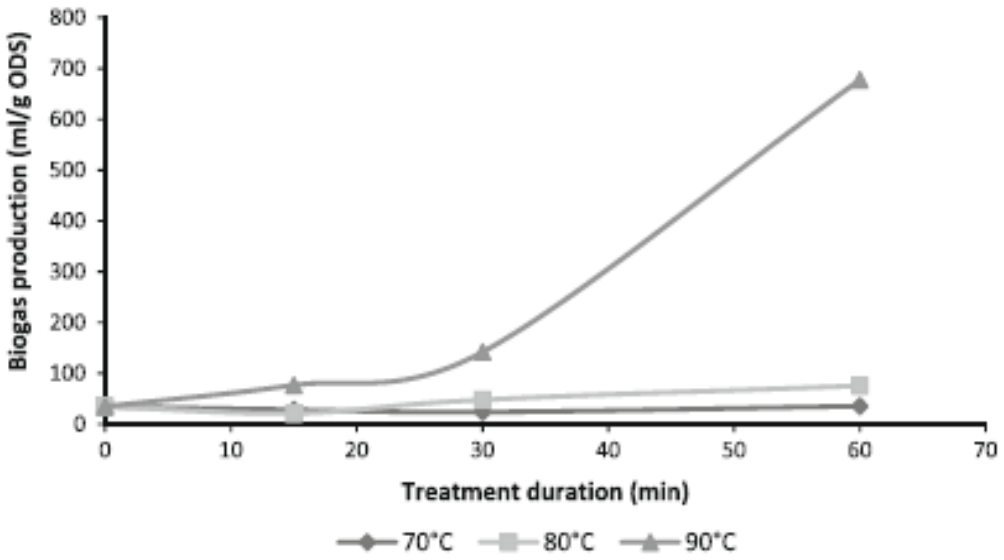

Figure 3.28 : Biogas production (mL/g Organic Dry Solid (ODS)) after 20 days for the different treatment temperature.

As shown in Figure 3.28, it was seen that low temperature thermal hydrolysis effectively influences the biogas production during the subsequent anaerobic digestion. For the treatment temperature of 70 ^{o}C, the gas volume slightly decreased for all pre-treatment times. This observation suggests that a temperature of 70 ^{o}C is too low to enhance the biogas production. The noticed decrease lies within the measurement uncertainty. At 80 and 90 ^{o}C on the other hand, a significant increase was observed. The gas production increases with increasing pre-treatment times for both temperatures.

Values obtained for % increment FVS/TVS ratio after thermal treatment of secondary sludge (dots) under different conditions of time and temperature and polynomial fit to the experimental points is shown in Figure 3.29.

Aerobic digestion studies conducted at Iowa State University reported that the residual SCOD of the ultrasound pretreated biosolids was significantly lower than the unsonicated biosolids at all SRTs as shown in Figure 3.30 (Khanal et al., 2006a). The SCOD removal showed an increasing trend with an increase in SRT for the digester fed with unsonicated sludge, except for a SRT of 10 days at which the efficiency declined slightly for unknown reasons. The respective mean SCOD removal efficiencies were 66, 62, 79 and 82% at SRTs of 8, 10, 12 and 15 days.

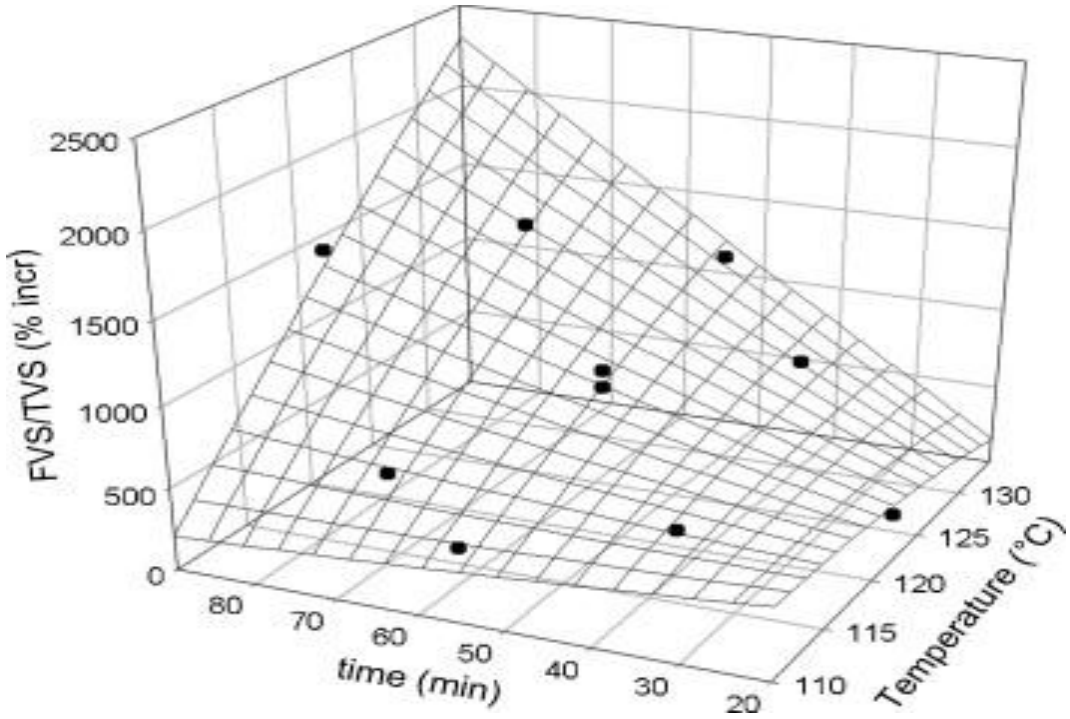

Figure 3.29 : Values obtained for % increment FVS/TVS ratio after thermal treatment of secondary sludge (dots) under different conditions of time and temperature and polynomial fit to the experimental points (surface).

The higher COD removal can be attributed to better mineralization of organics due to longer detention times. The digester fed with sonicated sludge showed consistently high SCOD removal of 92% even at a short SRT of 8 days.

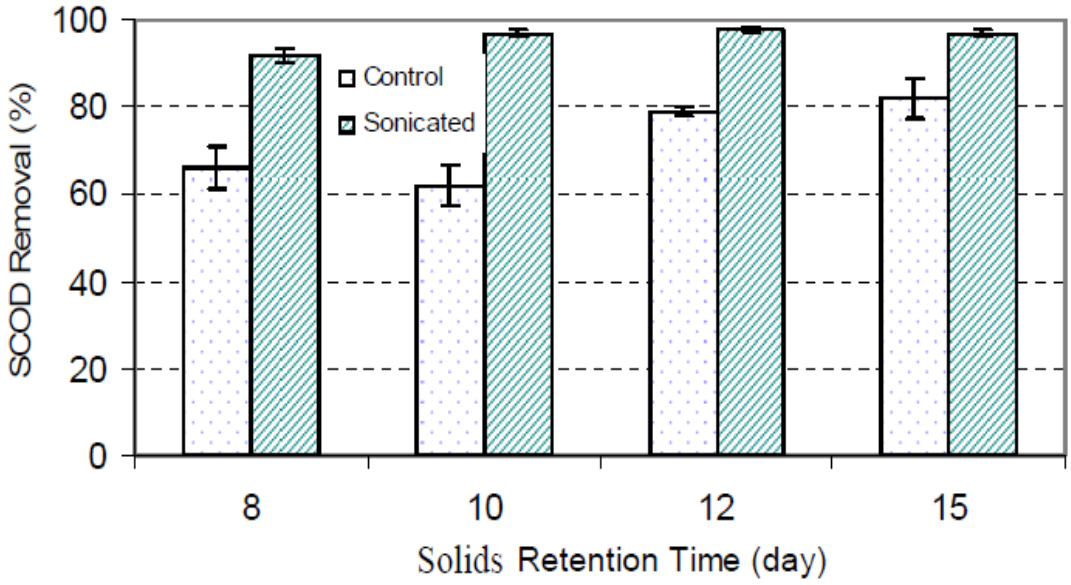

Figure 3.30 : SCOD removal for digesters fed with sonicated and unsonicated sludge at different SRTs (Khanal et al., 2006b).

Overview of some thermal pre-treatment studies is shown in Table 3.8.

Table 3.8: Overview of some thermal pre-treatment studies.

Reference	Treatment	Comments
Kim et al., (2003)	121 °C 30 min	Increase of VS reduction by 30%
Valo et al., (2004)	170 °C 15 min	59% increase of TS reduction 92% higher gas production
Ferrer et al., (2006)	70 °C 9–72 h	Studied thermophilic digestion Positive effect on gas production Higher temperature (110–134 °C) did not have any effect
Climent et al., (2007)	70–134 °C 90 min–9 h	Studied thermophilic digestion 50% increase of biogas production at 70 °C (9 h) No effect for high-temperature treatment
Bougrier et al., (2007)	135–190 °C	Increased methane production by 25% at the 190 °C treatment
Jeong et al., (2007)	120 °C 30 min	Increased methane production by 25%
Nges and Liu (2009)	25, 50, 70 °C 48 h	Increased methane production by 11% at 50 °C
Phothilangka et al., (2008)	Thermo-pressure-hydrolysis process	Increased biogas production by 80%
Perez-Elvira et al., (2008)	170 °C, 3 bar 30 min	Increased methane production by 50%

Impact of thermal pretreatments on primary sludge and waste activated sludge mesophilic anaerobic digestion is shown in Table 3.9.

Table 3.9: Impact of thermal pretreatments on primary sludge and waste activated sludge mesophilic anaerobic digestion

Reference	Thermal Treatment	Anaerobic Digestion	Results
Haug et al., (1978)	175 ^{o}C, 30 min	CSTR,HRT = 15 d	Increase of CH_4 production from 115 to 186 mL/g CODin (+ 62%)
Stuckey and McCarty (1978)	175 ^{o}C, 60 min	Batch, 25 d	Increase of convertibility of COD to CH_4 from 48 to 68 (+ 42%)
Li and Noike (1992)	175 ^{o}C, 60 min	CSTR,HRT = 5 d	Increase of gas production from 108 to 216 mL/g CODin (+ 100%)
Tanaka et al., (1997)	180 ^{o}C, 60 min	Batch, 8 d	Increase of CH_4 production (+ 90%)
Fjordside (2001)	160 ^{o}C	CSTR, 15 d	Increase of biogas production (+ 60%)
Gavala et al., (2003)	70 ^{o}C, 7d	Batch	Increase of CH_4 production from 8.30 to 10.45 mmol/g VSin (+ 26%)
Barjenbruch and Kopplow (2003)	121 ^{o}C, 60 min	CSTR, 20 d	Increase of biogas production from 350 to 420 mL/g VSSin (+ 20%)
Kim et al., (2003)	121 ^{o}C, 30 min	Batch, 7 d	Increase of biogas production from 3657 to 4843 L/m3 WASin (+ 32%)
Dohanyes et al., (2004)	170 ^{o}C, 60 s	Batch, 20 d	Increase of biogas production (+ 49%)
Valo et al., (2004)	170 ^{o}C, 60 min	Batch, 24 d	Increase of biogas production (+ 45%)
Valo et al., (2004)	170 ^{o}C, 60 min	CSTR, 20 d	Increase of CH_4 production from 88 to 142 mL/g CODin (+ 61%)
Graja et al., (2005)	175 ^{o}C, 40 min	Fixed reactor, HRT= 2.9 d	65 % reduction of TSS
Bougrier et al., (2006a)	170 ^{o}C, 30 min	Batch, 24 d	Increase of CH_4 production from 221 to 333 mL/g CODin (+ 76%)
Bougrier et al., (2006b)	170 ^{o}C, 30 min	CSTR, 20d	Increase of CH_4 production from 145 to 256 mL/g VSin (+ 51%)
Ferrer et al., (2008)	70 ^{o}C, 9 h	Batch, 10 d	Increase of biogas production (+ 30%)
Lu at al., (2008)	70 ^{o}C, 2 d	Batch, 13 d	Increase of CH_4 production (+ 48%)

3.2.4 Biological pretreatment

The biochemical sludge disintegration is based on enzyme activity. The compounds of the cell wall are cracked by the enzymatic lysis through an enzyme catalyzed reaction. Even Gram-positive bacteria with a high strength cell wall can be disintegrated using enzymes. Autolytic processes can be used at ambient temperatures or external enzymes can be added, resulting in additional treatment costs. Enzymatic lysis is of interest in combination with mechanical disintegration as well, because enzymes are also located in the intracellular liquid. They can cause a further disintegration of the cells after a mechanical disintegration by autolysis (Dohanyos et al., 1997).

The use of microbial enzymes for the enhancement of degradation of WAS is the basis for another process called the Enzymic Hydrolysis (EH) Process (Mayhew et al., 2002, 2003). The primary benefit described by the developers of this process is the pathogen kill; however, a further benefit is the enhancement of biogas production in anaerobic digestion.

During laboratory trials, a 10% improvement in biogas production was found (Mayhew et al., 2003). The EH stage, which has a retention time of 2 days, involves the use of a holding chamber where the WAS is kept at 42 1C (Mayhew et al., 2003). The process has been implemented at a municipal treatment plant in the UK.

Biological hydrolysis can be considered as a partial anaerobic sludge digestion. In conventional anaerobic digestion processes, acidogens and acetogens first solubilise and hydrolyse sludge microbes prior to the actual conversion to methane by the methanogens. By controlling the hydraulic retention time and temperature, it is possible to confine the anaerobic digestion of sludge to the acidogenic and acetogenic phase (hydrolysis and fermentation process) and take advantage of the soluble organics produced (Marjoleine et al., 1998).

Concerning the biological hydrolysis of activated sludge, Kitazume et al. (1991), studied sludge solubilisation by using acid-forming anaerobes. They isolated seven strains of high acid forming anaerobes (Clostridium bifermentans DYF strains) which solubilised volatile solids in activated sludge more than 50 %, besides converting most of the solubilised part of VFA, principally to acetic acid. Inoculating these isolated anaerobes contributed to accelerating the initial digestion rate more

than 20 % and increasing methane production more than 10 % in batch cultures running for 30 days.

Advantages of biological pre-treatment are:

- Low energy consumption.
- No stress on the equipment.

Disadvantages of biological pre-treatment are:

- High cost.
- The usage of enzymes to better the sludge stability is not clear.
- High generation of odours.

4. MATERIAL AND METHODS

4.1 Plans of Experiments

In the study firstly to select suitable ways and methods of disintegration different disintegration methods for the conditions of the dissolved COD yields (disintegration yield) were measured. The return activated sludge (RAS) sample was collected at return sludge line from the Paşaköy domestic wastewater treatment plant located in Kartal, in which the activated sludge process is used to treat the wastewater. After the initial sampling process is completed, chemical parameters such as CODc, CODf, SS, VSS, and pH were analyzed immediately. In order to set forth the influence of anaerobic digestion of selected disintegration method, Biogas & Methane content produced was measured. The sludge sample was preserved in cold storage room at 4°C prior to use to prevent biodegradation.

4.1.1 Application of disintegration methods

Thermal (heat), thermochemical (heat and chemical), ultrasonic methods have been applied to the sludge samples taken from the return line of Paşaköy Wastewater Treatment Plant in July and September 2009 to achieve different disintegration methods and different conditions of disintegration efficiencies.

The characteristic of return activated sludge (RAS) is shown in Table 4.1 and Table 4.2.

Table 4.1: Sludge characterization that thermal disintegration process applied to

Parameters	Unit	Value
SS	(mg/L)	12920
VSS	(mg/L)	8280
CODc	(mg/L)	167
CODf	(mg/L)	15
pH	-	6.95

Table 4.2: Sludge characterization that ultrasound disintegration process applied to

Parameters	Unit	Value
SS	(mg/L)	11880
VSS	(mg/L)	7720
CODc	(mg/L)	89
CODf	(mg/L)	15
pH	-	6.95

4.1.1.1 Thermal disintegration

In the experimental study conducted to determine the value of the thermal (heat) disintegration degree under different conditions ovens are used for the temperatures below 100°C and autoclaves are used for the temperatures above 100°C. 10, 30 and 60 minutes of intervals were applied.

Thermal disintegration process applied at three different temperature for three different time is shown in Table 4.3.

Table 4.3: Thermal disintegration process applied at three different temperatures for three different times

Time (Min.)	Temperature (^{0}C)		
	80	121	160
10	X	X	X
30	X	X	X
60	X	X	X

After thermal disintegration experiments centrifugation applied samples were held to TSS, VSS, CODc and CODf analysis.

4.1.1.2 Thermo-chemical disintegration

In the experimental study conducted to determine the value of the thermo chemical (heat and chemical) disintegration degree under different conditions ovens are used. NaOH for chemical pH adjustment was used. 80^0C, 100^0C and 120^0C intervals of temperatures and 8, 10 and 12 intervals of pH values and 10, 30 and 60 minutes of intervals were applied. That matrix is given in Table 4.4.

Table 4.4: Thermo-chemical disintegration process applied to the WAS at three different temperature and three different pH for 5 different time intervals

		Temperature (^{0}C)		
Time (Min.)	pH	80	100	120
	8	X	X	X
	10	X	X	X
10	12	X	X	X
	8	X	X	X
	10	X	X	X
20	12	X	X	X
	8	X	X	X
	10	X	X	X
30	12	X	X	X
	8	X	X	X
	10	X	X	X
60	12	X	X	X
	8	X	X	X
	10	X	X	X
120	12	X	X	X

After the applied thermo chemical (heat and chemical) disintegration experiments centrifugation applied samples were held to TSS, VSS, CODf, CODc and VFA analysis.

4.1.1.3 Ultrasound disintegration

In order to determine the degree of disintegration ultrasound, recycled sludge was exposed to ultrasound using an ultrasonic homogenizer in different conditions.

The RAS samples treated with the Sonix probe were placed inside a 50, 100 and 250 mL beaker. The sonix probe was then immerged in the beaker and stirred. By varying the sonication time between 1 and 30 minute, at %40, %60 ve %80 amplitude were used to treat the RAS samples with the sonix probe.

Matrix used in planning the experimental work is given in Table 4.5.

Table 4.5: Ultrasound disintegration process applied to the WAS of three different volume at three different amplitude for 5 different time intervals.

Volume (mL)	Time (Min.)	Amplitude (%)		
		40	60	80
50	1	X	X	X
	5	X	X	X
	10	X	X	X
	30	X	X	X
	60	X	X	X
100	1	X	X	X
	5	X	X	X
	10	X	X	X
	30	X	X	X
	60	X	X	X
250	1	X	X	X
	5	X	X	X
	10	X	X	X
	30	X	X	X
	60	X	X	X

The ultrasound treatment experiments were done according to the spesific energy calculation. The specific ultrasonic energy (Es) is defined as the product of the ultrasonic power (P) and the ultrasonic time (t) divided by the sample volume (V) and the initial total solids concentration (TSS).

$$E_S = P \times t / TSS \times V \quad \textbf{(4.1)}$$

Where;

P = Ultrasonic Power, (KW)

t = Ultrasonic time, (s)

V = Volume, (L)

TSS = Total Suspended Solid, (mg/L)

Es = Specific Ultrasonic Energy, (KJ/kg.DS)

4.1.2 Anaerobic digestion tests

Several recent reports have demonstrated the efficacy of ultrasonic as a method for disintegrating sludge and thereby accelerating the rate of anaerobic digestion process and improving methane yield (Tiehm et al., 2001; El-Hadj et al., 2007). Various ultrasonication parameters, including frequency (Tiehm et al., 2001), duration and intensity (Chu et al., 2001; Wang et al., 2006), have been studied as well as their effects on the characteristics of sludge.

In addition, the solubilization of organic matter during sludge anaerobic treatment usually drives some biochemical effects, such as the changes of enzymes activities. Some researchers reported that the hydrolytic enzymes, such as protease, glucosidase, acid and alkaline phosphatases, which were involved in the hydrolysis of organic matter, were observed in WAS anaerobic treatment system (Yuan et al., 2006; Feng et al., 2009). It has also been documented that the activities of hydrolytic enzymes usually depend on the substrate concentration, pH and temperature (Goel et al., 1998). It is well known that the hydrolysis of particulate organic matter is believed to be the rate-limiting step during WAS anaerobic digestion. If the activities of hydrolytic enzymes increased, the rate of WAS anaerobic digestion would be accelerated.

Previous studies have reported how ultrasonic energy, duration and intensity affect the sludge's physical and chemical characteristics of RAS, such as chemical oxygen demand (COD). To obtain the effect of ultrasonic disintegration on anaerobic digestion efficiency and methane production disintegrated sludge is mixed with return activated sludge in different proportions.

In this study, The effect of ultrasonic disintegration (sonicated 100 mL sample at 80% amplitude for 30 min) on biogas generation of anaerobic digesters was evaluated by using different ratios of disintegrated and untreated sludge as a reactor content at two F/M ratios (RUN I).

Food to microorganism (F/M) ratio is the ratio of substrate amount as waste activated sludge to the inoculum amount as anaerobic digested sludge added to the reactor. It is an important digester parameter in terms of volatile solids loading performance of the system (Pranshanth et al., 2006). According to Tanaka et al. (1997), F/M ratio should be in the range of 0.45-0.50 in order to solubilize cells efficiently. Pranshanth

et al. (2006) found the best value of F/M ratio between 0.570.68 for anaerobic digestion. In the study of Braguglia et al. (2006), they mentioned that the optimum range for F/M ratio was found between 0.5 and 2 for untreated excess sludge by Engelhart (2002) (Braguglia et al., 2006). Furthermore, for the untreated excess sludge batch digestion tests at different F/M ratios (0.15 and 8.37), the initial lag-phase in biogas production becomes longer with the increase in F/M ratio. Nevertheless, the specific biogas production was approximately constant for all ratios.

F/M = Sludge Mass Added / Seed Mass Added **(4.2)**

F = Food (g)

M = Microorganism (g)

Sludge Mass Added = $TCOD_{sludge}$ *V_{sludge} (g)

Seed Mass Added = V_{seed} * V_{seed} (g)

In this study, two different FM ratios of 1 and 0.5 are applied for anaerobic digesters.

Matrix presentation of anaerobic digesters experimental setup for RUN I is given in Table 4.6.

Table 4.6: Anaerobic digesters setup for RUN I

Anaerobic Reactor Content	FM =1	FM =0.5
•Control (untreated RAS)	X	X
•Disintegrated Sludge	X	X
•25% Disintegrated Sludge, 75% Untreated Sludge	X	X
•50% Disintegrated Sludge, 50% Untreated Sludge	X	X
•75% Disintegrated Sludge, 25% Untreated Sludge	X	X

The biogas generation from anaerobic reactors was evaluated in a series of batch anaerobic digestion tests during 30 days of incubation.

Serum bottles are used as a batch reactor. All the experiments were undertaken using 100 mL serum bottles capped with butyl rubber stoppers. All digesters were initially seeded with anaerobically digested sludge at a different volumes according to the I/S ratio. 45 mL of the samples (RAS and seed) were added to digesters and 5 mL of stock solutions were added. The reactor was purged with helium gas to eliminate

air from the reactor. The temperature of the digester was immediately increased to 37°C and maintained the mesophilic condition in the room. Serum bottles were kept in 37°C incubator until they stopped producing biogas.

Volume uses of serum bottles are shown in Table 4.7.

Table 4.7: Volume uses of serum bottles

	Volume (mL)
Total Volume	100
Working Volume	50
Stock Solutions	5

In this period, CODc, CODf, VS and TS parameters of control sludge and disintegrated sludge were analyzed periodically as shown in Table 4.8.

Table 4.8: Time intervals of CODc, CODf, VS and TS parameters analysis of contol and disintegrated sludge

F/M RATIOS	DAYS	SLUDGE
FM 0.5	Initial	Control Sludge
		Disintegrated Sludge
	3. Day	Control Sludge
		Disintegrated Sludge
	6. Day	Control Sludge
		Disintegrated Sludge
	15. Day	Control Sludge
		Disintegrated Sludge
	24. Day	Control Sludge
		Disintegrated Sludge
	Final	Control Sludge
		Disintegrated Sludge
FM 1	Initial	Control Sludge
		Disintegrated Sludge
	4. Day	Control Sludge
		Disintegrated Sludge
	7. Day	Control Sludge
		Disintegrated Sludge
	16. Day	Control Sludge
		Disintegrated Sludge
	25. Day	Control Sludge
		Disintegrated Sludge
	Final	Control Sludge
		Disintegrated Sludge

Biological nutrient removal (BNR) is widely used in modern municipal and industrial wastewater treatment plants (WWTP). A significant factor in the success of the BNR process is the availability of a suitable carbon source. Many authors have reported a specific ratio of carbon to phosphorus (P) and carbon to nitrogen (N), which can indicate the suitability of the wastewater for BNR treatment (Jonsson et al., 1996; Randall et al., 1992; Grady et al., 1999; Curto, 2001). The most common methods for increasing these ratios and hence make the wastewater treatable by a BNR process, are the pre-treatment of the wastewater (McCue et al., 2003) or the addition of extra carbon.

In full scale treatment plants, some part of the supernatant of the disintegrated sludge can be returned to the beginning of the system after the centrifuge process to supply the carbon demand for nutrient removal system.

In order to observe the effect of this application on anaerobic digestion, another experimental set up was carried out. Different percentages of centrifuged disintegrated sludge were subjected to anaerobic digesters by discarding some part of the supernatant to represent the possible effect of returned supernatant to the beginning of the system. The discarded supernatant amounts were in the range of 10 % to 50 % (RUN II). The same F/M ratios were applied as RUN I. Matrix presentation of anaerobic digesters experimental setup for RUN II is given in Table 4.9.

Table 4.9: Anaerobic digester setup for RUN II.

Anaerobic Reactor Content	FM =1	FM =0.5
•Disintegrated Sludge	X	X
•10% of Supernatant discarded after Centrifuge	X	X
•20% of Supernatant discarded after Centrifuge	X	X
•30% of Supernatant discarded after Centrifuge	X	X
•50% of Supernatant discarded after Centrifuge	X	X

The CODc values of disintegrated sludge and supernatant were 15409 and 6880 mg/L respectively.

Serum Bottles used in BMP test is shown in Figure 4.1.

Figure 4.1 : Serum bottles used in BMP test.

Inoculum

Inoculum was obtained from a pilot-scale anaerobic digester incubated at 37^{o}C for 30 days with sludge which was taken from Paşaköy Wastewater Treatment Plant. And new incubated seed was prepeared.

I/S ratio is choosen 1.5. According to this ratio, the amount of incolumn and sludge that mixed in the reactor was calculated.

I: Inoculum (VS mg/L)

S: Sludge (VS mg/L)

Volatile solid concentrations of seed and return sludge are shown in Table 4.10.

Table 4.10: Volatile solid concentrations of seed and return sludge

Sample	VS (mg/L)
Seed	42357
Sludge	14417

As the I/S ratio was choosen 1.5 the reactor solid matter was calculates as 3.85.

All the experiments were undertaken using 1000 mL serum bottles capped with butyl rubber stoppers.

Table 4.11: Volume uses of serum bottles

	Volume (mL)
Total Volume	1000
Working Volume	500
Stock Solutions	50

The composition of stock solution is shown in Table 4.12.

Table 4.12: The composition of the anaerobic reactors influents

Substances	Concentrations (mg/L)
Nutrients	
KH_2PO_4	408
$Na_2HPO_4.2H_2O$	534
NH_4Cl	360
NaCl	360
$MgCl_2.6H_2O$	120
$CaCl_2.2H_2O$	132
$NaHCO_3$	4000
Reducing Agent	
$Na_2S.9H_2O$	240
Anaerobic Control Agent	
Resazurin	5
Acid Stock Solution (I)	
HCl	1.8
H_3BO_3	0.062
$MnCl_2$	0.061
$FeCl_2$	0.944
$CoCl_2$	0.065
$NiCl_2$	0.013
$ZnCl_2$	0.068
$CuCl_2$	0.05
$AlCl_3$	0.05
$(NH_4)6Mo_7O_{24}$	0.05
Alkaline Stock Solution (II)	
NaOH	0.4
Na_2SeO_3	0.01
Na_2WO_4	0.029
Na_2MoO_4	0.021
Vitamins	
Biotin	0.02
Nicotinamid	0.2
P-Aminobenzoic acid	0.1
Thiamin (Vit B1)	0.2
Panthotenic acid	0.1
Pyridoxamine	0.5
Cyanocobalamine (Vit B12)	0.1
Riboflavine	0.1

4.2 Experimental Equipments

4.2.1 Ultrasound homogenizer

The WAS samples was sonicated using Sonics ultrasound unit, Bandelin- Sonoplus HD 2200 model.

The ultrasound unit has a maximum power output of 200W and operates at a frequency range of 20- 40 kHz. This unit is equipped with a horn. The power input can be set independently from 40 - 200 W. The amplitude can be also set independently from 20-100 %. The ultrasonic equipment is shown in Figure 4.2 and Figure 4.3.

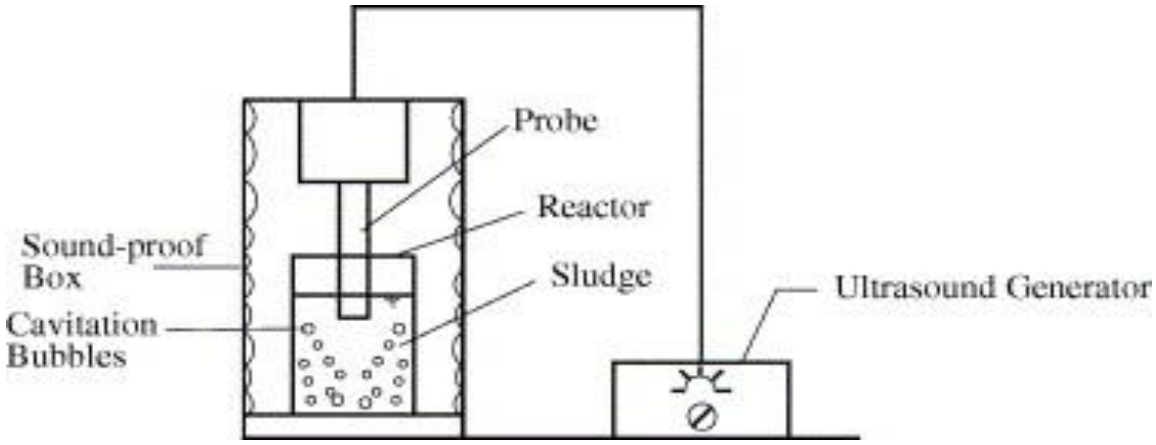

Figure 4.2 : Ultrasonic equipment

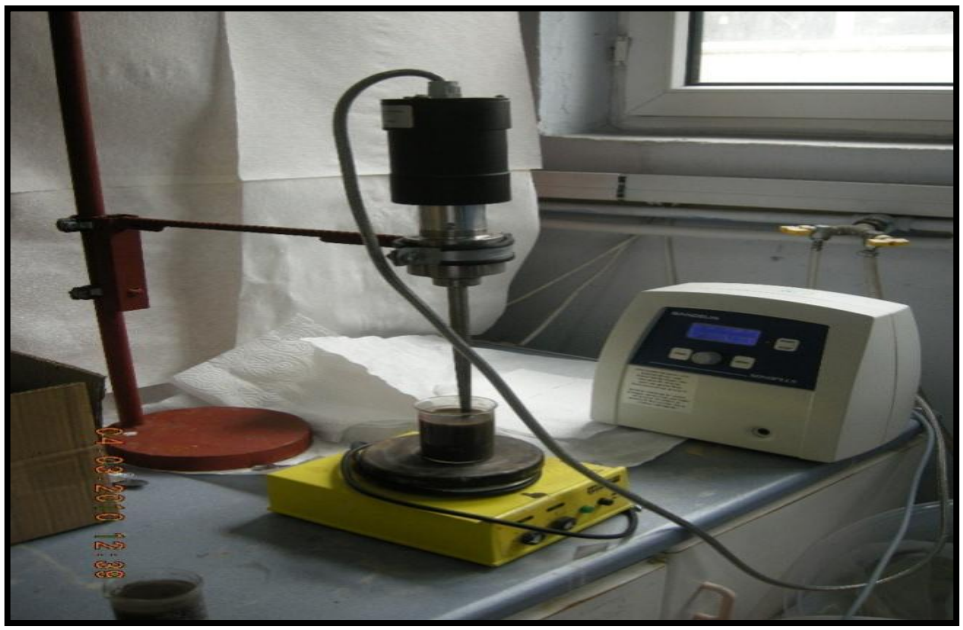

Figure 4.3 : Picture of ultrasound machine

4.2.2 Centrifuge equipment

The RAS samples are centrifuged with Hettich Zentrifugen, Universal 320 model centrifuge machine. The centrifuge equipment is shown in Figure 4.4.

Figure 4.4 : Centrifuge device

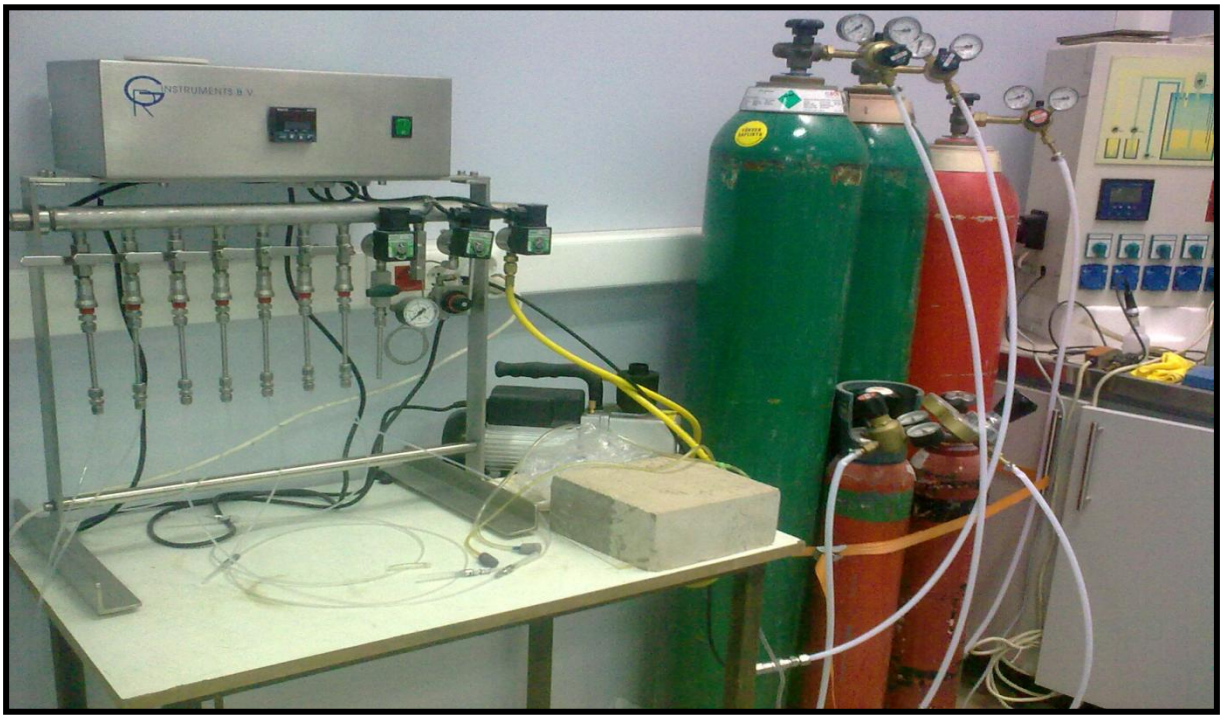

Figure 4.5 : Helium gas purged to the reactor.

4.2.3 Gas chromatography (GC)

The gas composition of the reactors are analyzed by Technical Manual, PR 2100 model gas chromatography. The carrier gas in the system was helium. The GC equipment is shown in Figure 4.6.

