THÈSE

En vue de l'obtention du

DOCTORAT DE L'UNIVERSITÉ DE TOULOUSE

Délivré par :

Institut National Polytechnique de Toulouse (INP Toulouse)

Discipline ou spécialité :

Génie des Procédés et de l'Environnement

Présentée et soutenue par :

M. NGOC TUAN LE
le lundi 9 décembre 2013

Titre :

OPTIMISATION OF SLUDGE PRETREATMENT BY LOW FREQUENCY SONICATION UNDER PRESSURE.
Optimisation du prétraitement de boues par ultrasons à très basses fréquences et sous pression.

Ecole doctorale :
Mécanique, Energétique, Génie civil, Procédés (MEGeP)

Unité de recherche :
Laboratoire de Génie Chimique (L.G.C.)
Directeur(s) de Thèse :
M. HENRI DELMAS
MME CARINE JULCOUR-LEBIGUE

Rapporteurs :
M. JEAN-YVES HIHN, UNIVERSITE DE BESANCON
Mme EVELYNE GONZE, INRA UNIVERSITE DE SAVOIE

Membre(s) du jury :
M. IORDAN NIKOV, POLYTECH LILLE, Président
M. HENRI DELMAS, INP TOULOUSE, Membre
Mme CARINE JULCOUR-LEBIGUE, INP TOULOUSE, Membre
Mme HÉLÈNE CARRERE, INRA NARBONNE, Membre
M. PASCAL TIERCE, SINAPTEC, Membre
M. XAVIER LEFEBVRE, INSA TOULOUSE, Membre

ACKNOWLEDGEMENTS

Apart from my efforts, the success of this work depends largely on the encouragement and guidelines of many others.

Foremost, I would like to express my sincere gratitude to my supervisors Prof. Henri DELMAS and Dr. Carine JULCOUR for the continuous support of my post-graduate work, for their patience, motivation, enthusiasm, and immense knowledge. Their guidance helped me in all the time of conducting the research and writing this thesis.

In addition, I would like to say a big thank you to the jury – Prof. Evelyne GONZE, Prof. Jean Yves HIHN, Prof. Helène Carrère, Prof. Iordan NIKOV, Mr. Pascal TIERCE, Dr. Xavier LEFEBVRE - for the precious time reading my thesis and valuable constructive comments.

I would like to acknowledge the financial support from the Ministry of Education and Training of Vietnam and Institut National Polytechnique of Toulouse (France).

Besides, my sincere thanks also goes to Alexandrine BARTHE (Ginestous), Berthe RATSIMBA, Laurie BARTHE, Ignace COGHE, Jean-Louis LABAT, Jean-Louis NADALIN, Lahcen FARHI (LGC), Bernard GALY, Christine REY-ROUCH, Marie-line PERN, Sylvie SCHETRITE (SAP, LGC), Xavier LEFEBVRE, Anil SHEWANI, Beatriz MORENTE, Delphine DELAGNES (INSA), and SinapTec Company for their technical and analytical support.

I appreciate my friends: Ngoc Chau PHAM, Alain PHILIP, Fillipa VELICHKOVA, Imane, BENHAMED, Benjamin BOISSIERE, Supaporn KHANGKHAM, Nicholas BRODU, Benjamin BONFILS, and others for their help, encouragement, and insightful comments for the whole time we were working together, and for all the fun we have had in the last three years.

Last but not the least, I would like to thank my parents LE Ut and NGUYEN Thi Chit for giving birth to me and supporting me spiritually throughout my life, my brothers and sisters for encouraging me, and my sweet love for everything.

LIST OF NOMENCLATURES AND ABBREVIATIONS

Label	***Unit***	***Definition***
A	m^2	Surface area of the probe
AD		Anaerobic Digestion
BMP		Biochemical Methane Potential
BP		35 mm diameter probe (big probe)
c	m/s	Velocity of sound
CCOD	g/L	Colloidal Chemical Oxygen Demand (concentration of supernatant liquid filtered between 0.2 µm and 1 µm pore size membrane)
COD		Chemical oxygen demand
CST	s	Capillary Suction Time
D[4,3]	µm	Volume moment mean particle diameter
DD_{COD}	%	Disintegration degree of sludge based on *COD* if not mentioned otherwise $DD_{COD} = (SCOD - SCOD_0) / (SCOD_{NaOH} - SCOD_0) * 100\ (\%)$
DNA		DeoxyriboNucleic Acid
D_{US}	(k)W/L	Ultrasonic density $D_{US} = P_{US} / V$
EPS		Extracellular Polymeric Substances
ES	(k)J/kg$_{TS}$	Specific energy input / Energy per total solid weight $ES = (P_{US} * t) / (V * TS)$
F_S	kHz	Sound frequency
γ	s^{-1}	Shear rate
I_{US}	(k)W/Im^2	Ultrasonic intensity $I_{US} = P_{US} / A$

K	Pa.s^n	Consistency coefficient (Herschel–Bulkley model)
μ_{app}	Pa.s	Apparent viscosity (τ / γ)
n		Flow behavior index (Herschel–Bulkley model)
OUR		Oxygen Utilization/Uptake Rate
P	bar (Pa)	Pressure in the bubble at its maximum size
P_a	bar (Pa)	Acoustic pressure $P_a = P_A \sin 2\pi F_S t$
P_A	bar (Pa)	Maximum amplitude of acoustic pressure $P_A = (2 * I_{US} * c * \rho)^{1/2}$
P_h	bar (Pa)	Hydrostatic pressure
P_m	bar (Pa)	Total solution pressure at the moment of transient collapse
PSD		Particle Size Distribution
P_{US}	(k)W	Ultrasonic power input
P_V	bar (Pa)	Vapour pressure of the liquid
ρ	kg/m^3	Density of the medium
RNA		RiboNucleic Acid
SCOD	g/L	Soluble chemical oxygen demand in the supernatant after treatment (concentration of supernatant liquid filtered through 0.2 µm pore size membrane)
$SCOD_0$	g/L	Soluble chemical oxygen demand in the supernatant before treatment
$SCOD_{NaOH}$	g/L	Soluble chemical oxygen demand after strong alkaline disintegration of sludge
SP		13 mm diameter probe (small probe)
SRF	m/kg	Specific Resistance to Filtration
SS	g/L	Suspended Solids
S_{TS}	%	Solubilisation yield of Total Solids

S_{VS}	%	Solubilisation yield of Volatile Solids
t	min	Sonication duration
τ	Pa	Shear stress
T	°C	Temperature
τ_0	Pa	Yield stress
TCOD	g/L	Total Chemical Oxygen Demand
TDS	g/L	Total Dissolved Solids
TOC	g/L	Total organic carbon
TS	g/L	Total solids
US		UltraSonication / UltraSound irradiation
V	L	Volume of sludge
VS	g/L	Volatile solids
WAS		Waste Activated Sludge
WWTP		WasteWater Treatment Plants

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

1. BACKGROUND OF THE PROBLEM

The activated sludge process is the most widely used biological treatment for eliminating organic and nitrogen pollutants in domestic wastewater. At the end of the process, a large amount of excess bacterial biomass (sludge) needs to be treated, *e.g.* more than a million tons of dry matter per year in France. Therefore, sludge management is a major issue as it represents about 50-60% of the total expense of wastewater treatment plants (*WWTP*) (Nowak, 2006; Banu *et al.*, 2009).

Incineration, ocean discharge, land spreading, and composting are the most common sludge disposal options used over the years, but no longer sustainable due to economic reasons or negative impacts on environment. Therefore, anaerobic digestion (*AD*) has been applied as an efficient and sustainable technology thanks to mass reduction, odor removal, pathogen decrease, less energy use, and energy recovery in the form of methane (CH_4). However, the first stage of *AD* process, hydrolysis, is the rate-limiting step of microbial conversion and requires a pretreatment that ruptures cell walls and facilitates the release of intracellular matters into the aqueous phase.

There are some very popular techniques applied in sludge pretreatment, *e.g.* biological (aerobic and anaerobic processes), mechanical (*US* pretreatment, lysis-centrifuge, liquid shear, grinding, etc.), chemical (oxidation, alkali, acidic pretreatment, etc.), electrical methods, and thermal hydrolysis (>100°C) (Carrère *et al.*, 2010).

Pilli *et al.* (2011) reported in their review that ultrasonication (*US*) is a feasible and promising mechanical disruption technique for sludge disintegration and microorganism lysis, with improvement in sludge biodegradability (Khanal *et al.*, 2007), increase in methane production (Onyeche *et al.*, 2002; Barber, 2005; Khanal *et al.*, 2007), no need for chemical additives (Mao *et al.*, 2004), less sludge retention time (Tiehm *et al.*, 1997), and sludge reduction (Onyeche *et al.*, 2002).

Many studies aiming at optimization of *US* efficiency have been conducted. However, there is lack of researches on the individual and integrated effects of some key *US* parameters as well as external conditions of sludge pretreatment, *i.e.* process conditions (stirrer speed, temperature, pressure), *US* parameters (power -P_{US}, intensity -I_{US}, specific energy input -*ES*, and frequency -F_S), and sludge characteristics (sludge type, total solids *TS* concentration, sludge pH). The objective of this work is therefore to optimize high-power low-frequency sonication pretreatment of sludge, and especially to emphasize for the first time the effects of hydrostatic pressure and frequency –down to audible range- which are expected to enhance sludge disintegration, to save energy input, and to facilitate the anaerobic digestion. Sludge ultrasonic pretreatment is generally assessed mainly based on disintegration degree (or solubilisation yield of chemical oxygen demand). Here we also add examination of particle size reduction, morphology changes, and the evolution of sludge viscosity.

2. ORGANIZATION OF THE STUDY

The *Introduction*presents the background of the environmental problem due to sludge massive production, and the potential use of ultrasound as sludge pretreatment. *Literature review* is discussed in details in **Chapter 1**. In this chapter, sludge type is depicted first. Researches in sludge *US* pretreatment field are collected and displayed in three main sections: brief background of *US* pretreatment of sludge, approaches to assess its efficiency, and optimization efforts in literature. **Chapter 2** introduces *Research methodology* where outline of research plan, sludge samples, sonication apparatus, and analytical methods are detailed. Findings of this work are shown in the next chapters. **Chapter 3** exhibits *Preliminary study of operation parameters* whereat effects of solid concentration, sludge type, sludge pH (alkaline addition), stirrer speed, and thermal effects are taken into consideration. In addition to *COD* solubilisation, the changes of particle size distribution, morphology, and viscosity are investigated. *Effect of ultrasound parameters* on sludge disintegration is presented in **Chapter 4**, including *US* power, intensity, and frequency. For the first time *Effect of hydrostatic pressure* is taken into account and reported in **Chapter 5**. This chapter aims at investigating the interaction between P_{US}, I_{US}, F_S, and pressure and their effects on isothermal sludge pretreatment. *Optimal sonication pretreatment of sludge* is described in **Chapter 6**. Optimum conditions of P_{US}, I_{US}, F_S, T, pressure, *TS*, and sequential sonication are discussed. Long term *AD* runs of some pretreated sludge are also carried out to quantify the effects of *US* pretreatment.

CHAPTER 1

LITERATURE REVIEW

Incineration, ocean discharge, land application, and composting are the common ways used for sludge disposal over the years, but they are no longer sustainable due to high costs and/or negative impacts on the environment. Therefore, anaerobic digestion (*AD*) of sludge has been applied as an efficient and sustainable technology for sludge treatment, allowing mass reduction, odor removal, pathogen decrease, and energy recovery in the form of methane.

AD of sludge is a complex and slow process requiring high retention time to convert degradable organic compounds to CH_4 and CO_2 in the absence of oxygen through four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Hydrolysis is known as the rate-limiting step, in which the intracellular biopolymers solubilize and convert to lower molecular weight compounds. This low rate of microbial conversion requires a pretreatment of sludge which ruptures the cell wall and facilitates the release of intracellular matter into the aqueous phase to improve biodegradability and enhance *AD*.