Figure 4.6 : Gas chromatography and the batch reactor

4.3 Analytical Methods

After the applied ultrasound disintegration experiments centrifugation applied samples were held to TSS, VSS, TS, VS, CODc, CODf and VFA analysis. And the methods are defined in below;

Total suspended solids (TSS)

Total suspended solids (TSS) content was determined by Standard Method (APHA, 2005). Glass fibre filter papers were pre-dried in an oven at 105°C for at least 1 hour and then cooled in a desiccator for 30 min. The pre-dried filter papers were weighed immediately prior to use. Well mixed sludge samples (5-100 mL, depending on solids contents) were filtered under vacuum through the pre-dried and pre-weighed filter papers. The filter papers were subsequently dried in an oven at 105°C for 1

hour, cooled in a desiccator and re-weighed. The suspended solids content was calculated according to equation ;

$$TSS(mg/L) = (A-B) \times 1000000 / C \quad \textbf{(4.3)}$$

A = Weight of filter and dried residue [g]

B = Weight of filter [g]

C = Sample volume filtered [mL]

Volatile suspended solids (VSS)

Volatile Suspended Solid (VSS) was determined by Standard Method (APHA, 2005). Filter papers supporting the suspended solids residue were ignited in a furnace at 550°C for 1hour. Following cooling in a desiccator, the filter papers were immediately re-weighed and the VSS concentration calculated according to equation

$$VSS(mg/L) = (A-B) \times 1000000 / C \quad \textbf{(4.4)}$$

Where:

A = Weight of filter and dried residue before ignition in [g]

B = Weight of filter and dried residue after ignition in [g]

C = Sample volume filtered in [mL]

Total Solid (TS)

Total Solid was determined by Standard Method (APHA, 2005). Porcelain crucible was ignited in a furnace at 550°C for 1hour. And then cooled in a desiccator, the Porcelain crucible was weighed. A well-mixed sample is evaporated in a porcelain crucible on a water-bath. And the sample dried to constant weight in an oven at 105°C for 1 hour, cooled in a desiccator and re-weighed. The total solid content was calculated according to equation

$$TS(mg/L) = (A-B) \times 1000000 / C \quad \textbf{(4.5)}$$

Where;

A = Weight of porcelain crucible and dried residue [g]

B = Weight of porcelain crucible [g]

C = Sample volume [mL]

Volatile Solid (VS)

Volatile solid was determined by Standard Method (APHA, 2005). After the TS determined this residue was ignited in a furnace at 550°C for 1hour, following cooling in a desiccator, the porcelain crucible were immediately re-weighed and the VS concentration calculated according to equation ;

$$VS(mg/L) = (A-B) \times 1000000 / C \quad \textbf{(4.6)}$$

Where;

A = Weight of porcelain crucible and dried residue [g]

B = Weight of porcelain crucible +inorganic residue [g]

C = Sample volume [mL]

Particle size analysis

Sludge particle sizes were measured using a Malvern Mastersizer 2000 particle analyser (Malvern Instruments Ltd, Worcestershire, UK). The Mastersizer uses an optical unit to detect the light scattering pattern of sludge particles dispersed in deionised water.

Chemical oxygen demand after centrifuge (CODc)

The samples (Disintegrated and RAS) were centrifuged at 9000 rpm for 15 minutes and the supernatant directly analyzed with ISO 6060 closed reflux**.**

Chemical oxygen demand, filtered after centrifuge (CODf)

The CODf release was used as a direct measurement of sludge disintegration. When RAS is sonicated, the intracellular materials from bacterial the cell was released into the aqueous phase. An increased CODf after ultrasonic treatment of sludge is an indication of sludge disintegration efficiency. The samples (Disintegrated and RAS) were centrifuged at 9000 rpm for 15 minutes and the supernatant was filtered through 0.45 μm pore millex-HV hydrophilic membrane filter. And analyzed with ISO 6060 closed reflux**.**

COD removal efficiency

The efficiency in the removal of the CODc (CODRem) was defined according to equation ;

$$COD_{Rem}(\%) = [COD_{Inf} - COD_{Eff}] / COD_{Inf} \times 100 \quad \textbf{(4.7)}$$

Where:

CODInf = The COD concentration in the influent, [mg/L COD]

CODEff = The COD concentration in the effluent, [mg/L COD]

Microscopic examination

Qualitative flocs structural characteristics were investigated with an Olympus BX50 phase contrast light microscope.

BMP

Methane composition was measured by gas chromatography with a packed column.

Manometer

Pressure of the gas is measured by manometer (Bar).

Volatile fatty acid (VFA)

VFA analysis were measured in recycled activated sludge and digested sludge. RAS and digested sludge was centrifuged at 9000 rpm for 15 minutes, and the supernetant was filtered through the 0,20μm pore size membrane filter. And the sample is

protected by adding phosphoric acid. Volatile fatty acid analysis was measured using Agilent, 6890 N model gas chromatograph.

pH

pH measured by Standard Method (APHA, 2005) with Orion 720A+ model pH meter.

4.4 Disintegration Degree (DD)

The degree of cell disruption can be measured using two biochemical parameters. The rate of oxygen demand and the COD release have been proven to be suitable.

$$DD = [COD_d - COD_i] / [COD_a - COD_i] \times 100 \quad \textbf{(4.8)}$$

Where;

COD_d = CODf concentration for disintegrated sample

COD_i = CODf concentration for untreated sample

COD_a = Max. CODf concentration can be obtained after alkaline hydrolysis

4.5 Alkaline Hydrolysis

The sludge (alkaline) hyrdrolysed by chemical disintegration with 1N sodium hydroxide (NaOH) for 10 minutes at 90°C. The alkaline hydrolysis of sludge is a method that the disintegration occurs at a maximum degree.

4.6 Measurement Methods of Biogas Production and Composition

The quality and quantity of digester gas produced can be used to evaluate digester performance. When cumulative gas collection becomes to constant value, it was indication of the steady state to be achieved. Daily biogas was measured by manometer. To analyze the composition (CH_4, CO_2, H_2 and N_2) Gas Chromatography attached with Helium as carrier gas was used.

Calculation of methane component in the sludge is shown below ;

% Component in the sample = ×100 [Area C / Area T] (**4.9)**

Where,

Area C = Area of peak of component of interest

Area T = Sum of areas all the peaks in the sample.

5. RESULTS AND DISCUSSIONS

5.1 Application of Disintegration Methods

In this part of the study, the effect of disintegration on CODf increase and VSS decrease are investigated by applying various disintegration methods to the return activated sludge (RAS) sample which was collected at return sludge line from the Paşaköy domestic wastewater treatment plant in order to select the most suitable disintegration method previous to anaerobic digestion studies to be conducted.

3 different disintegration methods are applied:

- Thermal disintegration
- Thermochemical disintegration
- Ultrasound disintegration

5.1.1 Thermal disintegration

Themal disintegration process is applied at different temperature for different time intervals to observe the effect of thermal disintedgration process on COD release and VSS reduction.

Thermal disintegration processapplied to the return activated sludge are 80°C, 121°C and 160°C with 10 , 30 and 60 minutes time intervals.

Total suspended solid (TSS) concentration of the return activated sludge that thermal disintegration applied is 12920 mg/L, volatile suspended solid (VSS) concentration is 8280 mg/L. CODc and CODf concentrations of return activated sludge after centrifuge is 167 mg/L and 15 mg/L.

CODc and CODf concentrations after thermal disintegration for three different temperature and three different time intervals are given in Figure 5.1 and Figure 5.2. The COD concentrations are referred as CODc since the analysis is applied to the centrifuge samples directly.

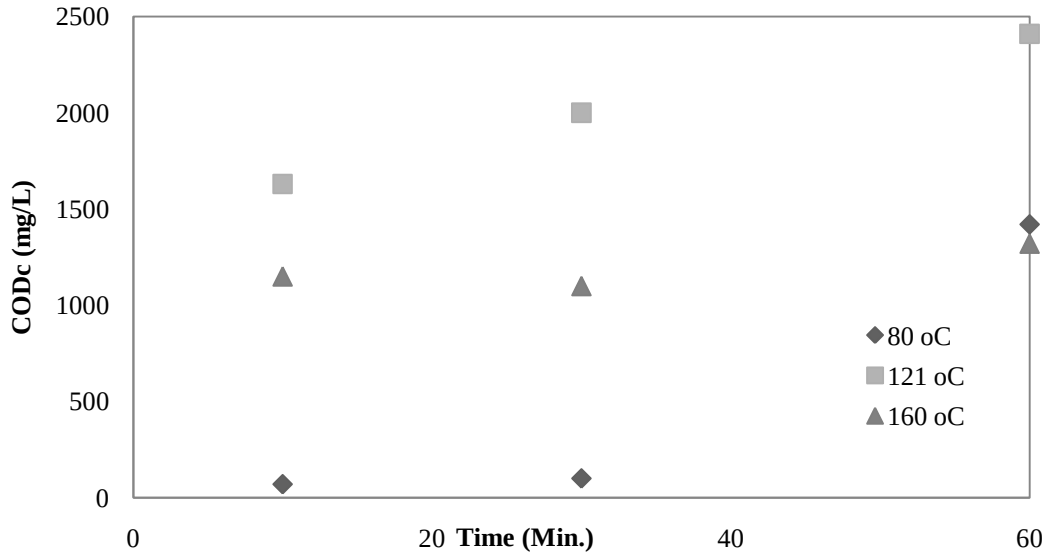

Figure 5.1 : CODc concentrations after thermal disintegration for three different temperature and three different time intervals.

As it can be seen from the Figure 5.1, the highest CODc release is obtained at 121 ^{o}C. Increasing the temperature to 160 ^{o}C doesnt increase CODc concentrations remarkably.

It also seems that temperature increaseat 10 minute to 30 minute was not very effective on CODc concentration increase except at 60 minute. Considering the full scale treatment plants, energy consumption and the costs will increase as the thermal treatment time increase, termal treatment is not practical for implementaion.

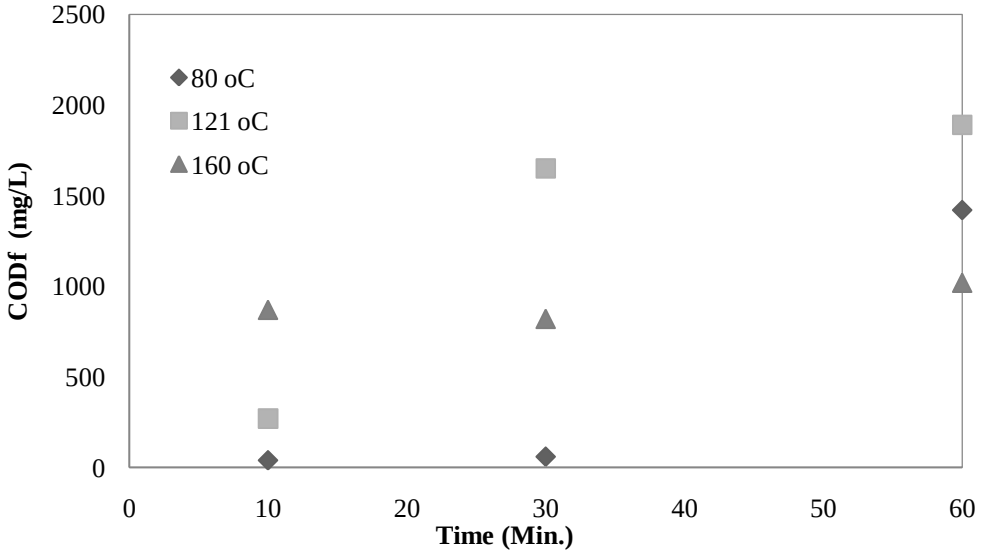

Figure 5.2 : CODf concentrations after thermal disintegration for three different temperature and three different time intervals.

As it can be seen in Figure 5.2 the CODf concentrations results are similar to the CODc concentration results. At low temperatures, CODf concentration increases only with long treatment time. Also the highest CODc release is interestingly obtained at 121 ^{o}C. Increasing the temperature to 160 ^{o}C decreases the CODc concentrations compared to 121 ^{o}C.

The alkaline hydrolysis of sludge is a method that the disintegration occurs at a maximum degree. So, the chemical treatment is applied to the return activated sludge to calculate the maximum disintegration degree.

The sludge (alkaline) hyrdrolysed by chemical disintegration with 1N sodium hydroxide (NaOH) for 10 minutes at 90°C. Maximum CODf concentration is obtained after alkaline hydrolysis.

Total suspended solid (TSS) concentration of the return activated sludge that chemical disintegration applied decrease from 12920 mg/L to 9680 mg/L, and volatile suspended solid (VSS) concentration decrease from 8280 mg/L to 4600 mg/L. It correspondes toTSS concentration decreaseof 25% and VSS concentration decrease of 45% for chemical disintegration.

CODc and CODf concentrations of chemically disintegrated return activated sludge after centrifuge is 4390 mg/L and 2280 mg/L.

Disintegration degrees of thermally treated sludge at three different temperatures for three different time intervals are calculated by comparing with the results of above mentioned chemical alkali treatment and shown in Table 5.1.

Table 5.1: Disintegration degrees of thermally disintegrated RAS

Time (Minute)	Temperature (^{o}C)		
	80	121	160
10	1.1	58.5	37.0
30	7.6	74.8	47.7
60	62.9	83.9	60.8

As it can be seen from the Table 5.1 the optimum temperature for thermal treatment is 121°C. Increasing the temperature from 121 ^{o}C to 160 ^{o}C decreases disintegration degree. At 80 ^{o}C increasing the time interval from 30 minute to 60 minute, increases the disintegration degree drastically. But when the temperature is increased to 121°C,

increasing the time interval from 30 minute to 60 minute, doesn't increase the disintegration degree noticably.

VSS/TSS rates of disintegrated sludge at different temperatures for different time intervals are shown in Figure 5.3.

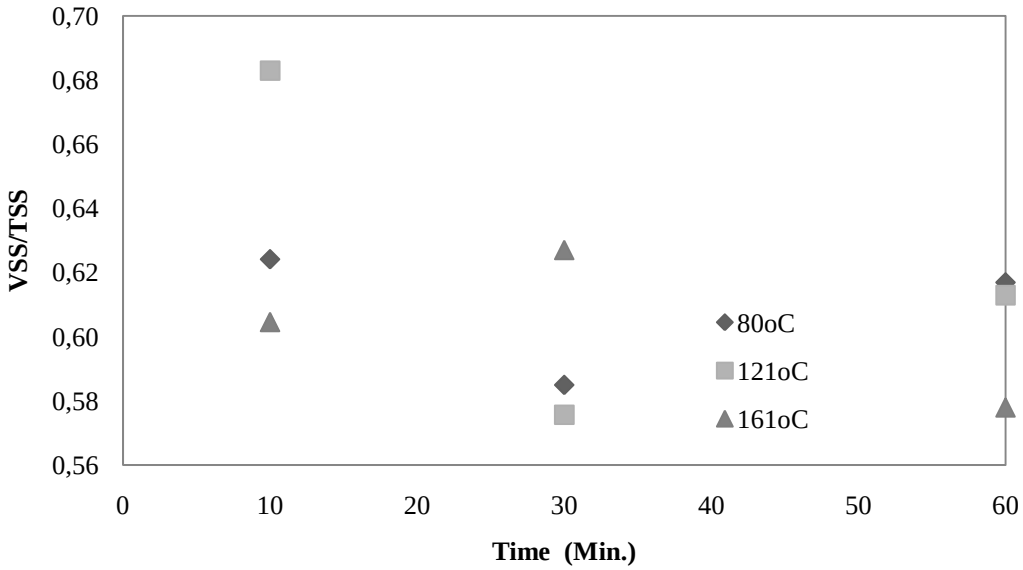

Figure 5.3 : VSS/TSS rates of disintegrated sludge at different temperatures for different time intervals.

VSS/TSS rates of return activated sludge before disintegration is 0.64. After disintegration VSS/TSS rates of disintegrated sludge is in the range of 0.58-0.68.

Table 5.2: VSS reductions at different temperatures

Temperature ^{o}C	VSS Reduction %
80	10-17
121	15-22
160	54-57

The VSS reductions according to the temperature increasing are calculated. As the temperature increase the VSS reduction percentages increase too.

5.1.2 Thermo-chemical disintegration

A thermochemical method for sludge pretreatment may be another option. Organic compounds have not been lost during the pretreatment because the thermochemical process does not oxidise any materials but only promotes hydrolysis and helps split

complex polymers into smaller molecules. The integration of a thermo-chemical treatment in the wastewater handling units at full-scale is rare and succesful implementations in the literature are limited. The reason is the unfavourable economic balance of this application due to the high energy requirement for heating a low-concentrated sludge and the increased reagent dosage.

As compared with the simple thermal treatment, the thermo-chemical treatment has an higher efficiency in sludge solubilisation when applied at the same temperature, however giving additional costs for reagents.

In this part of the study thermochemical disintegration process is applied at pH 8, pH10, pH12, and at three different temperatures of 80°C, 100°C and 120°C for different time interals. All the experiments are carried out with 250 mL sample volume.

The CODc and CODf (after centrifuge) concentrations of RAS and thermochemicaly disintegrated sludge at different temperatures are shown in the Figures from 5.4 to 5.9.

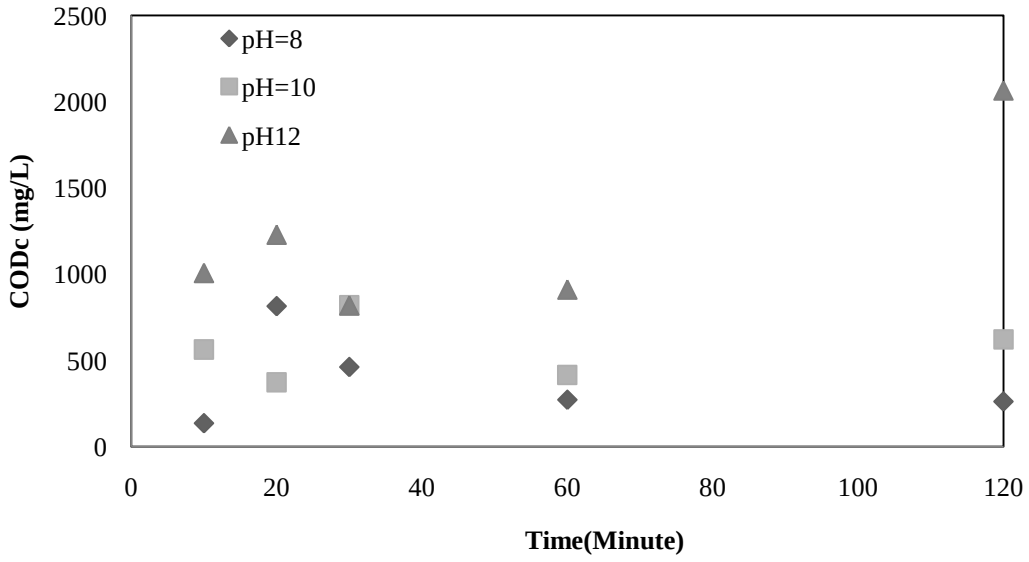

Figure 5.4 : CODc concentrations of thermochemically disintegrated sludge at 80^0C, at different pH values for different time intervals.

As can be seen from Figure 5.4, CODc concentrations of thermo chemically disintegrated sludge at 80^0C, at different pH values, fluctuate. The highest CODc increase is obtained at pH 12 and 120 minute.

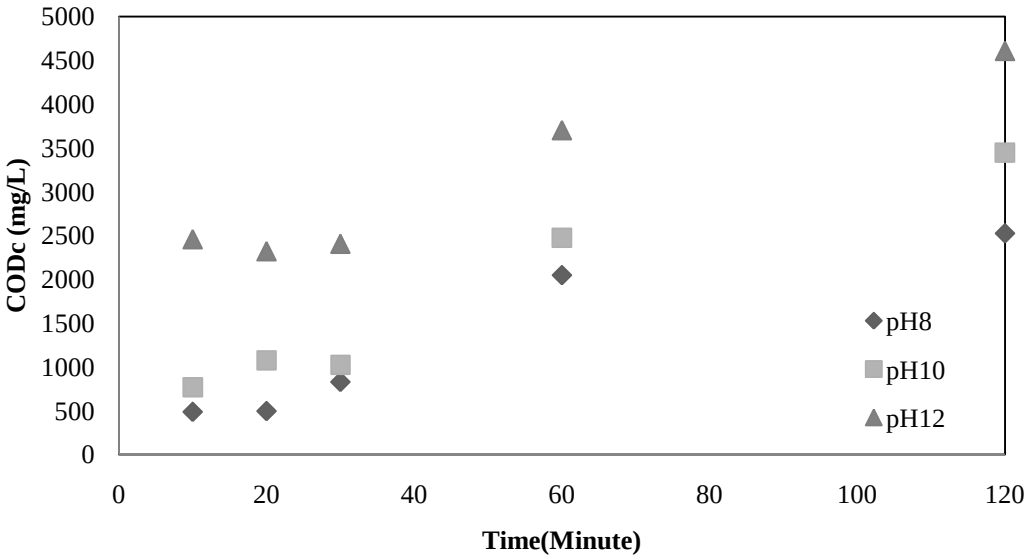

Figure 5.5 : CODc concentrations of thermochemically disintegrated sludge at 100^0C, at different pH values for different time intervals.

As shown in Figure 5.5, CODc concentrations of thermo chemically disintegrated sludge at 100^0C, at different pH values, fluctuate until the first 30 minute, after the first 30 minute CODc concentrations start to increase. Also as the pH increases, the CODc increases in thermo chemical disintegration.

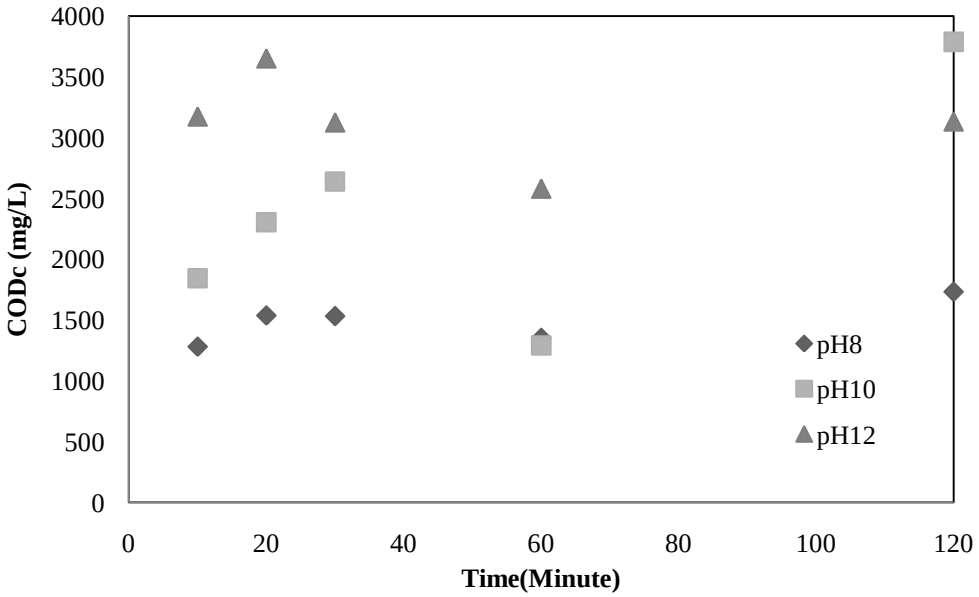

Figure 5.6 : CODc concentrations of thermochemically disintegrated sludge at 120^0C, at different pH values for different time intervals.

As shown in Figure 5.6, CODc concentrations of thermo chemically disintegrated sludge at 120^0C, at different pH values, first increase until the 20 minute then it starts

to decrease until 60 minute. After 1 hour it starts to increase again. According to the Figure 5.6, the results for pH 8 and pH 12 are similar, but pH 10 fluctuates which could be attributed to experimental error.

As shown in Figures, Thermo chemical pre-treatment allows us to overcome the hydrolysis rate-limiting step by lysing sludge cells and releasing extracellular and intracellular material.COD release from the cell increases as the applied temperature increase. Also as the pH increase, the COD release from the cell increases in thermo chemical disintegration.

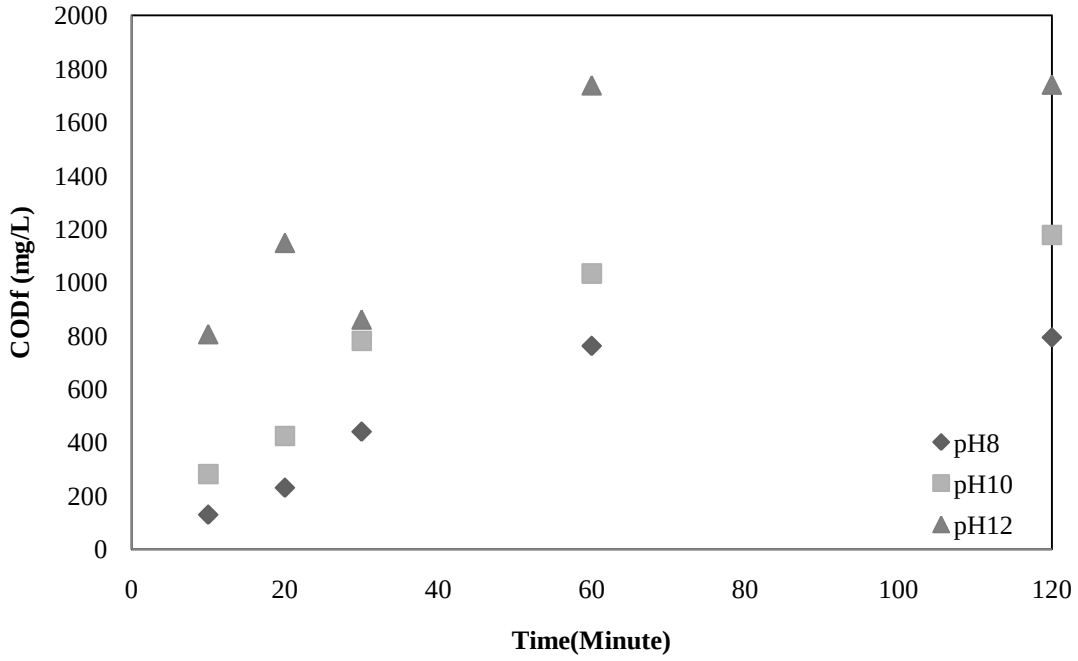

Figure 5.7 : CODf concentrations of thermochemically disintegrated sludge at 80^0C, at different pH values for different time intervals.

In thermochemical pretreatment at 80^0C, for pH 10 and pH 8 a rapid increase in CODf release is observed during the first 30 minute. Then a slowdown in increasing rate of CODf release was observed until a maximum value is reached. The results indicates that thedisintegration time longer than 60 min. doesn't cause significant increases in COD concentrations. The CODf release from the cell also increases as the pH increases after the 30 minute in thermochemical disintegration.

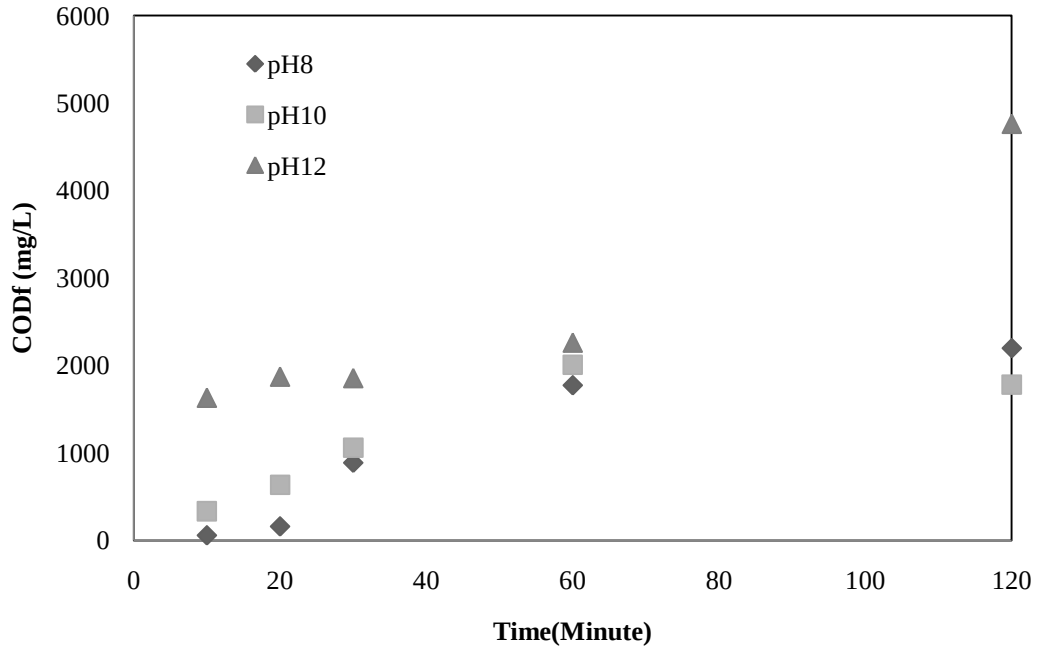

Figure 5.8 : CODf concentrations of thermochemically disintegrated sludge at 100^0C, at different pH values for different time intervals.

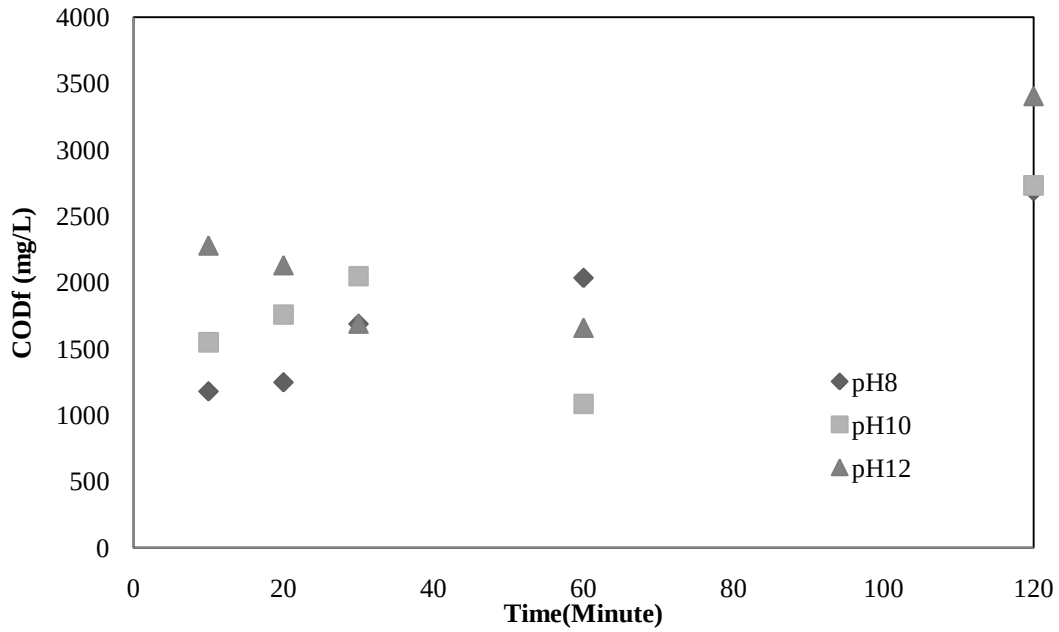

Figure 5.9 : CODf concentrations of thermochemically disintegrated sludge at 120^0C, at different pH values for different time intervals.

As shown in Figure 5.9, CODf concentrations of thermo chemically disintegrated sludge at 120^0C, at different pH values fluctuates until the first hour but CODf concentrations increase after first hour.

An increase in CODf release efficiency and decrease in VSS is used to evaluate the hydrolysis process. Disintegration Degrees and VSS reduction of RAS that thermochemical disintegration process is applied is calculated for different temperature values.

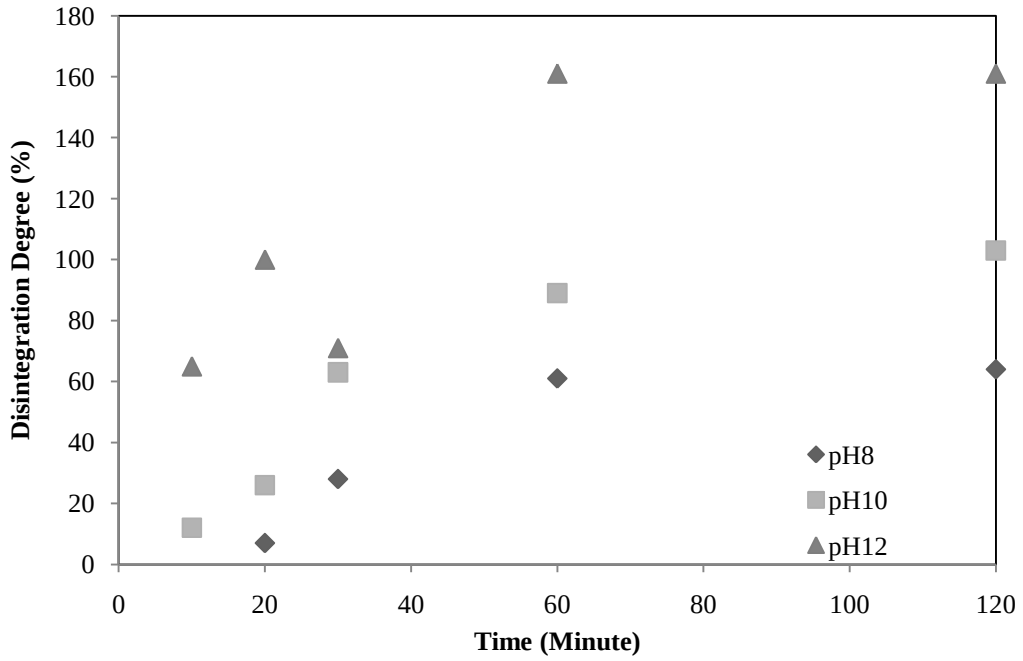

Figure 5.10 : Disintegration degree of disintegrated sludge at 80^{o}C for different pH values and different time intervals

As it is seen from the Figure 5.10, disintegration degree increases as the pH value increases. The highest disintegration degree is observed at pH 12. Also increasing the time interval more than 60 minute, doesn't cause any increase in disintegration degree. According to the results obtained, at 80^{o}C and 60 minute disintegration time can be considered as optimum for thermochemical disintegration.

VSS Reduction rates at 80^{o}C and at different pH values for different time intervals is given in Figure 5.11.

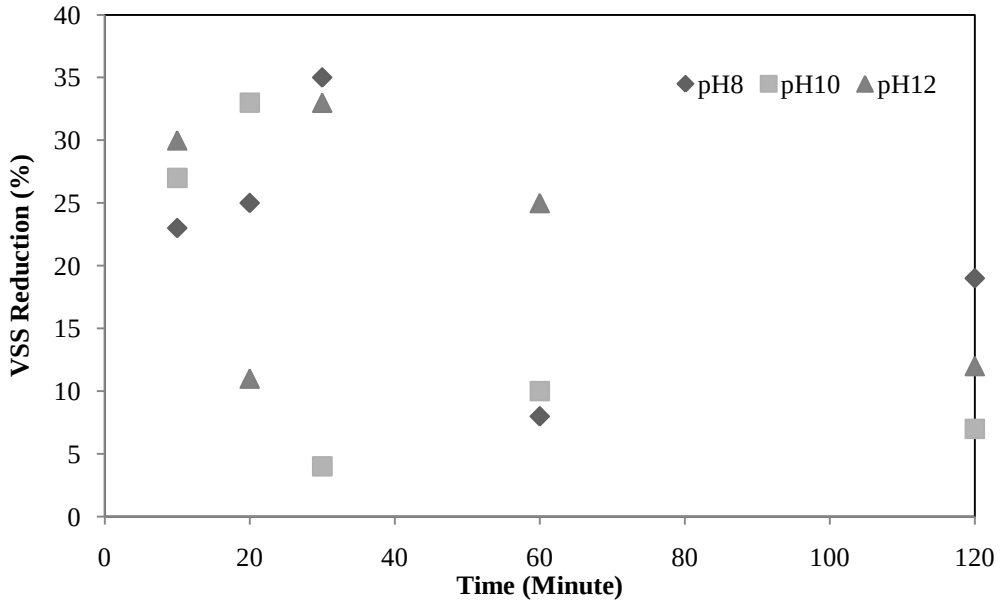

Figure 5.11 : VSS reduction rates at 80^{o}C and at different pH values for different time intervals

According to the Figure 5.11, the highest VSS reduction percentage is obtained at ph 8 and 30 minute. And the VSS concentration of disintegrated sludge at ph 8 and 30 minute is 2960 mg/L while the VSS concentration obtained after alkaline hydrolysis is 2600 mg/L.

Disintegration degrees of disintegrated sludge at 100^{o}C depending on the time for different pH values are shown in Figure 5.12. The figure supports the results given above.

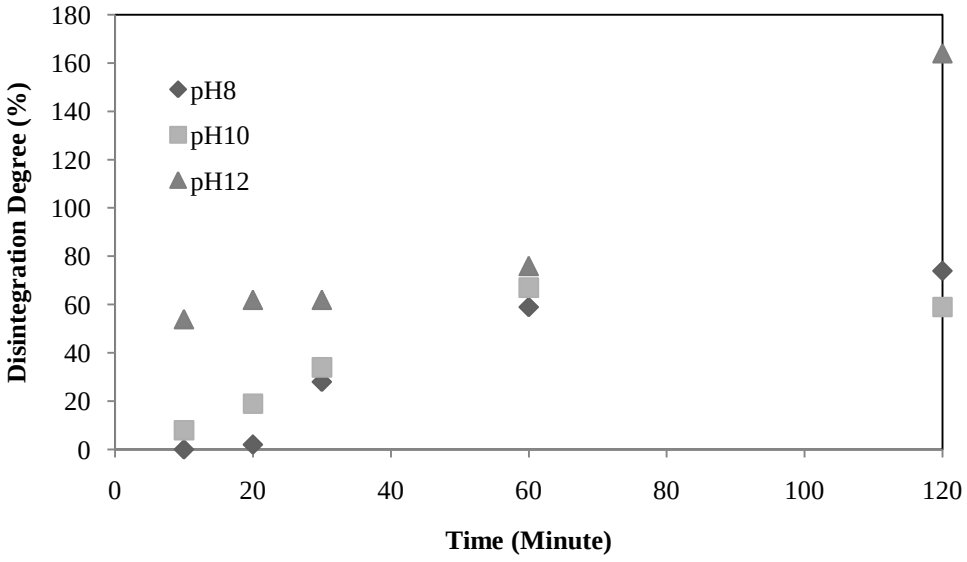

Figure 5.12 : Disintegration degree of disintegrated sludge at 100^{o}C for different pH values and different time intervals

VSS Reduction rates at 100°C and at different pH values for different time intervals are given in Figure 5.13.

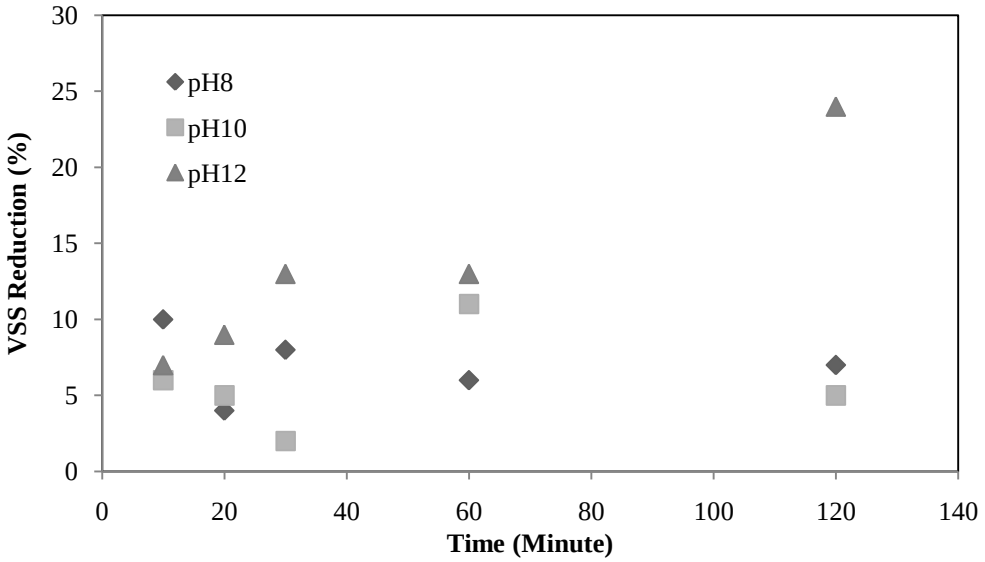

Figure 5.13 : VSS reduction rates at 100°C and at different pH values for different time intervals

Disintegration degrees of disintegrated sludge at 120°C depending on the time for different pH values are shown in Figure 5.14.

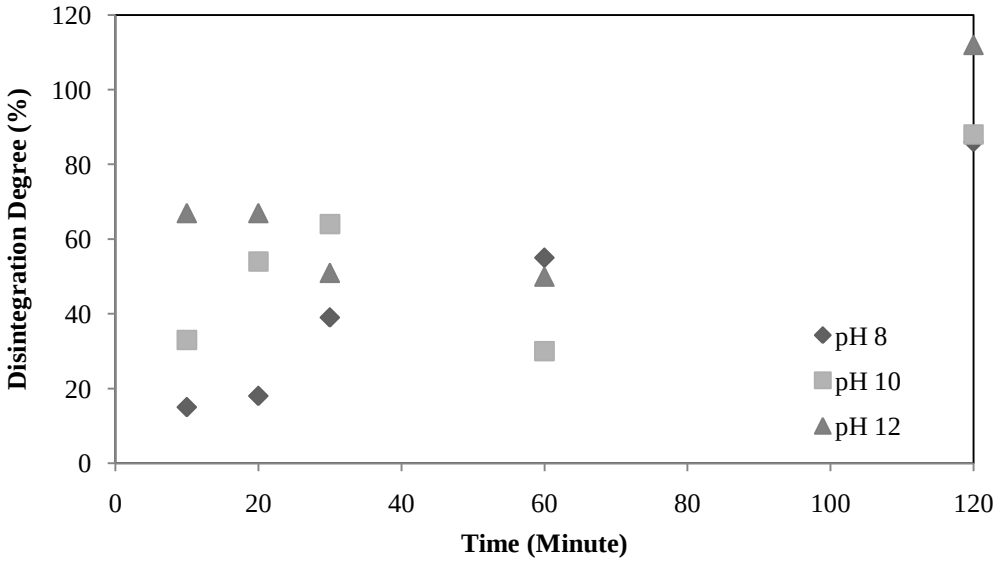

Figure 5.14 : Disintegration degree of disintegrated sludge at 120°C for different pH values and different time intervals

Disintegration degrees of thermo chemically disintegrated sludge at 120°C at different pH values fluctuate until the first hour but after first hour disintegration degrees start to increase. Figure 5.14 supports the results given above.

VSS Reduction rates at 120^{o}C and at different pH values for different time intervals are given in Figure 5.15.

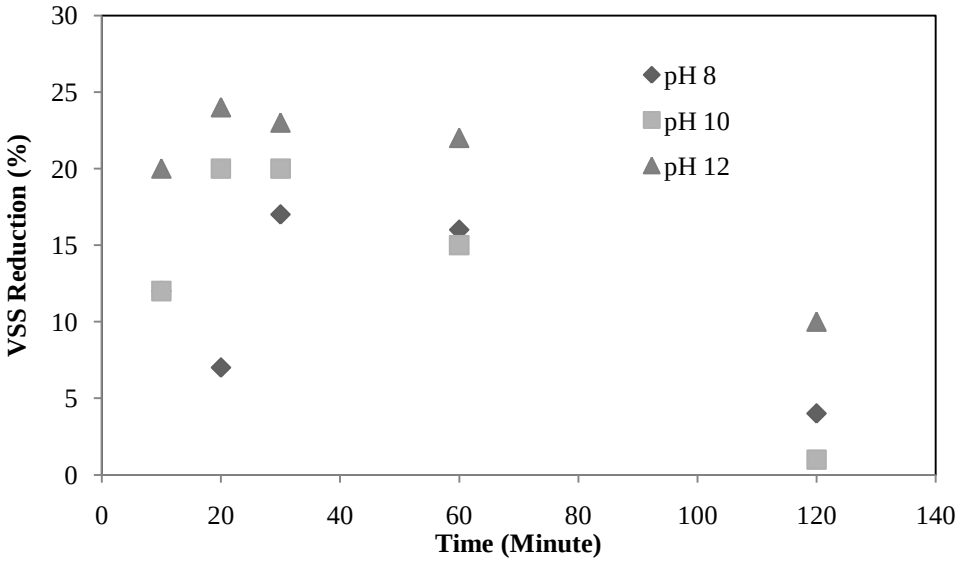

Figure 5.15 : VSS reduction rates at 120^{o}C and at different pH values for different time intervals

Experiments conducted on thermochemical preatreatment resulted in the CODf release efficiency which is increased during the first hour of the pretreatment process, in which about 20-50 % of CODf release efficiency is achieved.

5.1.3 Ultrasonic disintegration

Ultrasonic disintegration process is applied to the return activated sludge (RAS) sample collected from return sludge line from the Paşaköy domestic wastewater treatment plant at different times.

Sludge samples are collected in summer and autumn. The experiments conducted with the summer samples are referred as Stage I. And the experiments conducted with the autumn samples are referred as Stage II.

Stage I

Characterization of the return activated sludge before the disintegration process is performed. CODc concentration is 890 mg/L, CODf concentration of return activated sludge is 150 mg/L. TSS and VSS concentrations are 11880 mg/L and 7720 mg/L respectively.

After chemical disintegration process representing maximum disintegration, CODc concentration is 3960 mg/L, CODf concentration of chemically disintegrated return activated sludge is 2250 mg/L. TSS and VSS concentrations are 8560 mg/L and 3720 mg/L respectively.

TSS concentration decreases from 11880 mg/L to 8560 mg/L, and VSS concentration decreases from 7720 mg/L to 3720 mg/L during chemical disintegration process corresponding to 28 % decrease in TSS and 52 % decrease in VSS.

Ultrasonic disintegration process is applied to the return activated sludge at 60% amplitude at three different working volumes of 250 mL, 500 mL and 1000 mL for different sonication times of 10 minutes, 20 minutes and 30 minutes).

Figure 5.16 shows the CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times.

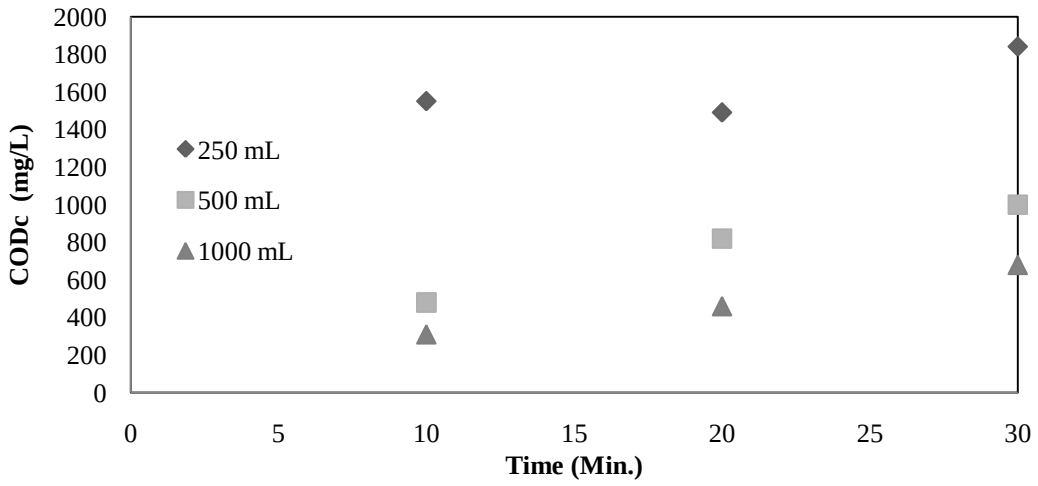

Figure 5.16 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times.

As shown in Figure 5.16, CODc concentrations increase by the increasing sonication time. As the volume that disintegration process applied decreases, the CODc concentration increases. The reason for that is the specific energy increase due to the decrease in sludge amount subjected to disintegration as the volume decreases.

Figure 5.17 indicates the CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times.

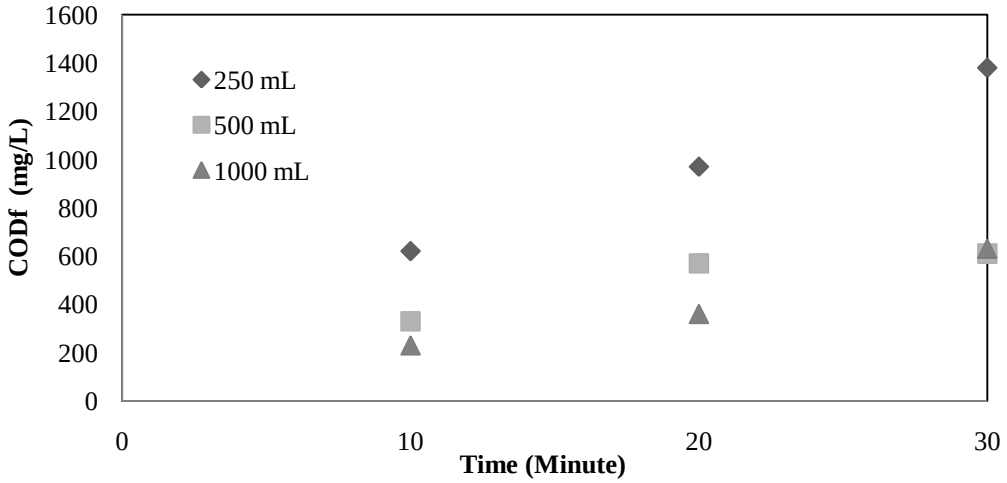

Figure 5.17 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times.

The results obtained on CODf concentration are similar to the CODc concentration results. CODf concentrations increase by the increasing sonication time. Also as the working volume decrease, CODf concentrations of the disintegrated sludge increase due to the increase in specific energies applied.

Specific energies and the disintegration degrees of the ultrasonicdisintegration studies are calculated and given in Table 5.3 and Table 5.4.

Table 5.3: Calculation of specific energies applied to the sludge in Stage I

Volume (mL)	Time (minute)	Amplitude (%)	Power (W)	Ultrasonic power (KW)	TSS (mg/L)	Specific Energy (KW.s/kg TS)
250	10	60	200	0.12	11880	24242
	20	60	200	0.12	11880	48485
	30	60	200	0.12	11880	72727
500	10	60	200	0.12	11880	12121
	20	60	200	0.12	11880	24242
	30	60	200	0.12	11880	36364
1000	10	60	200	0.12	11880	6061
	20	60	200	0.12	11880	12121
	30	60	200	0.12	11880	18182

Table 5.4: Disintegration degrees of ultrasonically disintegrated sludge in Stage I

Volume (mL)	Time (minute)	CODf (mg/L)			Disintegration Degree (%)
		Before Ultrasonic Dis.	After Ultrasonic Dis.	Chemical Disintegration	
250	10	150	620	2250	22.38
	20	150	970	2250	39.05
	30	150	1380	2250	58.57
500	10	150	330	2250	8.57
	20	150	610	2250	21.90
	30	150	570	2250	20.00
1000	10	150	230	2250	3.81
	20	150	360	2250	10.00
	30	150	630	2250	22.86

In Table 5.3, calculation of specific energy for different sonication times at different volumes is shown. According to this calculation, working with high volume of sludges decreases the specific energy applied to the sludge. Also increasing the sonication time causes an increase in specific energy values applied to the sludge.

In Table 5.4, calculation of disintegration degree for different sonication times at different volumes is shown. CODf concentrations increase in direct proportion with the disintegration degree.

The relation between the applied specific energy and the disintegration degree is shown in Figure 5.18.

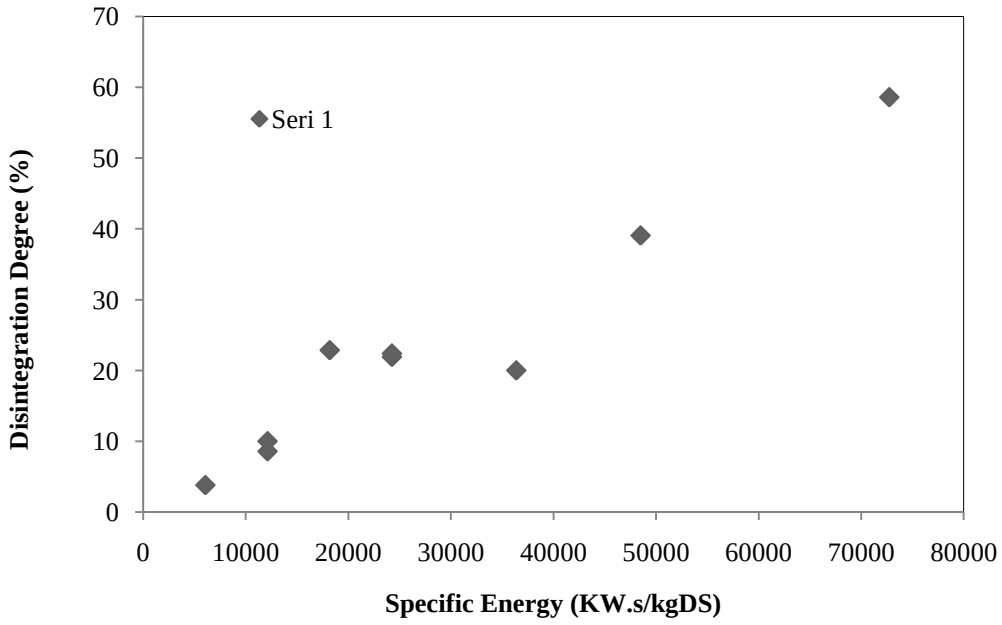

Figure 5.18 : Relation between the specific energy change and the disintegration degree

As seen in Figure 5.18, increasing the sonication time of ultrasounic disintegration leads to an increase up to 60% of the disintegration degree.

The specific energy that is applied to the sludge will also be lower in high working volumes resulting in low disintegration degreesobtained. The energy requirement for the implementation of the ultrasonic disintegration will be high in full scale treatment plants to obtain the high disintegration degrees. That is the most important disadvantage of this pretreatment method.

Stage II

Ultrasonic disintegration pretreatment method application with summer sample conducted at three different volume (50mL, 100mL, 250mL) ,three different amplitude percentage (40%, 60%, 80%) for different sonication time (1min., 5min., 10min., 30min., 60min.). The experiments are contacted under different condition lasting four days.and each condition is described below with the number of the day.

Day 1 : Ultrasonic Disintegration is applied to 50 mL sludge at 40 % and 60 % amplitude for 1, 5, 10, 30 and 60 minutes sonication times.

Day 2 : Ultrasonic Disintegration is applied to 50 mL sludge at 80% amplitude and 100 mL sludge at 40 % and 60 % amplitude for 1, 5, 10, 30 and 60 minute sonication times.

Day 3 : Ultrasonic Disintegration is applied to 100 mL sludge at 80% amplitude and 250 mL sludge at 40 % amplitude for 1, 5, 10, 30 and 60 minute sonication times.

Day 4 : Ultrasonic Disintegration is applied to 250 mL sludge at 60 % and 80 % amplitude for 1, 5, 10, 30 and 60 minutes sonication times.

Characterization of the return activated sludge is shown in Table 5.5.

Table 5.5: Characterization of the return activated sludge

DAY	TSS (mg/L)	VSS (mg/L)	CODf (mg/L)
1	12490	8000	110
2	12850	8250	225
3	12250	8050	120
4	13070	8600	64

For each of the four days, chemical disintegration is applied to the return activated sludge to calculate the disintegration degree. After chemical disintegration process CODf, TSS and VSS concentrations are measured and given in Table 5.6.

Table 5.6: The characterization of return activated sludge after chemical disintegration

DAY	TSS (mg/L)	VSS (mg/L)	CODc (After Centrifuge) (mg/L)	CODf (After Centrifuge) (mg/L)
1	9980	5430	3100	2640
2	9735	5215	3075	2765
3	7320	3920	3910	2950
4	9720	5215	2600	2300

CODc and CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at different volumes for different sonication times and for different amplitudes are shown in Figure 5.19 and 5.20.

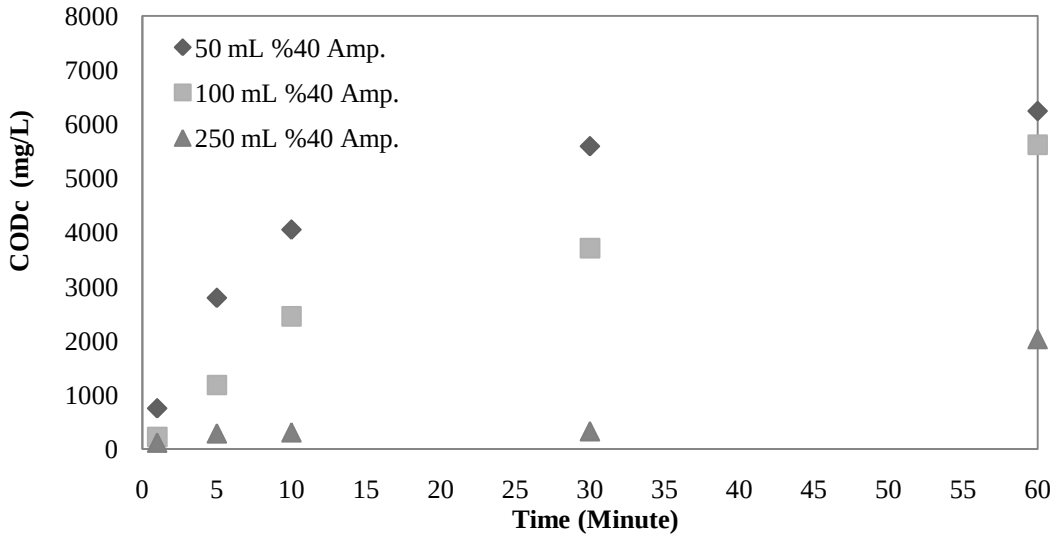

Figure 5.19 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 40 % amplitude at different volumes for different sonication times.

As shown in Figure 5.19, CODc concentrations for 50 mL and 100mL volume increase rapidly until the first 10 minutes. As the volume that disintegration is applied to decreases the CODc concentration increases due to the specific energy increase as mentioned before.

CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 40% amplitude at different volumes for different sonication times are shown in Figure 5.20.

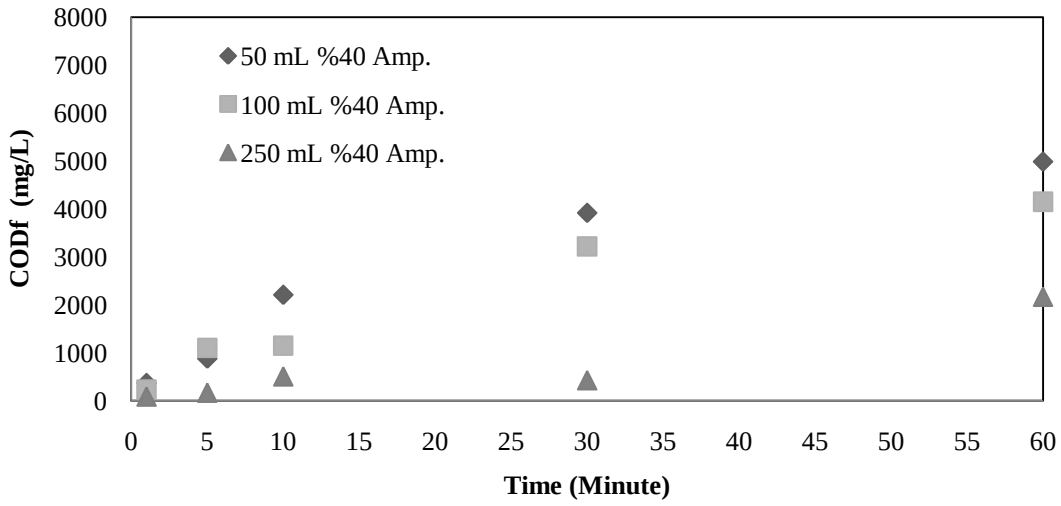

Figure 5.20 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 40% amplitude at different volumes for different sonication times.

As shown in the Figure 5.20, sonication time is remarkably effective on CODf increase together with the volume decrease.

CODc and CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60% amplitude at different volumes for different sonication times are shown in Figure 5.21 and Figure 5.22.

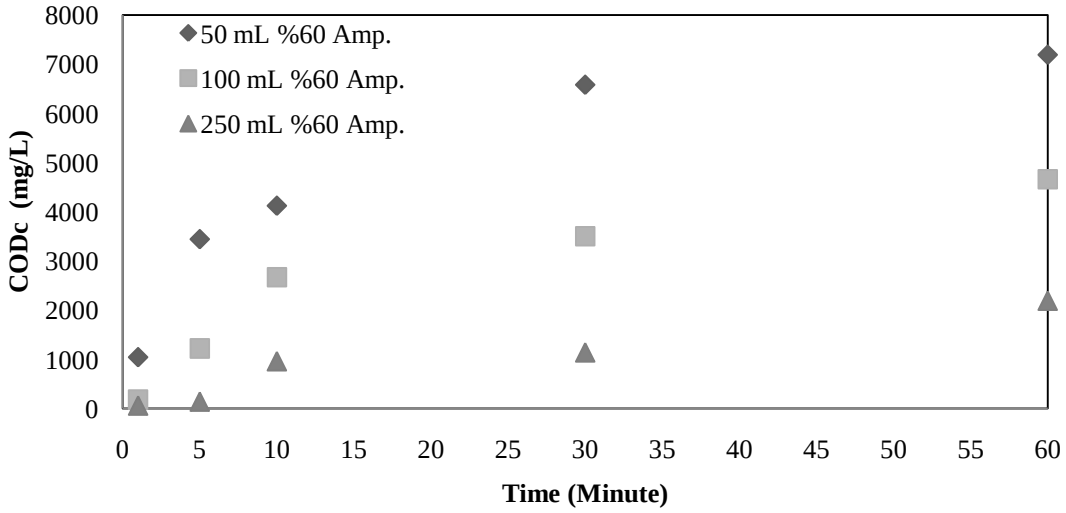

Figure 5.21 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60 % amplitude at different volumes for different sonication times.

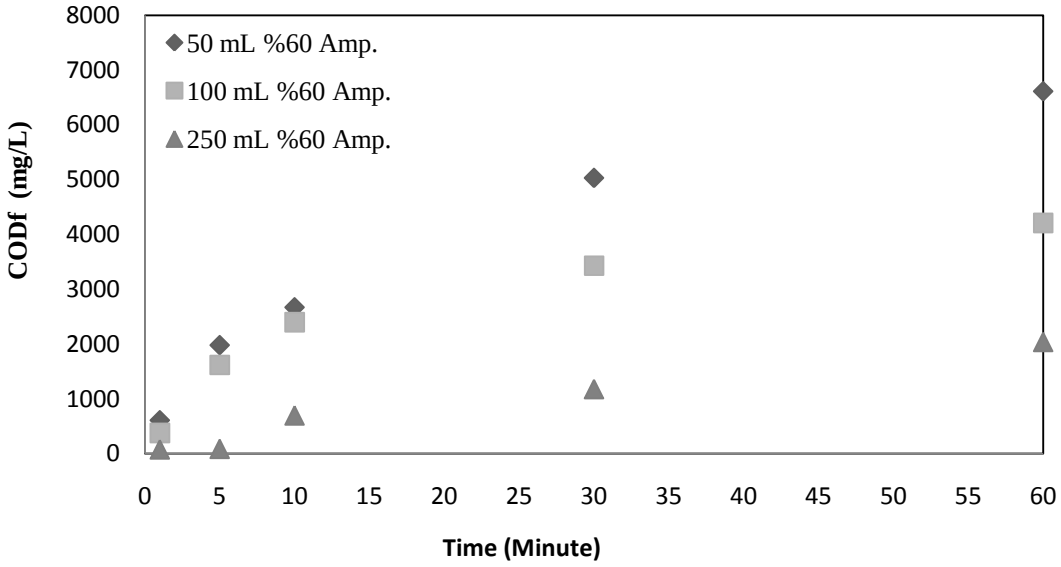

Figure 5.22 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 60% amplitude at different volumes for different sonication times.

As shown in the Figures sonication time is drastically effective on CODf increase. The volume decrease also effects the CODf concentration noticably. A significant increase is observed in COD concentrations of disintegrated sludge at 60% compared with the disintegrated sludge at 40% amplitude.

The highest increase in CODf concentration is observed for 50 mL sludge. CODf concentration increases from 4990 mg/L to 6610 mg/L when the amplitude is increased from 40% to 60%.

CODc and CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 80% amplitude at different volumes for different sonication times are shown in Figure 5.23 and Figure 5.24.

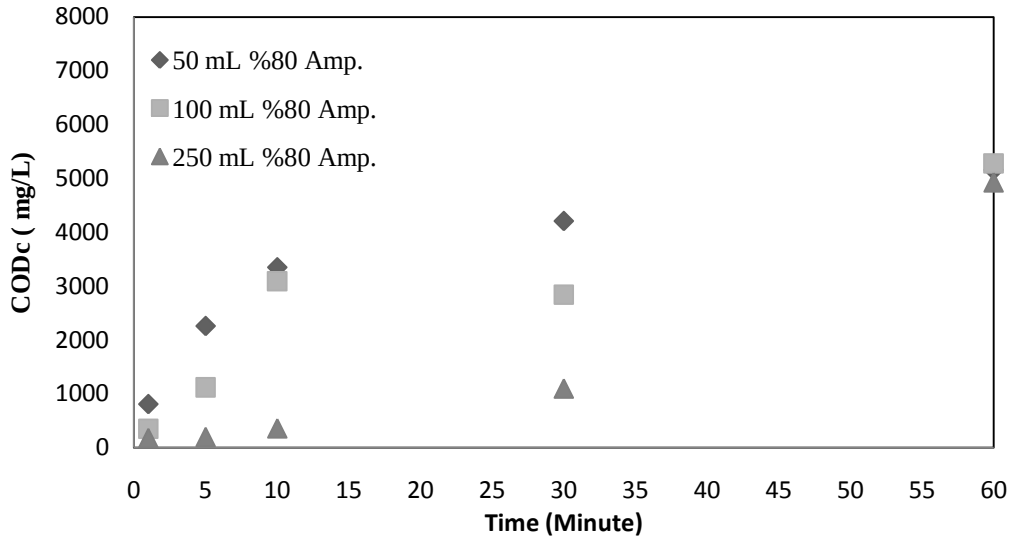

Figure 5.23 : CODc concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 80% amplitude at different volumes for different sonication times.

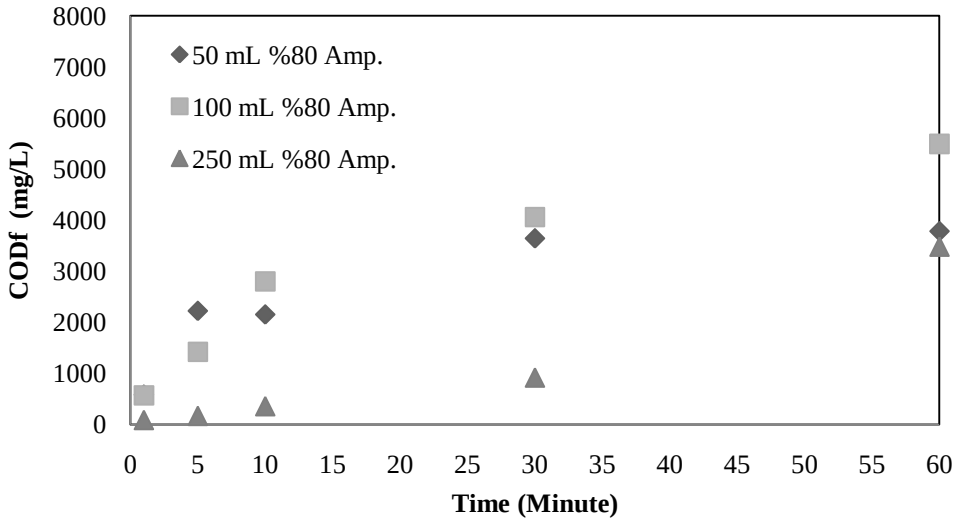

Figure 5.24 : CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 80% amplitude at different volumes for different sonication times.

As shown in the Figures CODc and CODf concentrations (after centrifuge) of ultrasonically disintegrated return activated sludge at 80% amplitude are similar to the previous results obtained at 40% and 60% amplitude. In Table 5.7 calculation of specific energies that applied to the sludge in stage II is given. Also disintegration degrees of ultrasonically disintegrated sludge in stage II is calculated and shown in Table 5.8.

Table 5.7: Calculation of specific energies that applied to the sludge in Stage II

Volume (mL)	Time (minute)	40% Amplitude			60% Amplitude			80% Amplitude		
		Ultrasonic power (KW)	TSS (mg/L)	Specific Energy (KW.s/kg TS)	Ultrasonic power (KW)	TSS (mg/L)	Specific Energy (KW.s/kg TS)	Ultrasonic power (KW)	TSS (mg/L)	Specific Energy (KW.s/kg TS)
50	1	0.08	12490	**7686**	0.12	12490	**11529**	0.16	12850	**14942**
	5	0.08	12490	**38431**	0.12	12490	**57646**	0.16	12850	**74708**
	10	0.08	12490	**76861**	0.12	12490	**115292**	0.16	12850	**149416**
	30	0.08	12490	**230584**	0.12	12490	**345877**	0.16	12850	**448249**
	60	0.08	12490	**461169**	0.12	12490	**691753**	0.16	12850	**896498**
100	1	0.08	12850	**3735**	0.12	12850	**5603**	0.16	12250	**7837**
	5	0.08	12850	**18677**	0.12	12850	**28016**	0.16	12250	**39184**
	10	0.08	12850	**37354**	0.12	12850	**56031**	0.16	12250	**78367**
	30	0.08	12850	**112062**	0.12	12850	**168093**	0.16	12250	**235102**
	60	0.08	12850	**224125**	0.12	12850	**336187**	0.16	12250	**470204**
250	1	0.08	12250	**1567**	0.12	13070	**2204**	0.16	13070	**2938**
	5	0.08	12250	**7837**	0.12	13070	**11018**	0.16	13070	**14690**
	10	0.08	12250	**15673**	0.12	13070	**22035**	0.16	13070	**29380**
	30	0.08	12250	**47020**	0.12	13070	**66106**	0.16	13070	**88141**
	60	0.08	12250	**94041**	0.12	13070	**132211**	0.16	13070	**176282**

Table 5.8: Disintegration degrees of ultrasonically disintegrated sludge in Stage II

Volume (mL)	Time (min)	40% Amplitude				60% Amplitude				80% Amplitude			
		CODf (mg/L)			Disintegration Degree (%)	CODf (mg/L)			Disintegration Degree (%)	CODf (mg/L)			Disintegration Degree (%)
		Before Ultrasonic Dis.	After Ultrasonic Dis.	Chemical Disintegration		Before Ultrasonic Dis.	After Ultrasonic Dis.	Chemical Disintegration		Before Ultrasonic Dis.	After Ultrasonic Dis.	Chemical Disintegration	
50	1	110	372	2640	**10.36**	110	610	2640	**19.76**	225	584	2765	**14.13**
	5	110	879	2640	**30.40**	110	1984	2640	**74.07**	225	2222	2765	**78.62**
	10	110	2214	2640	**83.16**	110	2673	2640	**101.30**	225	2150	2765	**75.79**
	30	110	3922	2640	**150.67**	110	5028	2640	**194.39**	225	3640	2765	**134.45**
	60	110	4986	2640	**192.73**	110	6612	2640	**257.00**	225	3783	2765	**140.08**
100	1	225	230	2765	**0.20**	225	384	2765	**6.26**	120	569	2950	**15.87**
	5	225	1104	2765	**34.61**	225	1616	2765	**54.76**	120	1417	2950	**45.83**
	10	225	1152	2765	**36.50**	225	2400	2765	**85.63**	120	2794	2950	**94.49**
	30	225	3216	2765	**117.76**	225	3432	2765	**126.26**	120	4055	2950	**139.05**
	60	225	4147	2765	**154.41**	225	4209	2765	**156.85**	120	5494	2950	**189.89**
250	1	120	132	2950	**0.42**	64	165	2300	**4.52**	64	400	2300	**15.03**
	5	120	171	2950	**1.80**	64	250	2300	**8.32**	64	1016	2300	**42.58**
	10	120	507	2950	**13.67**	64	650	2300	**26.21**	64	1423	2300	**60.78**
	30	120	430	2950	**10.95**	64	900	2300	**37.39**	64	2480	2300	**108.05**
	60	120	2173	2950	**72.54**	64	2500	2300	**108.94**	64	3015	2300	**131.98**

Disintegration degrees of ultrasonically disintegrated sludge at three different amplitude and three different volumes for different sonication times are calculated to observe the effect of ultrasonic disintegration, sonication time volume and amplitude. The results are given from Figure 5.25 to 5.27.

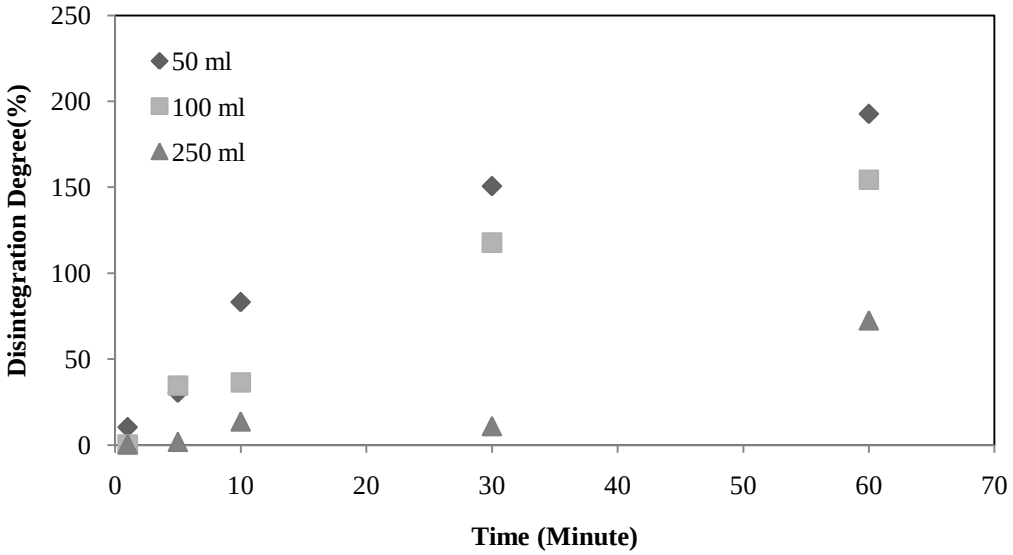

Figure 5.25 : Disintegration degrees of disintegrated sludge depending on the sonication time at 40% amplitude for three different volumes.