There are some very popular techniques used in sludge pretreatment, such as biological, thermal, mechanical, chemical, and electrical methods. Biological treatment provides a moderately better performance over the mesophilic digestion with mild energy input. Mechanical methods (*US* pretreatment, lysis centrifugation, liquid shear disruption, grinding, *etc*.) also provide a moderate performance improvement with moderate electrical input. Meanwhile, thermal hydrolysis (>100°C) provides a significant increase in performance with a substantial thermal energy consumption. Chemical methods (oxidation, alkali, acidic pretreatment, *etc*.) are also applied in sludge pretreatment (Carrère *et al*., 2010). Recent studies have taken intense electric fields into account (Kopplow *et al*., 2004; Rittmann *et al*., 2008; Salerno *et al*., 2009; Keles *et al*., 2010; Mahmoud *et al*., 2010; Pham, 2011; Rynkiewicz, 2011).

In their review, Pilli *et al*. (2011) claimed *ultrasonic irradiation (US)* to be a feasible and promising mechanical disruption technique for sludge disintegration and microorganism lysis according to the treatment time and power, equating to specific energy input *(ES)*. Some positive characteristics of this method are efficient sludge disintegration (Pilli *et al*., 2011), improvement in biodegradability and bio-solid quality (Khanal *et al*., 2007), increase in biogas/methane production (Onyeche *et al*., 2002; Barber *et al*., 2005; Khanal *et al*., 2007), no need for chemical additives (Mao *et al*., 2004), less sludge retention time (Tiehm *et al*., 1997), and sludge reduction (Onyeche *et al*., 2002).

1.1. SLUDGE TYPES AND PROPERTIES

Primary sludge is produced through the mechanical wastewater treatment process. It occurs after the screen and the grit chamber and contains untreated wastewater contaminations. The sludge amassing at the bottom of the primary clarifier is also called primary sludge. It is decayable and must be stabilized before being disposed of (Liu and Liptak, 1999). The composition of this sludge depends on the characteristics of the collecting area. Primary sludge is easily biodegradable since it consists of more easily digestible carbohydrates and fats (faeces, vegetables, fruits, textiles, paper, *etc*.). Biogas therefore is more easily produced from primary sludge but the methane content of the gas is lower.

Activated sludge comes from the secondary wastewater treatment. In the secondary treatment, different types of bacteria and microorganisms biodegrade the organic matter and consume oxygen to live, grow and multiply. The resulting sludge from this process is called waste activated sludge (*WAS*). Normally, a part of the *WAS* is returned back to the system (called return activated sludge) and the remaining is removed at the bottom of the secondary clarifier (called excess sludge or secondary sludge). Overall, the sludge has the same properties, but different names regarding its usage. *WAS* consists largely of biological mass, *i.e.* proteins (30%), carbohydrates (40%) and lipids (30%) in particulate form (Lin *et al.*, 1999), as well as large amount of pathogens. It causes odour problems and thus must be stabilized. Besides, activated sludge is more difficult to digest than primary sludge.

Activated sludge floc is a heterogeneous mixture of particles, microorganisms, colloids, organic polymers and cations whose composition depends on the origins (Forster 1976; Urbain *et al.*, 1993). Flocs have three structural levels (Fig. 1.1): microflocs, which are primarily particles of 2.5 µm in size, secondary particles (13 µm) linked together by exo-polymers and forming tertiary structures having a mean diameter of 125 µm (Jorand et al.,1995; Chu *et al*., 2001).

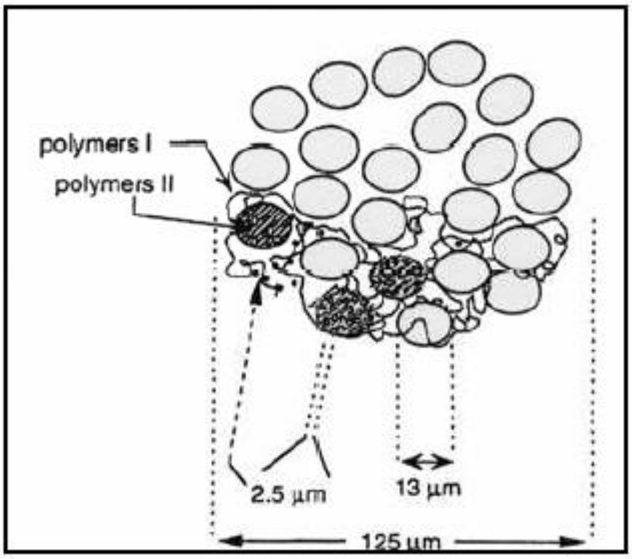


Fig 1.1: Model of an activated sludge floc (Jorand *et al*., 1995)

Digested sludge is the residual product after *AD* of primary and activated sludge. The digested sludge is reduced in mass, less odorous, and safer in the aspect of pathogens and easier dewatered than the primary and activated sludge types (Liu and Liptak, 1999).

1.2. BRIEF BACKGROUND OF SONICATION

The diagram of sonication range is presented in Fig. 1.2

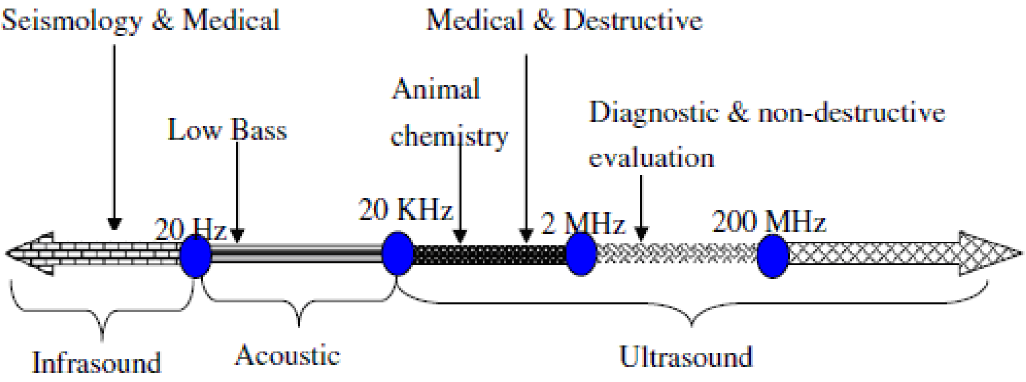


Fig 1.2: Diagram of sonication range (Pilli et al., 2011)

When an acoustic field is applied, the sonic vibrations create an acoustic pressure (P_a) which must be considered to be additional to the ambient hydrostatic pressure (P_h) already present in the medium:

$$P_a = P_A \sin 2 \pi F_S t$$

where F_S is the sound frequency and P_A is the maximum pressure amplitude of the wave. The intensity of the wave (I) is the energy transmitted per time unit and per surface unit of fluid:

$$I = P_A^{2} / (2\,\rho\, c) = (\rho\, c / 2)\, (a\, \omega)^2$$

where ρ is the density of the medium, c is the velocity of sound in that medium, a is the amplitude (half the height difference between a peak and a trough), and ω is the angular frequency (= $2\pi\, F_S$).

When propagating in a solution, ultrasound waves generate compressions (they cause a positive pressure on the liquid by pushing molecules together) and rarefactions (they cause a negative pressure by pulling molecules one from each other). If a sufficiently large negative pressure is applied during rarefaction, acoustic cavitation will take place.

It is now clearly stated that most of ultrasound outstanding effects are due to acoustic cavitation. Acoustic cavitation is a very complex highly non-linear phenomenon which occurs at given acoustic pressure conditions (needing rather high ultrasound intensity, > 1 W/cm^2 in water at room conditions). Micro-bubbles are generated from nuclei -favored by dissolved gas, wall defects, and liquid impurities- during the low pressure half periods (bubble formation and expansion). They may oscillate a few periods, undergoing a slow average growth due to the so called –rectified diffusion” process (up to several µm) and suddenly, reaching a critical size, they dramatically grow during the low pressure half period and collapse violently in a very short fraction of the high pressure half period. Most often the bubble breaks up after the collapse point, giving smaller bubbles ready to reproduce the same scenario: oscillatory growth, driven by rectified diffusion, then sudden collapse (as schematized on Fig. 1.3). Such a fast collapse being nearly adiabatic gives rise to extreme conditions inside and around the collapsing bubble.

Theoretical considerations by Noltingk and Neppiras (1950), Flynn (1964), Neppiras (1980), and Lorimer and Mason (1987), assuming adiabatic collapse of the bubbles, allow for the calculation of the maximal temperature *(T_{max})* and pressure *(P_{max})* within the bubble at the end of collapse (bubble rebound):

$$T_{\max} = T_o \left\{ \frac{P_m\ (\gamma - 1)}{P} \right\}$$

$$P_{\max} = P \left\{ \frac{P_m (\gamma - 1)}{P} \right\}^{\left(\frac{\gamma}{\gamma - 1}\right)}$$

where T is the ambient temperature, γ is the ratio of the specific heats of gas (or gas vapour) mixture, P is the pressure in the bubble at its maximum size and is usually assumed to be equal to the vapour pressure (P_V) of the liquid. P_m is total solution pressure at the moment of transient collapse ($P_m = P_h + P_a$).

Such models and experimental validations suggest that final collapse leads to a temperature as high as 5000 K at the bubble center, a pressure of 500 bar, and a high radial velocity -up to the sound speed- then shock waves at the bubble rebound. These cavitation characteristics have different impacts on the sonicated media: high temperature peaks produce very active free radicals (mainly OH• in aqueous media), giving the way to intense radical chemistry either inside or at the interface of the cavitation bubble depending on the volatility of the target dissolved molecules. On the other hand, high pressure, high velocity gradients, and shock waves have mainly physical effects through very strong micro turbulence and intense local mixing, increasing heat and mass transfer. These physical effects are even more efficient in multiphase systems and especially on solid surfaces due to asymmetrical collapse with projection of a very fast jet towards the solid close to cavitation bubbles. This is the main cause of ultrasonic cleaning and also of most of ultrasonic solid processing, such as sludge disintegration.

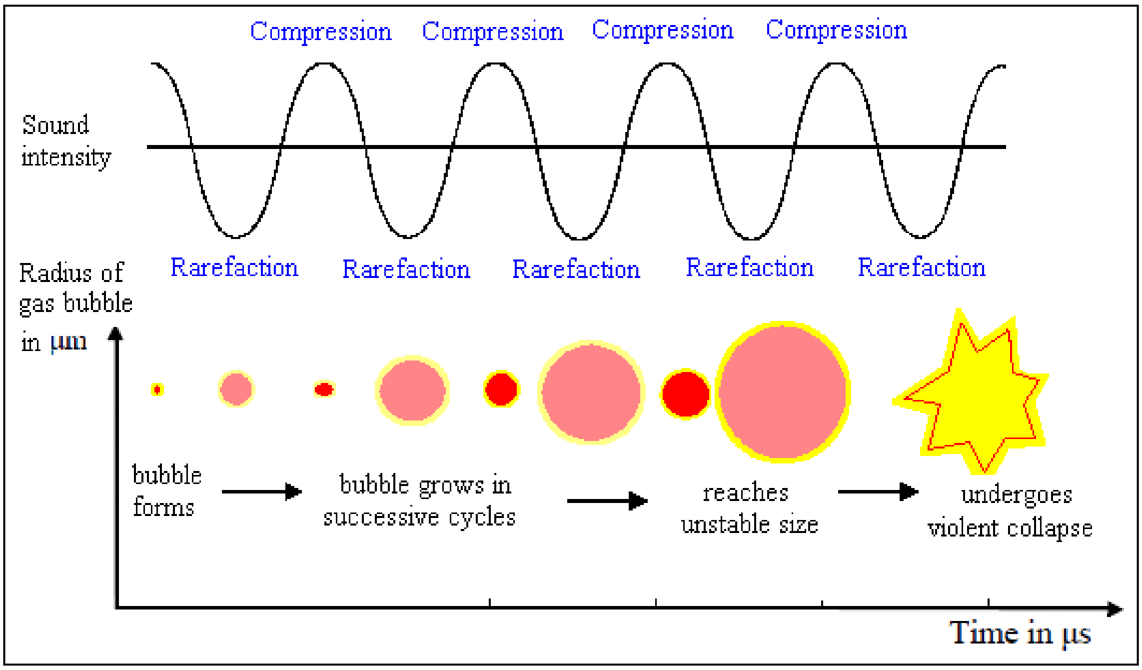


Fig 1.3: Formation and collapse process of a cavity

When applied to solid suspension and especially for sludge treatment the power/energy may be expressed in many ways as given in Table 1.1: specific energy input *ES*, *US* dose, *US* density, and *US* intensity.

Table 1.1: Expressions of *US* energy for sludge disintegration

No.	Parameter	Expression	Unit	Reference
1	Specific energy input	$ES = (P_{US} * t) / (V * TS)$	J/kg$_{TS}$	Feng *et al.*, 2009
2	Ultrasonic dose	$DO_{US} = P_{US} * t / V$	J/L	Tiehm *et al.*, 2001
3	Ultrasonic density	$D_{US} = P_{US} / V$	W/L	Tiehm *et al.*, 2001
4	Ultrasonic intensity	$I_{US} = P_{US} / A$	W/cm^2	Neis *et al.*, 2000

P_{US}: power input (W), *t:* sonication duration (s), *V*: volume of sludge (L), *TS*: total solid concentration (kg/L), *A*: surface area of the probe (cm^2)

The piezoelectric generator is one of the most common techniques for generating ultrasound. This apparatus is comprised of three major parts: converter, booster, and horn (or probe). In *the converter* (transducer), the piezoelectric ceramics is put in the electric fields with varying polarity which causes changes in its dimension. These repeated changes create ultrasound of a specific frequency. *The booster* is designed to control (increase or decrease) the amplitude of the ultrasonic energy before it is delivered to the liquid through the horn (sonotrode). These three parts are stacked by clamping at the nodal points of either the converter or the booster. *The horn,* like the booster, also contributes to the amplification of the *US*; therefore the half or full wavelength design of the horn depends on the application of this apparatus. Furthermore, the design of the horn, enhanced by the power input levels, impacts on the intensity of the sonication, which indicates the magnitude of the ultrasonic motion, in other words, the amplitude of the vibration. An example of *US* set-up is presented in Fig. 1.4.

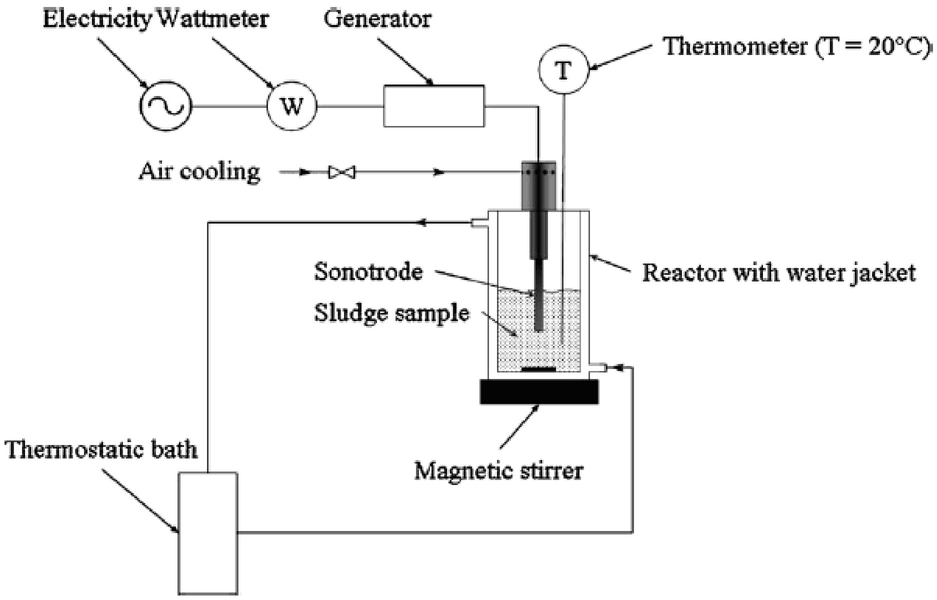


Fig 1.4: Ultrasonic set-up (Kidak et al., 2009)

Wang *et al*. (2005) indicated that the mechanisms implied in *US* sludge disintegration are hydro-mechanical shear forces, oxidizing effect of OH•, H•, N•, and O• produced under *US*, and thermal decomposition of volatile hydrophobic substances in the sludge due to the increase in temperature during sonication. The effect of hydro-mechanical shear forces is nevertheless much higher than that of radicals.

1.3. EVALUATION APPROACHES OF SLUDGE ULTRASONIC PRETREATMENT EFFICIENCY

Ultrasonic irradiation (US) is a feasible and promising mechanical disruption technique for sludge disintegration, biodegradation acceleration, and *AD* enhancement. Ultrasonic cell lysis was first studied at lab-scale in the 1960s, but it was initially found uneconomical due to limitations of the *US* equipment at that time (Roxburgh *et al*., 2006). In the last fifteen years, researches on *US* application for sludge disintegration have developed, as illustrated by the works of Chiu *et al*. (1997), Tiehm *et al*. (1997, 2001, 2002), Wang *et al*. (1999), Neis *et al*. (2000), Chu *et al*. (2002), Onyeche *et al*. (2002), Gonze *et al*. (2003), Bougrier *et al*. (2006), Cao *et al*. (2006), Bragulia *et al*. (2006), *etc*. Advances in *US* technology in the last decade have enabled commercial applications, especially for wastewater treatment. Fig. 1.5 depicts options for installation of *US* systems in *WWTP* (Ultrawaves GmbH - Water & Environmental Technologies).

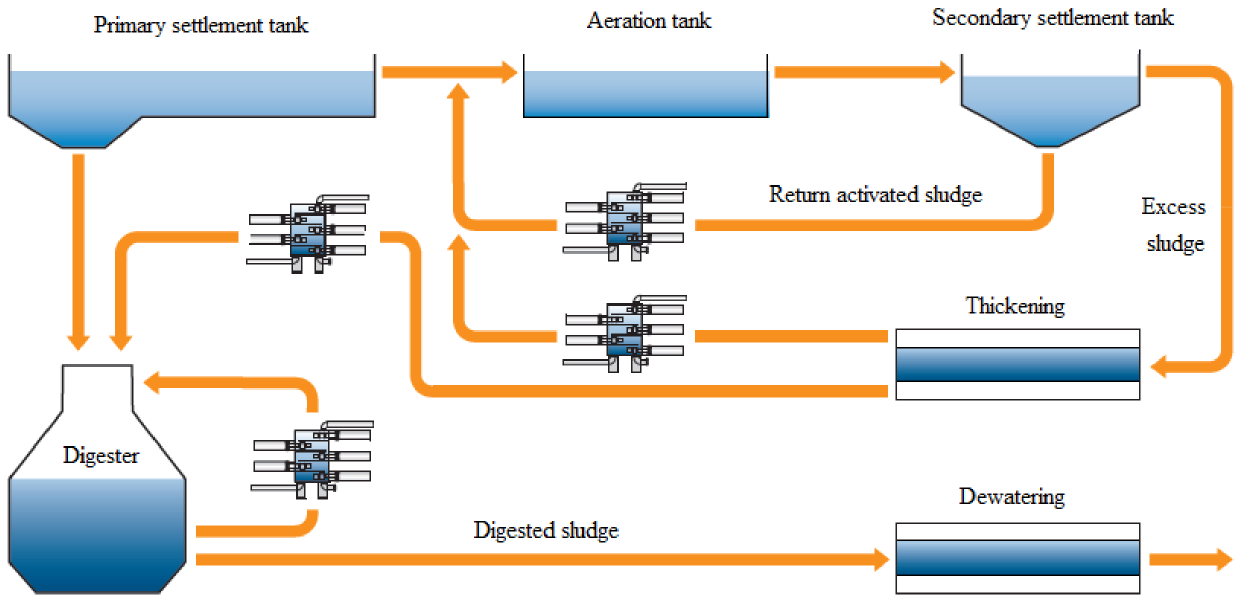


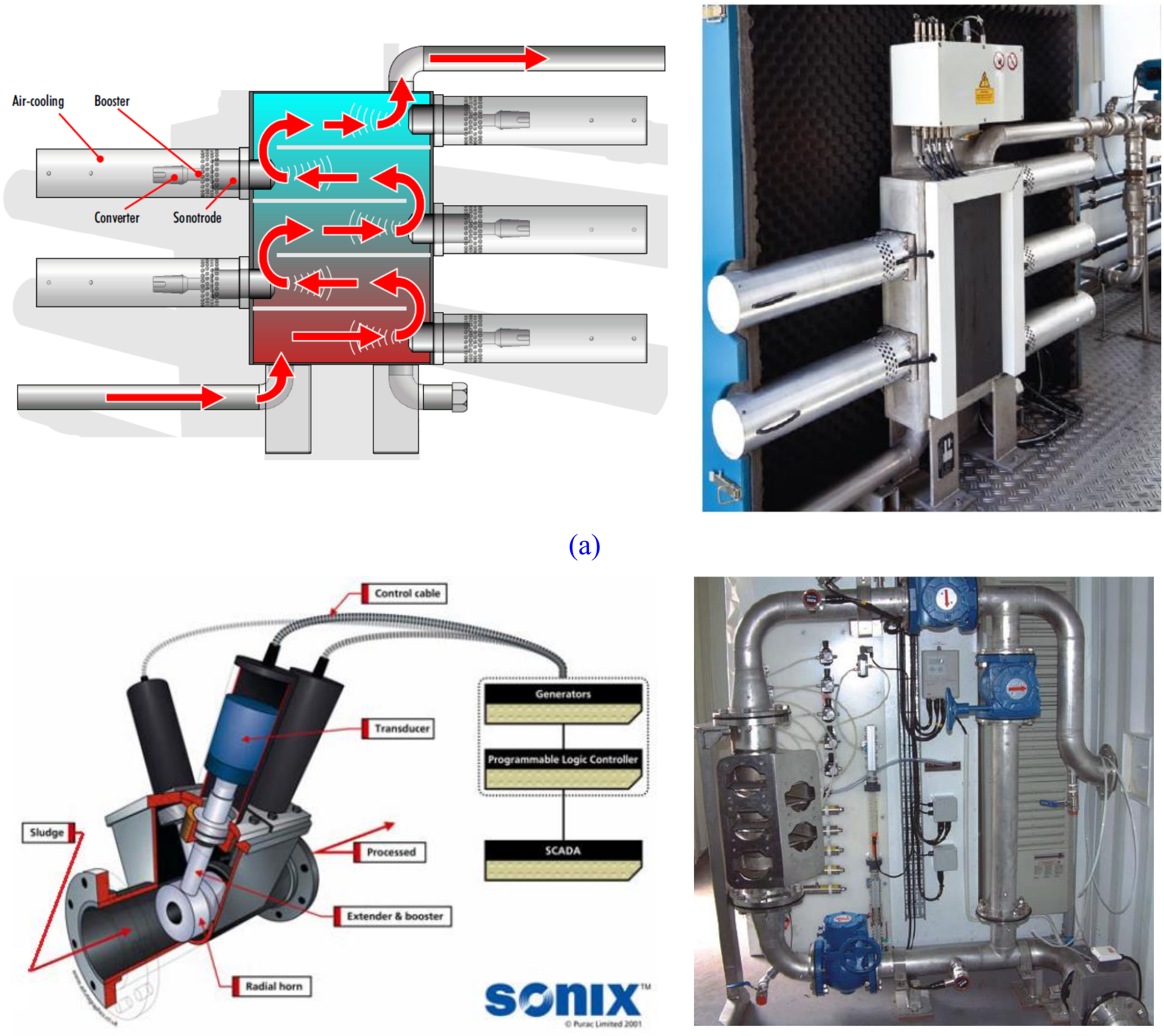
Fig 1.5: Integration of the US technology in WWTP (Ultrawaves GmbH - Water & Environmental Technologies)

Ultrawaves and *Sonix*^{TM}, whose configurations were described in Fig. 1.6, have the largest number of full-scale trials and full-scale installations in wastewater treatment, *i.e.* over 30 installations in Europe, the United States, Asia, and Australia. *Ultrawaves* is a commercial business born from the research activities at the Technical University of Hamburg-Harburg, has different trademarks such as Eimco Sonolyser, Dumo, Euro-open KFT, Sonoflux (sold by Stereau in France), *etc*. *Sonix*™ technology is supplied under licence from Sonico - a joint venture company between Purac Ltd and Atkins Water. *Sonotronic Nagel* is a worldwide provider and manufacturer of ultrasonic equipment serving a variety of industries for the last 30 years. *Sonolyzer* technology is the product of years of development between Ultrawaves and Sonotronic Nagel. For *WAS* pretreatment, *US* installations have been applied in many *WWTP*, especially in Germany, since 2000 with different capacities (Table 1.2). In general, *US* system has been operated at 20 kHz and P_{US} up to 48 kHz. According to Roxburgh *et al*., (2006), the largest installation is at Mangere *WWTP* in New Zealand, from Sonico.