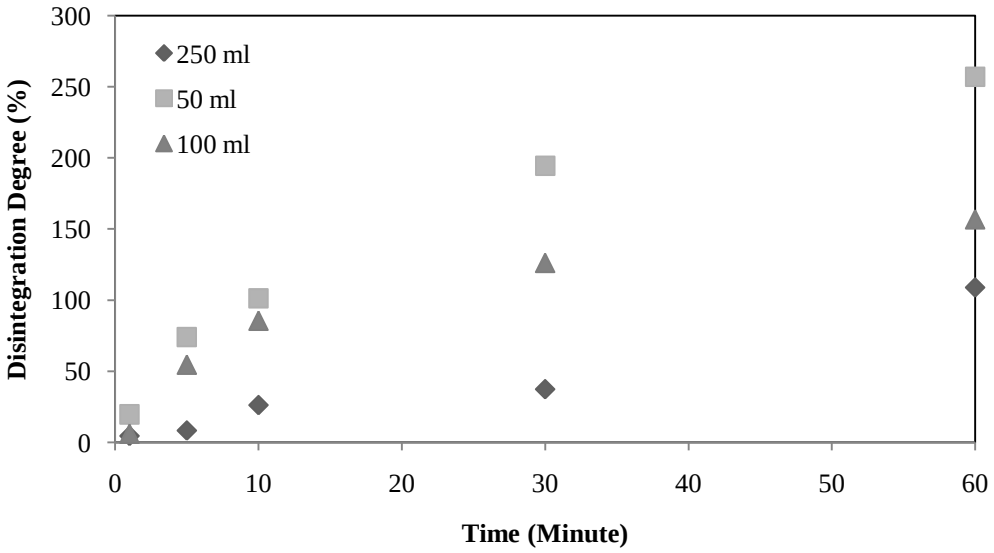

Figure 5.26 : Disintegration degrees of disintegrated sludge depending on the sonication time at 60% amplitude for three different volumes.

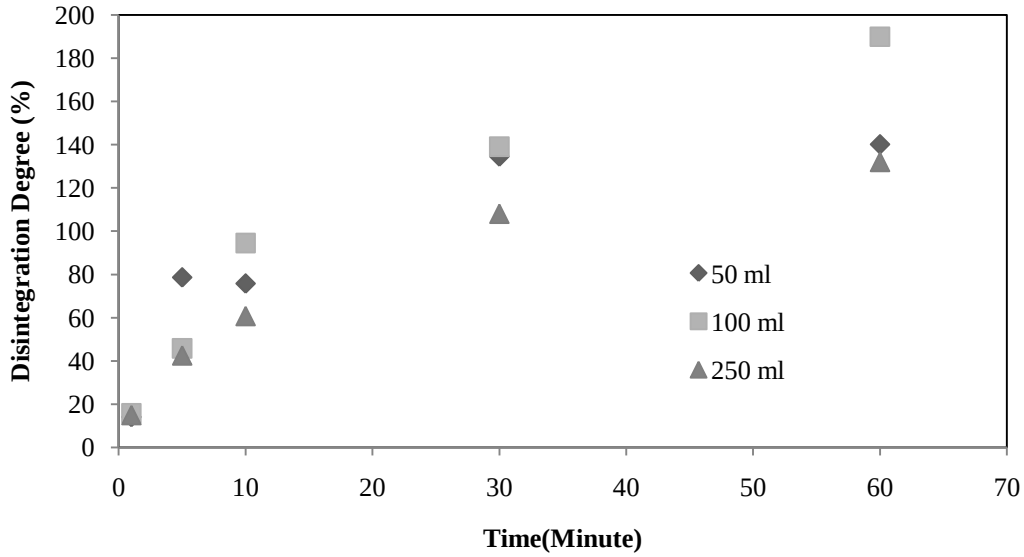

Figure 5.27 : Disintegration degrees of disintegrated sludge depending on the sonication time at 80% amplitude for three different volumes.

As the amplitude increases, disintegration degree (%) increases because of the high energy input applied. As seen from the Figures sonication time is effective on disintegration degree. At 40 % amplitude percentage, increasing sonication time from 30 minute to 60 minute causes **% 22** and **% 84** increase in disintegration degree for 50 mL and 250 mL respectively. It indicates that sonication time is more effective in higher working volumes.

As the sonication time increase, energy consumption of the system increase as well. For this reason, for sonication time more than 30 minute seems not practical for ultrasonic disintegration.

VSS/TSS values of disintegrated sludge at three different amplitude and three different volumes for different sonication times are also calculated and shown in the Figures from 5.28 to 5.30.

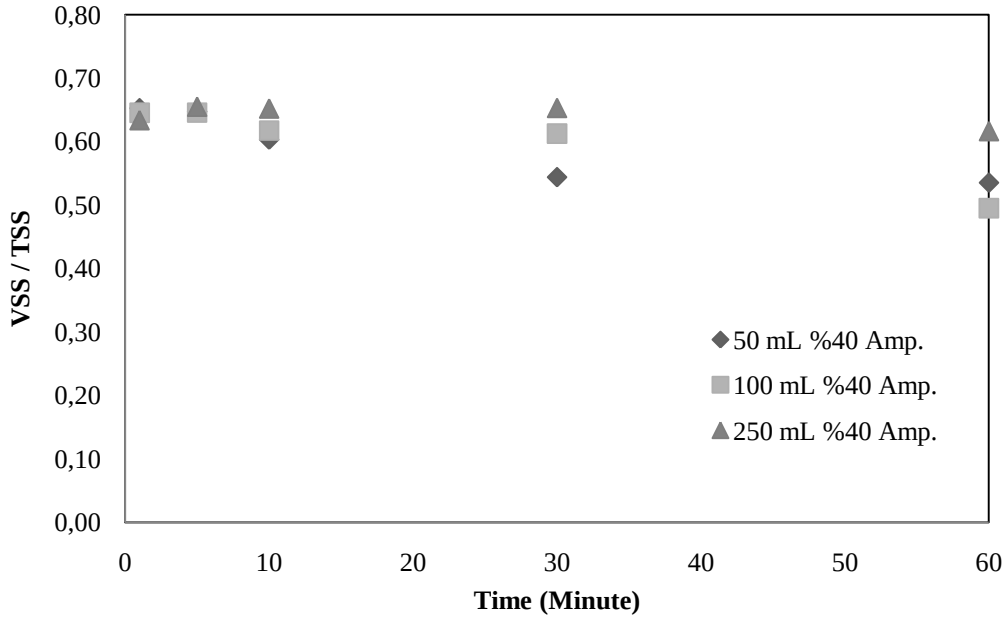

Figure 5.28 : Effect of sonication time on VSS/TSS values of disintegrated sludge at 40% amplitude for three different volumes.

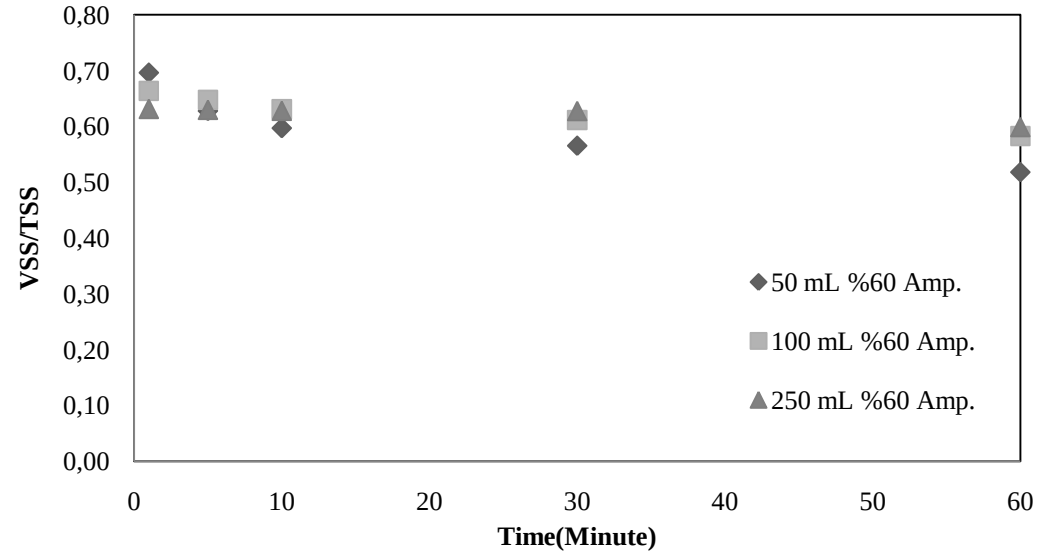

Figure 5.29 : Effect of sonication time on VSS/TSS values of disintegrated sludge at 60% amplitude for three different volumes.

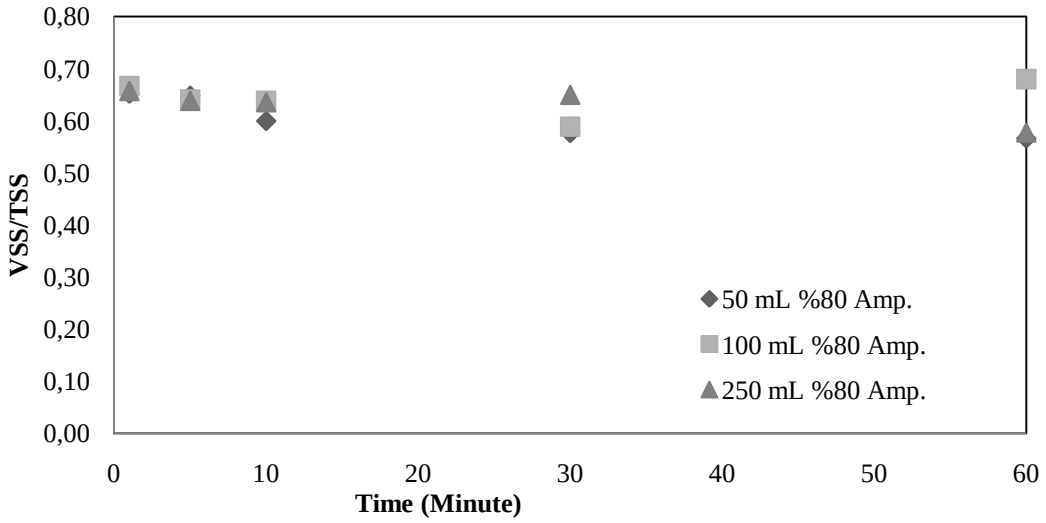

Figure 5.30 : Effect of sonication time onVSS/TSS values of disintegrated sludge at 80% amplitude for three different volumes.

VSS/TSS values of disintegrated sludge depending on the sonication time for three different volumes also tend to decrease for all amplitude percentages.

VSS reduction of disintegrated sludge at three different amplitude and three different volumes for different sonication times are also calculated. VSS reduction increases with the incresing sonication time.. For example VSS reduction of 50 mL disintegrated sludge at 60% amplitude for 30 minute is 11% while the VSS reduction of 100 mL disintegrated sludge at 60% amplitude for 30 minute is 5%.

The change in the disintegration degrees of disintegrated sludge depending on the specific energy, at three different amplitude and three different volumes for different sonication times is calculated and shown in Figure 5.31.

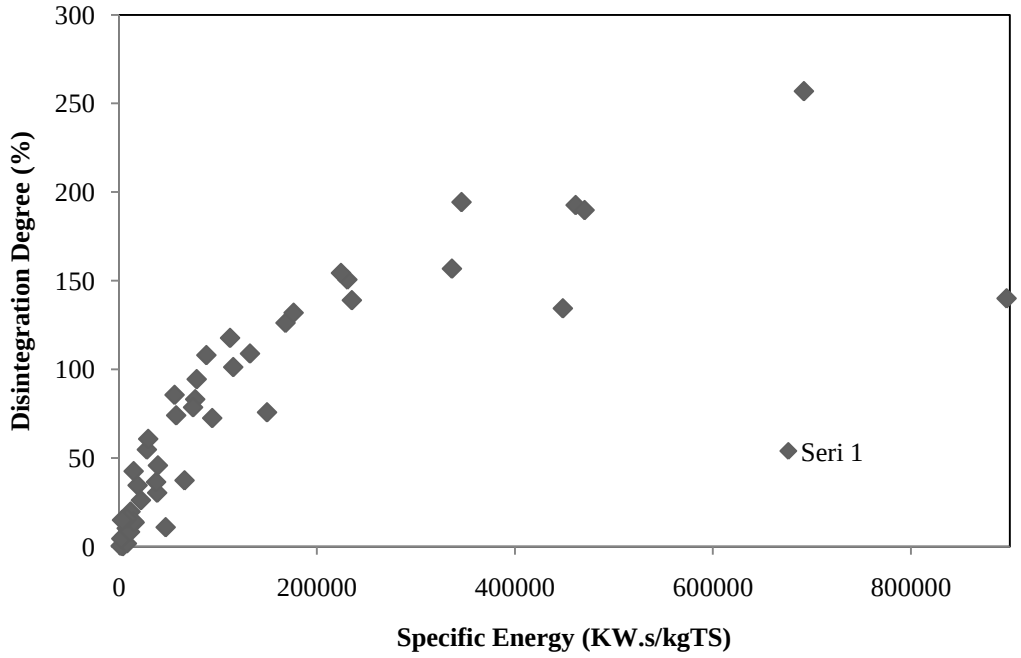

Figure 5.31 : The changes of disintegration degrees with specific energy

Disintegration degree and specific energy is directly proportional. As the specific energy increases disintegration degree increases too. Also in high working volumes specific energy that is applied to the sludge will be lower and eventually low disintegration degree is obtained.

When sludge was exposed to ultrasonic waves, an increase on temperature was also observedduring the ultrasonic disintegration experiments. The increased temperature generated in the sonication chamber during the ultrasonic treatment was investigated. A significant increase of temperature was observed at long sonication duration. The power input and sonication duration have a significant influence in the temperature of the sludge sample which might effect COD solubilisation in a positive way.

Bougrier et al., (2005), in their studies showed that for ultrasonic specific energy between 0 and 7000 kJ/kg TS, biogas production increased with energy supplied, but for energy supplied of 7000 and 15000 kJ/kg TS, biogas production was almost the same. The optimum ultrasonic energy was thus about 7000 kJ/kgTS. Nevertheless, Benabdallah El-Hadj et al., (2006), found that optimum specific energy of 11000kJ/kgTS promoted the best solubilization yield and enhanced biogas production in the subsequent anaerobic stabilization under both mesophilic and thermophilic conditions. Therefore, no specific conclusion can be drawn regarding the value of optimum specific energy.

5.1.3.1 Particle size analysis before and after ultrasonic disintegration

Praticle size distribution of return activated sludge and ultrasonically disintegrated sludge is observed to obtain the change in the particule size distribution with disintegration pretreatment.

The particle size distribution of return activated sludge before disintegration pretreatment is shown in Figure 5.32. Before the disintegration treatment, particle sizes of the sludge distribute in the range of 0.479 μm- 954.993 μm. Also the particle size corresponding to 50% by volume is 48.17 μm.

As shown in Figure 5.32. particle size corresponding to 10% by volume for return activated sludge is 14.4 μm and 90% by volume is 114.2 μm.

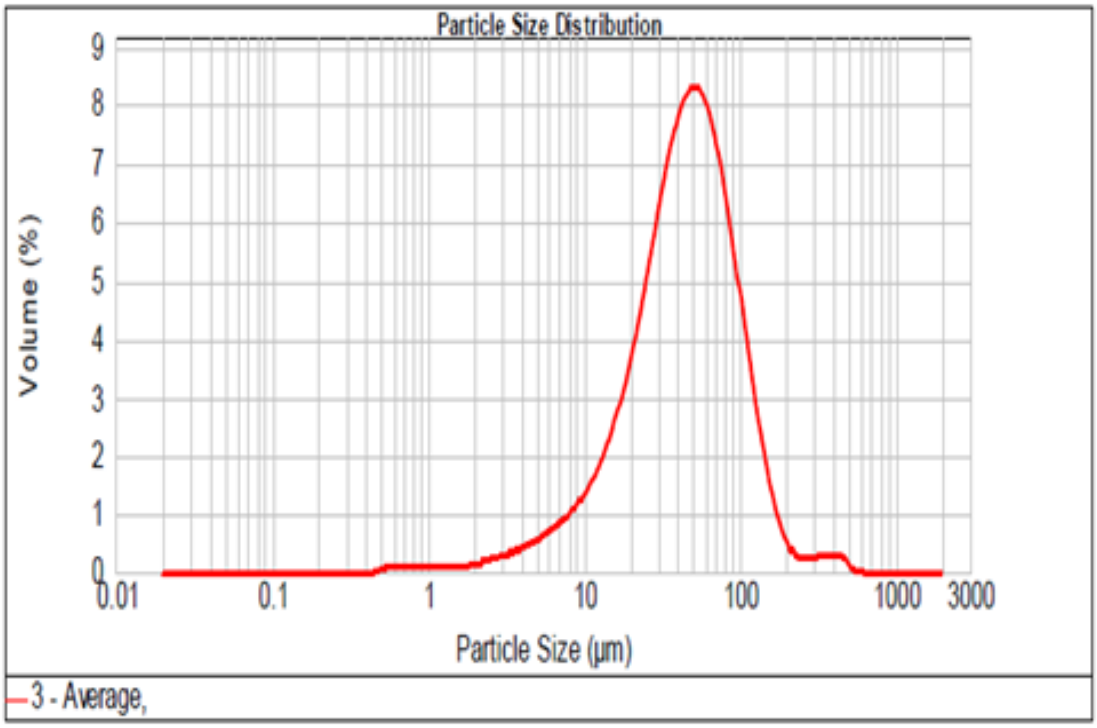

Figure 5.32 : Particle size distribution of return activated sludge before disintegration process.

The particle size distribution of ultrasonically disintegrated sludge at100 mL volume and 80% amplitude for 30 minute is shown in Figure 5.33.

After the disintegration pre-treatment, particle size corresponding to 50% by volume is 7.45 μm.

As shown in Figure 5.33 after the disintegration process particle size corresponding to 10% by volume for return activated sludge is 0.71 µm and 90% by volume is 89.1 µm.

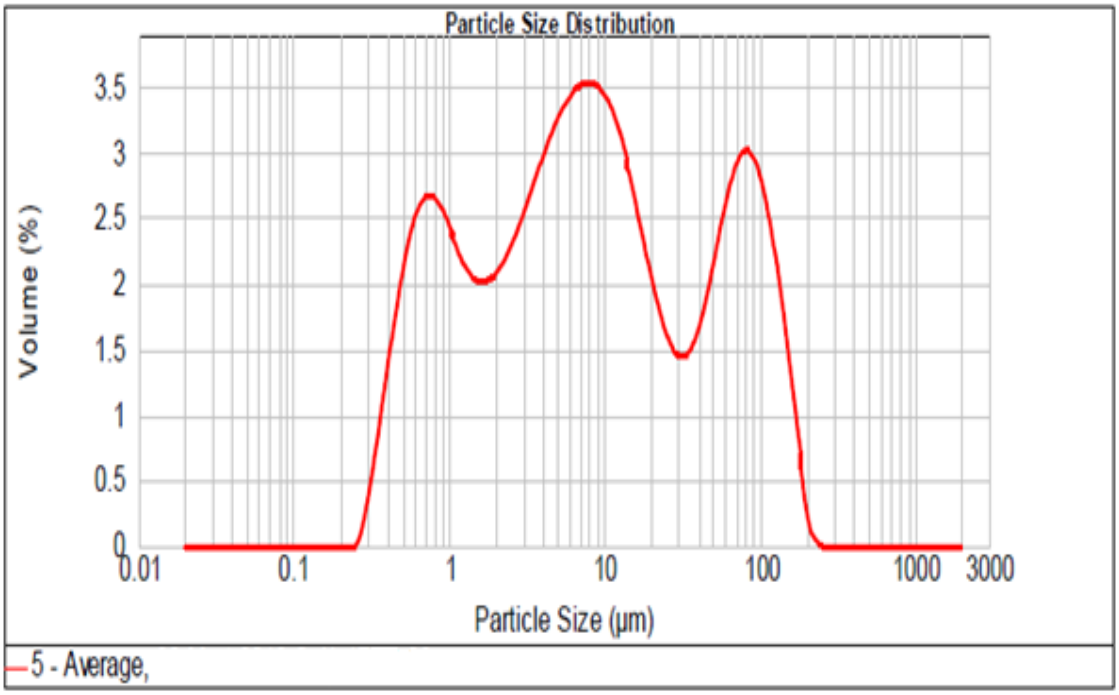

Figure 5.33 : Particle size distribution of return activated sludge after disintegration process applied.

Consequently the results of the particle size distribution show that the disintegration process is able to decrease the size of the particles. Particle size distribution shows that after disintegration not only most of the porous flocs are destroyed, but also some of the microflocs with the simultaneous release of polymeric compounds which link the microflocs to each other (Jorand et al.,1995).

In this study, with ultrasonic disintegration, the particle size corresponding to 50% by volume decreased to 7.45 µm, while it is 48.17 µm before disintegration process.

5.1.3.2 Light microscopic images

Microscope was used to observed sludge structure of ultrasonically treated and nonsonicated RAS sample. The Figure 5.34 shows the light microscope image of nonsonicated RAS sample and ultrasonically treated sludge of 100 mL at 80% amplitude for 30 minute.

From Figure 5.34 to 5.36 reveals that many smaller sludge cell formed sludge floc, which was bounded by extra cellular substances. When sludge was disintegrated at 80% amplitude for sonication duration of 30s, the sludge flock was deagglomerated into individual particles.

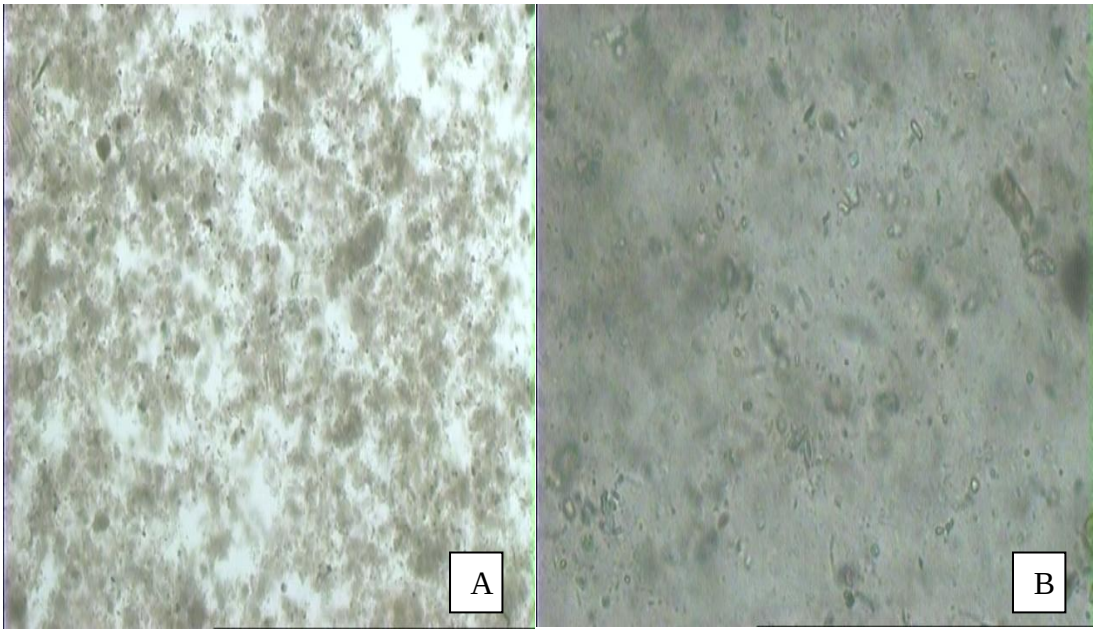

Figure 5.34 : Microscopic images with 40X objective of A) Untreated B) Ultrasonically treated Sludge

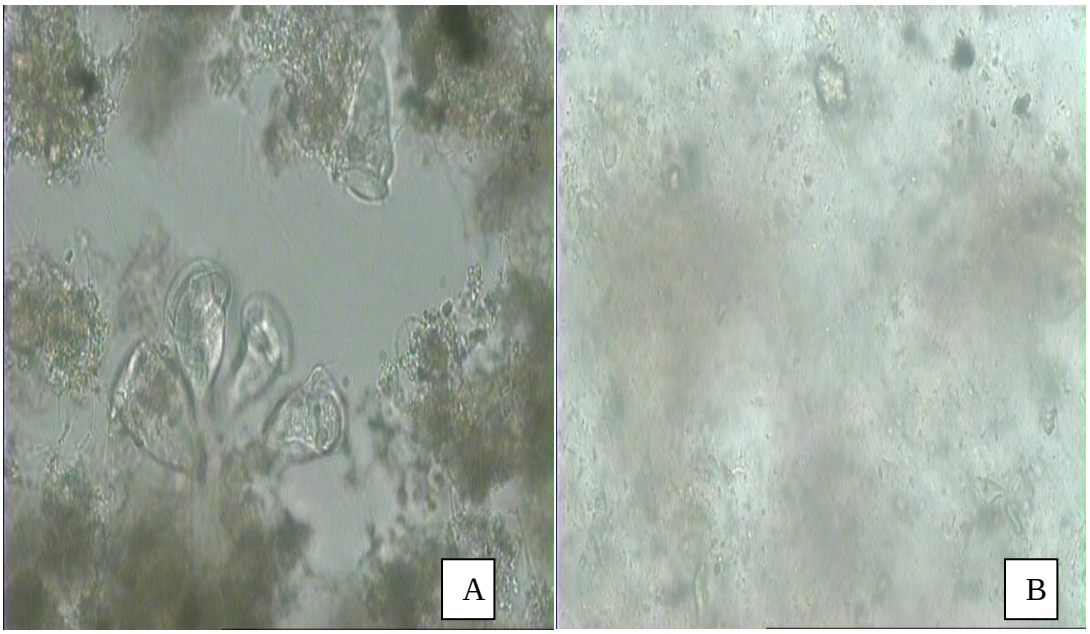

Figure 5.35 : Microscopic images with 20X objective of A) Untreated B) Ultrasonically treated Sludge

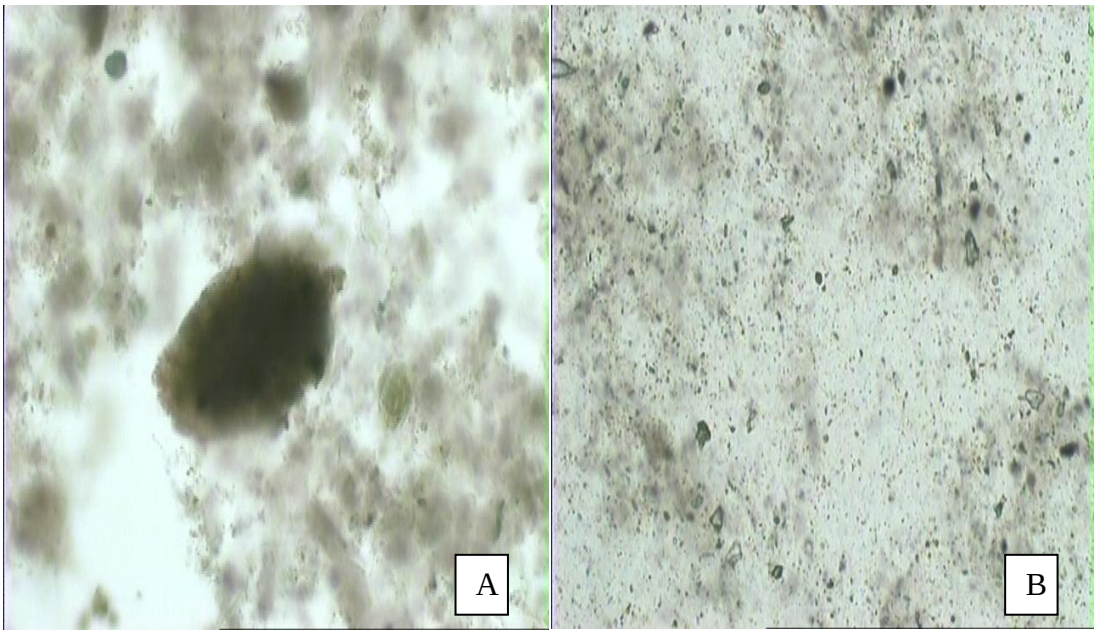

Figure 5.36 : Microscopic images with 10X objective of A) Untreated B) Ultrasonically treated Sludge

5.1.4 Selection of disintegration method

Comparing the results attained from 3 different disintegration method applications, ultrasound disintegration was choosen for the anaerobic stabilization experiments to determine the effect on gas production during anaerobic degradation.

Ultrasonic disintegration is applied to the sludge at different specific energies to determine the release of CODf at the different sonication condition. As a result, ultrasonic disintegration at 80% amplitude which is resulted in 40700 KJ/kg.DS specific energy for 30 minute and 100 mL by volume is selected for anaerobic digestion experiments to evaluate the impact of ultrasonic pretreatment on the digestibility of batch anaerobic digestion.

5.2 Effect of Disintegration on Anaerobic Digestion Efficiency at F/M ratios of 1 and 0.5

5.2.1 Experimental results of RUN I with different ratios of disintegrated and untreated sludge

The effect of ultrasonic disintegration (sonicated 100 mL sample at 80% amplitude for 30 min) on biogas generation of anaerobic digesters was evaluated by using different ratios of disintegrated and untreated sludge as a reactor content at two F/M ratios.

Characterization of sludge

In order to concentrate the sludge that is taken from Paşaköy WWTP, sludge is allowed to settlefor one day and than the supernetant of the sludge is discarded. The total solid concentration was around 13250 mg/L before this one day settling period. Total solid (TS) concentration is increased to 70670 mg/L together with volatile solid (VS) concentration of 63005 mg/L and CODc concentrations of 15409 mg/L before disintegration with this settling period. CODc concentrations of the sludge after ultrasonic disintegration is 16670 mg/L.

The sludge characteristics before and after disintegration are given in Table 5.9 together with the seed properties which is used to provied deired Food to Microorganism ratio in the anaerobic reactors.

Table 5.9: Characterization of the sludge types

	TS mg/L	VS (mg/L)	VS/ TS
SEED	52540	38750	0.74
Before disintegration	70670	63005	0.89
Disintegrated Sludge	18680	10735	0.57

Sludge and Seed Volume Calculations

All digesters were initially seeded with an aerobically digested sludge at different volumes according to F/M ratios. The amount of inoculums- seed (I) and sludge (S) amounts (I/S ratio) in the mixture of the reactors were calculated according to the formula below:

$$I/S = [A \times V_I] \ / \ [B \times V_s] \qquad \textbf{(5.1)}$$

A = Inoculums concentration VS mg/L

B = Sludge concentration as VS mg/L

V_s = Volume of Sludge, (mL)

V_i = Volume of Seed, (mL)

The reactors are fed with seed and sludge either untreated or sonicated at different percentages at required F/M ratios and the calculations are shown in the Table 5.10 and 5.11.

Table 5.10: Sludge and seed volume calculations for RUN I (F/M =1)

RUN	FM=1								
	Seed VSS (mg/L)	V_{inoc} (mL)	Seed Mass Added (g)	CODc	V_{sl} (mL)	Sludge Mass Added (g)	Sludge VSS (mg/L)	I/S	F/M (Sludge added/ Seed added)
Control	38750	13	0.496	15409	32	0.496	63005	0.2	1
25% Dis. + 75% Un.	38750	13	0.496	15409	32	0.496	50630	0.3	1
50% Dis. + 50% Un.	38750	13	0.496	15409	32	0.496	34745	0.5	1
75% Dis. + 25% Un.	38750	13	0.496	15409	32	0.496	20905	0.8	1
Disintegrated sludge	38750	13	0.496	15409	32	0.496	10735	1.5	1

Table 5.11: Sludge and seed volume calculations for RUN I (F/M =0.5)

RUN	FM=0.5								
	Seed VSS (mg/L)	V_{inoc} (mL)	Seed Mass Added (g)	CODc	V_{sl} (mL)	Sludge Mass Added (g)	Sludge VSS (mg/L)	I/S	F/M (Sludge added/ Seed added)
Control	38750	20	0.772	15409	25	0.386	63005	0.5	0.5
25% Dis. + 75% Un.	38750	20	0.772	15409	25	0.386	50630	0.6	0.5
50% Dis. + 50% Un.	38750	20	0.772	15409	25	0.386	34745	0.9	0.5
75% Dis. + 25% Un.	38750	20	0.772	15409	25	0.386	20905	1.5	0.5
Disintegrated sludge	38750	20	0.772	15409	25	0.386	10735	2.9	0.5

5.2.1.1 Biogas productions in RUN I

The biogas produced in each reactor was monitored by measuring daily gas pressure by manometer. Bottles were mixed manually before each gas measurement. And the pressure values are converted to the biogas amount by the help of the formulas below:

$$PxV = nxRxT \quad \textbf{(5.2)}$$

P = Pressure (atm)

V = Volume (L)

N = Amount of substance (mole)

R = Universal gas content (l atm/mole/K)

T = Temperature (Kelvin)

$$V = 22.4 \text{ L/mole (at STP)} \quad \textbf{(5.3)}$$

$1\text{mbar} = 0.98692.10^{-3}\ \text{atm}$

The total biogas production amounts of control sludge and disintegrated sludge at different percentage is measured for two F/M ratios. And the total biogas production amounts are shown in the Figures 5.37 and 5.38.

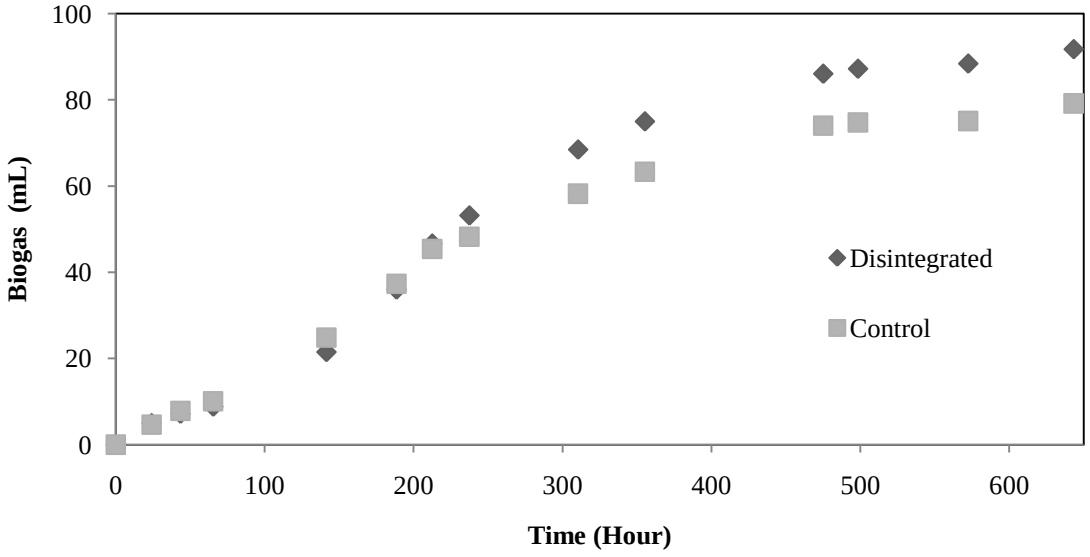

Figure 5.37 : Total biogas production of disintegrated sludge and untreated sludge for F/M 1.

As shown in Figure 5.37, total biogas production of disintegrated sludge is higher than total gas production of untreated (control) sludge. For both sludge types, total biogas production increase rapidly until the 10th day, then increase of total biogas production begins to decrease over time. After the 20th day, the increase of total biogas production decreases more and the amount of total gas production becomes constant.

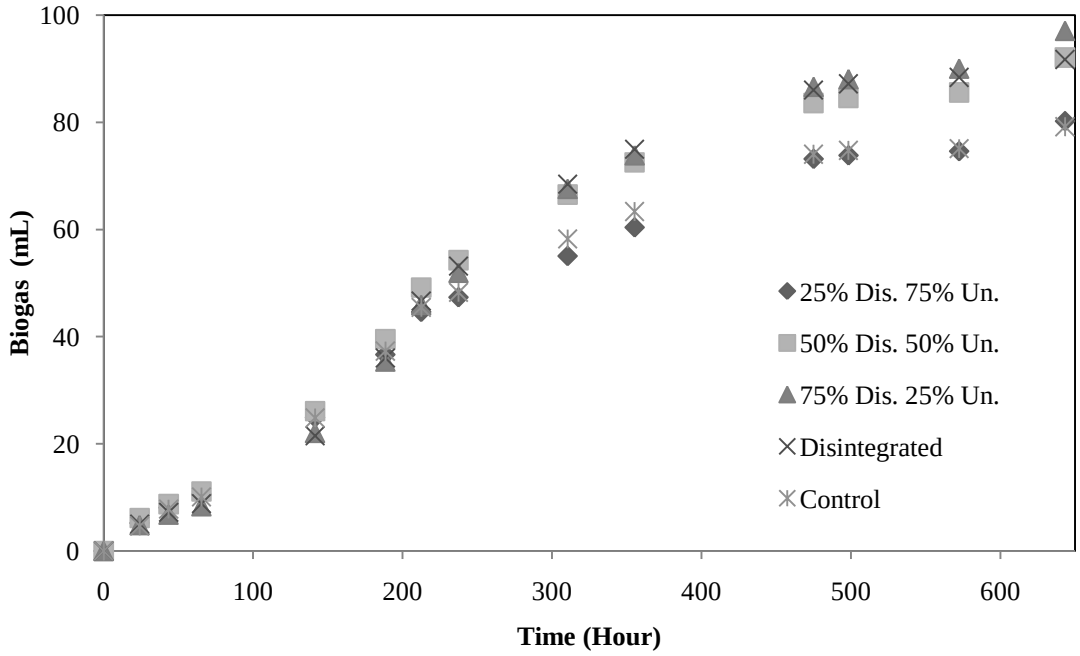

Figure 5.38 : Total biogas production of sludge disintegrated at different percentages for F/M 1.

As shown in Figure 5.38 for F/M 1, there is not a remarkable difference between total biogas production of control sludge and total biogas production of 25% disintegrated sludge + 75 % untreated sludge. As the percentage of disintegrated sludge increases, total biogas production increases.

Total biogas production of disintegrated sludge and untreated sludge for F/M 0.5 is shown in Figure 5.39.

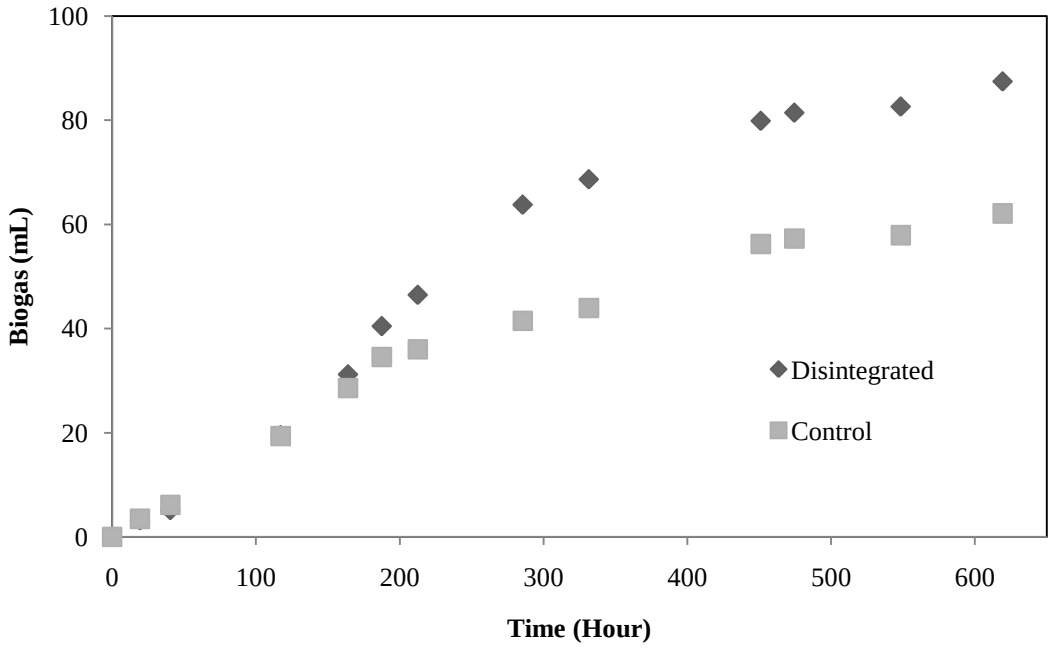

Figure 5.39 : Total biogas production of integrated sludge and untreated sludge for F/M 0.5.

As shown in Figure 5.39, total biogas production of disintegrated sludge is higher than total gas production of untreated (control) sludge. Also the results of total biogas production of the first week are very close to each other. For both sludge types, total biogas production increase rapidly until the day 12th, then increase of total biogas production begins to decrease over time. After the day 20th, the increase of total biogas production decreases more and the amount of total gas production becomes constant. Compared with F/M 1, total biogas production for F/M 0.5, becomes constant more quickly.

Total biogas production of sludge disintegrated at different percentages for F/M 0.5 is given in Figure 5.40.

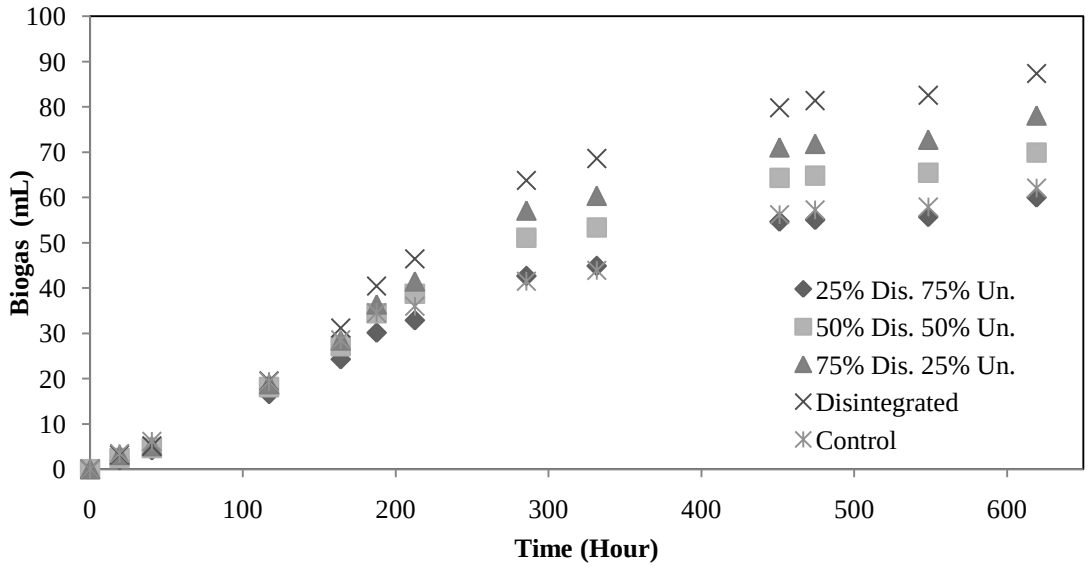

Figure 5.40 : Total biogas production of sludge disintegrated at different percentages for F/M 0.5.

As shown in Figure 5.40 for FM 0.5, there is no big difference between total biogas production of control sludge and total biogas production of 25% disintegrated sludge + 75 % untreated sludge. The results of total biogas production of the first week are very close to each others. As the percentage of disintegrated sludge increases, total biogas production increases. The highest total biogas production is obtained with disintegrated sludge.

Total biogas amount of control sludge at different F/M ratio is shown in Figure 5.41.

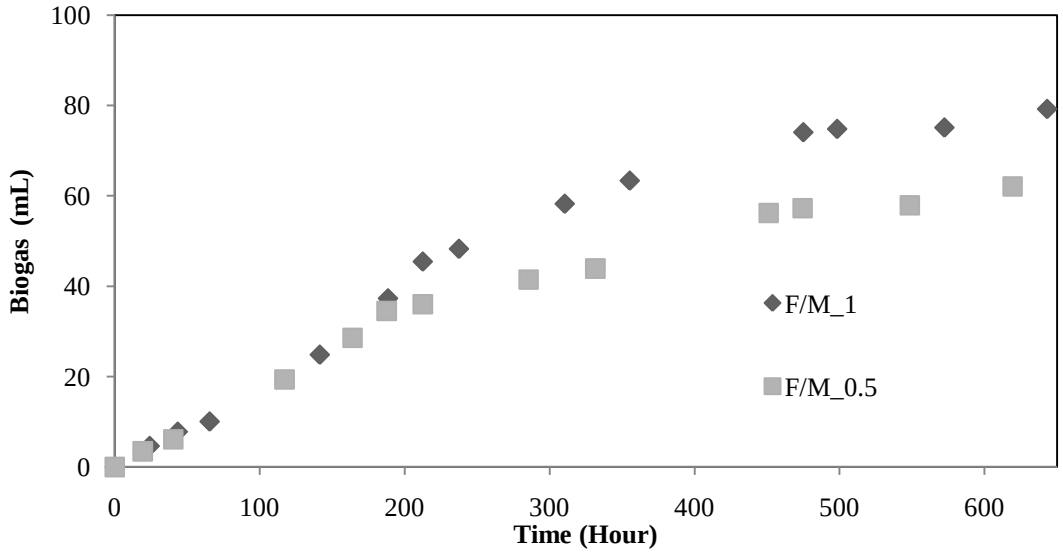

Figure 5.41 : Total biogas amount of control sludge at different F/M ratio.

For different I/S and F/M ratios biogas production amount of control sludge is shown in Figure 5.41. As shown in Figure 5.41 as the I/S decreases and F/M ratios increases, the total biogas production increases.

Total biogas amount of disintegrated sludge at different F/M ratio is shown in Figure 5.42.

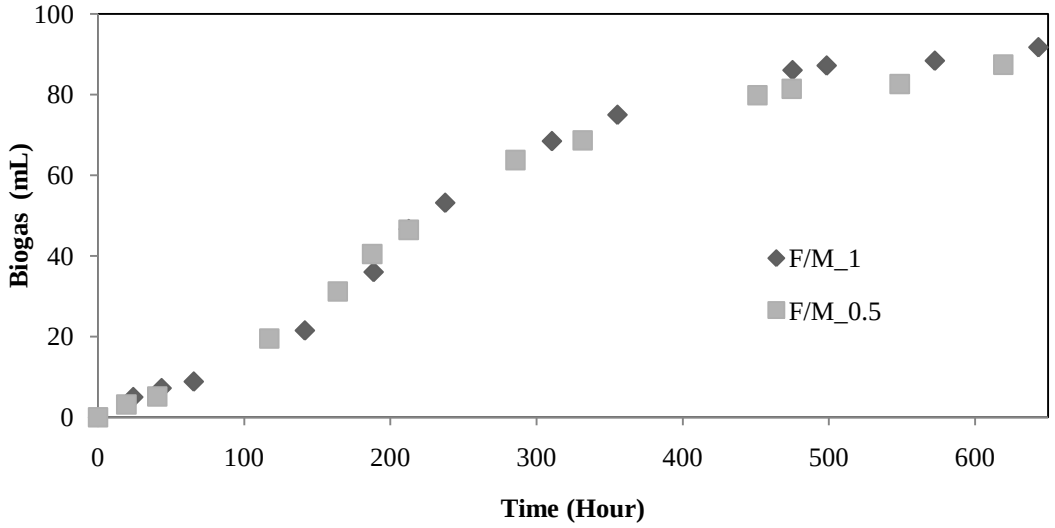

Figure 5.42 : Total biogas amount of disintegrated sludge at different F/M ratio.

Compared with biogas production amount of control values, biogas production amount of disintegrated sludge at different F/M ratios doesn't change too much as can be seen from Figure 5.42. According to these results, the lower difference between control and its sonicated reactor in terms of total gas production is found in the reactors with F/M ratio of 0.5. This difference is higher when the F/M ratio is 1.

In Figure 5.43, the comparison of 50% disintegrated sludge and 50% untreated sludge values for different FM ratios is shown. The results of this figure support the previous results obtained.

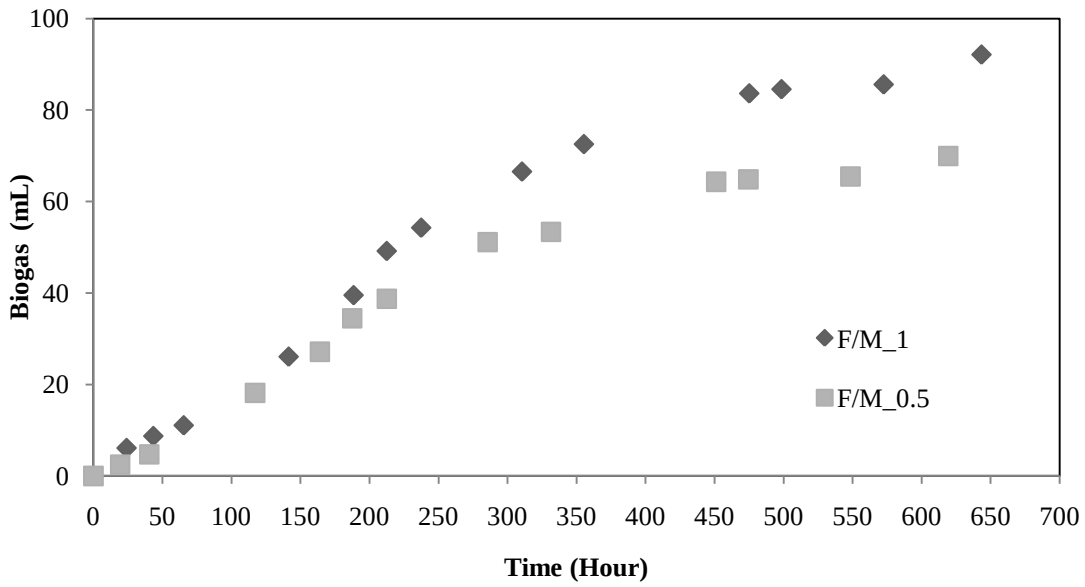

Figure 5.43 : Total biogas amount of 50% disintegrated sludge at different F/M ratios.

In the study of Braguglia et al. (2006), it was found that the ultrasound pretreatment was effective on hydrolysis kinetics and biogas production for all investigated F/M ratios. The VS degradation data for untreated and sonicated sludge during continuous anaerobic digestion were well correlated by a first order kinetic equation. The hydrolysis rate values (0.06-0.17 d-1) increased with decreasing F/M for untreated sludge. The hydrolysis rate of sonicated sludge (0.13-0.23 d-1) was found higher than untreated ones. Moreover, it was obtained that at all F/M ratios, biogas production was higher for sonicated sludge. Initially for the F/M ratio of 2, the biogas production occurred slowly due to accumulation of soluble organic substances caused a kinetic discoupling between hydrolysis and methanogenesis. However, after a while the biogas production increased and overtook the others.

For all F/M ratios, biogas production is higher for sonicated sludge and these results supports the the Braguglia's study.

At the end of the anaerobic digestion period , the amount of biogas production of control sludge and disintegrated sludge increase from **79mL to 92mL** at F/M 1 while the biogas production increase from **62mL to 87mL** at F/M 0.5. It means disintegration process applied before anaerobic digestion cause an **17%** increase in the amount of biogas production at F/M, at the end of the anaerobic digestion period while it cause an **40%** increase in the amount of biogas production at F/M 0.5.

5.2.1.2 Sludge reduction in RUN I

After 30 days of anaerobic digestion period, reactors are opened and analyzed. The initial and final TS, VS, CODc and final CODf values are given in Table 5.12. According to these results, there is **3 % - 55 %** and **14% - 30 %** difference in CODf and VS values respectively to compare the control and reactors mixed with disintegrated sludge at different percentages for F/M 1. Also **9 % - 37 %** and **9 % - 10 %** difference in CODf and VS values are observed respectively to compare the control and reactors mixed with disintegrated sludge at different percentages for F/M 0.5. On the other hand, the CODc destruction of sonicated reactors is lower than control reactors.

VS reduction in 100% disintegrated sludge is higher than the VS reduction in control sludge for both F/M ratios. On the other hand CODf reduction in disintegrated sludge is lower than the VS reduction in control sludge for both F/M ratios.

At the end of the anaerobic digestion period, VS reduction percentages of control sludge and disintegrated sludge increase from **5% to 19%** at F/M 1 while the VS reduction increase from **24% to 34%** at F/M 0.5

Also during the 30 days of anaerobic digestion period, control and disintegrated reactors are opened and analyzed at specific time intervals for both F/M ratios. And the reduction in VS and CODf concentrations by the time is shown in Table 5.13, as shown in the Table 5.13, reduction in VS and CODf concentration increase by day for F/M 1 and F/M 0.5.

Table 5.12: Reduction in CODf and VS values for all configurations of digesters at different F/Ms

RUN		INITIAL				FINAL				CODf Reduction (%)	VS Reduction (%)
		CODf	CODc	TS mg/L	VS mg/L	CODf	CODc	TS mg/L	VS mg/L		
FM1	Control	1880	2075	20067	8967	360	398	20853	8553	81	5
	Disintegrated	2010	2010	22000	9350	441	624	18680	7580	78	19
	%25 Dis. %75 Un.	335	335	24250	12700	381	426	19840	8253	-	35
	%50 Dis. %50 Un.	865	778	22100	10000	396	441	17580	7327	54	27
	%75 Dis. %25 Un.	586	607	21350	11200	434	472	19313	7573	26	32
FM 0.5	Control	1698	1698	25400	12550	405	486	23113	9513	76	24
	Disintegrated	1029	1080	27700	14250	441	502	23633	9393	57	34
	%25 Dis. %75 Un.	398	356	23850	11850	422	503	21947	9153	-	23
	%50 Dis. %50 Un.	670	670	24710	10840	360	383	22740	8893	46	18
	%75 Dis. %25 Un.	1232	1254	26600	11075	755	785	23553	9380	39	15

Table 5.13: CODf and VS reduction during the digestion of digesters at different F/Ms

			CODf	CODc (mg/L)	TS	VS (mg/L)	CODf Reduction (%)	VS Reduction (%)
FM 0.5	Initial	**Control**	1698	1698	25400	12550	0	0
		Disintegrated	**1029**	**1080**	**27700**	**14250**	**0**	**0**
	3. Day	**Control**	1245	1245	21400	9200	27	27
		Disintegrated	**2491**	**2512**	**28100**	**12167**	**-**	**15**
	6. Day	**Control**	1059	1142	21000	9100	38	27
		Disintegrated	**2242**	**2366**	**25200**	**10300**	**-**	**28**
	15. Day	**Control**	454	568	24393	10660	73	15
		Disintegrated	**624**	**639**	**26360**	**18007**	**39**	**-**
	Final	**Control**	405	486	23113	9513	76	24
		Disintegrated	**441**	**502**	**23633**	**9393**	**57**	**34**
FM 1	Initial	**Control**	1880	2075	20067	8967	0	0
		Disintegrated	**2010**	**2010**	**22000**	**9350**	**0**	**0**
	4. Day	**Control**	1453	2348	21100	12333	23	-
		Disintegrated	**3114**	**3259**	**21657**	**9870**	**-**	**-**
	7. Day	**Control**	1287	1308	23850	14980	32	-
		Disintegrated	**3010**	**3051**	**20560**	**12035**	**-**	**-**
	16. Day	**Control**	584	616	22420	9867	69	-
		Disintegrated	**830**	**882**	**19493**	**8020**	**59**	**14**
	25. Day	**Control**	357	405	19780	8613	81	4
		Disintegrated	**545**	**623**	**19040**	**7673**	**73**	**18**
	Final	**Control**	360	398	20853	8553	81	5
		Disintegrated	**441**	**624**	**18680**	**7580**	**78**	**19**

5.2.1.3 Biochemical methane potential (BMP) in RUN I

The impact of the ultrasonic disintegration on the anaerobic digestibility efficiency at different F/M ratios is evaluated by the methane accumulation using BMP test. All the experiments are carried out in identical conditions such as temperature and pressure.

The Table 5.14 and 5.15 show the results of methane content of total biogas that is produced during the anaerobic digestion. Methane content of produced biogas in control and disintegrated sludge reactors at different percentages is analyzed by gas chromatograph at different days during the anaerobic digestion. The Methane, Carbon dioxide, Nitrogen, Oxygen and Hydrogen gas contents of biogas is observed by gas chromatograph. The sum of the Methane, Carbon dioxide and Hydrogen gases represents the total biogas. According to this relation the methane percentage of total produced biogas is calculated.

Table 5.14: Methane percentages (%) of control and disintegrated sludge at different percentages by the time at F/M 1.

Day	FM_1														
	Control			Disintegrated			25% Dis, 75% Un.			50% Dis, 50% Un.			75% Dis, 25% Un.		
	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.
4	4563.17	746.35	**16**	4346.14	504.57	**12**	3855.62	646.57	**17**	4759.31	810.52	**17**	4144	541.18	**13**
9	7450.54	3660.77	**49**	7045.71	3446.26	**49**	7415.32	3626.19	**49**	7544.95	3824.02	**51**	6713.5	3094.61	**46**
16	7457.04	3979.87	**53**	8842.25	4860.32	**55**									
28	8767.67	4778.05	**54**	9580.17	5329.02	**56**	8878.06	4969.26	**56**	9450	5418.4	**57**	8628.2	4838.03	**56**

Table 5.15: Methane percentages (%) of control and disintegrated sludge at different percentages by the time at F/M 0.5.

Day	FM_O.5														
	Control			Disintegrated			25% Dis, 75% Un.			50% Dis, 50% Un.			75% Dis, 25% Un.		
	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.
3	3963.93	559.41	**14**	3817.04	449.09	**12**	3584.1	394.99	**11**	3765.5	459.69	**12**	3780.82	370.50	**10**
8	6605.79	3252.53	**49**	6308.84	2960.69	**47**	5983.37	2623.75	**44**	6450.19	2908.02	**45**	6448.56	2984.67	**46**
15	7310.09	3908.78	**53**	7764.34	4475.22	**58**									
27	8529.06	4593.39	**54**	8269.67	4722.17	**57**	7387.18	3842.85	**52**	7798.22	4122.2	**53**	7982.3	4346.59	**54**

Gas composition of biogas is measured three times during the anaerobic digestion by gas chromatograph to observe the change in methane production during the 28 days anaerobic digestion period.

For F/M 0.5, while the methane percentage of produced biogas in control reactors change ± 0.2, the methane percentage of produced biogas in disintegrated reactors change ± 0.6.

In the first four day of digestion, the methane percentage of produced biogas in control reactors is **14%** for F/M 1 and **16%** for F/M 0.5. As seen from the Tables methane percentage values show a large increase until the 8^{th} and 9^{th} days at both F/M ratios. After this increase methane percentage of the produced biogas remains almost the same until the end of the anaerobic digestion period a lot.

The amount of produced methane gas in disintegrated reactor is **41 mL**, while the amount of produced methane gas in control (unsonicated) reactor is **34 mL** in the day 16^{th} at F/M 1.

Similarly, the amount of produced methane gas in disintegrated reactor in the day 15^{th} is **40 mL**, while the amount of produced methane gas in control (unsonicated) reactor is **24 mL** at F/M 0.5 ratio

At the end of the anaerobic digestion period, the amount of methane gas of control sludge and disintegrated sludge increase from **43 mL to 51 mL** at F/M 1 while the VS reduction increase from **33 mL to 50 mL** at F/M 0.5. It is concluded that the difference of produced methane amount between control and disintegrated sludge increase at lower F/M ratios**.**

Table 5.16 shows VS values of sludge added to the reactors for F/M 1 and F/M 0.5. VS values added are calculated to observe the change in normalized mL CH_4/gVSSadded with respect to time of anaerobic digestion at both F/M ratios which is shown in Figure 5.44 and Figure 5.45 for F/M 1 and F/M 0.5 respectively.

Table 5.16: VS (g) values of sludge added to the reactors for F/M 1 and F/M 0.5.

RUN	g VS-added	
	FM_1	FM_0.5
Control	2.02	1.58
Disintegrated sludge	0.34	0.27
25% Dis. Sludge + 75% Un.	1.62	1.27
50% Dis. Sludge + 50% Un.	1.11	0.87
75% Dis. Sludge + 25% Un.	0.67	0.52

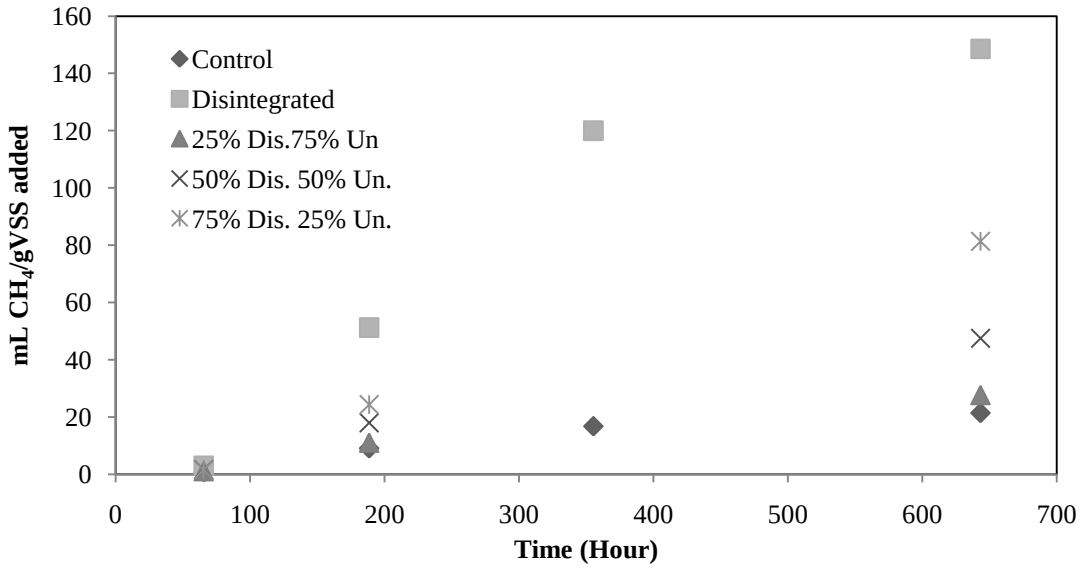

Figure 5.44 : Change in normalized mL CH_4/gVS $_{added}$ with respect to time of anaerobic digestion for F/M 1

When mL CH_4/gVS $_{added}$ values are normalized according to time intervals of anaerobic digestion, as it is clear from Figure 5.44 for F/M 1 ratio, mL CH_4/gVS $_{added}$ values increase by the increasing disintegration percentage of the return activated sludge that is aerobically digested.

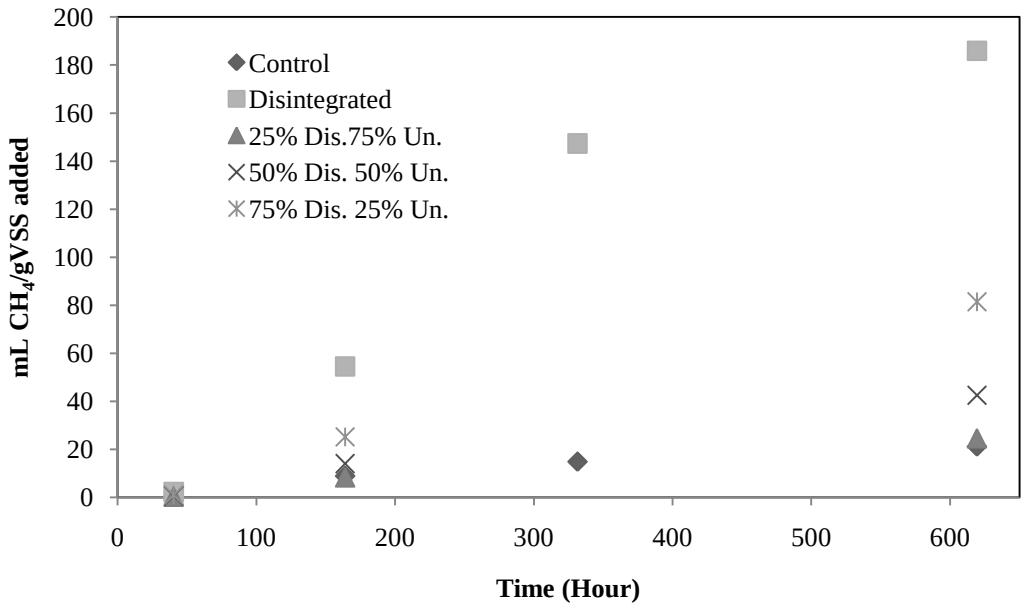

Figure 5.45 : Change in normalized mL CH_4/g VS $_{added}$ with respect to time of anaerobic digestion for F/M 0.5.

The similar results are obtained for F/M 0.5 ratio as can be seen from Figure 5.45. When mL CH_4/g VS $_{added}$ values are normalized according to time intervals of anaerobic digestion, mL CH_4/gVS $_{added}$ values increases by the increasing disintegration percentage of the return activated sludge that is anaerobically digested.

When the results given in Figure 5.44 and 5.45 are compared, there is no big difference between the control reactors at different F/M ratios in terms of mL CH_4/g VS $_{added}$ with respect to time of anaerobic digestion.

Comparison of mL CH_4/g VS $_{added}$ values with respect to time of anaerobic digestion for disintegrated sludge at different F/M ratios is given in Figure 5.46.

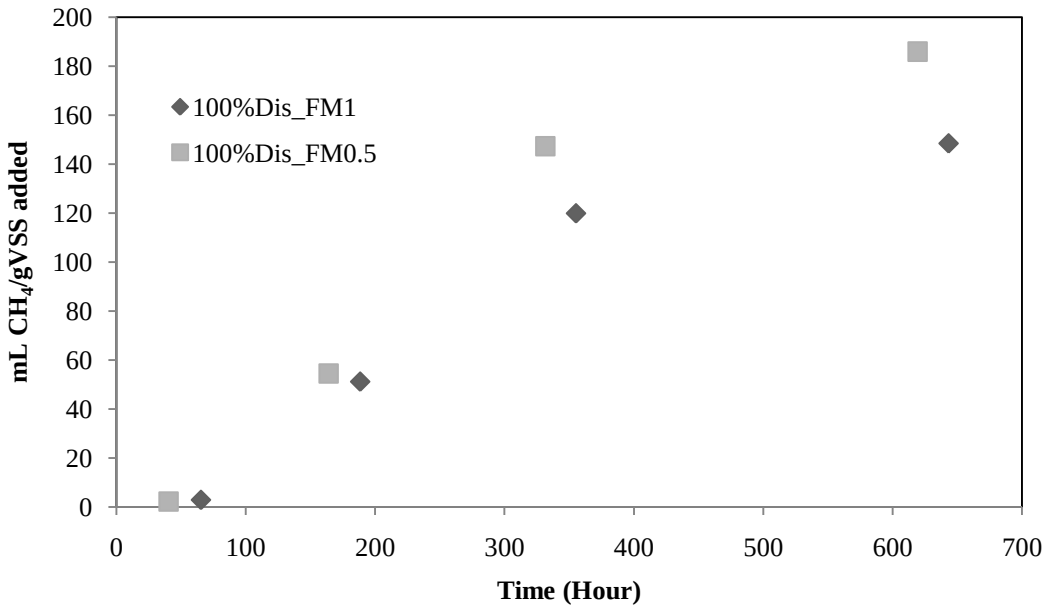

Figure 5.46 : Comparison mL CH_4/g VS $_{added}$ with respect to time of anaerobic digestion for disintegrated sludge at different F/M ratios

As it is shown in the Figure 5.46 as the F/M ratio decreases the amount of mL CH_4/g VS $_{added}$ increases.

As a result, the methane volume per amount of VS added is **149 mL** CH_4/g VS $_{added}$ for disintegrated reactor, while **21 mL** CH_4/g VS $_{added}$ for control reactor at the end of the 28 days anaerobic digestion period for F/M 1. The methane volume per amount of VSS added is **186** mL CH_4/g VS $_{added}$ for disintegrated reactor at the end of the 27 days anaerobic digestion period for F/M 0.5. Decreasing the F/M ratio from 1 to 0.5 for disintegrated sludge, causes **20%** increase in terms of mL CH_4/g VS $_{added}$.

Wang et al. (2006), conducted the experiment to determine the BMP value for different specific energy applied to the raw WAS. Under both mesophilic and thermophilic conditions, the biogas production was improved with increasing specific energy inputs. At low specific energy, the total methane produced increased significantly between 12.5–17.5% and 11.0–19.7% under thermophilic and mesophilic conditions, respectively. However, the enhancement in the biogas yield was only 1.6% (thermophilic) and 2.5% (mesophilic) when the applied specific energy was changed from 11000 to 15000 kJ/kg TS. From recorded methane improvement at the tested specific energy, show that 11000 kJ/kg TS was the optimum specific energy for the raw WAS.

5.2.2 The experimental results of RUN II with different percentages of centrifuged disintegrated sludge content

In full scale treatment plants, some part of the supernatant of the disintegrated sludge can be returned to the beginning of the system after the centrifuge process to supply the carbon demand for nutrient removal system.

In order to observe the effect of this application on anaerobic digestion, another experimental set up is carried out. Different percentages of centrifuged disintegrated sludge are subjected to anaerobic digesters by discarding some part of the supernatant to represent the possible effect of returned supernatant to the beginning of the system. The discarded supernatant amounts are in the range of 10 % to 50 % (RUN II). The same F/M ratios are applied as RUN I.

CODc concentrations of return activated sludge is 15409 mg/L and CODc concentration of supernatant is 6880 mg/L. Different percentages of supernatant obtained by centrifuging for 15 minutes at 9000 rpm is discarded before entering the anaerobic reactors.

By changing the percentages of discarded supernatant after centrifuge, CODc concentration of the mixed sludge entering the anaerobic reactors changes. So, the volume of the sludge added to the reactor is adjusted accordingly to obtain the constant F/M ratios.

The reactors are fed with seed and sonicated RAS mixed with supernatant at different percentages at required F/M ratios and calculated as shown in Table 5.17 and 5.18.

Table 5.17: Sludge and seed volume calculations for RUN II (F/M =1)

RUN	F/M 1								
	Seed VSS (mg/L)	V_{inoc} (mL)	Seed Mass Added (g)	CODc	V_{sl} (mL)	Sludge Mass Added (g)	Sludge VSS (mg/L)	I/S	F/M(Sludge added/ Seed added)
Disintegrated sludge	38750	13	0.504	15409	32	0.493	10735	1.5	1
10% supernatant discarded	38750	13	0.518	16357	32	0.518	14510	1.1	1
20% supernatant discarded	38750	14	0.543	17541	31	0.543	19045	0.9	1
30% supernatant discarded	38750	15	0.575	19064	30	0.575	22030	0.9	1
50% supernatant discarded	38750	17	0.666	23937	28	0.666	28450	0.8	1

Table 5.18: Sludge and seed volume calculations for RUN II (F/M = 0.5)

RUN	F/M 0.5								
	Seed VSS (mg/L)	V_{inoc} (mL)	Seed Mass Added (g)	CODc	V_{sl} (mL)	Sludge Mass Added (g)	Sludge VSS (mg/L)	I/S	F/M(Sludge added/ Seed added)
Disintegrated sludge	38750	20	0.775	15409	25	0.386	10735	2.9	0.5
10% supernatant discarded	38750	21	0.798	16357	24	0.399	14510	2.3	0.5
20% supernatant discarded	38750	21	0.829	17541	24	0.414	19045	1.8	0.5
30% supernatant discarded	38750	22	0.865	19064	23	0.432	22030	1.7	0.5
50% supernatant discarded	38750	25	0.964	23937	20	0.482	28450	1.7	0.5

5.2.2.1 Biogas production in RUN II

Total biogas amounts produced during the anaerobic digestion period for different percentages of discarded supernatant at F/M 1 are given in Figure 5.47.

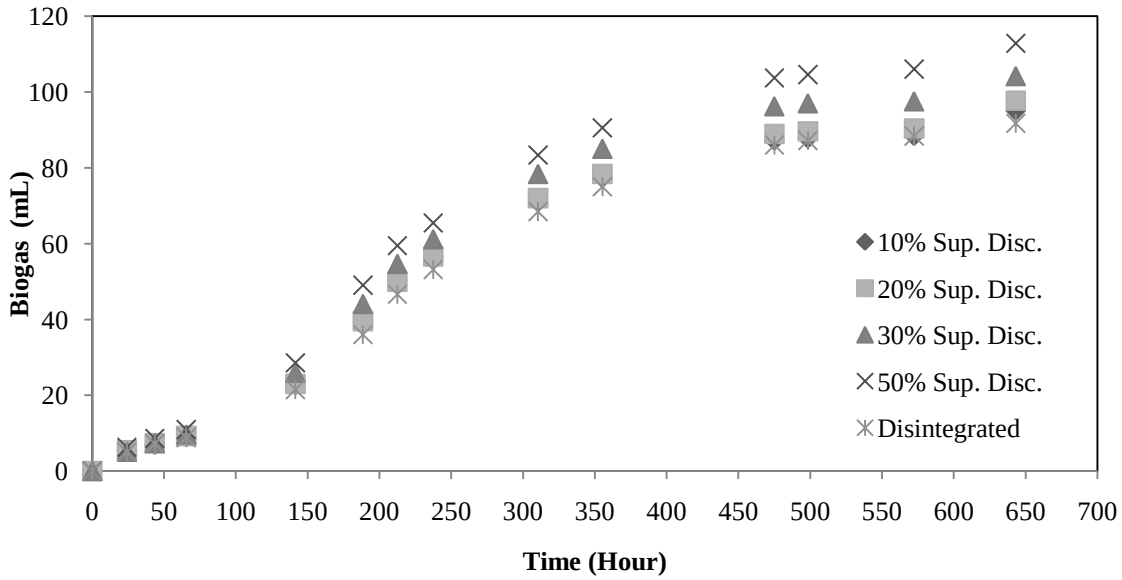

Figure 5.47 : Total biogas amount produced during the anaerobic digestion period for different percentages of discarded supernatant at F/M 1.