Table 1.2: Full scale US applications

	WWTP	**Country**	**Capacity (*PE*)**	***US* system**	**Application year**	**Substrate / Stage**	**Ref.**
1	Heiligenstadt	Germany	52 000	Ultrawaves (20 KHz, 5 generators, 5 kW/generator, *V* = 29 L)	2003	Return sludge (For Aerobic Stabilization - *AS*)	Ultrawaves – Royce Water Technologies
2	Leinetal	Germany	50 000		2003		
3	Tanba City	Japan			2004		
4	Bamberg	Germany	230 000		2004	Primary and Thickened *WAS* for *AD*	Rossier *et al.* 2007; Ultrawaves – Royce Water Technologies
5	Meldorf	Germany	70 000		2004	(For *AD*)	
6	Zeist	Netherlands	75 000		2005		
7	Hennef	Germany	65 000		2006		
8	Kleinsteinbach	Germany	40 000		2006		Ultrawaves – Royce Water Technologies
9	Marselisborg-Arhus	Denmark	220 000		2006		
10	Pecs	Hungary	200 000		2006	Return sludge (For *AS*)	
11	Datansha	China	550 000		2006		
12	Bath	England	550 000		2006		Rossier *et al.* 2007
13	Slupsk	Germany	250 000		2007		
14	Detmold	Germany	95 000	*DMS*, 14 kW	2000	Mixed sludge	Rossier *et al.* 2007
15	Mannheim	Germany	725 000	*DMS*, 24 kW	2001	Primary : *WAS* = 1 : 1, for *AD*	Bartholomew 2002; Rossier *et al.* 2007
16	Russelsheim	Germany	80 000	*DMS*, 10 kW	2001	Mixed sludge	
17	Wiesbaden	Germany	360 000	*DMS*, 48 kW	2002	Mixed sludge	
18	Kavlinge	Sweden	100 000	Sonix^{TM}, 3-6 kW	2002	*WAS*	Rossier *et al.* 2007
19	Mangere	New Zealand	800 000	Sonix^{TM}	2005	*WAS*	
20	Rzeszow	Poland	220 000	*VTA GSD*	2003		Rossier *et al.*

21	Villach	Austria	200 000		2003		2007
22	Eberstadt	Germany	200 000		2003	Primary : *WAS* = 1/3 : 2/3	
23	Zemtralklarwerk Darmstadt	Germany	240 000		2004		
24	Halle Nord	Germany	300 000		2004		
25	GroBostheim	Germany	35 000		2004		
26	Kitzbuhel	Austria	46 500		2005		
27	Winsen/Luhe	Germany	50 000		2005		
28	Penthaz	Switzerland	10 000		2006		
29	Obersee	Germany	25 000		2006		
30	Sud	Germany	40 000	6 kW	2000	*WAS* for *AD*	Bartholomew 2002
31	Darmstadt	Germany	180 000	16 kW	2000	Primary : *WAS* = 1/3 : 2/3, for *AD*	



(a)

(b)

Fig 1.6: Configurations of (a) Ultrawaves and (b) SonixTM reactor

Some achievements from Sonix™ (a high-power *US* system for conditioning sludge) have been reported. For instance, *TS* and *VS* reduction in digesters were 40% and 50%, respectively for untreated sludge and 60% and 70%, respectively for sonicated sludge (Hogan *et al.*, 2004). Xie *et al.* (2007) showed an increase in biogas production of 15-58% (average of 45%) in the full-scale *US* installation for mixed sludge treatment. For the full-scale part-stream *US* plants in Germany, Austria, Switzerland, Italy, and Japan, biogas, *VS* reduction, and sludge dewaterability were increased by 20–50% (volume/kg fed), 20–50%, and 3–7%, respectively (Barber, 2005).

It is clear that many processing factors significantly affect cavitation and consequently the efficiency of sludge pretreatment. Therefore, assessment, comparison, and selection of optimal ultrasonic conditions for actual application of sludge pretreatment are sorely necessary. An extensive review of approaches to evaluate sludge ultrasonic pretreatment efficiency is presented with regard to changes in:

- *Physical properties*: particle size, sludge mass and volume reduction, dewaterability, settleability, turbidity, and microscopic examination.

- *Chemical properties*: increase in soluble chemical oxygen demand (*SCOD*), nucleic acids, proteins, polysaccharides, release of NH_3, total organic carbon (*TOC*), *etc*.

- *Biological properties*: heterotrophic count and specific oxygen uptake rate.

1.3.1. Physical change-based evaluation of sludge *US* pretreatment efficiency

1.3.1.1. Particle size reduction

US pretreatment is very effective in reducing the particle size of sludge particles**,** which is analyzed by different techniques: sieves, sedimentation, electric-ozone sensing, microscopy, and laser diffraction which is usually used. The efficiency of size reduction depends on *US* parameters (P_{US}, D_{US}, *US* duration, *ES)* and sludge characteristics.

The floc size reduction improves (sludge disintegration efficiency also improves) with the increase in both P_{US} and D_{US} (Show *et al.* 2007; Pilli *et al.*, 2011), *e.g.* 60% and 73% at 2 W/mL and 4 W/mL, respectively (Mao *et al.*, 2004). Chu *et al.* (2001) showed that after 40 min *US* at 0.11 W/mL, the architecture of flocs was basically the same as that of the raw sludge (although the floc structure became looser and some filamentous bacteria were exposed). Meanwhile, the structural integrity of flocs was almost completely broken down after 40 min *US* at 0.33 W/mL. Thereby, there is a critical P_{US} value beyond which the sludge flocs could be sufficiently disintegrated.

Besides, the particle size also reduces owing to the increase in *US* duration (Tiehm *et al.*, 1997; Show *et al.*, 2007), but beyond 10 min of sonication, the particle size can exhibit a reverse trend (Gonze *et al.*, 2003) due to re-flocculation of the particles. However, this phenomenon was not recorded by Show *et al.* (2007) even after 20 min of sonication.

In terms of *ES*, 1000 kJ/kg_{TS} may be the disruption threshold of usual flocs (Feng *et al.*, 2009a). Following the increase in *ES*, *US* causes a decrease in particle size (Tiehm *et al.*, 2001; Gonze *et al.*, 2003; Feng *et al.*, 2009a). For example, the volume occupied by particles of less than 1 µm increased from 0.1% in the raw sludge to 1.5% in the pretreated one at *ES* of 14550 kJ/kg_{TS} (Bougrier *et al.*, 2005). Mean particle size of sludge decreased from 33.8 µm to 10.1–13.3 µm when *ES* increase in the range of 0-15000 kJ/kg_{TS} (El-Hadj *et al.*, 2007).

Show *et al.* (2007), Na *et al.* (2007), and Pilli *et al.* (2011) agreed that flocs above 4.4 microns showed more disruption probability as they exhibit a larger surface area and less strong binding forces.

With regard to the sludge type, the particles of flocculated sludge in *AD* were reduced by more than 50% in size after *US* compared to those of raw sludge (Chu *et al.*, 2002). Similarly, within 20 min of sonication, the disintegration was more significant in secondary sludge (85%) than in primary sludge (71%) because the former contains mostly biomass (microbial cells) whereas the latter mainly consists of settle-able solids (fibers and less degradable cellulosic material) (Mao *et al.*, 2004).

For sludge *TS* concentration, the size reduced more in lower *TS* sample. d_{50} of sludge with 2% *TS* decreased by 6.5 fold at 0.67 W/mL. Higher *TS* concentrations (4% and 6%) required more D_{US} (0.83 W/mL and 1.03 W/mL, respectively) to gain the same level of particle size reduction (Akin *et al.*, 2006).

In short, *US* pretreatment significantly decreases the particle size of sludge, especially in the very first period of sonication. Sludge particle size reduction is sometimes used to assess the degree of sludge disintegration.

1.3.1.2. Sludge mass reduction or solubilisation

The sludge mass reduction results mainly from solubilisation of the organic matters and is usually measured by the decrease in the suspended solid (*SS*) concentration. During *US* (0–30 min, 0.5 W/mL, 9.945 g_{SS}/L of raw sludge), *SS* reduction increase was almost linear with *US* duration, indicating the continuous and stable sludge floc disintegration, mass reduction, and cell lysis (Zhang *et al*., 2007). This parameter was also presented as *matter solubilisation* in Bougrier *et al*. (2006).

Apart from *SS* concentration, total dissolved solids also reflect the mass transfer from the solid into the aqueous phase. Feng *et al.* (2009a) proved the amount of soluble matters in the supernatant to be strongly affected by *US*, *e.g.* in *ES* range of 500-26000 kJ/kg$_{TS}$, the increase in total dissolved solids was 3-46% as compared to untreated sludge.

Other parameters used to assess the sludge reduction, subsequently the efficiency of sludge *US* disintegration, were the solubilisation of total solids (S_{TS}) and of volatile solids (S_{VS}). Salsabil *et al.* (2009) observed that S_{TS} increased linearly with in *ES* (3600 - 108000 kJ/kg$_{TS}$) and reached 14.7% at ES_{max}. Meanwhile, S_{VS} initially increased fast in the *ES* range of 0-31500 kJ/kg$_{TS}$ (reaching 15.8 %) and then slowed down at higher *ES* values (reaching 23% at ES_{max}). The main purpose of sludge disintegration is to transfer organic matters from the solid to the aqueous phase. The increase in soluble organic compounds can be correlated with *VS* reduction (as both *COD* and *VS* represent the organic matters of sludge). A higher S_{VS} is important for eliminating/shortening the hydrolysis step of *AD*. In addition, increasing *VS* reduction directly improves methane production during *AD*. Therefore, S_{VS} is comparatively more meaningful than S_{TS} in terms of sludge disintegration (Salsabil *et al.*, 2009; Erden and Filibeli, 2009).

1.3.1.3. Dewaterability of sludge

The capillary suction time (*CST*) and the specific resistance to filtration (*SRF*) tests (related to permeability) are both commonly used to estimate *sludge dewaterability*. Both tests are known to be empirically related but the *SRF* (based on an analysis of pressure drop for flow through a porous medium) is much more expensive and time consuming compared with the *CST* test. For *CST* test, sludge is poured into a small open tube resting on a piece of filter paper. The capillary suction pressure generated by the standard filter paper is used to extract water from the sludge. The rate at which water permeates through the filter paper varies, depending on the condition of the sludge and the filterability of the cake formed on the filter paper. The time taken for the water front to pass between these two electrodes (placed at a standard interval from the funnel) constitutes the *CST*.

Most authors agree with Gonze *et al.*(2003) that are two opposite effects of *US* on sludge dewaterability: positive for short time *US* (or low *ES*) then negative for longer *US* duration (higher *ES*).

Feng *et al*. (2009) found an increase of sludge dewaterability for an *ES* range of 0 - 2200 kJ/kg$_{TS}$, but a decrease when *ES* exceeded 2200 kJ/kg$_{TS}$, especially beyond 4400 kJ/kg$_{TS}$. Li *et al*. (2009) indicated that when DD_{COD} was too low (<2%), floc structure exhibited a limited change and sludge dewaterability was almost unchanged. When DD_{COD} was proper (2-5%), the incompact sludge flocs can be disrupted to smaller fragments and then be re-flocculated to tighter particles with the help of conditioning agents, subsequently resulting in an improvement of sludge dewaterability. When DD_{COD} was high (>7%), sludge particle size was significantly decreased, a number of fine particles were then produced, leading to the deterioration of sludge dewaterability.