As shown in Figure 5.47, total biogas production of disintegrated sludge is lower than total gas production of sludges at different percentages of discarded supernatant. The results of total biogas production of the first 10 days are very close to each other at each set. The amounts of total biogas increase rapidly in the first ten days. After the first 10 days until the end of the anaerobic digestion period as the percentage of discarded supernatant of sludge increase, the total biogas amount produced increase too.

Total biogas amount produced during the anaerobic digestion period for different percentages of discarded supernatant at F/M 0.5 is given in Figure 5.48.

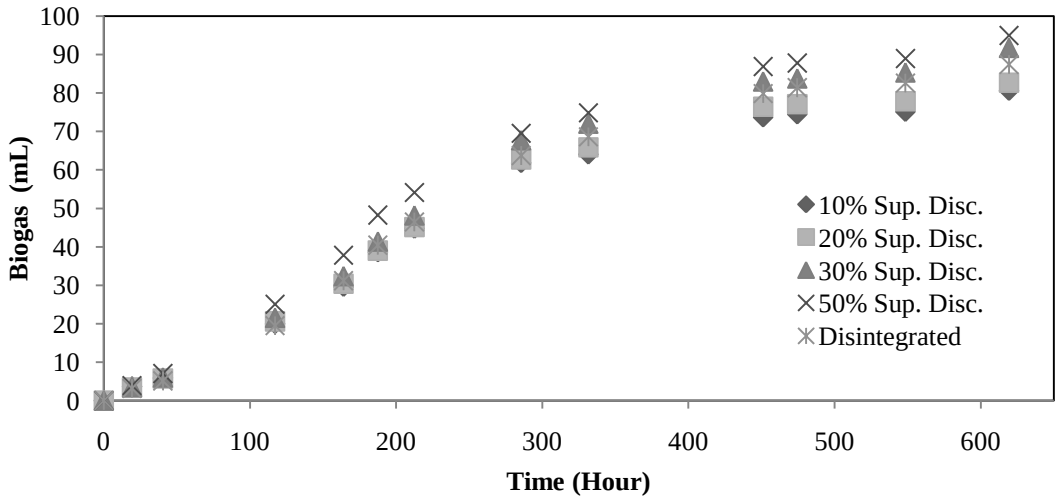

Figure 5.48 : Total biogas amount produced during the anaerobic digestion period for different percentages of discarded supernatant at F/M 0.5.

As shown in Figure 5.48, for F/M 0.5, total biogas production of disintegrated sludge is lower than total gas production of 50% and 30% of supernatant discarded. The results of total biogas production of the first 12 days are very close to each other except the 50 % of discarded supernatant. The amount of total biogas increases rapidly in the first twelve days. After the first twelve days until the end of the anaerobic digestion period as the percentage of centrifuged sludge increases, the total biogas amount produced increases too.

Figure 5.49 and Figure 5.50 show the comparison of 10% and 50% of discarded supernatant values for different F/M ratios.

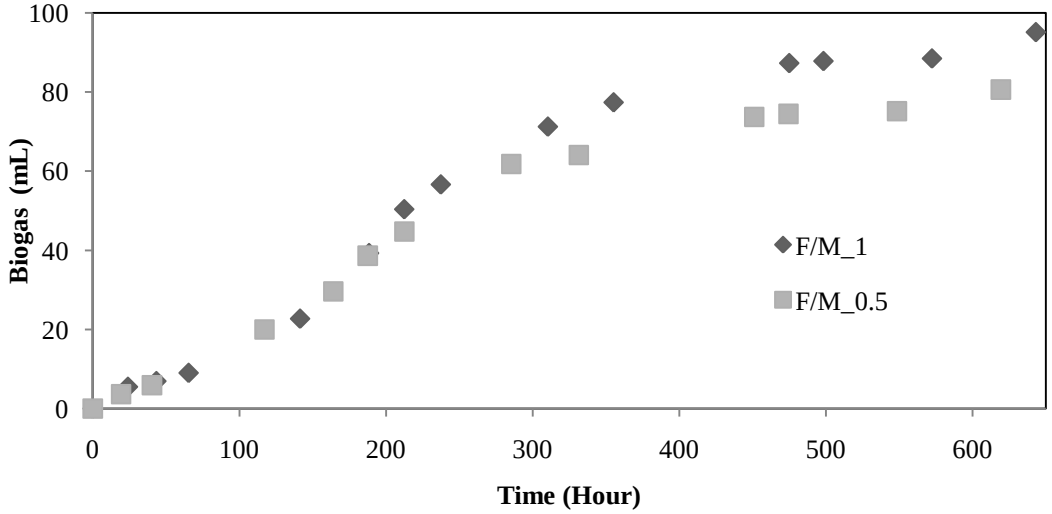

Figure 5.49 : Comparison of 10% of discarded supernatant values for different F/M ratios

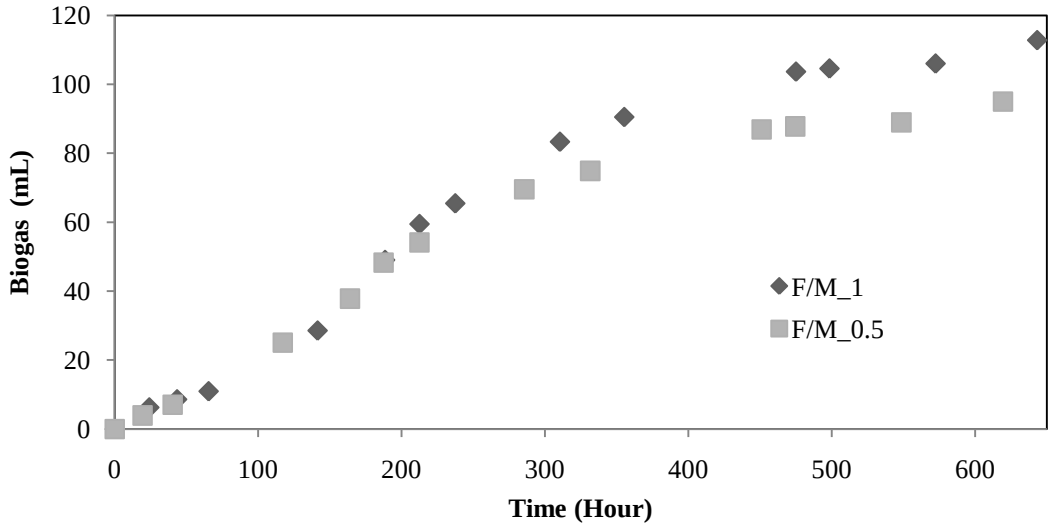

Figure 5.50 : Comparison of 50% of discarded supernatant values for different F/M ratios

As shown in Figure 5.49 and Figure 5.50 as the F/M ratio increase the amount of total biogas that is produced during the anaerobic digestion increase too. For both Figures in the first 10 days of anaerobic digestion, the total biogas amounts are so close to each other. After the first 10 days the difference of total produced biogas between F/M 1 and F/M 0.5 change.

5.2.2.2 Sludge reduction in RUN II

After 30 days of anaerobic digestion period, reactors are opened and analyzed. The initial and final TS, VS, CODc and final CODf are given in Table 5.19.

Disintegrated sludge has the lowest VS reduction. VS reduction increases as the percentages of discarded supernatant sludge increase for F/M 1. Similarly, VS reduction increases as the percentages of centrifuged sludge increase for F/M 0.5, except the 10% of discarded centrifuged sludge supernatant. VS reduction percentages of disintegrated sludge and reactor mixed at 50 percentage of discarded centrifuged sludge supernatant increase from **19% to 41%** at F/M 1 while the VS reduction increase from **23% to 30%** at F/M 0.5. It means that as the F/M ratio increases the difference of VS reduction between disintegrated reactor and reactor mixed at 50 percentage of centrifuged sludge increase too.

For F/M 1 and F/M 0.5 disintegrated sludge has the highest CODf reduction. Also as the percentages of discarded centrifuged sludge supernatant increase the CODf reduction percentages increase too.

5.2.2.3 Biochemical methane potential (BMP) in RUN II

Gas composition of biogas is measured three times during the anaerobic digestion by gas chromatograph to observe the change in methane production during the 30 days anaerobic digestion period.

In the first four day of digestion, the methane percentage of produced biogas is 10%-12% for F/M 1 and F/M 0.5. As seen from the Tables methane percentage values show a large increase until the 8^{th} and 9^{th} days at both F/M ratios. After this increase until the end of the anaerobic digestion period increase in methane percentages of the produced biogas decrease.

As seen from the Table 5.20 and Table 5.21 for both F/M ratios as the discarded centrifuged sludge supernatant increase, the percentage of produced methane during the anaerobic digestion process increases too. The methane percentages of disintegrated sludge is **0.56** while the process the methane percentages of 50% centrifuged disintegrated sludge is **0.59.** At the end of the anaerobic digestion process for F/M 1 produced methane amount of disintegrated sludge and 50% discarded centrifuged sludge supernatant, increase from **51 mL** to **67 mL** resulting in. **24%** increase on produced methane gas amount**.** High percentages of methane can be obtained at higher F/M ratios.

Table 5.19: Reduction in CODf and VS values for all configurations of digesters at different F/M ratios.

RUN		INITIAL				FINAL				CODf Reduction (%)	VS Reduction (%)
		CODf	CODc	TS mg/L	VS mg/L	CODf	CODc	TS mg/L	VS mg/L		
F/M1	Disintegrated sludge	2010	2010	22000	9350	441	624	18680	7580	**78**	**19**
	10 % supernatant discarded	1286	1286	23800	11800	487	518	20407	8273	**62**	**30**
	20 % supernatant discarded	2117	2159	27400	11900	590	615	19407	7860	**72**	**34**
	30 % supernatant discarded	1080	1337	27850	13700	465	480	19833	8053	**57**	**41**
	50% Supernatant discarded	1445	1466	36300	16850	490	510	24673	9867	**66**	**41**
F/M 0.5	Disintegrated sludge	1029	1080	27700	12250	441	502	23633	9393	**57**	**23**
	10 % supernatant discarded	951	951	25010	10250	421	521	22807	8960	**56**	**13**
	20 % supernatant discarded	817	775	28150	13250	457	563	24693	9380	**44**	**29**
	30 % supernatant discarded	893	851	30135	14320	472	563	26873	10747	**47**	**25**
	50% Supernatant discarded	1029	1183	39400	18100	623	649	32247	12640	**39**	**30**

Table 5.20: Methane percentages (%) of disintegrated sludge and centrifuged sludge at different percentages by the time at F/M 1.

	F/M_1														
Day	Disintegrated			10% Supernatant Disc.			20% Supernatant Disc.			30% Supernatant Disc.			50% Supernatant Disc.		
	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.
4	4346.14	504.57	**12**	4326.73	474.18	**11**	4654.75	438.68	**9**	4675.85	591.06	**13**	4689.37	569.41	**12**
9	7045.71	3446.26	**49**	7102.41	3483.24	**49**	7495	3686.73	**49**	7826.71	3959.58	**51**	8183.88	4174.82	**51**
16	8842.25	4860.32	**55**												
28	9580.17	5329.02	**56**	9084.26	5126.47	**56**	9547.85	5473.2	**57**	9967.8	5845.1	**59**	10256.6	6054.8	**59**

Table 5.21: Methane percentages (%) of disintegrated sludge and centrifuged sludge at different percentages by the time at F/M 0.5.

	F/M_O.5														
Day	Disintegrated			10% Supernatant Disc.			20% Supernatant Disc.			30% Supernatant Disc.			50% Supernatant Disc.		
	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.	Methane	Total	Methane Percent.	Total	Methane	Methane Percent.	Total	Methane	Methane Percent.
3	3817.04	449.09	**12**	3825.09	401.48	**10**	3896.8	385.09	**10**	3859.6	418.65	**11**	3949.51	437.87	**11**
8	6308.84	2960.69	**47**	6298.8	2869.89	**46**	6712.72	3115.4	**46**	6950.6	3071.34	**44**	7366.64	3505.45	**48**
15	7764.34	4475.22	**58**												
27	8269.67	4722.17	**57**	8304.66	4635.27	**56**	8006.8	4328.5	**54**	8421.2	4743.23	**56**	9130.9	5191.69	**57**

5.3 Disintegration Effects on Anaerobic Digestion Efficiency at F/M ratios of 5, 2, 1 and 0.5

In order to observe the effect of F/M ratio on biogas and methane production anaerobic digestion tests are dublicated. In this part of the study, four different F/M ratios of 5, 2, 1 and 0.5 are applied to the anaerobic digesters. Sludge and seed volume calculations for different F/M ratios are shown in Table 5.22. VS concentration of seed and sludge is 37430 mg/L and 10686 mg/L. and TS concentration of RAS is 19024 mg/L. Also CODc concentration of disintegrated sludge is 13368 mg/L. The reactors are fed with seed and sludge either untreated or sonicated at different percentages at required F/M ratios and calculated as below:

For anaerobic digestion experiments, ultrasonic disintegration at 80% amplitude for 30 minute and 100 mL by volume is selected which is resulted in 151387 KW.s/kg.DS specific energy.

Anaerobic digestion tests last 27 days. During the 27 days of anaerobic digestion period, biogas amount of control, disintegrated reactors at different percentages and centrifuged at different ratios are measured.

Table 5.22: Sludge and seed volume calculations for different F/M ratios for RUN I (Second Experiments)

RUN	Seed VSS (mg/L)	V_{inoc} (mL)	Seed Mass Added (g)	CODc	V_{sl} (mL)	Sludge Mass Added (g)	F/M (Sludge added/ Seed added)
Control	37430	3	0.11	13368	42	0.56	
%25 Dis. %75 Un.	37430	3	0.11	13368	42	0.56	
%50 Dis. %50 Un.	37430	3	0.11	13368	42	0.56	**5**
%75 Dis. %25 Un.	37430	3	0.11	13368	42	0.56	
Disintegrated	37430	3	0.11	13368	42	0.56	
Control	37430	7	0.26	13368	38	0.52	
%25 Dis. %75 Un.	37430	7	0.26	13368	38	0.52	
%50 Dis. %50 Un.	37430	7	0.26	13368	38	0.52	**2**
%75 Dis. %25 Un.	37430	7	0.26	13368	38	0.52	
Disintegrated	37430	7	0.26	13368	38	0.52	
Control	37430	12	0.45	13368	33	0.45	
%25 Dis. %75 Un.	37430	12	0.45	13368	33	0.45	
%50 Dis. %50 Un.	37430	12	0.45	13368	33	0.45	**1**
%75 Dis. %25 Un.	37430	12	0.45	13368	33	0.45	
Disintegrated	37430	12	0.45	13368	33	0.45	
Control	37430	18	0.67	13368	27	0.34	
%25 Dis. %75 Un.	37430	18	0.67	13368	27	0.34	
%50 Dis. %50 Un.	37430	18	0.67	13368	27	0.34	**0.5**
%75 Dis. %25 Un.	37430	18	0.67	13368	27	0.34	
Disintegrated	37430	18	0.67	13368	27	0.34	

The biogas produced in each reactor was monitored by measuring daily gas pressure by manometer. Bottles are mixed manually before each gas measurement. And the pressure values are converted to the biogas amount.

5.3.1 The experimental results of RUN I (Second experiments)

The total biogas production amounts of control sludge and disintegrated sludge at different percentage is measured for four F/M ratios at the second part of experimental study.

5.3.1.1 The experimental results of RUN I for F/M 0.5

The total biogas production amounts of disintegrated sludge and untreated sludge for F/M 0.5 are shown in Figure 5.51.

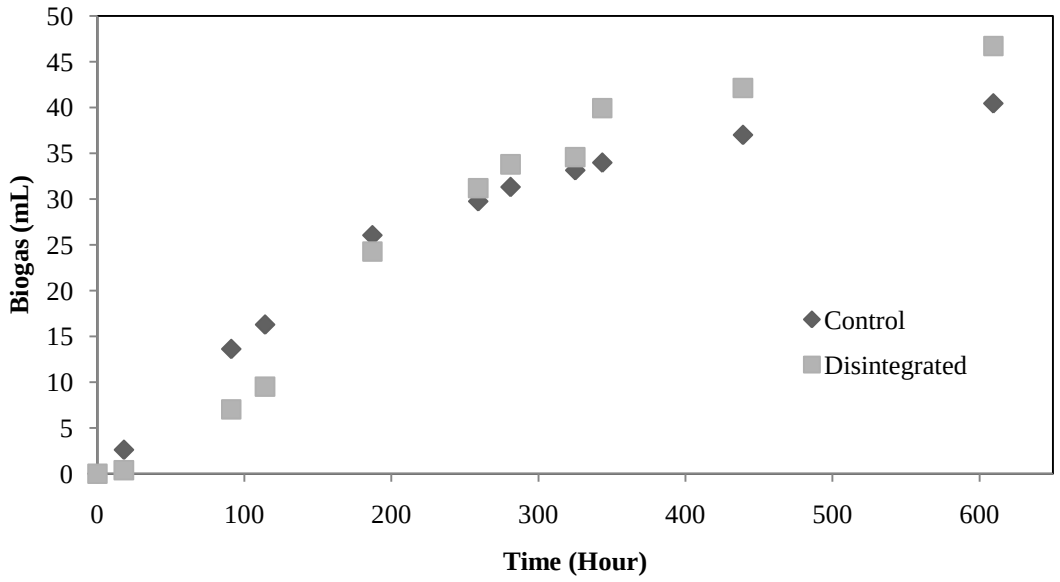

Figure 5.51 : Total biogas production of disintegrated sludge and untreated sludge for F/M 0.5.

As shown in Figure 5.51, total biogas production of disintegrated sludge is higher than total gas production of untreated (control) sludge. Until the 12th day, the amount of total biogas production of control sludge is higher than the biogas amount of disintegrated sludge. After the 12th day, biogas amount of disintegrated sludge is higher than the biogas amount of control sludge.

Biogas production of control and disintegrated sludge at different percentages for F/M 0.5 is shown in Figure 5.52.

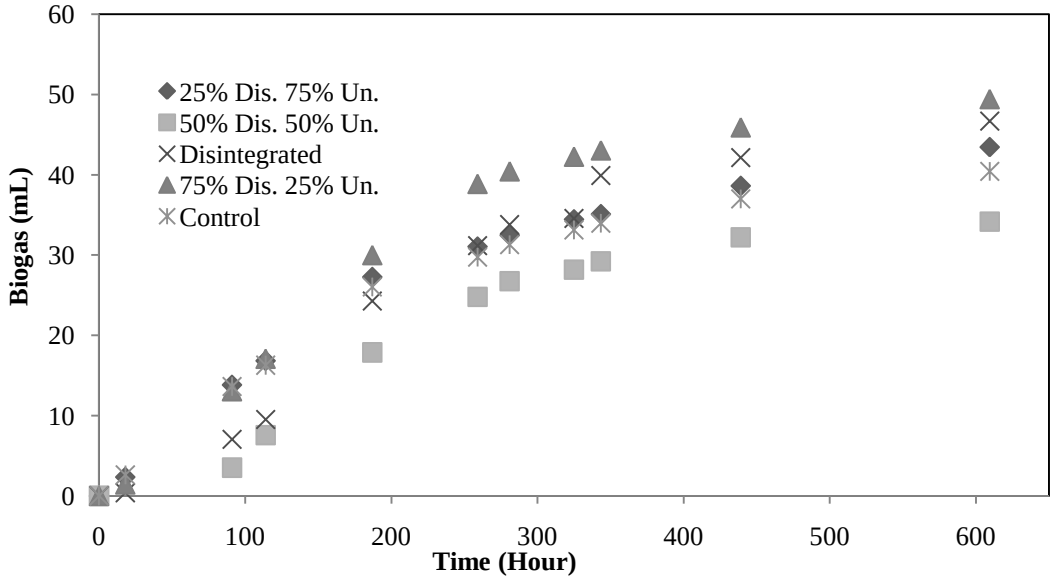

Figure 5.52 : Biogas production of control and disintegrated sludge at different percentages for F/M 0.5

As seen from Figure 5.52, the highest biogas amount is obtained at 75% disintegrated sludge. The biogas production amount of control sludge is higher than the biogas amount of 50% disintegrated sludge for F/M 0.5.

5.3.1.2 The experimental results of RUN I for F/M 1

Total biogas production of disintegrated sludge and untreated sludge for F/M 1 is given in Figure 5.53.

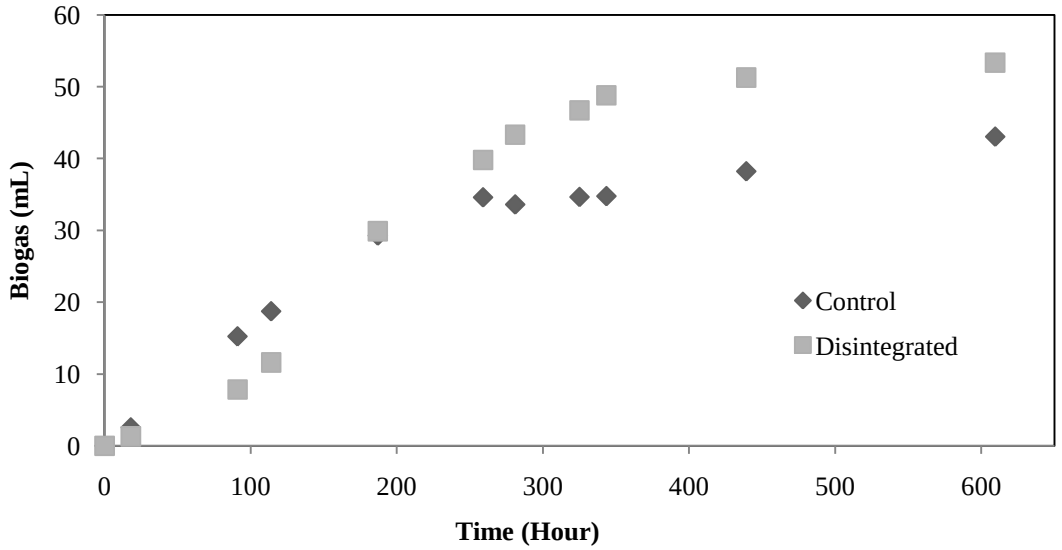

Figure 5.53 : Total biogas production of disintegrated sludge and untreated sludge for F/M 1.

As shown in Figure 5.53, total biogas production of disintegrated sludge is higher than total gas production of untreated (control) sludge. For both sludge types, total biogas production increases rapidly until the 10th day, and then increase of total biogas production begins to decrease over time. After the 20th day, the increase of total biogas production decreases more and the amount of total gas production becomes constant.

Biogas production of control and disintegrated sludge at different percentages for F/M 1 is given in Figure 5.54.

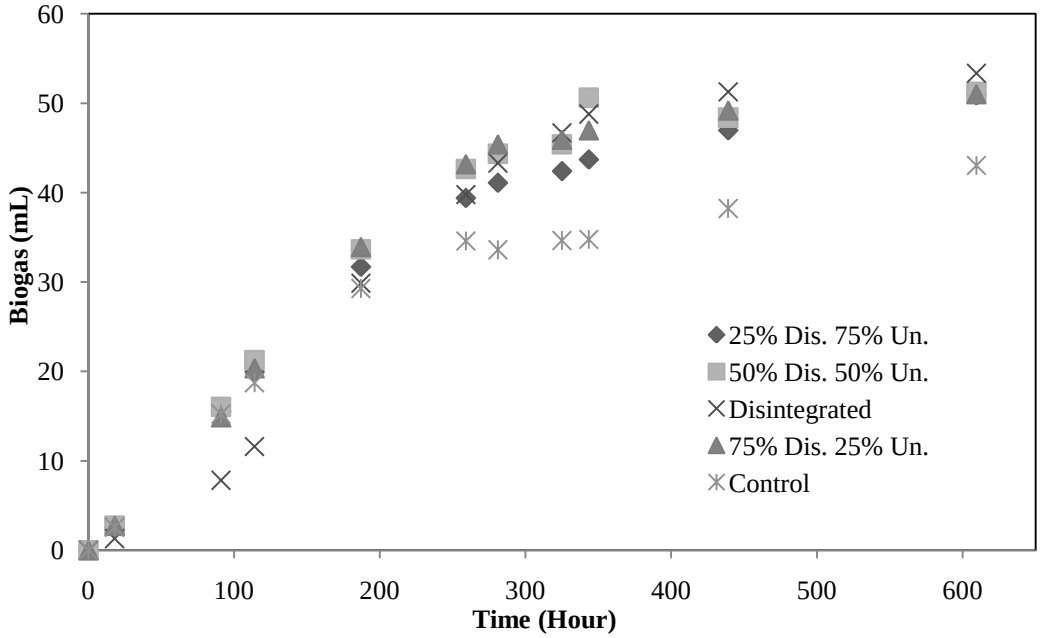

Figure 5.54 : Biogas production of control and disintegrated sludge at different percentages for F/M 1

As shown in Figure 5.54, for F/M 1, the biogas production amounts of disintegrated sludge at different percentages are close to each other. On the other hand the biogas production amount of disintegrated sludge at different percentages is higher than control sludge.

5.3.1.3 The experimental results of RUN I for F/M 2

Total biogas production of disintegrated sludge and untreated sludge for F/M 2 is given in Figure 5.55.

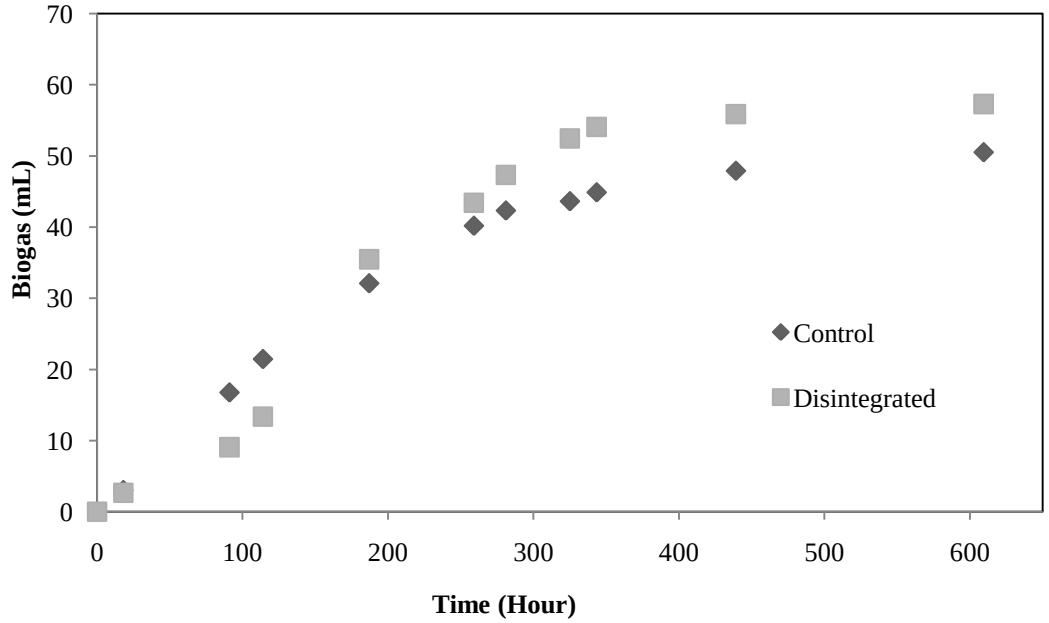

Figure 5.55 : Total biogas production of disintegrated sludge and untreated sludge for F/M 2.

As shown in Figure 5.55, total biogas production of disintegrated sludge is higher than total gas production of untreated (control) sludge. Total biogas amount at the end of the anaerobic digestion increase from **50 mL** to **57 mL** by disintegration of sludge resulting in **14%** increase.

Biogas production of control and disintegrated sludge at different percentages for F/M 2 is given in Figure 5.56.

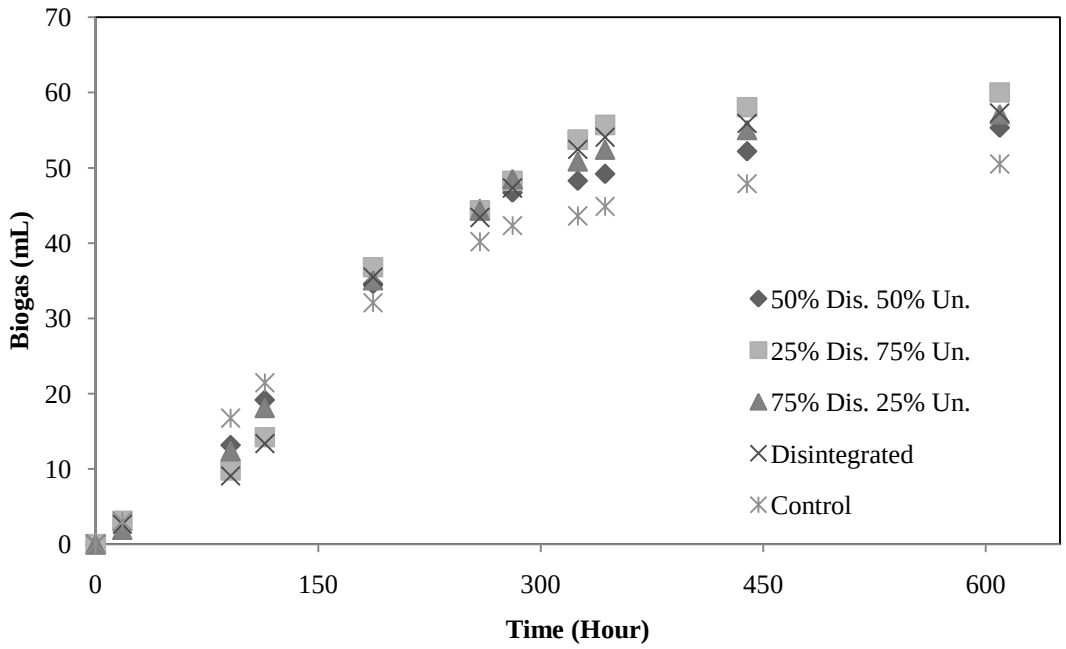

Figure 5.56 : Biogas production by time at F/M 2 for control and disintegrated sludge at different percentages

As shown in Figure 5.56, Biogas amount of contol sludge and disintegrated sludge at different percentages fluctuate during the first week of anaerobic digestion period. The highest amount of biogas is obtained at 25% disintegrated sludge + 75 % untreated sludge while the control sludge has the lowest biogas amount at F/M 2. Additionally, as the percentage of disintegrated sludge mixed to the sludge increases, total biogas production increases except for 25 % disintegrated sludge.

5.3.1.4 The experimental results of RUN I for F/M 5

Total biogas productions of disintegrated sludge and untreated sludge for F/M 5 are given in Figure 5.57.

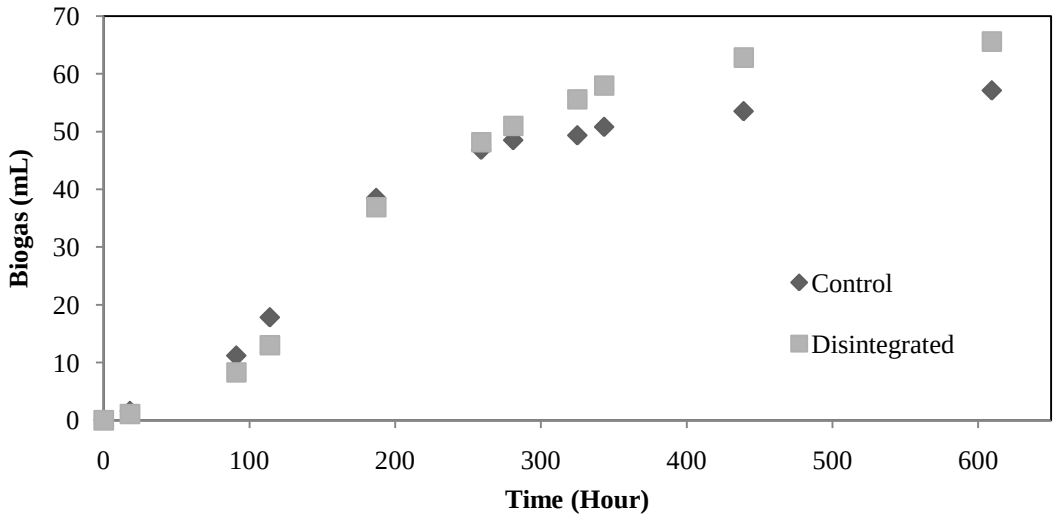

Figure 5.57 : Total biogas production of disintegrated sludge and untreated sludge for F/M 5.

As shown in Figure 5.57, total biogas production of disintegrated sludge is higher than total gas production of untreated (control) sludge. Total biogas amount at the end of the anaerobic digestion increases from **57 mL** to **66 mL** corresponding to a **16%** increase.

Biogas production of control and disintegrated sludge at different percentages for F/M 5 is given in Figure 5.58.

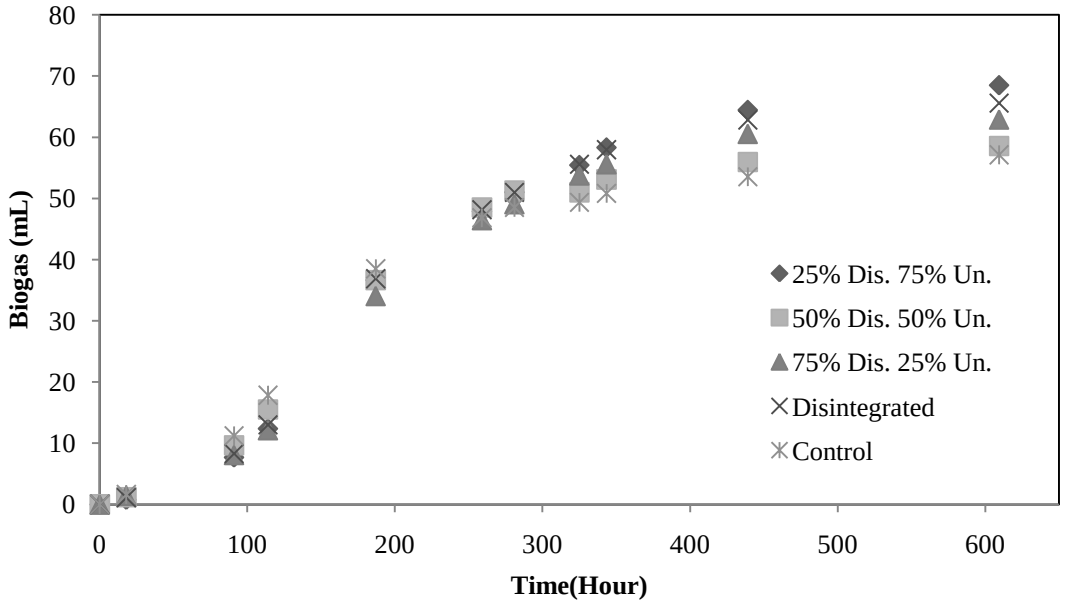

Figure 5.58 : Biogas production by time at F/M 5 for control and disintegrated sludge at different percentages

As shown in Figure 5.58, the highest amount of biogas is obtained at 25% disintegrated sludge + 75 % untreated sludge while the control sludge has the lowest biogas amount at F/M 2. As the percentage of disintegrated sludge mixed to the sludge increases, total biogas production increases as well except the results of 25 % disintegrated sludge. Comparing with the other F/M ratios, biogas amount of control sludge are closes the biogas amount of disintegrated sludge at F/M 5.

At different F/M ratios biogas production amount of control sludge and disintegrated sludge are shown in Figure 5.59 and Figure 5.60.

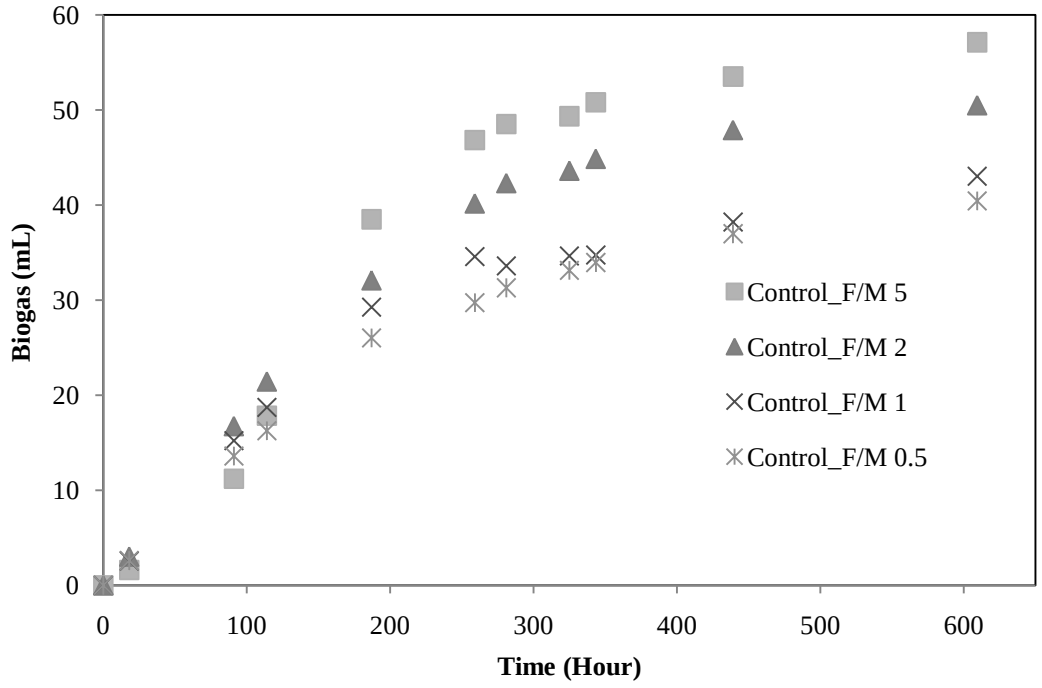

Figure 5.59 : Biogas amount of control sludge at different F/M ratios

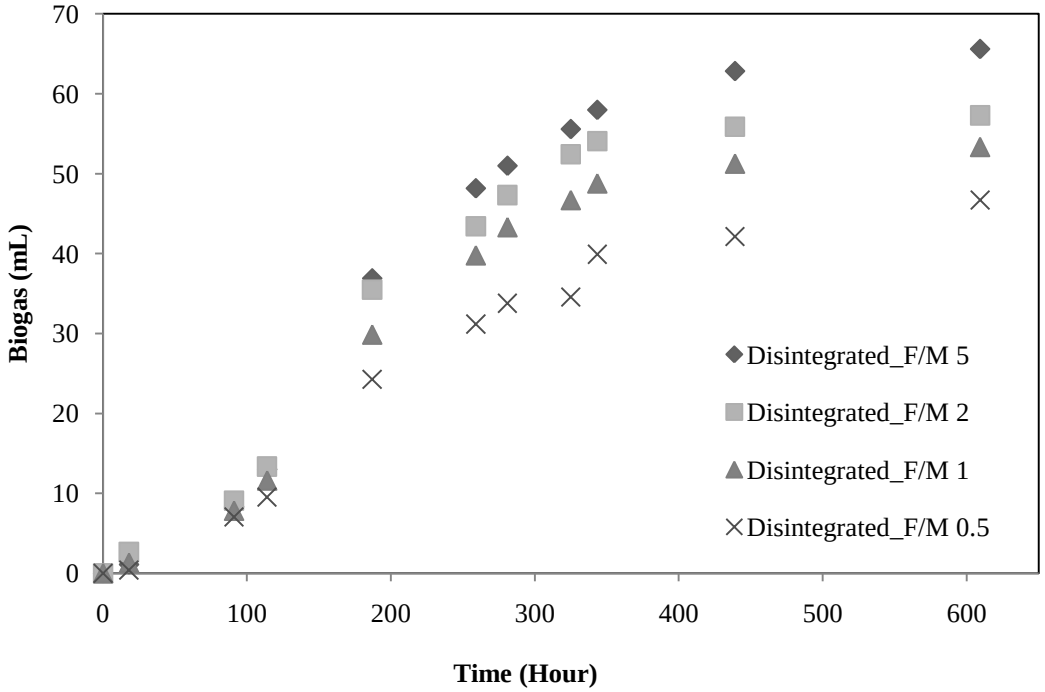

Figure 5.60 : Biogas amount of disintegrated sludge at different F/M ratios

As the F/M ratio increase the biogas amount increase for both, control sludge and disintegrated sludge. The results of the Figures support the first anaerobic digestion test results. At the end of the anaerobic digestion period, by increasing F/M from 0.5 to 5 the amount of biogas of disintegrated sludge increases from **47 mL** to **66 mL** corresponding to a **40 %** increase.

In the second experiment set, the biogas amount of disintegrated sludge and control sludge is higher at the end of the anaerobic digestion period, comparing with the first experiment set. The results of second set of experiments can be attributed to low VS concentration of sludge.

5.3.1.5 Effect of ultrasonic disintegration on biochemical methane potential (BMP)

The impact of the ultrasonic disintegration on the anaerobic digestion efficiency at different FM ratios is also evaluated by the methane accumulation in the BMP test. All the experiments are carried out under identical conditions such as temperature and pressure.

The Table 5.23 shows the results of methane content of total biogas that produced during the anaerobic digestion. Methane content of produced biogas of control and

disintegrated sludge at different percentages is analyzed by gas chromatograph at different days during the anaerobic digestion. The sum of the Methane, Carbon dioxide and Hydrogen gases represent the total biogas. According to this relation the methane percentage of total produced biogas is calculated.

Table 5.23: Methane percentages (%) of control and disintegrated sludge at different percentages by the time at four different F/M ratios.

Day	Control	Disintegrated	25% Dis. 75% Un.	50% Dis. 50% Un	75% Dis. 25% Un	F/M
4	10	10	9	10	9	
10	42	45	43	44	43	F/M 0.5
27	52	52	50	52	5	
Day	Control	Disintegrated	25% Dis. 75% Un.	50% Dis. 50% Un	75% Dis. 25% Un	
4	11	12	9	13	12	
10	45	49	47	47	48	F/M 1
27	52	54	52	52	53	
Day	Control	Disintegrated	25% Dis. 75% Un.	50% Dis. 50% Un	75% Dis. 25% Un	
4	12	14	10	13	13	
10	46	50	46	57	49	F/M 2
27	54	59	56	56	58	
Day	Control	Disintegrated	25% Dis. 75% Un.	50% Dis. 50% Un	75% Dis. 25% Un	
4	12	13	9	13	12	
10	47	49	48	49	50	F/M 5
27	55	60	55	56	58	

Gas composition of biogas is measured three times during the anaerobic digestion by gas chromatograph to observe the change in methane production during the 27 day of anaerobic digestion period.

In the first four day of digestion, the methane percentage of produced biogas is between 9% - 13% for different F/M ratios. As seen from the Table methane percentage values show a large increase until the 10^{th} days at all F/M ratios. After this rapid increase until the end of the anaerobic digestion period methane percentages of the produced biogas don't change remarkably.

At the day 10, the amount of produced methane gas in disintegrated reactor is **18 mL**, while the amount of produced methane gas in control (unsonicated) reactor is **14 mL** at F/M 0.5. Similar to the F/M 0.5, the amount of produced methane gas in disintegrated reactor is **28 mL**, while the amount of produced methane gas in control (unsonicated) reactor is **24 mL** at F/M ratio of 5 for the same day.

At the end of the anaerobic digestion period, by increasing F/M from 0.5 to 5 the amount of methane gas of disintegrated sludge increase from **24 mL** to **40 mL** causing a **67%** increase.

5.3.2 The experimental results of RUN II

Different percentages of centrifuged disintegrated sludge are subjected to anaerobic digesters by discarding some part of the supernatant after centrifuge for 15 minutes at 9000 rpm.

By changing the percentages of discarded supernatant of the disintegrated return activated sludge after centrifuge, CODc of the mixed sludge changes according to these percentages. To obtain the constant F/M ratios, volume of the sludge added to the reactor is adjusted accordingly.

The reactors are fed with seed and sonicated RAS mixed with supernatant at different percentages at required F/M ratios and calculated as given in Table 5.24. Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 0.5 is given in Figure 5.61.

Table 5.24: Sludge and seed volume calculations of sludge mixed with supernatant after centrifuge at different percentages for different F/M ratios for RUN II (Second Experiments)

RUN	Seed VSS (mg/L)	V_{inoc} (mL)	Seed Mass Added (g)	CODc	V_{sl} (mL)	Sludge Mass Added (g)	F/M (Sludge added/ Seed added)
Disintegrated sludge	37430	3	0.11	13368	42	0.56	
10% Supernetant Disc.	37430	3	0.11	14434	42	0.56	
20% Supernetant Disc.	37430	3	0.11	15767	42	0.56	5
30% Supernetant Disc.	37430	4	0.14	17481	41	0.72	
50% Supernetant Disc.	37430	5	0.19	22965	40	0.92	
Disintegrated sludge	37430	7	0.26	13368	38	0.51	
10% Supernetant Disc.	37430	7	0.27	14434	38	0.55	
20% Supernetant Disc.	37430	8	0.30	15767	37	0.58	2
30% Supernetant Disc.	37430	8	0.32	17481	37	0.65	
50% Supernetant Disc.	37430	10	0.39	22965	35	0.80	
Disintegrated sludge	37430	12	0.45	13368	33	0.44	
10% Supernetant Disc.	37430	12	0.47	14434	33	0.48	
20% Supernetant Disc.	37430	13	0.49	15767	32	0.50	1
30% Supernetant Disc.	37430	14	0.53	17481	31	0.54	
50% Supernetant Disc.	37430	17	0.64	22965	28	0.64	
Disintegrated sludge	37430	18	0.67	13368	27	0.36	
10% Supernetant Disc.	37430	19	0.71	14434	26	0.38	
20% Supernetant Disc.	37430	20	0.75	15767	25	0.39	0.5
30% Supernetant Disc.	37430	21	0.79	17481	24	0.42	
50% Supernetant Disc.	37430	24	0.90	22965	21	0.48	

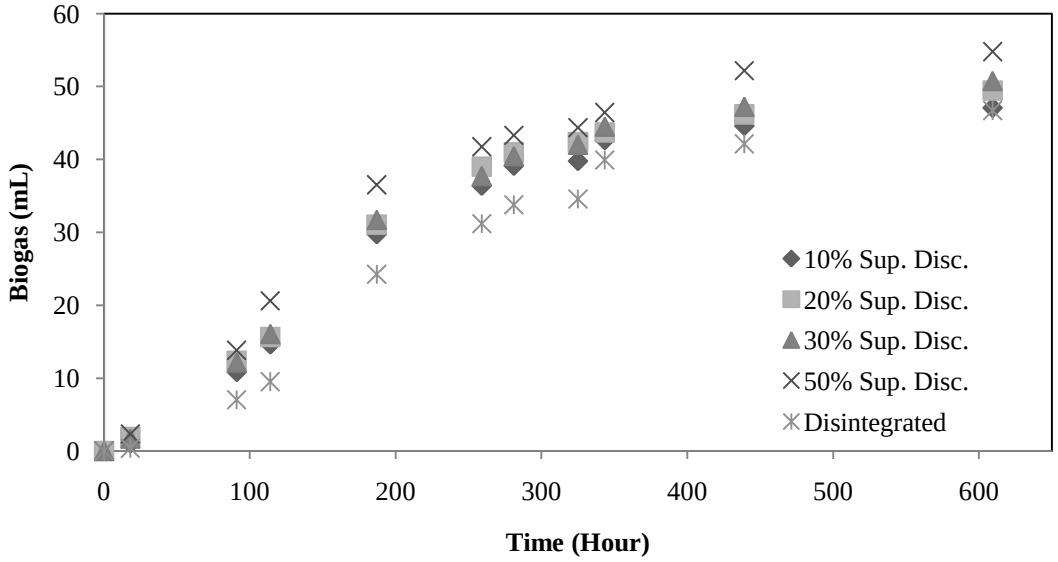

Figure 5.61 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 0.5.

The amount of biogas of disintegrated sludge is 47ml at the end of the anaerobic digestion period while the biogas amount of 50% centrifuged sludge is 55 mL. Biogas amounts of 30%, 20% and 10% centrifuged sludges are close to each other.

Total Biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 1 and F/M 2 are given in Figure 5.62 and 5.63 respectively.

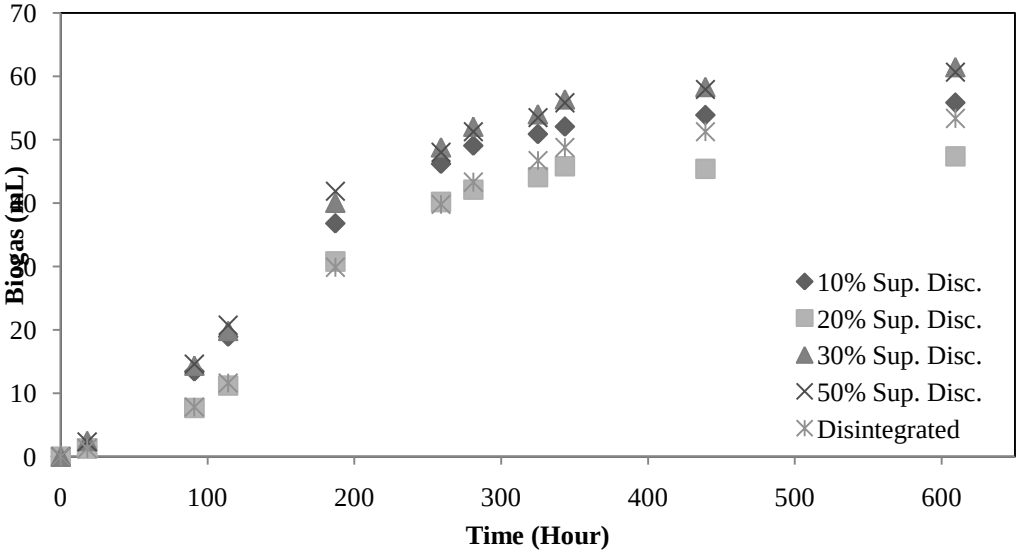

Figure 5.62 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 1.

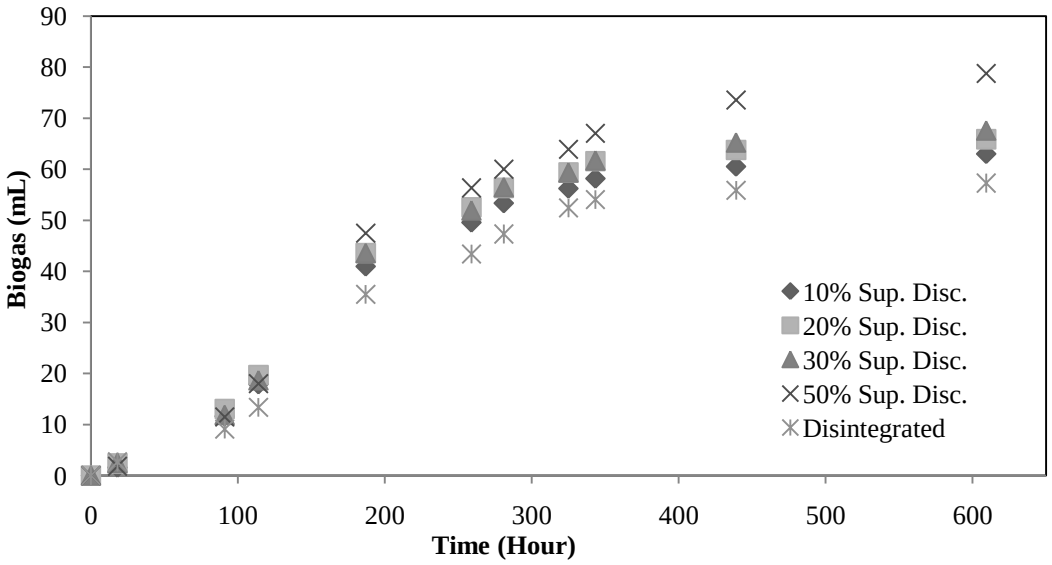

Figure 5.63 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 2.

As shown in Figure 5.63, the lowest biogas amount is obtained at disintegrated sludge. The amount of biogas of disintegrated sludge is 57 mL at the end of the anaerobic digestion period while the biogas amount of 50% centrifuged sludge is 79 mL.

Total Biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 5 is given in Figure 5.64.

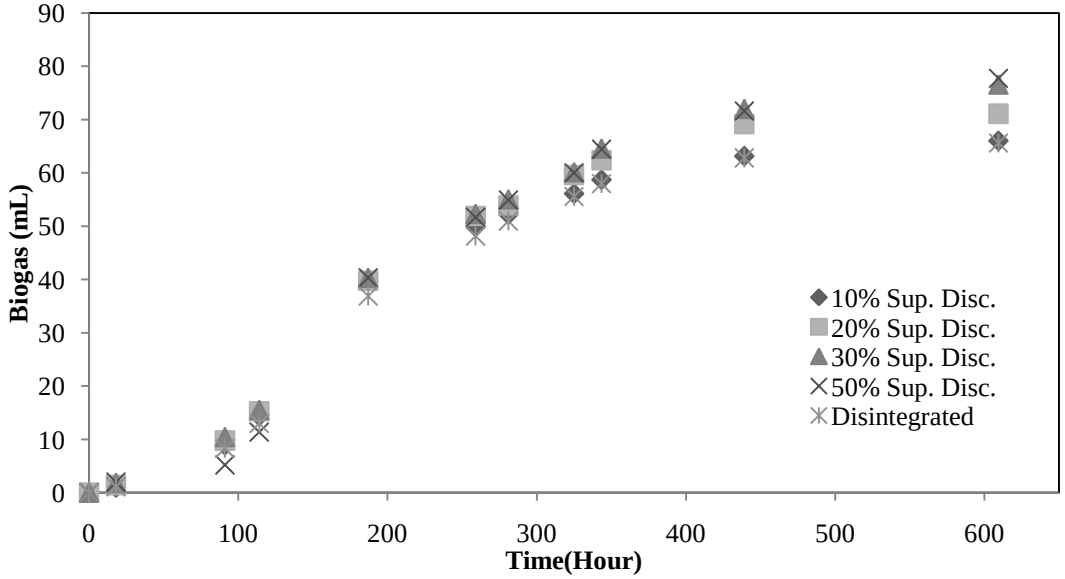

Figure 5.64 : Total biogas amount produced during the anaerobic digestion period for different centrifuge percentages at F/M 5.

As shown in Figures total biogas production of disintegrated sludge is lower than total gas production of sludge at different centrifuge percentages for all F/M ratios except F/M 1. The results of the second experiments support the results of the first experiments.

Comparison of biogas amount of 50% supernatant discarded sludge for different F/M ratios is shown in the Figure5.65.

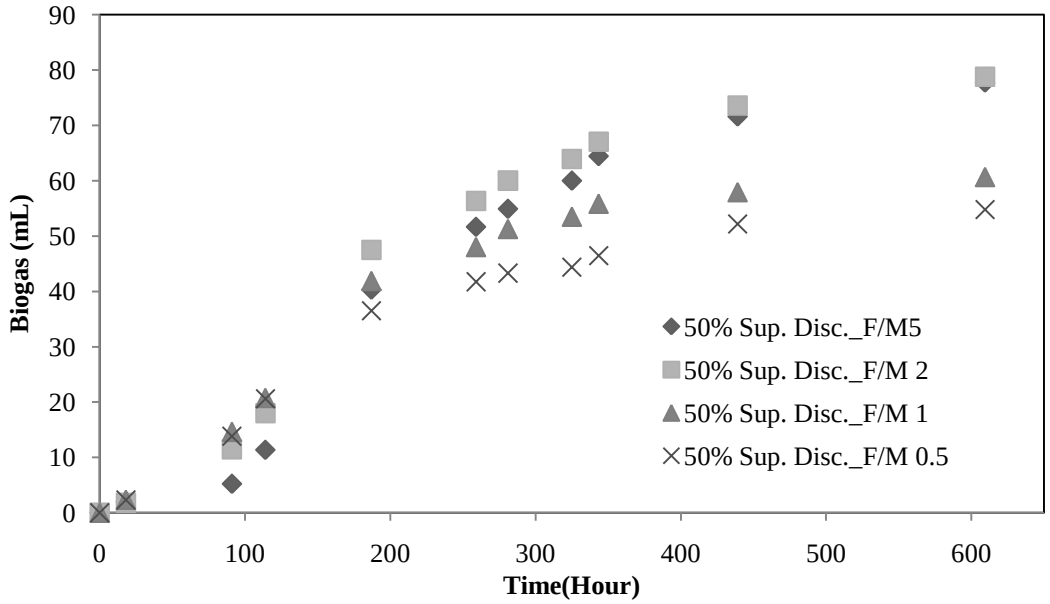

Figure 5.65 : Comparison of biogas amount of 50% supernatant discarded sludge for different F/M ratios

As shown in Figure 5.65, as the F/M ratio increases the amount of total biogas that is produced during the anaerobic digestion increases, except f or F/M 5 ratio. In the first 10 days of anaerobic digestion, the total biogas amounts are very close to each other. After 10 days the difference between total produced biogas amounts at different F/M ratios increases. For F/M 0.5, the amount of biogas of 50% supernatant discarded sludge is **55mL** at the end of the anaerobic digestion period while the biogas amount of 50% centrifuged sludge is **78 mL** at F/M ratio of 5.

Gas composition of biogas is measured three times during the anaerobic digestion by gas chromatograph to observe the change in methane production during the 27 days anaerobic digestion period and given in Table 5.25.

Table 5.25: Methane percentages (%) of disintegrated sludge and supernatant discarded sludge at different percentages at different F/M ratios.

Day	Disintegrated	10% Supernetant Disc.	20%Supernetant Disc.	30% Supernetant Disc.	50% Supernetant Disc.	
4	1	9	10	10	11	
10	45	44	46	45	47	F/M 0.5
27	52	50	53	53	54	
Day	Disintegrated	10% Supernetant Disc.	20%Supernetant Disc.	30% Supernetant Disc.	50% Supernetant Disc.	
4	12	11	9	13	12	
10	49	49	49	51	51	F/M 1
27	54	56	57	54	55	
Day	Disintegrated	10% Supernetant Disc.	20%Supernetant Disc.	30% Supernetant Disc.	50% Supernetant Disc.	
4	14	11	9	13	13	
10	50	51	51	52	53	F/M 2
27	59	59	59	60	61	
Day	Disintegrated	10% Supernetant Disc.	20%Supernetant Disc.	30% Supernetant Disc.	50% Supernetant Disc.	
4	13	11	9	13	12	
10	49	49	50	51	51	F/M 5
27	60	57	58	59	63	

As seen from the Table 5.25, methane percentage values show a rapid increase until the 10^{th} days for all F/M ratios. After this rapid increase, increase in methane percentages of the produced biogas decrease until the end of the anaerobic digestion period.

At F/M 5, the amount of methane gas of disintegrated sludge is **40 mL** at the end of the anaerobic digestion period while the methane amount of 50% supernatant discarded sludge is **49 mL.**

At F/M 0.5, the amount of methane gas of disintegrated sludge is **24 mL** at the end of the anaerobic digestion period while the methane amount of 50% supernatant discarded sludge is **30 mL.**

As seen from the Table 5.25, as the centrifuged percentage of disintegrated sludge increases the percentage of produced methane during the anaerobic digestion process increases at all F/M ratio. Indicating that high percentage of methane gas is obtained at higher F/M ratios.

5.4 Economic Efficiency

Using disintegration for improving the anaerobic digestion a high degree of disintegration is necessary in order to realize a noticeable acceleration and enhancement of the degradation. This leads to a relatively high energy input and requires quite big machines. Additional costs are caused by the increased amount of flocculent needed because of the high content of small particles. The backflow of nitrogen is increased mainly because of the increase in degree of degradation and in some cases the dewatering result can be a little poorer. That brings out corresponding investment and running costs. A cost effective application can be obtained if the WTP has problems with the sludge treatment which can be reduced by the disintegration. This is the case for overloaded digesters, for sludges of low biodegradability and for high disposal costs.

The capital costs and the operational and maintenance (O&M) costs vary considerably among treatment processes. Mechanical disintegration is highly promising for enhancing digestion efficiency, owing to the method's relatively low capital costs and energy consumption and that it does not release harmful off-gases.

Comparing the pretreatment methods concerning the efficiency of COD-release and energy consumption, ultrasound and thermal pre-treatment are using a higher amount of energy. If the disintegration is used to improve the anaerobic digestion, a high degree of disintegration is necessary in order to realize a noticeable acceleration and enhancement of the degradation. This leads to a relatively high-energy input and requires fairly large machines.

The upgrading of the plant is assumed to be done by integrating a sonication unit and the new situation is assumed to consist of operational costs for a sonication unit additionally. Concurrently, the increased biogas and decreased transportation and disposal costs can be counted as revenues and savings of the upgraded situation.

Since there are conflicting results about the improvement of dewaterability and polymer consumption following pretreatment in literature, the effects originating from sludge dewatering (positive or negative) was not taken into account during cost calculations. Costs other than electricity consumption such as labor, insurance, maintenance etc. were not exclusively evaluated in cost analysis with the assumption that the major operating costs originate from the electricity use of sonication.

Energy balance is shown in Figure 5.66.

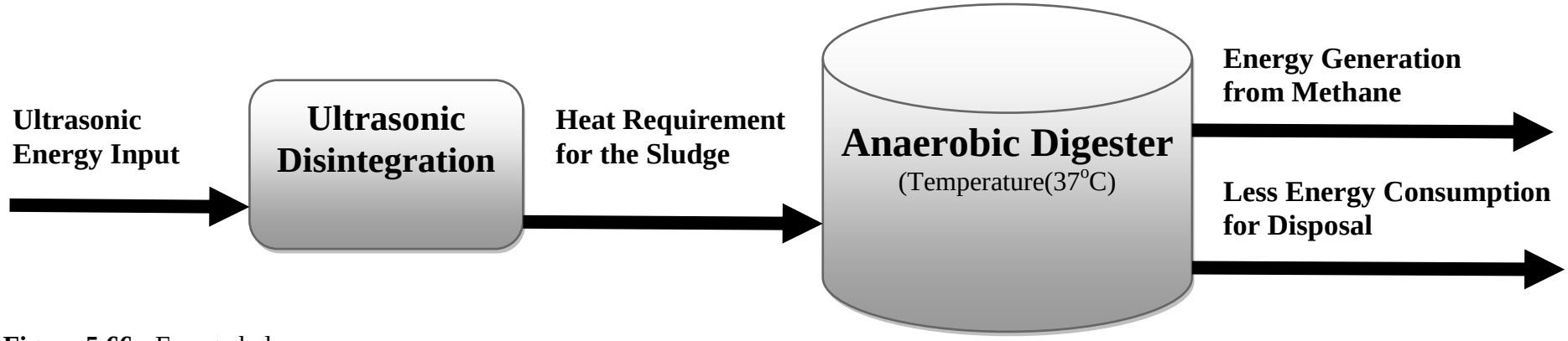

Figure 5.66 : Energy balance

The defined baseline situation has some assumptions given.

Assumptions:

- Calorific Value of Methane = 35800 kJ/m^3 (Barber, 2005)
- Temperature of sludge after ultrasonic disintegration = > 37 ^oC
- Temperature of anaerobic digester = 37 ^oC
- Disposal Cost per sludge volume = 65 YTL/ ton sludge
- Distance to the nearest disposal site = 15 km.
- Transport cost = 1.2 YTL/km (Truck capacity = 1 ton)
- Avarage price of energy = 0.215 YTL/kWh (TEDAŞ, 2010)

5.4.1 Cost analysis

For cost analysis, the results of the first experiments that ultrasonic disintegration is applied to the sludge with a specific energy of 40700 kWs/kg DS before the anaerobic digestion are choosen. And the results of F/M 0.5 are taken for the calculations.

Operating cost of ultrasound

The operating costs are dominated by the electrical power consumption. The average price in Turkey is approximately 0.215 YTL/kWh (TEDAS, 2010). And the specific energy that applied to the sludge for 30min at 80% amplitude is 40700 kWs/kg DS. Then the operating cost is 24295 YTL/Ton.

Transportation and disposal costs

The sludge solid reduction after anaerobic digestion of the sonicated sludge, (F/M=0.5) (first experiments) with respect to that of the untreated sludge, the transportation and disposal costs will decrease. For the transport, a truck with a capacity of 1 ton is assumed and transport cost of 1.2 YTL/km considering a 15 km far disposal site was taken. Disposal cost of 1 ton of sludge was taken as 65 YTL.

Revenue from methane generation

Increase in the methane production per VS from 21 mL CH_4/gVS_{added} to 186 mL CH_4/gVS_{added} after anaerobic digestion of the sludge sonicated at F/M ratio of 0.5 with respect to that of untreated sludge, the gain as renewable energy was calculated. When the calorific value of methane is 35800 kJ/m^3 (Barber, 2005), the methane revenue for control sludge is 43 YTL/Ton. However, this value increases to 843 YTL/Ton, when the sludge is sonicated before digestion.

Summary table for cost analysis is shown in Table 5.26.

Table 5.26: Summary table for cost analysis

	YTL/ton	
	Without Ultrasound	With Ultrasound
Operational cost(ultrasound)	-	24295
Transportation cost	18	10
Disposal cost	65	35
Methane Revenue	43	843

According to the calculations energy balance is negative. It is due to the high specific energy that applied to the sludge during the ultrasonic disintegration. But at the same time, the increase in the methane revenue is really high for the sonicated sludge.

5.4.2 Case study

A case study is prepared to observe the possible cost analysis; what would be the results of energy balance if the sonication time is decreased from 30 min. to 10 min. and the amplitude percentage is decreased from 80% to 60%.

Assumptions

- 10175 kWs/kg DS (100mL, 60% amplitude, 10 min.)
- Solid reduction decrease 14%
- Methane production decrease 17%

Summary table for cost analysis of case study is shown in Table 5.27.

Table 5. 27: Summary table for cost analysis of case study.

	YTL/ton	
	Without Ultrasound	With Ultrasound
Operational cost(ultrasound)	-	608
Transportation cost	18	12
Disposal cost	65	40
Methane Revenue	43	714

Ultrasound is an energy consuming technology with a high investment cost. However, the benefits gained from pretreatment such as more methane production and less sludge disposal break even with the associated costs after a certain operation period. By choosing shorter sonication time, energy balance can became positive as shown in Table 5.27.

Considering all costs of ultrasonication, besides being environment-friendly; its application can be more profitable.

6. CONCLUSION

The ultrasonic pretreatment of return activated sludge was applied in order to improve the anaerobic digestion efficiency. Ultrasonic disintegration efficiency was first examined mainly in terms of the effect of ultrasonic density and specific energy input. 40%, 60% and 80 % amplitudes were used to treat the RAS samples at varying sonication times between 1and 30 minute. At longer sonication duration and high ultrasound power input, better disintegration was observed as a result higher release of intercellular and extracellular polymeric substances in the aqueous phase, measured as CODf. The highest increase in CODf concentration was observed for 50 mL sludge volume used. CODf concentration increased from 4,990 mg/L to 6,610 mg/L when the amplitude was increased from 40% to 60%. For the anaerobic digestion tests ultrasound disintegration under the conditions of 100 mL of volume, 80% amplitude and 30 minutes of duration is selected to observe noticeable improve in the digestion efficiency during anaerobic tests.

The effect of ultrasound pretreatment before anaerobic digestion was studied for four different F/M ratios of 0.5, 1, 2 and 5, and five different percentages of treated sludge mixed with un-treated sludge. The percentages of treated sludge subjected to anaerobic digestion were varied from 0%, 25%, 50%, 75% and 100%. The percentage of 0% refers to control experiments with un-treated return sludge. The evaluation relied on biogas production, VS reduction and the content of the produced biogas.

In the first part of the experimental study, two different F/M ratios of 0.5 and 1 were studied, the amount of biogas production of disintegrated sludge increased 17% compared to un-treated sludge at F/M 1, while the biogas production increase was 40% at F/M 0.5 at the end of the anaerobic digestion period.

VS reduction in disintegrated sludge was higher than the VS reduction in control sludge for both F/M ratios. On the other hand CODf increase in disintegrated sludge was lower than the VS reduction in control sludge for both F/M ratios.

VS reduction percentages of un-treated (control) sludge and disintegrated sludge were 5% and 19% respectively at F/M 1, while the VS reduction increased from 24% (untreated sludge) to 34% at F/M 0.5 during the anaerobic digestion period.

Similarly,VS reduction of disintegrated sludge and reactor mixed at 50 % of discarded centrifuged sludge supernatant were 19% and 41% respectively at F/M 1, while 23% and 30% at F/M 0.5 indicating that as the F/M ratio increases the difference in VS reduction also increases.

At the end of the anaerobic digestion period, the amount of methane gas of disintegrated sludge increased from 43mL in the control sludge to 51 mL at F/M 1, while the the amount of methane gas increased from 33 mL to 50 mL at F/M 0.5. Adversly, decreasing the F/M ratio from 1 to 0.5, causes 25% increase in terms of mL CH_4/gVS_{added} for disintegrated sludge.

Since the results obtained from the first part of the experiments for biogas production and methane percentages were very close to each other at F/M and 0.5 and F/M 1 which might be misleading in terms of interpretation of the data. In the second part of the experimental study, these experiments were duplicated together with two additional F/M ratios of 2 and 5.

In the second experiments, total biogas amount at the end of the anaerobic digestion increased from 50 mL to 57 mL by disintegration of sludge resulting in 14% increase for F/M 2, while 43 mL to 53 mL resulting in 23% increase for F/M 1. Consequently, the amount of biogas production was increased 40% by increasing F/M from 0.5 to 5.

Similarly, by increasing F/M from 0.5 to 5 the amount of methane gas of disintegrated sludge increased from 24 mL to 40 mL resulting in 67% increase. It is obviously because of higher soluble COD entering to anaerobic reactors for higher F/M ratios. Therefore, the results also imply that higher F/M ratios should be applied to get higher gas productions from the anaerobic digestion applications.

In full scale treatment plants, considering that some part of the supernatant of the disintegrated sludge can be returned to the beginning of the system after the centrifuge process to supply the carbon demand for nutrient removal system, different percentages of centrifuged disintegrated sludge are subjected to anaerobic digesters by discarding some part of the supernatant to represent the possible effect

of returned supernatant to the beginning of the system. The discarded supernatant amounts are in the range of 10 % to 50 % (RUN II).

No remarkable decrease was observed in methane gas measurements for all F/M ratios as the percentage of supernetant discarded was increased. There was even a slight increase in methane gas produced. Produced methane gas also increased by increasing F/M ratio in all experiments regardless of the different percentages of discarded supernatant.

For example, the amount of methane gas of disintegrated sludge produced at the end of the anaerobic digestion period was 24 mL, while the methane amount of 50% centrifuged sludge was 30 mL at F/M 0.5 and similarly 40 mL and 49 mL respectively for F/M 5.

The results presented in this study confirmed that complete or partial sonication of return sludge can be used to produce quantities of potential biogas amounts in subsequent anaerobic digestion compared to non-sonicated sludge. It was obvious from the results that F/M ratio is one of the major parameters for anaerobic digestion of pre-treated sludge. The increase of F/M ratio importantly can increase the biogas production. Interestingly, it was also observed that disintegration of sludge may not be appropriate selection to obtain higher biogas productions. The results have proved that it should be investigated both the effect of F/M ratio and percentage of pre-treated sludge at the same time for the cost effectiveness and higher efficiency in anaerobic digestion. The results also implied that in nutrient removal activated sludge systems, returning some part of the disintegrated sludge supernatant to the beginning of the system can also be used to supply substrate for further nutrient removal without deteriorating the efficiency of anaerobic digestion.

REFERENCES

Ahn, K.H., Park, K.Y., Maeng, S.K., Hwang, J.H., Lee, J.W., Song, K.G., Choi, S., 2002: Ozonation of wastewater sludge for reduction and recycling, *Water Sci Technol* **46**(10), pp. 71–7.

APHA, 2005: Standart Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, D.C.

ATV, 2003: Müller, J., Tiehm, A., Böcker, K., Eder, B., Kopp, J., Kunz, P., Neis, U., Oles, J., Otte-Witte, R., Schmelz, K.G. and Seiler, K., 2003: Thermische, chemische und biochemische Desintegrationsverfahren, Report of ATV/DVWK – Specialist group "Sewage Sludge Disintegration". *Korrespondenz Abwasser*, **50**(6).

Barber, W.P, 2005: The effects of ultrasound on sludge digestion. *Journal of the Chartered Institution of Water and Environmental Management*, **19**(11), pp. 2-7.

Barjenbruch, M. and Kopplow, O., 2003: Enzymatic, mechanical and thermal pre-treatment of surplus sludge, *Adv. Environ. Res.* **7**(3), pp. 715–720.

Barr, K.G., Solley, D.O., Starrenburg, D.J. and Lewis, R.G., 2008: Evaluation, selection and initial performance of a large scale centralised biosolids facility at Oxley Creek Water Reclamation Plant, Brisbane, pp. 1579-1586.

Bartholomew, R., 2002: Ultrasound Disintegration of Sewage Sludge: An Innovative Wastewater Treatment Technology PA Department of Environmental Protection, Bureau of Water Supply and Wastewater Management. From http://www.dep.state.pa.us/DEP/DEPutate/WatermgtWSM/ WSM_TAO / InnovTech / ProjReviews/ Ultrasound- Disintegr. Htm

Benabdallah El-Hadj, T., Dosta, J., Marquez-serrano, R., Mata-Alvarez, J., 2007: Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene, *Water Research*, **41**(1), pp. 87-94.