According to Chu *et al*. (2001), sludge dewaterability decreases gradually with an increase in *US* duration because of the subsequent increase in small particles. After 5 min of sonication at 0.528 W/mL, Wang *et al*. (2006b) observed that *SRF* and *CST* increased from 1.67 x 10^{12} m/kg and 82 s, respectively for raw sludge to 1.33 x 10^{14} m/kg and 344 s, respectively for pretreated sludge. They linked this phenomenon to floc structure disruption, cell lysis, and release of biopolymers from extracellular polymeric substances (*EPS*) and bacteria into aqueous phase.

The authors stated that sludge particles are disintegrated to smaller size with higher surface area causing adsorption of more water, thus slowing the release of water from sludge. Moreover, the release of *EPS* in the solution creates a thin layer on the surface of the filtrating membrane acting as a barrier against the water, consequently reducing sludge dewaterability (Chen *et al*., 2001; Houghton *et al*., 2002; Wang *et al*., 2006b; Feng *et al*., 2009b). It was proved that both *EPS* and particle size have effects on sludge dewaterability but the former is considered prevalent (Feng *et al*., 2009b).

On the other hand, *SRF* and *CST* increase with the decrease in free water of the sludge, which means dewaterability shows a positive correlation with free water content. Nevertheless, despite *US* transforms interstitial water retained by *EPS* and inside cells into free water, the negative adsorption effect is predominant; thereby sludge dewaterability is deteriorated at high *ES*.

1.3.1.4. Settleability and Turbidity of sludge

Settling velocity is one of the most important settling parameters of sludge in routine process control and plays an important role in controlling the excess sludge emission and sludge bulking (Feng *et al*., 2009a).

The settleability of sludge is not enhanced by *US* treatment (Chu *et al.*, 2001). It is deteriorated when increasing *ES* due to the breakdown of flocs, decrease in particle size, and increase in *EPS* concentration in the liquid phase (Feng *et al*. 2009a).

On the contrary, the turbidity of sludge usually increases with *ES* due to particle size reduction (Tiehm *et al.*, 2001) and subsequent release of micro-particles into supernatant, which settle very slowly (Feng *et al*. 2009a).

Sludge settleability and turbidity are rarely used individually, but combined with other parameters to evaluate the efficiency of sludge *US* pretreatment.

1.3.1.5. Microscopic examination of sludge

Microscope imaging displays sludge floc and cellular level before and after sonication, thus it can be used to evaluate the disintegration degree of sludge (Chu *et al.*, 2001; Khanal *et al.*, 2006).

US pretreatment reduces average size of flocs and creates a lot of separate cells and short filaments pieces - Actinomyces (Dewil *et al*. 2006). Feng *et al*. (2009a) found that neither the floc structure nor the microbial cells were totally disintegrated, even at *ES* of 26000 kJ/kg$_{TS}$ (*TS* of 14.4 g/L), because there was still a network of filamentous bacteria in the photomicrographs of the treated sludge. Meanwhile, Chu *et al.* (2001) observed flocs and cell walls to be almost completely broken down after 40 min of *US* at 0.33 W/ml (P_{US} of 82.5 W, *ES* of 96100 kJ/kg$_{TS}$, *TS* of 8.3 g/L). This controversy may be due to different experimental conditions. It is therefore clear that *US* has considerable effects on microbial disruption but the efficiency of the disruption should be presented enclosed with process parameters (P_{US}, *ES*, *TS*, *etc*.).

1.3.2. Chemical change-based evaluation of sludge *US* pretreatment efficiency

Chemical evaluation mainly focuses on sludge disintegration efficiency (Khanal *et al.*, 2007), reflected by the degree of sludge disintegration (DD_{COD}) based on a chemical digestion reference. Besides, the ratio of soluble *COD* to total *COD (SCOD/TCOD)* is also used as it represents the release of organic matters from solid to liquid phase after *US* (*TCOD* being not significantly affected by *US* as oxidation remains very limited). Apart from *SCOD*, nucleic acids, *EPS*, ammonium nitrogen, and total organic carbon (*TOC)* concentrations are also considered as the important parameters in chemical evaluation.

1.3.2.1. Degree of disintegration (DD_{COD})

Both cellular/extracellular matter and organic debris/*EPS* of sludge are disintegrated by *US*, leading to the solubilisation of solid matters and the increase in organic matters/*EPS* concentrations in aqueous phase; thereby *SCOD* of sludge increases (Zhang *et al*., 2007). That is why the release of those components, especially *SCOD* can be used to assess sludge disintegration efficiency (Tiehm *et al*., 2001; Rai *et al*., 2004; Wang *et al*., 2006a; Nickel and Neis, 2007).

There are different approaches to determine DD_{COD} after *US*.

$$DD_{COD} = (SCOD_{US} - SCOD_0) / (SCOD_{NaOH} - SCOD_0) * 100\ (\%)$$

(Li *et al*., 2009)

where - $SCOD_{US}$ is supernatant *COD* of the sonicated sample (mg/L);

- $SCOD_0$ is supernatant *COD* of original sample (mg/L);

- $SCOD_{NaOH}$ is the *COD* release in the supernatant after NaOH digestion (the sludge sample being mixed with 0.5 M NaOH at room temperature for 24 h)

$$DD_{COD} = (SCOD_{US} - SCOD_0) / (TCOD - SCOD_0) * 100\ (\%)$$

(Bougrier *et al*., 2006; Zhang *et al*., 2007)

$$DD_{COD} = [(SCOD_{US} - SCOD_0) / COD_{Max}] * 100\ (\%)$$ (Braguglia *et al.* 2008)

where; COD_{max} is *COD* of the reference sample after complete chemical solubilisation with H_2SO_4.

It was proved that *US* sludge disintegration depends on various factors, such as F_S, I_{US}, *US* duration, D_{US}, *ES*, temperature, *TS*, sludge type/properties, *etc*., among which *US* duration, *ES*, *TS,* and temperature are the most important (Gronroos *et al*., 2005).

1.3.2.2. Nucleic acid assessment

Nucleic acids are biological molecules essential for life, and include deoxyribonucleic acid (*DNA*) and ribonucleic acid (*RNA*). Together with proteins, nucleic acids make up the most important macromolecules. The increase in nucleic acid concentration represents cell lysis, thus it is also used to evaluate the efficiency of sludge *US* pretreatment.

Zhang *et al*. (2007) measured the concentration of nucleic acids after *US* treatment and found a linear relationship between cell lysis and D_{US} (0.1-1.5 W/mL for 30 min *US*) as well as sonication time (0-30 min *US* at 0.5 W/mL).

1.3.2.3. Protein assessment

Proteins are important building blocks of bacteria with many different functions in the living cell (they catalyze chemical and biochemical reactions in living cell and outside). It was found about 70–80% of the extracellular organic carbon contained in *WAS* to be in form of proteins and saccharides (Neyens *et al*., 2004).

Under *US*, the activated sludge is disintegrated, cells are ruptured, and consequently *EPS* and cellular substances are released into the aqueous phase, resulting in an increase in protein and polysaccharide levels. It can be inferred that the rise of soluble protein increases the *AD* efficiency (Saad *et al*., 2008), thus it was used to evaluate the efficacy of sludge *US* pretreatment (Akin *et al*., 2006; Wang *et al*., 2006a; 2006b). Besides, Ca^{2+} and Mg^{2+} play a key role in binding the *EPS*. Sonication first causes a fast increase in Ca^{2+} and Mg^{2+} concentrations in the aqueous phase, but then these concentrations decrease as the cations are adsorbed by smaller sludge particles formed during *US* (Wang *et al*., 2006a).

The amounts of proteins, polysaccharides, and *DNA* in the supernatant first increase fast when *US* is applied (Feng *et al*., 2009a; 2009b). Then the release of proteins and polysaccharide slows down when sludge is almost disintegrated, but *DNA* concentration drops due to temperature increase during *US* which would denature the *DNA* (Wang *et al*., 2006a). Among those components, protein is the most released due to large quantities of exoenzymes in the flocs: a ratio of protein to polysaccharide of about 5.4 was found by Feng *et al*. (2009a).

However, the protein measurement is not common and not yet well accepted for evaluating sludge ultrasonic disintegration efficiency. Therefore, *COD* measurement is preferred for this purpose due to its simplicity and easiness in daily operation (Pilli *et al*., 2011).

1.3.2.4. The release of ammonia and soluble organic nitrogen assessment

The ammonia nitrogen concentration increases following the increase in *ES* due to the disintegration of bacterial cells and release of intracellular organic nitrogen into the aqueous phase, which is subsequently hydrolyzed to ammonia (Khanal *et al*., 2006; Akin, 2008). The disintegration of organic nitrogen from non-biological debris is also an important contribution to ammonia nitrogen (Khanal *et al*., 2007).

Bougrier *et al.* (2005) and Salsabil *et al.* 2009 claimed that total Kjeldahl nitrogen (sum of organic nitrogen and ammonia nitrogen) in the whole sludge is constant regardless of *ES*, which means *US* does not lead to nitrogen mineralization or volatilization. Following an increase in *ES*, organic nitrogen in particles decreases meanwhile organic nitrogen in soluble phase and ammonia concentrations increase. Different estimations of solubilisation of organic nitrogen were obtained: about 40% at 15000kJ/kg_{TS}-220W (Bougrier et al. 2005) and about 19.6% at 108000kJ/kg_{TS}-60W (Salsabil *et al.* 2009). Very little organic nitrogen is transformed into ammonium (NH_4^+-N).

In short, the release of ammonia and soluble organic nitrogen in the aqueous phase could be another useful indicator to assess sludge *US* pretreatment efficacy. However, a correlation between nitrogen release data and subsequent *AD* efficiency under different conditions is required to obtain a standardized method based on NH_3 data (Pilli *et al*., 2011).

1.3.2.5. TOC assessment

In agreement with *TCOD*, *TOC* of sludge (solid + liquid) stays almost constant as the organics only pass from solid to liquid phase during *US* treatment without significant oxidation. After 90 min of sonication at 200 W, Kidak *et al.* (2009) observed that the solubilisation of organics (based on *TOC* measurement in the supernatant) reached 7.9% and 22.8% for industrial and municipal sludge, respectively. This increase of *TOC* in the liquid phase was consistent with the results obtained from the *COD* analysis.

To measure *TCOD* of sludge, a pre-digestion (hydrolysis) step is needed which somehow may not allow the solubilisation of all solid particles. Besides, there are also some refractory organics which are not oxidized by the oxidizing agents used in *COD* tests. Therefore, *TOC* measurement -based on combustion- is more accurate due to those difficulties in *COD* analysis.

1.3.3. Biological change-based evaluation of sludge ultrasonic pretreatment efficiency

Evaluation of biological properties is usually based on heterotrophic count and specific oxygen uptake rate.

The breakdown of bacterial cell walls due to *US* can be evaluated by biological utilization tests. The sludge microbiological activity is characterized using Oxygen Utilization/Uptake Rate (*OUR*). *OUR* measurement therefore could be used to evaluate the sludge *US* disintegration efficiency.

In general, sludge microbial activity decreases when DD_{COD} increases during *US* sludge treatment. Nevertheless, Li *et al.* (2009) found that microbial activity was first enhanced and *OUR* increased about 20–40% when DD_{COD} was in the range 0-20%. This indicates that the flocs were slightly disrupted, but the cell lysis did not occur at this stage. In other words, the microbial activity would go up when the micro-floc aggregates are separated from the sludge flocs. When DD_{COD} was 20–40%, *OUR* still increased but by less than 20%, which means that some microorganisms were damaged. When DD_{COD} was over 40%, inactivation of microbes occurred, *i.e.* most bacteria were disrupted at different degrees, and sludge microbial activity decreased significantly. In other words, cells started to lyse only when DD_{COD} was over 40% as presented in Fig. 1.7.