Bien J.B., Malina G., Bien J.D. and Wolny L., 2004: Enhancing anaerobic fermentation of sewage sludge for increasing biogas generation, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng*. **39**(4), pp. 939-949.

Bilitewski, B., Härdtle, G., Marek, K., 1997: Waste Management. Springer, Berlin, ISBN: 3-540-59210-5.

Bitton, G., 1999: *Wastewater Microbiology, (2nd ed.)*. Wiley-Liss Inc, New York.

Boehler, M. and Siegrist, H., 2006: Potential of activated sludge disintegration, *Water Sci. Technol*. **53**(12), pp. 207-216.

Borrely, S.I., Cruz, A.C., Del Mastro, N.L., Sampra, M.H.O. and Somessari, E.S., 1998: Radiation processing of sewage and sludge. A Review Prog. Nucl. Energy, **33**, Nos. 1–2, pp. 3–21.

Bougrier C., Carràre H. and Delgenès J.P., 2005: Solubilisation of waste-activated sludge by ultrasonic treatment, *Chem. Eng. J.* **106**(2), pp. 163-169.

Bougrier, C., Delgen`es, J.P., Carr`ere, H., 2006: Combination of thermal treatments and anaerobic digestion to reduce sewage sludge quantity and improve biogas yield. *Proc. Saf. Environ. Protect,* **84**(B4), pp. 280–284.

Bougrier, C., Albasi, C., Delgenes, J.P. and Carrere, H., 2006a: Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability, *Chemical Engineering and Processing*, **45**(8), pp. 711-718.

Bougrier, C., Battimelli, A., Delgenes, J.P. and Carrere, H., 2007a: Combined ozone pretreatment and anaerobic digestion for the reduction of biological sludge production in wastewater treatment. *Ozone: Science and Engineering*, **29**(3)**,** pp. 201-206.

Bougrier, C., J.P. Delgenes & H. Carrere, 2007: Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge, *Biochemical Engineering Journal*, **34**(1), pp. 20-27.

Bougrier, C., Delgenes, J. P., and Carrere, H., 2008: Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. *Chemical Engineering Journal*, **139**(2), pp. 236-244.

Braguglia, C.M., Mininni, G., Tomei, M.C. and Rolle, E., 2006: Effect of feed/inoculum ratio on anaerobic digestion of sonicated sludge, *Water Sci. Technology*, **54**(5), pp. 77–84.

Braguglia, C.M., Mininni, G. and Gianico, A., 2008: Is sonication effective to improve biogas production and solids reduction in excess sludge digestion?, *Water Sci. Technology*, **57**(4), pp. 479-483.

Brown, J.P., Clark, P., Hogan, F., 2003: Ultrasonic sludge treatment for enhanced anaerobic digestion at Orange County Sanitation District, WEFTEC 2003 Conference, Los Angeles, California. Water Environment Federeation, Alexandria, Virginia.

Caffaz, S., Santianni, D., Cerchiara, M., Lubello, C., Stecchi, R., 2005: Reduction of excess biological sludge with ozone: experimental investigation in a full-scale plant. In: IOA *17th World Ozone Congress*, Strasbourg, France.

Campanella, L., Ferri, T, Petronio, B.M. and Piccolo, A., 1989: Effect of speciation in sludges on the adsorption of leached metals from soil. Science and Total Environment, **79**, pp. 223–231.

Carballa, M., Manterola, G., Larrea, L., Ternes, T., Omil, F., Lema, J.M., 2007: Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products. *Chemosphere*, **67**, Issue 7, April 2007, pp. 1444-1452.

Carrere, H., Bougrier, C., Castets, D. and Delgenes, J.P., 2008: Impact of initial biodegradability on sludge anaerobic digestion enhancement by thermal pretreatment, *J. Environ. Sci. Health Part AToxic/Hazard. Subst. Environ. Eng.* **43**(13), pp. 1551-1555.

Cartmell, E., Clay, S., Smith, R. and Withey, S., 2004: Application of mechanical pre-treatments for improving the digestibility of waste activated sludge. Proceedings, 10th World Congress Montre´ al, Canada.

Chu, C.P., Feng, W.H., Tsai, Y.H., Lee, D.J., 1997: Undirectional freezing of waste activated sludge: the presence of sodium chloride. *Environ. Sci. Technology*. **31**(5), pp. 1512-1517.

Chu, C.P., Feng, W.C., Chang, B.V., Chou, C.H., Lee, D.J., 1999: Reduction of microbial density level in wastewater activated sludge via freezing and thawing, *Water Research*, **33**(16), pp. 3532–5.

Chu, C. P., Chang, B. V., Liao, G. S., Jean, D. S. and Lee, D. J., 2001: Observation on changes in ultrasonically treated waste-activated sludge, *Water Research*, **35**(4) 1038-1046.

Chu, C.P., Lee, D.J., You, C.S., Tay, J.H., 2002: Weak ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids. *Water Research*, **36**, 2681– 2688.

Climent, M., Ferrer, I., Baeza, M.D., Artola, A., Vazquez, F. and Font, X., 2007: Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions, *Chem. Eng. J.* **133** (1-3), pp. 335-342.

Cui, R. and Jahng, D., 2004: Nitrogen control in AO process with recirculation of solubilized excess sludge, *Water Research,* **38**(5), pp. 1159–1172.

Curto, P. R., 2001: Determining the potential for enhanced biological phosphorus removal based on wastewater characteristics. *MSc Thesis,* Cranfield University, Beds, UK.

Davidsson Å., 2007: Increase of biogas production at wastewater treatment plants – Addition of urban organic waste and pre-treatment of sludge, PhD-thesis, Water and Environmental Engineering Department of Chemical Engineering Lund University, ISBN 978-91-7422-143-5.

De Mes, T.Z.D., Stams, A.J.M., Reith, J.H., Zeeman, G., 2003: Methane production by anaerobic digestion of wastewater and solid wastes. In: Reith, J.H., Wijffels, R.H., Barten, H. (eds.), Bio-methane & Bio-hydrogen. Status and Perspectives of Biological Methane and Therlands, pp. 58-102.

Dewil, R., Baeyens, J., Goutvrind, R., 2006: Ultrasonic treatment of waste activated sludge. *Environ. Progress*, **25**(2), pp. 121-128.

Dohányos, M., Zábranská, J. and Jenícek, P., 1997: Enhancement of anaerobic sludge digestion by using of a special thickening centrifuge. *Wat. Sci. Tech*, **36**(11), pp.145–153.

Dohányos, M., Zábranská, J., Jenícek, P., Stepová, J., Kutil, V. & Horejs, J., 2000: The intensification of sludge digestion by the disintegration of activated sludge and the thermal conditioning of digested sludge, *Water Science and Technology*, **42**(9), pp. 57-64

Dohányos, M., Zábranská, J., Kutil, V. & Jenícek, P., 2004: Improvement of anaerobic digestion of sludge, *Water Science and Technology*, **49**(10), pp. 89-96.

Eastman, J.A., and Ferguson, J.F., 1981: Solubilization of particulate organic carbon during the acid stage of anaerobic digestion. J. WPCF **53**(3), pp. 352–366.

Ecke, H. and Lagerkvist, A., 2000: Anaerobic treatment of putrescible refuse (ATPR). Report 2000:01, The Division of Waste Science & Technology, Lulea University of Technology, Lulea, Sweden, 47. (http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva- 4581)

Egemen, E., Corpening, J., Nirmalakhandan, N., 2001: Evaluation of an ozonation system for reduced waste sludge generation. *Water Sci Technol* **44**(2–3), pp. 445–52.

Elliott, A. and Mahmood, T., 2007: Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues, *Water Research,* **41**(19), pp. 4273-4286.

Engelhart, M., 2002: Anaerober Abbau Mechanish Desintegrierten Ueberschussschlammes. Institut für Siedlungswasserwirtschaft-Technische Universität Braunschweig, Heft 68.

Enpure, 2008: Sonix reference list, Enpure Ltd. Last Access: 07 March 2008, from: http://www.enpure.co.uk/profile/show_doc.php?id=348.

Erden, G. and Filibeli A., 2009: Ultrasonic pre-treatment of biological sludge: consequences for disintegration, anaerobic biodegradability, and filterability, *J. Chem. Technol. Biotechnoogy,*. **85**(1), pp. 145-150.

Etzel, J.E., Born, G.S., Stein, J., Helbing, T.J. and Baney, G., 1969: Sewage sludge conditioning and disinfection by gamma irradiation. *Am J Public Health*, **59**, pp. 2067–3076.

Everett, J.G., 1973: Resent developments in heat treatments, *J. Water Pollut. Control Fed.*, **50**, 1, pp. 73-75.

Feng, X., Deng, J., Lei, H., Bai, T., Fan, Q., Li, Z., 2009: Dewaterability of waste activated sludge with ultrasound conditioning. *Bioresource Technology*, **100**, pp. 1074–1081.

Fernandez-Polanco, F., Velazquez, R., Perez-Elvira, S.I., Casas, C., del Barrio, D., Cantero, F.J., Fdz-Polanco, M., Rodriguez, P., Panizo, L., Serrat, J. and Rouge, P., 2008: Continuous thermal hydrolysis and energy integration in sludge anaerobic digestion plants, *Water Sci. Technol.*, **57**(8), pp. 1221-1226.

Ferrer, I., Climent, M., Baeza, M.M., Artola, A., Vazquez, F., Font, X., 2006: Effect of sludgepretreatment on thermophilic anaerobic digestion. In: Proceedings of the IWA Specialized Conference on Sustainable Sludge Management: State-of-the-Art, Challenges and Perspectives, Moscow, Russia, May 29–31, 2006, pp. 235–241.

Ferrer, I., Ponsá, S., Vázquez, F. and Font X., 2008: Increasing biogas production by thermal (70 °C) sludge pre-treatment prior to thermophilic anaerobic digestion. *Biochemical Engineering Journal*, **42**, Issue 2, 1 November 2008, pp. 186-192.

Fjordside, C., 2001: An operating tale from Næstved Sewage Treatment Plant, *Municipal wastewater treatment Nordic Conference*, Copenhagen (Denmark).

Gavala, H.N., Yenal, U., Skiadas, I.V., Westermann P. and Ahring, B.K., 2003: Mesophilic and thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature, *Water Res.*, **37**(19), pp. 4561–4572.

Garuti, G., Dohanyos, M. and Tilche, A., 1992a: Anaerobic–Aerobic combined process for the treatment of sewage wit nutrient removal: the ANANOX process, *Water Sci. Technol.*, **25**(7), pp. 383–394.

Garuti, G., Dohanyos, M. and Tilche, A., 1992b: Anaerobic–aerobic wastewater treatment system suitable for variable population in coastal areas: the ANANOX process. *Water Sci. Technol.*, **25**(12), pp. 185–195.

Gene, F. P., 1986: Fundamentals of anaerobic, Environmental Engineering, 112, pp. 867-920.

Goel, R., Mino, T., Satoh, H., Matsuo, T., 1998: Enzyme activities under anaerobic and aerobic conditions in activated sludge sequencing batch reactor, *Water Research*, **32**, 7, pp. 2081–2088.

Gerardi, M.H., 2003: The Microbiology of Anaerobic Digesters, John Wiley & Sons, ISBN 0-471-20693-8.

Grady, L.C.P., Daigger, G.T., Lim, H.C., 1999: Biological Wastewater Treatment, second ed., revised and expanded. Marcel Dekker, New York.

Graja, S., Chauzy, J., Fernandes, P., Patria, L. and Cretenot, D., 2005: Reduction of sludge production from WWTP using thermal pretreatment and enhanced anaerobic methanisation, *Water Sci. Technol.* **52**(1–2), pp. 267–273.

Hall, J., 1999: Ecological and economical balance for sludge management options, WRc plc, Medmenham, Marlow, SL7 2HD, United Kingdom.

Harrison, S.T.L., 1991: Bacterial cell disruption: a key unit operation in the recovery of intracellular products, *Biotechnology Advances,* **9**(2), pp. 217-240.

Haug, T.R., Stuckey, D.C., Gossett, J.M., McCarty, P.L., 1978: Effect of thermal pretreatment on digestibility and dewaterability of organic sludges, *J. Water Pollut. Control. Fed.,* **50**, pp. 73-85.

Hielscher, 2005: Ultrasound technology. Last Access: 21 April 2005, from: http://www.hielscher.com/.

Hiraoka, M., Takeda, N., Sakai, S. and Yasuda A., 1984: Highly efficient anaerobic digestion with thermal pretreatment, *Water Sci. Technol.,* **17**, pp. 529–539.

Hogan, F., Mormede, S., Clark, P., Crane, M., 2004: Ultrasonic sludge treatment for enhanced anaerobic digestion, *Water Science and Technology,* **50**(9), pp. 25-32.

Horst, C. and Hoffmann, U., 1999: Design, operation and characterization of ultrasound reactors. In: *Ultrasound in environmental engineering*, **25**, pp. 77-90, Technical University of Hamburg, Hamburg.

Ince, N. H., Tezcanli, G., Belen, R. K. and Apikyan, I. G., 2001: Ultrasound as a catalyzer of aqueous reaction systems: The state of the art and environmental applications, *Applied Catalysis B: Environmental,* **29,** pp. 167-176.

Jarvis, Å., 2004: Biogas Förnybar energi från organiskt avfall, brochure, Swedish Biogas Association.

Jeong, G.C., Cha, S., Choi, S. and Jeon, C., 2007: Evaluation of methane production by the thermal pretreatment of waste activated sludge in an anaerobic digester, *J. Ind. Chem. Eng.*, **13**, pp. 856–863.

Jonsson, K., Johansson, P., Christensson, M., Lee, N., Lie, E., Welander, T., 1996: Operational factors affecting enhanced biological phosphorus removal at the waste water treatment plant in Helsingborg, Sweden, *Water Sci. Technol*., **34**(1–2), pp. 67–74.

Jorand, F., Zartarian, F., Thomas, F., Block, J.C., Bottero, J.Y., Villemin, G., Urbain, V. and Manem. J., 1995: Chemical and structural (2D) linkage between bacteria within activated sludge flocs, *Water Research,* **29**, Issue 7, July 1995, pp. 1639-1647.

Kamiya, T. and Hirotsuji, J., 1998: New combined system of biological process and intermittent ozonation for advanced wastewater treatment, *Water Science and Technology,* **38**(8-9 pt 7)**,** pp. 145-153.

Kaynak, G.E., Filibeli, A., 2007: Sludge Disintegration Using Fenton's Peroxidation. IWA Conferance- Facing Sludge Diversities:Challanges, Risks and Opportunities, Antalya, 28-30 March 2007.

Kepp, U., Machenbach, I., Weisz, N., and Solheim, O.E., 2000: Enhanced Stabilisation of Sewage Sludge through Thermal Hydrolysis - Three Years of Experience with Full Scale Plant, *Water Sci. Technol.*, **42**(9), pp. 89-96.

Khanal, S.K., Isik, H., Sung, S., van Leeuwen, J., 2006a: Effect of ultrasonic pretreatment on aerobic digestion of waste activated sludge. A Review. Critical Revised *in Water Science and Technology.*

Khanal, S.K., Isik, H., Sung, S., van Leeuwen, J., 2006b: Ultrasound conditioning of waste activated sludge for enhanced aerobic digestion of waste activated sludge. In CD-ROM Proceedings of IWA Specialized Conference - Sustainable Sludge Management: State of Art, Challenges and Perspectives, May 29-31, 2006, Moscow, Russia.

Khanal, S.K., Isik, H., Sung, S., Van Leeuwen, J., 2006c: Ultrasound pretreatment of waste activated sludge: evaluation of sludge disintegration and aerobic digestion. In CD-ROM Proceedings of IWA World Water Congress and Exhibition, Sep 10-14, 2006, Beijing, China.

Kim, Y.U. and Kim, B.I., 2003: Effect of ultrasound on dewaterability of sewage sludge, Japanese J. Appl. Phys. Part 1 **42**(9A), pp. 5898-5899.

Kim, J., Park, C., Kim, T.H., Lee, M., Kim, S., Kim, S.W. and Lee, J., 2003: Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge, *J. Biosci. Bioeng.,* **95**(3), pp. 271-275.

Kim, D.H., Jeong, E., Oh, S.E. and Shin, H.S., 2010: Combined (alkaline + ultrasonic) pretreatment effect on sewage sludge disintegration, *Water Research,* **44**, Issue 10, May 2010, pp. 3093-3100.

Kitazume, M., Ueyama, S. & Benno, Y., 1991: Solubilization of activated sludge by isolated acid-forming anaerobes. Hakkokogaku Kaishi, 5, 363È72.

Kurth, F., 2002: Full-scale commercial operation of ultrasound disintegration plants in Germany. In Proceedings of: *Proceedings of the 7th European Biosolids and Organic Residuals Conference*, Wakefield, 18-20 November 2002.

Lee, J. W., Cha, H.Y., Park, K.Y., Song, K.G. and Ahm, K.H., 2005: Operational strategies for an activated sludge process in conjuction with ozone oxidation for zero excess sludge production during winter season. *Water Research,* **39**, pp. 1199-1204.

Lehne, G., Müller, A. J., Schwedes, J., 2001: Mechanical disintegration of sewage sludge, *Water Science&Technology,* **43**(1), pp. 19-26.

Li, Y.Y. and Noike, T., 1992: Upgrading of anaerobic digestion of waste activated sludge by thermal pre-treatment. *Wat. Sci. Tech*., 3È4 857È66.

Lin, J.G., Chang, C.N. and Chang, S.C., 1997: Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization, *Biores. Technol.*, **62**, pp. 85-90.

Liu, D.H., Liptak, B.G.(Eds.)., 1999: Environmental Engineers' Handbook, 2nd Edition, CRC Press LLC, Boca Raton, Florida, Chapter 7: Wastewater Treatment, URL: http://www.engnetbase.com/books/78/fm.pdf.

Lu, J.G., Hariklia N., Skiadas, I.V., Mladenovska, Z. and Ahring, B.K., 2008: Improving anaerobic sewage sludge digestion by implementation of a hyper-thermophilic prehydrolysis step, *Journal of Environmental Management,* **88**, Issue 4, September 2008, pp. 881-889.

Machnicka, A., Suschka, J. and Grübel, K.,. 2005: The Intensification of Sewage Sludge Anaerobic Digestion by Partial Disintegration of Surplus Activated Sludge and Foam w: Integration and Optimization of Sanitation Systems In Urban Areas: proceedings of Polish-Swedish seminars, Cracow, March 17-18, 2005, p: 87-94, Report no. 13, pp. 87-94.

Manterola, G., Uriarte, I. and Sancho, L., 2008: The effect of operational parameters of the process of sludge ozonation on the solubilisation of organic and nitrogenous compounds, *Water Research,* **42**(12)**,** pp. 3191-3197.

Marjoleine, P.J., Weemaes and Willy, H., 1998: Evaluation of Current Wet Sludge Disintegration Techniques *J. Chem. T echnol. Biotechnol.* **73,** pp. 83-92.

Martel, C.J., 1989: Dewater ability of freeze-thaw conditioned sludges, *J. Water Pollution Control Fed.,* **61**(2), pp. 237-241.

Mayhew, M., Le, M., Ratcliff, R., 2002: A novel approach to pathogen reduction in biosolids: the enzymic hydrolyser, *Water Sci. Technol.,* **46**(4/5), pp. 427–434.

Mayhew, M., Le, M., Brade, C., Harrison, D., 2003: The United utilities 'enzymic hydrolysis process'—validation of phased digestion at full-scale to enhance pathogen removal. In: WEF Proceedings of the Residuals and Biosolids Conference, Baltimore.

McCarty, P.L., 2001: The developmental of anaerobic treatment and its future, *Water Science and Technology,* **44**(8)**,** pp. 149-156.

McCue, T., Shah, R., Vassiliev, I., Liu, Y.H., Eremektar, F.G., Chen, Y., Randall, A.A., 2003: Evaluation of influent prefermentation as a unit process upon biological nutrient removal, *Water Sci. Technol*., **47**(11), pp. 9–15.

Metcalf & Eddy., Inc. 2003: Wastewater Engineering. McGraw-Hill, a business unit of The McGraw-Hill Companies, Inc., New York.

Metcalf & Eddy., 1991: Wastewater engineering: treatment, disposal and reuse, 3rd ed., New York: McGraw-Hill; pp. 529–91.

Miklas, Scholz., 2006: Wetland Systems to Control Urban Runoff. 1st ed. Oxford, UK, pp. 164-168.

Minervini, D., 2008: The Potential of Ultrasound Treatment for Sludge Reduction. School of Applied Sciences Department of Sustainable Systems Centre for Water Science. Cranfield University.

Mines, R.O., Northenor, C.B., Murchison, M., 2008: Oxidation and ozonation of waste activated sludge, *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* **43**(6), pp. 610--618.

Montusiewicz, A., Lebiocka, M., Ro_zej, A., Zacharska, E., Pawłowski, L., 2010: Freezing/thawing effects on anaerobic digestion of mixed sewage sludge. *Bioresource Technology*, **101**, pp. 3466-3473.

Mustapha, S. and Forster, C.F., 1985: Examination into the gamma irradiation of activated sludge, *Enzyme Microbiology Technology*, **7**, pp. 179–181.

Müller, C.D., 2006: Shear forces, Floc structure and their impact on anaerobic digestion and biosolids stability, Civil and Environmental Engineering.Virginia Polytechnic Institute and State University, Blacksburg.

Muller, C., Abu-Orf, M., Blumenschein, C., Novak, J., 2005: The impact of ultrasound energy on mesophilic anaerobic digestion. In: WEF Proceedings of the Residuals and Biosolids Management Conference, Covington, KY.

Müller, J.A., Winter, A., Strünkmann, G., 2004: Investigation and assessment of sludge pretreatment processes, *Water Science and Technology*, **49**(10), pp. 97-104.

Müller, J.A., 2003: Conditioning, Thickening and dewatering of mechanically disintegrated excess sludge, *Separation Science and Technology*, **38**(4), pp. 889–902.

Müller, J., 2000: Disintegration as a key step in sewage sludge treatment. *Wat. Sci. Tech.*, **41**(8), pp.123–130.

Müller, J.A., 2000a: Disintegration as a key-step in sewage sludge treatment, *Water Science Technology*, **41**(8), pp. 123–130.

Müller, J.A., 2000b: Pretreatment processes for the recycling and reuse of sewage sludge, *Water Science Technology*, **42**(9), pp. 167–174.

Müller, J.A., 2000c: Prospects and problems of sludge pre-treatment Processes, *Water Science Technology*, **44**(10), pp. 121–128.

Navaneethan, N., 2007: Anaerobic Digestion Of Waste Activated Sludge With Ultrasonic Pretreatment, Asian Institute of Technology School of Environment, Resources and Development. Thailand.

Neis, U., Nickel, K. and Tiehm, A., 1999: Enhancement of anaerobic sludge digestion by ultrasonic disintegration. In: Disposal and Uutilisation of Sewage Sludge: Treatment Methods and Application Modalities, IAWQ Specialised Conference on Sludge Treatment, 13–15 October 1999, Athens, Greece, pp. 129–136.

Neis, U., Nickel, K. and Tiehm, A., 2000: Enhancement of anaerobic sludge digestion by ultrasonic disintegration, *Water Science and Technology*, **42**, No 9, pp 73–80.

Neis, U., Nickel, K. and Tiehm, A., 2001: Ultrasonic disintegration of sewage sludge for enhanced anaerobic biodegradation. In: *Advances in sonochemistry*. Editor(s): Mason, T. J. and Tiehm, A., **6,** pp. 59-90. Elsevier Science.

Neis, U., Nickel, K., and Lunden, A., 2008: Improving anaerobic and aerobic degradation by ultrasonic disintegration of biomass, J. Environ. Sci. Health Part A-Toxic/Hazard. *Subst. Environ. Eng.,* **43**(13), pp. 1541-1545.

Neyens, E., Baeyens, J., Weemaes, M., De Heyder, B., 2003: Alkaline thermal sludge hydrolysis, *J Hazard Mater,* **97**(1–3), pp. 295–314.

Nges, I.A. and Liu, J., 2009: Effects of anaerobic pre-treatment on the degradation of dewatered-sewage sludge, *Renewable Energy,* **34**, Issue 7, July 2009, pp. 1795-1800.

Nowak, O., 2006: Optimizing the use of sludge treatment facilities at municipal WWTPs, *Journal of Environmental Science and Health Part A* **41**(2006), pp. 1807–1817.

Onyeche, T.I., Schlafer, O., Bormann, H., Schroder, C., Sievers, M., 2002: Utrasonic cell disruption of stabilized sludge with subsequent anaerobic digestion, Ultrasonic, **40**, pp. 31-35.

Ostrem, K., 2004: Greening Waste: Anaerobic Digestion For Treating The Organic Fraction Of Municipal Solid Wastes, Earth Engineering Center Columbia University.

Otte-Witte, R., Wünsch, M., Hodder, M., 2000: Sludge disintegration by Lysate thickening centrifuge, 5th Biosolids Conference, Wakefield, UK.

Örmeci, B., Vesilind, P.A., 2001: Effect of dissolved organic material and cations on freeze-thaw conditioning of activated and alum sludges, *Water Res.*, **35**(18), pp. 4299-4306.

Panda, K.K., and Mathews A.P., 2008: Mass transfer of ozone in a novel in situ ozone generator and reactor, *J. Environ. Eng.-ASCE,* **134**(10), pp. 860-869.

Panter, K., 2002: A comparison of methods for pre–treating surplus activated sludge prior to anaerobic digestion. In Proceedings of: *The 7th European Biosolids and Organic Residuals Conference*, Wakefield, 18-20 November 2002.

Park, K.Y., Ahn, K.H., Maeng, S.K., Hwang, J.H., Kwon, J.H., 2003: Feasibility of sludge ozonation for stabilization and conditioning, *Ozone: Science&Engineering,* **25(**1), pp. 73- 80.

Peltola, R.J., Laine, V.H., Kautola, H. and Kymalainen, M.A.L., 2004: Impact grinding as pre-treatment method for biowaste and sludge, Proceedings, 10th World Congress Montre´ al, Canada.

Pérez-Elvira, S.I., Nieto Diez, P. and Fdz-Polanco, F., 2006: Sludge minimization technologies, *Environmental Science and Bio/Technology*, **2006**(5), pp. 375-398.

Perez-Elvira, S.I., Fernandez-Polanco, F., Fernandez-Polanco, M., Rodriguez, P. and Rouge, P., 2008: Hydrothermal multivariable approach. Full-scale feasibility study. *Electronic Journal of Biotechnology* **11**.

Perez-Elvira, S., Fdz-Polanco, M., Plaza, F.I., Garralon, G. and Fdz-Polanco, F., 2009: Ultrasound pretreatment for anaerobic digestion improvement, *Water Sci. Technol.*, **60**(6), pp. 1525-1532.

Phothilangka, P., Schoen, M. A. , Huber, M., Luchetta, P. , Winkler, T. and Wett B., 2008: Prediction of thermal hydrolysis pretreatment on anaerobic digestion of waste activated sludge, *Water Science & Technology*—WST, **58**, No 7, pp. 1467–1473.

Pickworth, B., Adams, J., Panter, K., & Solheim, O. E., 2006: Maximising biogas in anaerobic digestion by using engine waste heat for thermal hydrolysis pre-treatment of sludge, *Water Sci. Technol*., **54**(5), pp. 101-108.

Portenlänger, G., 1999: Mechanical and radical effects of ultrasound. In: *Ultrasound in environmental engineering*, **25,** pp. 11-22. Technical University of Hamburg, Hamburg.

Pranshanth, S., Kumar, P., and Mehrotra, I., 2006: Anaerobic Degradability: Effect of Particulate COD, *J. Environ. Eng.*, **132**(4), pp. 488–496.

Pursell, N., 2002: Sustainable sewage sludge treatment at avonmouth. In Proceedings of: *The 7th European Biosolids and Organic Residuals Conference*, Wakefield, 18-20 November 2002.

Rajan, R.V., Lin, J.G. and Ray, B.T., 1989: Low-level chemical pretreatment for enhanced sludge solubilization, *Res. J. Water Pollut. Control Fed.*, **61**, pp.1678-1683.

Randall, W.C., Barnard, L.J., Stensel, H.D., 1992: Design and retrofit of wastewater treatment plants for biological nutrient removal, *Water Qual. Manage. Lib*., 5.

Reed, S., Bouzoun, J., Medding, W., 1986: Arational method for sludge dewatering via freezing. *J. Water Pollution Control Fed.*, **58**(9), pp. 911-916.

Riedel, Jr. D.J., 2009: An Investigation into the Mechanisms of Sludge Reduction Technologies. Virginia Polytechnic Institute and State University. Blacksburg, VA.

Sakai, Y., Fukase, T., Yasui, H. and Shibata, M., 1997: Activated sludge process without excess sludge production, *Water Science and Technology*, **36**(11)**,** pp. 163-170.

Saktaywin, W., Tsuno, H., Nagare, H., Soyama, T., Weerapakkaroon, J., 2005: Advanced sewage treatment process with excess sludge reduction and phosphorus recovery, *Water Research*, **39**(5), pp. 902–910.

Salsabil, M.,R., Prorot, A., Casellasa, M., Dagot, C., 2009: Pre-treatment of activated sludge: Effect of sonication on aerobic and anaerobic digestibility. *Chemical Engineering Journal*, **148**, pp. 327–335.

Sanchez, B., Alonso, J.M.Q. and Oviedo, M.D.C., 2006: Use of microbial activity parameters for determination of a biosolid stability index, *Bioresource Technology* **97**(2006), pp. 562–568.

Sandino, J., Santha, H., Rogowski, S., Anderson, W., Sung, S., Isik, F., 2005: Applicability of ultrasound pre-conditioning of was to reduce foaming potential in mesophilic digesters. In: WEF Proceedings of the Residuals and Biosolids Management Conference, Covington, KY.

Scheminski, A., Krull, R. and Hempel, D.C., 1999: Oxidative treatment of digested sewage sludge with ozone, *Wat. Sci. Tech.*, **42**(9), pp. 151–158.

Schrank, S.G., Jose, H.J., Moreira, R.F.P.M., Schroder, H.F., 2005: Applicability of Fenton and H2O2/UV reactions in the treatment of tannery wastewaters, Chemosphere 60, 644–655.

Sievers, M., Ried, A., Koll, R., 2004: Sludge treatment by ozonation evaluation of full-scale results. *Water Science and Technology,* **49**(4), pp. 247–253.

Spinosa, L., 2001: Evolution of sewage sludge regulations in Europe, *Water Science and Technology*, **44**(10), pp. 1-8.

Spinosa, L. and Vesilind, P. A., 2001: Sludge into biosolids: Processing, disposal and utilization. IWA Publishing, London.

Stuckey, D.C., Mc Carty, P.L., 1978: Thermochemical pretreatment of nitrogenous materials to increase methane yield, *Biotechnol. Bioeng. Symp*., **8**, pp. 219-233**.**

Sykes, R.M., 2003: *Biological wastewater treatment processes*. *In*: Chen, W-F. & Liew, J.Y.R. (eds.), The Civil Engineering Handbook, 2nd Edition, CRC Press LLC, Boca Raton, Florida.

TAKY, 2004: Tehlikeli Atıkların Kontrolü Yönetmeliği, 14 Mart 2005 Tarih ve 25755 Sayılı Resmi Gazete, Çevre ve Orman Bakanlığı.

Tanaka, S., Kobayashi, T., Kamiyama, K., Bildan, M.L., 1997: Effects of thermochemical pre-treatment on the anaerobic digestion of waste activated sludge, *Water Sci Technol*., **36**(8), pp. 209–215.

Tchobanoglous, G., Burton, F.L. and Stensel, H.D., 2003: Wastewater engineering: Treatment, disposal and reuse, *4th ed. rev. and up.* Metcalf and Eddy, Inc. - McGraw-Hill Education, Boston.

TEDAS, 2010: Official Web Site of Turkiye Elektrik Dagitim Anonim Sirketi (TEDAS) Geneli 2010 Yili Fonsuz Tarifesi, www.tedas.gov.tr.

Tiehm, A., Nickel, K. and Neis, U., 1997: The use of ultrasound to accelerate the anaerobic digestion of sewage sludge, *Wat. Sci. Tech.*, **36**(11), pp. 121–128.

Tiehm, A., Nickel, K., Zellhorn, M., Neis, U., 2001: Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, *Water Reserach*, **35**(8), pp. 2003– 2009.

TKKY, 2005: Toprak Kirliliği Kontrolü Yönetmeliği, 31/05/2005 tarih ve 25831 sayılı Resmi Gazete, Çevre ve Orman Bakanlığı.

Ultrawaves, 2008a: The Ultrawaves reactor. Last Access: 30 April 2008, from: http://www.ultrawaves.de/en/the_ultrawaves_reactor.htm.

United Tech, I., 2003: Anaerobic Digestion, UTI Web Design.

U.S. Environmental Protection Agency, 1987: Design Manual-Phosphorus Removal, U.S. EPA/625/1-87/001, Cincinnati, Ohio.

Valo, A., Carrère, H. and Delgenès, J.P., 2004: Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion, *J. Chem. Technol. Biotechnol,*. **79**(11), pp. 1197-1203.

Wang, Q., Kuninobu, M., Kakimoto, K., Ogawa, H. I. and Kato, Y., 1999: Upgrading of anaerobic digestion of waste activated sludge by ultrasonic pretreatment, *Bioresource Technology*, **68**, pp. 309-313.

Wang, F., Lu, S., Ji., M., 2006: Components of released liquid from ultrasonic waste activated sludge disintegration, Ultrason. Sonochem., **13**, pp. 334–338.

Wang, F., Lu, S., Ji, M., 2005: Components of released liquid from ultrasonic waste activated sludge disintegration, *Ultrasonics Sonochemistry*, **13**(4), pp. 334-338.

Wang, F., Wang, Y., Ji, M., 2005: Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration, *Journal of Hazardous Materials*, **B123**, pp. 145–150.

Wang, F., Wang, Y., Ji, M., 2005a: Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration, *Journal of Hazardous materials*, **B 123**, pp. 145-150.

Winter, A., 2002: Minimisation of costs by using disintegration at a full-scale anaerobic digestion plant, *Water Sci. Technol.*, **46**(4–5), pp. 405–412.

Winter, J., Temper, U., 1987: Microbiology of the anaerobic wastewater treatment, Sewage Waste Recycle 38, pp. 14-21.

Wolff, H.J., Nickel, K., Houy, A., Lundén, A. and Neis, U., 2007: Two years experience on a large German STP with acoustic disintegration of waste activated sludge for improved anaerobic digestion. In Proceedings of: *Bioenergy for our future, 11th IWA World Congress on Anaerobic Digestion*, Brisbane, Australia, 23-27 September.

Woodard, S.E. and Wukasch, R.F., 1994: A hydrolysis/thickening/filtration process for the treatment of waste activated sludge, *Water Science Technology*, **30**, pp. 29-38.

Xie, R., Xing, Y., Ghani, Y.A., Ooi, K.E. and Ng, S.W., 2007: Full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge, *J. Environ. Eng. Sci*., **6**(5), pp. 533-541.

Xie, B., Liu, H. and Yan, Y., 2009: Improvement of the activity of anaerobic sludge by low-intensity ultrasound, *Journal of Environmental Management,* **90**, Issue 1, January 2009, pp. 260-264.

Yasui, H., Komatsu, K., Goel, R., Li, Y.Y., Noike, T., 2005: Full-scale application of anaerobic digestion process with partial ozonation of digested sludge, *Water Science and Technology*, **52**(1–2), pp. 245–252.

Yeager, J.G. and O'Brien, R.T., 1983: Irradiation as a means to minimise public health risks from sludge-borne pathogens, *J. WPCF*, **55**(7), pp. 977–983.

Yeom, I.T., Lee, K.R., Lee, Y.H., Ahn, K.H. and Lee, S.H., 2002: Effects of ozone treatment on the biodegradability of sludge from municipal wastewater treatment plants, *Water Science and Technology,* **46**(4-5)**,** pp. 421-425.

Yuan, H.Y., Chen, Y.G., Zhang, H.X., Zhou, Q., Gu, G.W., 2006: Improved bioproduction of short-chain fatty acids (SCFAs) from excess sludge under alkaline conditions, *Environ. Sci. Technol*., **40**(6), pp. 2025-2029.

Zabranska, J., Dohanyos, M., Jenicek, P., Kutil, J., 2006: Disintegration of excess activated sludge – evaluation and experience of full-scale applications, *Water Sci. Technol.*, **53**, pp. 229-236.

Zhao, Y.X., Yin, J., Yu, H.L., Han, N. and Tian, F.J., 2007: Observations on ozone treatment of excess sludge, *Water Science and Technology,* **56**(9), pp. 167-175.

CURRICULUM VITAE

Candidate's full name: Ezgi KURDOĞLU

Place and date of birth: Elbistan/ 23.10.1984

Permanent Address: Acıbedem Cad. Genç Sok. Beyazsaray apt. 18/5 Acıbadem /İSTANBUL

Universities and Colleges attended: İstanbul Technical University / Osmangazi Anatolian High School