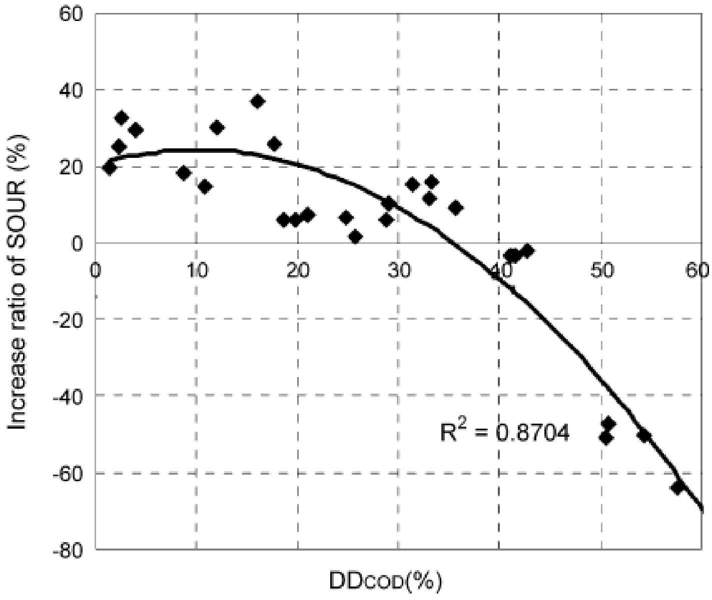


Fig 1.7: Relationship between sludge microbial activity and disintegration degree during ultrasonic treatment (Li et al., 2009)

DD_{OUR} is considered as *the degree of inactivation* and calculated as follows:

$$DD_{OUR}\ (\%) = (1 - OUR/OUR_0) * 100 \qquad \text{(Rai et al., 2004)}$$

where *OUR* and OUR_0 is the oxygen uptake rate of sonicated and original sample, respectively.

DD_{OUR} first increases quickly with the increase in *ES*, but the increase then slows down, above *ES* of 40 kJ/g_{TS} according to Rai *et al.* (2004). It could be inferred that DD_{OUR} is directly proportional to DD_{COD}. However, Zhang *et al.* (2007) observed a big difference between DD_{OUR}

(95.5%) and DD_{COD} (30.1%), indicating some chemical reactions might have happened and inhibited cell metabolisms without disrupting the sludge structure. Akin (2008) also noticed that microbes were inactivated well prior to their disintegration, *e.g.* the percentage of microbial inactivation ranged from 53% to 69% (corresponding to different *TS*) after 60 s of *US* and the *OUR* values changed insignificantly for longer duration. According to Pilli *et al.* (2011), *OUR* data therefore should not be used to assess the degree of sludge disintegration.

Chu *et al.* (2001) proposed the following scenario to describe the sonication of a biological sludge. *In the first stage* (0–20 min), mechanical forces break down the porous flocs into small particles and release extracellular polymers. *In the second stage* (20–60 min), the biomass is inactivated and organic matters are dissolved. *In the final stage* (> 60 min), sonication has essentially no effect on sludge if the bulk temperature has been controlled; if it is not controlled, the total coliform could be disinfected effectively if time exceeds 60 min. Of course these results based on sonication times only give the general trend.

Zhang *et al.* (2007) showed that the sludge inactivation efficiency increased significantly after 10 min of sonication and the biomass inactivation stage was 10–30 min, which was different from Chu *et al.* (2001) maybe due to the different D_{US} applied: 0.5 W/ml as compared to 0.3 W/ml by Chu *et al.* (2001). After 30 min of sonication, the sludge *OUR* decrease ratio was 95.5%, which indicated that biological cells were almost completely inactivated. The above hypothesis was therefore modified as follows: sludge disintegration and cell lysis occur continuously during sonication, but sludge inactivation occurs mainly in the second stage (10–30 min). It could be concluded that D_{US} and *US* duration are important parameters affecting inactivation of sludge.

Besides, Li *et al.* (2009) mentioned two main stages in *US* sludge pretreatment process: sludge flocs are changed and disintegrated at first, and then the exposed cells are disrupted. *In the first stage*, some organic matters contained in the flocs are dissolved, *SCOD* increases slightly, and *OUR* also increases due to the enhancement of oxygen and nutrients consumption. *In the second stage*, some cells are exposed and damaged by *US* cavitation, leading to the release in intracellular organic matters, the further increase in *SCOD*, and the significant decrease in *OUR*. Due to the heterogeneity of sludge and the differences in the external resistances of many types of zoogloea and bacteria, activation and inactivation might both occur in the same time and the comprehensive effectiveness is under the influence of various *US* parameters.

1.4. OPTIMIZATION OF ULTRASONIC PRETREATMENT OF SLUDGE

The ambient conditions of the sonicated system can significantly affect the intensity of cavitation and consequently affect the efficiency (rate and/or yield) of the desired operation. The cavitation effect is influenced by many factors: gas and particulate matter, solvent, field type (standing or progressive wave), types of *US* cavitation (related to F_S, D_{US}, I_{US}), attenuation, temperature, external pressure, and sample preparation, etc. (Lorimer and Mason, 1987; Thompson and Doraiswamy, 1999; Pilli *et al.*, 2011). This section aims at presenting main parameters significantly affecting the cavitation in order to optimize sludge *US* pretreatment efficacy.

1.4.1. Ultrasonic frequency

Acoustic cavitation is a phenomenon that is mainly related to the sound pressure amplitude, its frequency, through the bubble size variations (Leighton, 2007). For a given frequency and sound pressure amplitude, there is a critical size range in which the initial size of the bubbles must fall to nucleate cavitation (Leighton, 1994). The critical size range increases with the increase in acoustic pressure amplitude and the decrease in frequency.

Sound frequency has a significant effect on the cavitation process because it alters the critical size of the cavitation bubble (Thompson and Doraiswamy, 1999). In general, the increase in acoustic frequency leads to the decrease in cavitation physical effects (Crum, 1995; Rochebrochard *et al.*, 2012) due to the decrease in radius range that will provide cavitation (Leighton, 2007). It was added that at very high frequencies, the finite time of the rarefaction cycle is too short to allow a bubble to grow and collapse (Lorimer and Mason, 1987). Moreover, even if a bubble is produced during rarefaction, the compression cycle occurs too fast to collapse the bubble (Thompson and Doraiswamy, 1999). On the other hand, at higher sound frequencies, although cavitation is less violent, there are more cavitation events and thus more radicals to be produced and consequently a promotion of chemical reactions (Crum, 1995). Meanwhile, lower sound frequencies have stronger shock waves and favour mechanical effects (Zhang *et al.* 2008). This more violent collapse at low frequencies is due to the resonance bubble size being inversely proportional to the acoustic frequency (Laborde *et al.* 1998).

The optimum frequency is system-specific and depends on whether intense temperatures and pressures (enhanced by lower frequencies) or single electron transfer reactions (enhanced by higher frequencies) are looked for. The choice of frequency therefore depends on the expected type of ultrasound effects: mechanical, due to shock waves and high local shear stresses, or chemical, connected to free radical formation. For example, 20-60 kHz are used for ultrasonic cleaning baths (Lorimer and Mason, 1987; Entezari *et al.* 1997) or metal corrosion (Whillock and Harvey, 1997; Doche *et al.*, 2003), 20-600 kHz for sonochemical degradation of carbon tetrachloride (Francony and Petrier, 1996), trichloroethylene (Drijvers *et al.* 1996), methylene blue (Kobayashi *et al.* 2012), or octylbenzene sulfonate (Deojay *et al.* 2011), 20-900 kHz for sonochemical oxidation of iodide (Entezari and Kruus, 1996) or large-scale sonochemical reactors (Asakura *et al.* 2008). However, in several reactions, the alteration of frequency (20-900 kHz) has no apparent effect, such as in the dissociation of carbon disulfide (Entezari *et al.*, 1997).

With regard to sludge pretreatment**,** ultrasound mechanically disrupts the floc matrix and cell structure. Tiehm *et al.* (2001) and Zhang *et al.* (2008) found that DD_{COD} decreased owing to the increase in frequency (41-1068 kHz and 25-150 kHz, respectively), indicating that mechanical effects, instead of free radicals, are responsible for the biodegradability enhancement. It is therefore important to note that in most works sludge disintegration is the most significant at low frequencies (Pham *et al.* 2009**;** Carrère *et al.* 2010; Pilli *et al.*, 2011). However, the lowest investigated values of frequency in this field have been restricted to around 20-25 kHz. Lower frequency could then be interesting in sludge disintegration and needs detailed investigation.

1.4.2. Temperature

Theory-based, increasing temperature (*T*) will decrease surface tension and raise the equilibrium vapour pressure of the medium**,** leading to easier bubble formation (due to the decrease of the cavitation threshold). However, these kinds of cavitation bubbles contain more vapors that reduce the *US* energy produced by cavitation because they cushion the implosion (and so lower both T_{max} and P_{max})**,** thus reducing the amount of free radicals produced within the bubble and also mechanical effects as shock waves. Besides, great numbers of cavitation bubbles generated simultaneously will provoke attenuation or dampening effect on the propagation of *US* energy from the emitter through the system (Lorimer and Mason, 1987).

Nevertheless, in terms of sludge disintegration, it is important to note that sludge ultrasonic pretreatment efficacy increases following an increase in the bulk temperature as temperature alone favors *COD* release.

It was proved that the *US* treatment has two simultaneous effects: (i) vigorous agitation caused by the formation and explosion of tiny bubbles, and (ii) the increase in the bulk temperature. Chu *et al.* (2001), Gronroos *et al.* (2005), Li *et al.* (2009) and Kidak *et al.* (2009) concluded that the higher the temperature of sludge samples, the more efficient the *US* disintegration was. This is opposite to most power *US* applications as cavitation intensity is higher at low temperature.

Li *et al*. (2009) indicated that the *T* effect is limited when *US* duration is short. For example, after 1 min of *US* at 4 W/mL, DD_{COD} was 9% for both samples without and with *T* control (maintained at 20°C). On the other hand, after 5 min at 0.8 W/mL, DD_{COD} was 27% and 23% for the uncontrolled and controlled *T* samples, respectively. It was also noted that cavitation explosion and bulk temperature increase have equal influence on sludge floc disintegration and cell lysis (Chu *et al*., 2001).

It could be suggested that for any scale up operation, on one hand, the process should be carried out without cooling to make use of thermal solubilisation; on the other hand, the extreme *T* must be controlled neither to damage the mechanical equipment nor to fully inhibit transient cavitation. In other words, the *US* system should be controlled at the possible highest *T* in order to both take advantage of *US* (cavitation and temperature effects) and to maintain the system (Kidak *et al*., 2009). This suggests a probable optimum temperature.

1.4.3. Hydrostatic Pressure

Despite ultrasonic sludge treatment has reached commercial developments and given rise to many works, none of them has been carried out to investigate the effect of pressure. Changing the hydrostatic pressure will change the resonance condition of cavitation bubbles via their equilibrium radius and then may drive the system toward resonance conditions (Thompson and Doraiswamy, 1999). At resonance conditions, the rate and yield of reactions will increase (Cum *et al*. 1988, 1990, 1992). More probably, both the cavitation threshold and the intensity of cavity collapse should increase following an increase in external pressure (Lorimer and Mason, 1987), suggesting a possible optimum pressure. Brett and Jellinek (1956) stated that bubbles could be visible for gas-applied pressure as high as 16 atm. Nevertheless, nearly all the *US* experiments have been carried out at atmospheric pressure. Only a few studies have been focusing on how increasing static pressure affects cavitation.

Most works on pressure effects concern sonoluminescence and no consensus emerges about an optimum value as reported by Chendke and Fogler (1983a, 1983b). The early works of Finch (1965) indicated that the greatest sonoluminescence intensity was observed in water at a static pressure of about 1.5 atm (over an investigated range of 1-8 atm), but Chendke and Fogler (1983b) recommended a value of 6 atm to promote sonoluminescence in nitrogen-saturated water. In aqueous carbon tetrachloride solutions, the intensity of the sonoluminescence did not show any monotonous behavior: it first went up to 6 atm, then reached a minimum at 8 atm, got a new maximum at 12 atm, and was finally almost inhibited above 18 atm (Chendke and Fogler, 1983a). Pilling and Ridley (1986) examined cavitation in superplastic flow (Supral 220, Al-7475E and Al-Cu-Li alloy) with varying superimposed hydrostatic pressures (up to 47.5 bar) and found that increasing superimposed pressure decreases volume fraction of cavities. Chokshi *et al.* (1990, 1993) also indicated a significant reduction of the cavitation damage level in a superplastic 7475 Al alloy and Al-Li alloy under hydrostatic pressure (30 bar). On the contrary, Dezhkunov et al. (1997) found a strong effect of hydrostatic pressure (1-12 atm) on cavitation when measuring the aluminum foils erosion and the sonoluminescence intensity. The erosion rate as a function of the hydrostatic pressure reached a maximum value at 4.5 atm and decreased afterwards until it disappeared at 6 atm. Whillock and Harvey (1997) investigated the effects of hydrostatic pressure on the corrosion of 304L stainless steel in an ultrasonic field. An increase in pressure up to 4 bar at a constant temperature caused a strong increase in corrosion rate. Hydrostatic pressure retards both cavity nucleation (reduction of the total number of cavities) and cavity growth (decrease in the sizes of cavities). As a result, larger *US* intensity is required to induce bubble oscillations and implosions.

More recent pressure effects again focused attention. Gaitan *et al.* (2010) found that the collapse strength is intensified at elevated static pressures in part due to an increased differential pressure between the external liquid and the interior of the bubble. Bader *et al* (2012b) extended the work of Gaitan *et al.* (2010) and found the increase in the collapse strength of transient cavitation events at elevated static pressure (up to 300 bar) to be more strongly dependent on the increased acoustic energy stored in the resonant system (*i.e.* increased peak negative pressure) rather than the increased differential pressure. The overpressure acts to suppress cavitation and increase the amount of stored energy which leads to an increase in the collapse strength and therefore shock wave amplitudes. Besides, the cavitation threshold increases linearly with the static pressure, thus the acoustic pressure amplitude required to reach the cavitation threshold also increases (Bader *et al.*, 2012a). Yasui et al. (2011) showed an enhancement of acoustic energy radiated by a bubble per acoustic cycle either by the excess static pressure for relatively high acoustic amplitudes and low viscosities of liquids or by a reduced static pressure for relatively low acoustic amplitudes and high viscosities. The optimal static pressure which maximizes the acoustic energy increases as the acoustic amplitude increases or viscosity of liquid decreases, which qualitatively agrees with Sauter et al. (2008).

Closer to the present subject, Neppiras and Hughes (1964) investigated the influence of pressure (up to 5.8 atm) on the disintegration of yeast cells and found an optimum value of 4 atm. As mentioned the effect of pressure on sludge pretreatment has hardly been investigated but should deserve attention.

1.4.4. Energy aspects

Concerning the economy of the process of *US* sludge disintegration, the operation cost is directly linked to *ES* - the *US* energy per unit weight of dry sludge provided to the suspension. The fact that *US* sludge disruption is an energy-driven process was effectively proved by the usual verification that *ES* is by far the main parameter (Tiehm *et al.*, 2001; Rai *et al.*, 2004; Gronroos *et al.*, 2005; Bougrier *et al.*, 2004, 2005; Khanal *et al.*, 2006; Feng *et al.*, 2009; *etc.*), even if many authors remained concerned with only *US* power, time of irradiation, and to a less extend *US* intensity and *US* dose (Mao *et al.*, 2005; Wang *et al.*, 2005; Zhang *et al.*, 2007; Na *et al.*, 2007; El-Hadj *et al.*, 2007; *etc.*).

Knowing this fundamental result, the questions to be solved are: is there an optimum power or power density, an optimum sludge concentration, and later how to extrapolate? What is the effect of the equipment size?

1.4.4.1. Ultrasonic power

As a general trend it is usually accepted that ultrasound power has positive effect in most *US* applications taking advantage of either chemical or physical effects. Nevertheless, very high power or intensity may be detrimental. Ratoarinoro *et al.* (1995) and Contamine *et al.* (1994) explained that at high $P_{US,}$ the formation of a dense cloud of cavitation bubbles around the probe blocks the energy transmitted from emitter to the solution. The optimum P_{US} also depends on F_S: different optimal values were found for P_{US} depending on F_S when investigating the corrosion rate of 304L stainless steel; no optimum value was observed at 20 kHz (Whillock and Harvey, 1997).

In the case of sludge pretreatment, it is proved that the solubilisation of organics increases when applying elevated P_{US} or D_{US}. For example, at *ES* of 100000 kJ/kg$_{TS}$, DD_{COD} were 52.3% and 71.3% for P_{US} of 100W and 200W, respectively (Kidak *et al.*2009). At the same *ES* of 40 kWh/kg$_{TS}$, *SCOD* increased by 1.2-1.9 fold corresponding to the D_{US} range of 0.18-0.52 W/mL (Show *et al.* 2007), and by 1.2-4.8 fold for 2-4 W/mL (Mao *et al.*, 2004). Chu *et al.* (2001) indicated the total solubilized *COD* fraction (*SCOD/TCOD*) during 40min at 0.33 W/mL to be much higher than that during 2 h at 0.11 W/mL.

According to Kidak *et al.* (2009), at a given *ES*, *"high P_{US} - short US duration"* should be preferred for heterogeneous sludge like municipal sludge, in agreement with Gronroos *et al.* (2005), Zhang *et al.* (2007), and Show *et al.* (2007). Conversely, *"low P_{US} and long US duration"* better works for homogenous sludge like industrial sludge. It could be reasoned that particles in municipal sludge (like fibrous particles coming from toilet papers) are resistant to *US* disruption; thus P_{US} should be increased to break these particles. On the other hand, the settled bacteria (the major components in industrial sludge) are broken to soluble materials even at low P_{US}; more solubilisation consequently could be obtained when increasing the *US* duration.

It is clear that P_{US} and D_{US} are important parameters in *WAS* disintegration that must be considered in terms of cost-benefit purpose in full-scale application.

1.4.4.2. Ultrasonic intensity

Above the cavitation threshold, increasing I_{US} leads to a rise in the maximum pressure and temperature within a transient collapse (Lorimer and Mason, 1987), improving all mechanical effects, and then the degree of sludge disintegration (DD_{COD}) (Quarmby *et al.* 1999; Neis *et al.*, 2000; Pilli *et al.*, 2011). For instance, Neis *et al.* (2000) found that DD_{COD} was more than double by increasing I_{US} from 6 to 18 W/cm^2.

However, Lorimer and Mason (1987) noted that I_{US} cannot be increased indefinitely since a subsequent pressure amplitude increase may result in so large bubbles during rarefaction that the time available for their collapse is insufficient. This is rather similar to the explanation of optimum power due to the damping of *US* wave by an excess of cavitation bubbles near the emitter (Contamine *et al.* 1994; Ratoarinoro *et al.* 1995).

Apart from bubble formation, *bubble behavior* is also associated with I_{US}. As discussed, the disruptive effect of transient bubbles in a short *US* duration is more noticeable than that of stable bubbles with long *US* duration. Thus, I_{US} may be considered as a more predominant parameter than *US* duration in terms of bubble behavior, thereby the *US* process can be optimized by increasing I_{US} to minimize energy use (Show *et al.*, 2007).

In addition, I_{US} is the quotient of P_{US} and the surface area of the probe (*A*). Most researches (Wang *et al.*, 2005; Show *et al.*, 2007; Zhang *et al.*, 2008b; Liu *et al.*, 2009; Li *et al.*, 2010) have varied only $P_{US,}$ meanwhile the magnitude of the effect of each factor needs further investigation in connection with scale-up purpose.

1.4.4.3. Ultrasonic duration and specific energy input

In earlier studies, sonication time was most often used although as already mentioned *ES* has more significance and should be preferred. It was proved that the solubilisation of *WAS* increases gradually with an increase in *US* duration at same *US* conditions (Lorimer and Mason, 1987; Wang *et al.*, 1999; Mao *et al.*, 2004; Show *et al.*, 2007). For example, to get 50% and 75–80% increase in solubilisation, it required at least 30–40 min and 90 min of sonication, respectively (Shimizu *et al.*, 1993).

In addition, *VS* reduction and biogas production in *AD* increase gradually with an increase in *US* duration. Tiehm *et al.* (2001) reported a *VS* reduction by 27% and 56.7% after 30 and 150 min of sonication at 41 kHz, respectively. Simultaneously the methane percentage in biogas increased, by 9.7% after 150 min of *US*.

In terms of *ES*, different ranges were investigated. Generally, *SCOD* increases with an increase in *ES*. Considering together the disintegration efficiency and the energy input, different *ES* values were suggested: 4000 kJ/L (Na *et al.* 2007), 10000 kJ/kg_{TS} (Bougrier *et al.* 2005), 12000 kJ/kg_{TS} (Neis *et al.*, 2000), 35000 kJ/kg_{TS} (Khanal *et al.* 2006), 50000 kJ/kg_{TS} (Wang *et al.*, 2006a).

In addition, according to Kidak *et al.* (2009), higher reactor volume resulted in a decrease in DD_{COD} due to the difficulties in creating homogeneous sonication, as intense damping occurs in the sludge suspension. This is a complex problem faced when trying to scale up this process.

In conclusion, it is clear that experimental results are required to account for P_{US}, I_{US}, and D_{US} (through optimal solid concentration) and not only for *ES*.

1.4.5. Sludge type, and total solid concentration of sludge

Mao *et al.* (2004) proved the *SCOD* in secondary sludge to be higher than that in primary sludge.

Regarding *TS* concentration, high solid loading in the liquid generally makes more cavitation sites and then more intense hydro-mechanical shear forces (Neis *et al.* 2000; Mao *et al.*, 2004; Akin *et al.*, 2006; Show *et al.*, 2007; Zhang *et al.*, 2008b; Kidak *et al.*, 2009; Pilli *et al.*, 2011). However, the effect of *TS* depends on many factors, *e.g.* reactor configuration (reactor size, transducer type), *T*, P_{US}, and sludge characteristics (Gronroos *et al.*, 2005). An optimum *TS* concentration can be found, which is explained by opposite effects. The increase in *TS* provides more cells and aggregates to be in contact with cavitation bubbles; thereby, the P_{US} required to generate cavitation is more efficiently consumed. However, at high sludge loading, the acoustic pressure field decreases faster from the emitter due to the degraded propagation of *US* waves in a denser suspension. Consequently, acoustic cavitation intensity is reduced. For example, *SCOD* increased from 1000 to 5800 mg/L when *TS* varied between 0.98% and 2.6%, but it decreased to 3200 mg/L when *TS* was 3.6% (Akin *et al*., 2006). According to Kidak *et al*. (2009), DD_{COD} hiked up with an increase in *TS* within the range 4-12 g/L, but it severely decreased at a *TS* of 24 g/L. Show *et al*. (2007) found the optimum range of *TS* to be between 2.3% and 3.2% at constant energy input.

1.4.6. pH of sludge

According to Wang *et al*. (2005), the effects of sonication parameters and sludge properties on solubilisation of the chemical oxygen demand (*COD*) can be rated as follows: sludge *pH* > sludge concentration > ultrasonic intensity > ultrasonic density. This suggests that *pH* adjustment to a suitable value prior to *US* pretreatment is an important step.

Sludge cells were proved to be disintegrated and dissolved by acidic treatment, solubilisation being only significantly affected by the acid dose (Woodard and Wukash, 1994). The optimal *pH* values for reducing volatile suspended solids and excess sludge subsequently was found to vary between 1.5 (Woodard and Wukash, 1994) and 3 (Neyens *et al*., 2003). However, acidic pretreatment alone exhibits a very low performance as compared to *US* pretreatment for releasing organic matters into the liquid phase and Apul (2009) reported the sludge acidification to be detrimental to *US* pretreatment performance, especially at low pH values.

On the other hand, alkaline pretreatment enhances sludge solubilisation, anaerobic biodegradability, and methane production (Kim *et al*., 2003; Valo *et al*., 2004). Besides, the combination of alkaline and *US* gives better performances of *TS* solubilisation as compared to both thermo-acidic and *US*-acidic pretreatments (Liu *et al*., 2008). Moreover, Chu *et al*. (2001) showed that extracellular polymeric substances (*EPS*) and gels surrounding cells limit the efficiency of ultrasonic treatment on sludge disintegration. Adjusting the pH of sludge to alkali value promotes *EPS* hydrolysis and gel solubilisation. After that, cell walls cannot maintain an appropriate turgor pressure (Jin *et al*., 2009) and easily disrupt. Therefore, the combined alkaline-*US* pretreatment, based on different mechanisms of sludge disintegration (modification of structural properties and intense mechanical shear force), is expected to take advantage of both and achieve a better efficiency of sludge pretreatment. Some synergetic effects were even noticed (Kim *et al*., 2010). At near-neutral pH conditions (pH 7-8), waste activated sludge (*WAS*) solubilisation obtained from combined, chemical, and *US* (1.9 W/mL, 60 s) pretreatments was

18, 13.5, and 13%, respectively (Bunrith, 2008). At higher pH values (pH 11-13), the solubilisation reached 60-70% with the combined method (*ES* 7500-30000 kJ/kg_{TS}) while it never exceeded 50% in individual pretreatments (Jin *et al.*, 2009; Kim *et al.*, 2010). Methane production yield derived from full stream combined-pretreated sludge (pH 9, *ES* 7500 kJ/kg_{TS}) was also 55% higher than that from the control (Kim *et al.*, 2010) which seems rather questionable.

The chemicals used for increasing the pH of sludge also affect *WAS* solubilisation efficacy, where NaOH > KOH > $Mg(OH)_2$ and $Ca(OH)_2$ (Kim *et al.*, 2003; Jin *et al.*, 2009). Ca^{2+} and Mg^{2+} are key substances binding cells with *EPS*. As a result, their presence may enhance the reflocculation of dissolved organic polymers (Jin *et al.*, 2009), leading to a decrease in soluble *COD*. On the other hand, overconcentration of Na^+ (or K^+) was reported to cause subsequent inhibition of *AD* (Carrère *et al.*, 2010).

1.5. CONCLUSIONS

According to the literature review, studies about *US* sludge disintegration have expressed *US* effect using different reference properties. There is still no fully comprehensive method to evaluate the efficiency of sludge *US* pretreatment. However, some main parameters commonly used for this purpose are DD_{COD}, proteins, particle size reduction, *etc.* due to their simplicity, easiness, and predominant accuracy in daily operation.

Regarding *US* parameters, apart from *ES* recognized as the main one, P_{US}, I_{US}, and frequency seem to have significant effects. However, static pressure effect has been only marginally studied due to the complex equipment required. The magnitude of the effect of P_{US} and probe size in terms of I_{US} has not been clearly detailed and should to be investigated at constant *ES*. Besides, investigation on the effect of *pH* alkalization prior to *US* process has been restricted to limited concerned parameters (initial *pH* or alkaline dose and *ES*). In addition, investigating very low frequency (acoustic frequency) seems interesting but has not yet been taken into consideration. Their effects therefore should be varied separately and simultaneously with other related parameters, *i.e.* process conditions, ultrasonic properties, and sludge characteristics, to optimize sludge *US* pretreatment process.

CHAPTER 2

RESEARCH METHODOLOGY

2.1. INTRODUCTION

Regarding sludge *US* pretreatment, I_{US} has positive effects, but the respective magnitude of the effect of P_{US} and probe size has not been looked into. Besides, sludge disintegration is known to take advantage of low frequency but audible frequency has not yet been considered. In addition, hydrostatic pressure is an important parameter, but has hardly been investigated in terms of sludge *US* pretreatment. Thereby several issues need to be elucidated or confirmed in order to optimize sludge disintegration:

- How important are the effects of P_{US}, I_{US}, and F_S on sludge pretreatment efficiency? Which parameter between P_{US} and probe size is more meaningful in terms of I_{US} effect on sludge pretreatment efficiency? Does a very low frequency down to audible range (12 kHz) really improve the efficiency of sludge disintegration?

- Is there an optimal hydrostatic pressure for sludge *US* pretreatment? If any, how do the other parameters (sludge type, sludge concentration, temperature, *ES*, P_{US}, I_{US}, F_S) affect this optimum and what is the expected gain in terms of energy saving? It should be recalled that the effect of external pressure (above atmosphere) will be investigated for the first time in this context.

- How does the *US* procedure (continuous or sequential treatment at optimum conditions) affect the efficiency of sludge disintegration and *AD* afterwards?

In order to answer these questions, different experiments have been conducted to determine optimum values of important parameters related to sludge pretreatment efficacies. The corresponding tasks, shown in Fig. 2.1, are:

- To investigate usual operation parameters: sludge type, *TS*, sludge pH (alkaline dose, holding time), stirrer speed, and *T* profile (―adiabatic” or isotherm operation mode).

- To quantify the effect of *US* parameters on sludge disintegration: P_{US}, I_{US}, and F_S.

- To study the effect of pressure on sludge *US* pretreatment at various P_{US}, I_{US} and F_S.

- To finally optimize *US* process selecting continuous or sequential treatment.

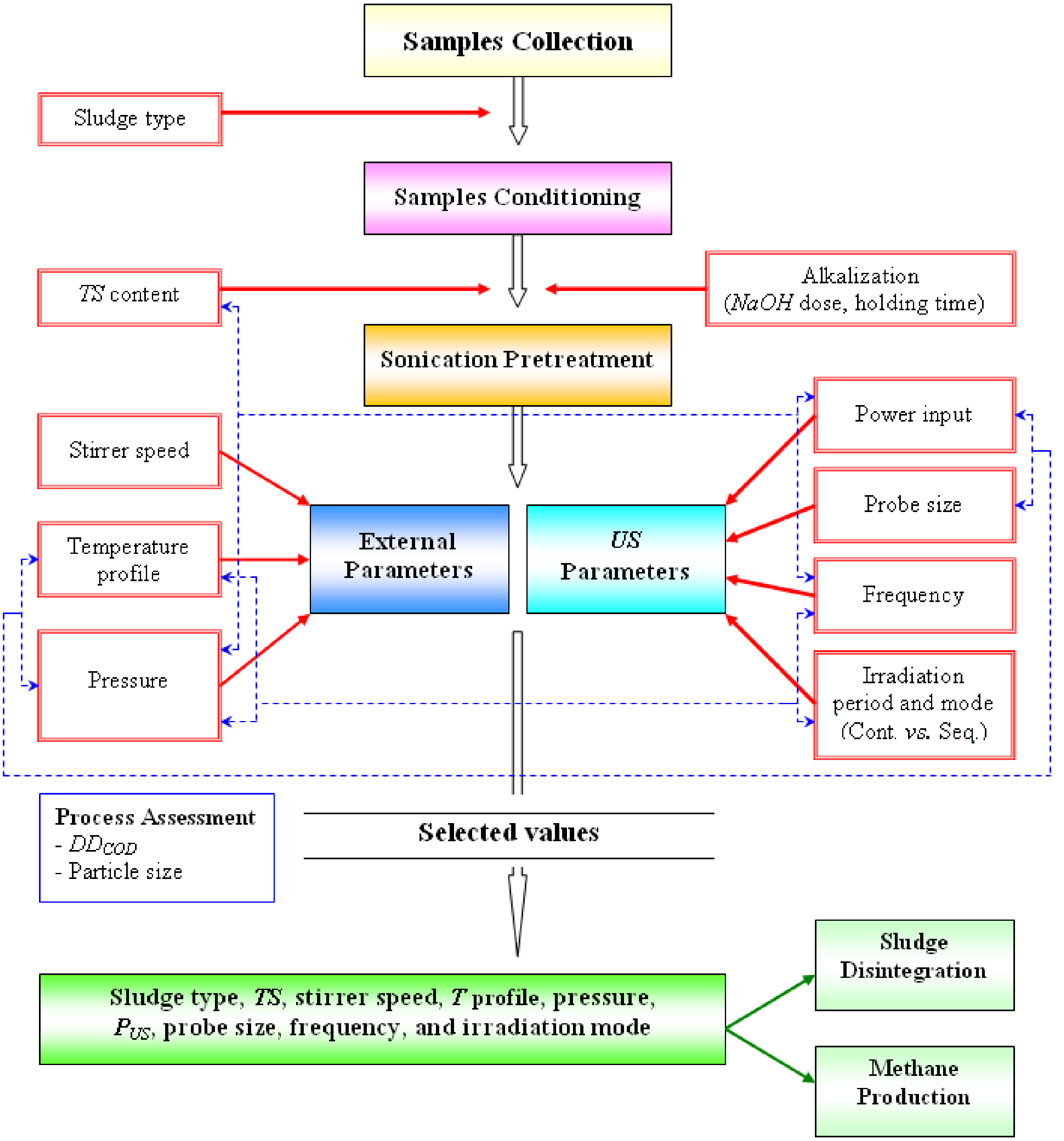


Fig 2.1: Outline of research plan

A multifactorial analysis was not selected at the early stage of the research due to the very different importance of the abovementioned parameters. Moreover, the available equipment at that time only allowed single frequency, single probe size, and limited power input. Therefore, parameters were mainly investigated separately, their combined effect being evaluated at the end of the research.

2.2. SLUDGE SAMPLES

Due to the changes in *US* equipment (probes, generator, frequency, *etc.*) along this work, four times of sludge sampling were needed and conducted at Ginestous wastewater treatment plant (*WWTP)* in Toulouse (France) and INSA with a sufficient amount for all experiments in each part of this work: mixed sludge (solid form, after centrifugation), secondary sludge (liquid form), and digested sludge (liquid form, after *AD* of the secondary sludge, from INSA). The properties of initial sludge samples are given in Table 2.1-2.4.

Secondary and mixed sludges were collected at the sampling point *B6* from *G1* and *B30* from *G4*, respectively (Figure 2.2). The *G1* site (activated sludge process, average load) is the oldest of Ginestous *WWTP*. Its average and maximum (for short periods) processing capacity (only carbon pollution) is 75000 m^3/day and 90000 m^3/day, respectively (375000 to 450000 population equivalent). The *G4* site (a new unit, established in 2004) treats all the water from *G1*, *G2*, and *G3* to eliminate nitrogen pollution by nitrification and clarify water by filtration. Its maximum processing capacity is 160000 m^3/day (800000 population equivalent).

Mixed and most of secondary sludge samples were conditioned in 100 g and 1 L plastic bottles, respectively and preserved in a freezer. Kidak *et al.* (2009) reported that this preliminary maintaining step might change some physical characteristics of the sludge (for instance particle size), but it should not significantly affect *COD* solubilisation results. It was confirmed in a first step of this work, the difference in sludge disintegration between fresh sludge (without freezing) and frozen sludge was less than 5% and 8% on the whole *ES* range (7000-75000 kJ/kg_{TS}) for mixed and secondary sludges, respectively. Digested sludge was sampled in 1 L plastic bottles and preserved at a constant temperature of 3-4^{o}C. Some preliminary experiments were also conducted with fresh secondary sludge samples kept at 3-4°C (without any freezing).

When performing experiments, the required amount of sludge was defrosted (for frozen sludge) and diluted with distilled water (up to 500 mL per experiment) to prepare synthetic sludge samples with a given *TS* content.

Photos of sludge samples are shown in Fig. 2.3.

Table 2.1: Characteristics of sludge samples from first sampling (Oct. 2011)

Parameter	**Value**		
	Mixed sludge	Secondary sludge	Digested sludge
Raw sludge samples			
pH	6.3	6.6	7.4
Total solids (*TS*)	285 mg/g	37.5 g/L	14.0 g/L
Volatile solids (*VS*)	238 mg/g	32.2 g/L	11.9 g/L
VS/TS	83.5 %	85.8 %	84.7 %

Table 2.2: Characteristics of mixed sludge from second sampling (Jan. 2012)

Parameter	**Value**
Raw sludge sample	
pH	6.3
Total solids (*TS*)	270 mg/g
Volatile solids (*VS*)	233 mg/g
VS/TS	86.2 %

Table 2.3: Characteristics of secondary sludge from third sampling (Oct. 2012)

Parameter	**Value**
Raw sludge sample	
pH	6.3
Total solids (*TS*)	31.9 g/L
Volatile solids (*VS*)	26.4 g/L
VS/TS	82.8 %

Table 2.4: Characteristics of secondary sludge from fourth sampling (Apr. 2013)

Parameter	**Value**
Raw sludge sample	
pH	6.3
Total solids (*TS*)	34.2 g/L
Volatile solids (*VS*)	30.2 g/L
VS/TS	88.3 %

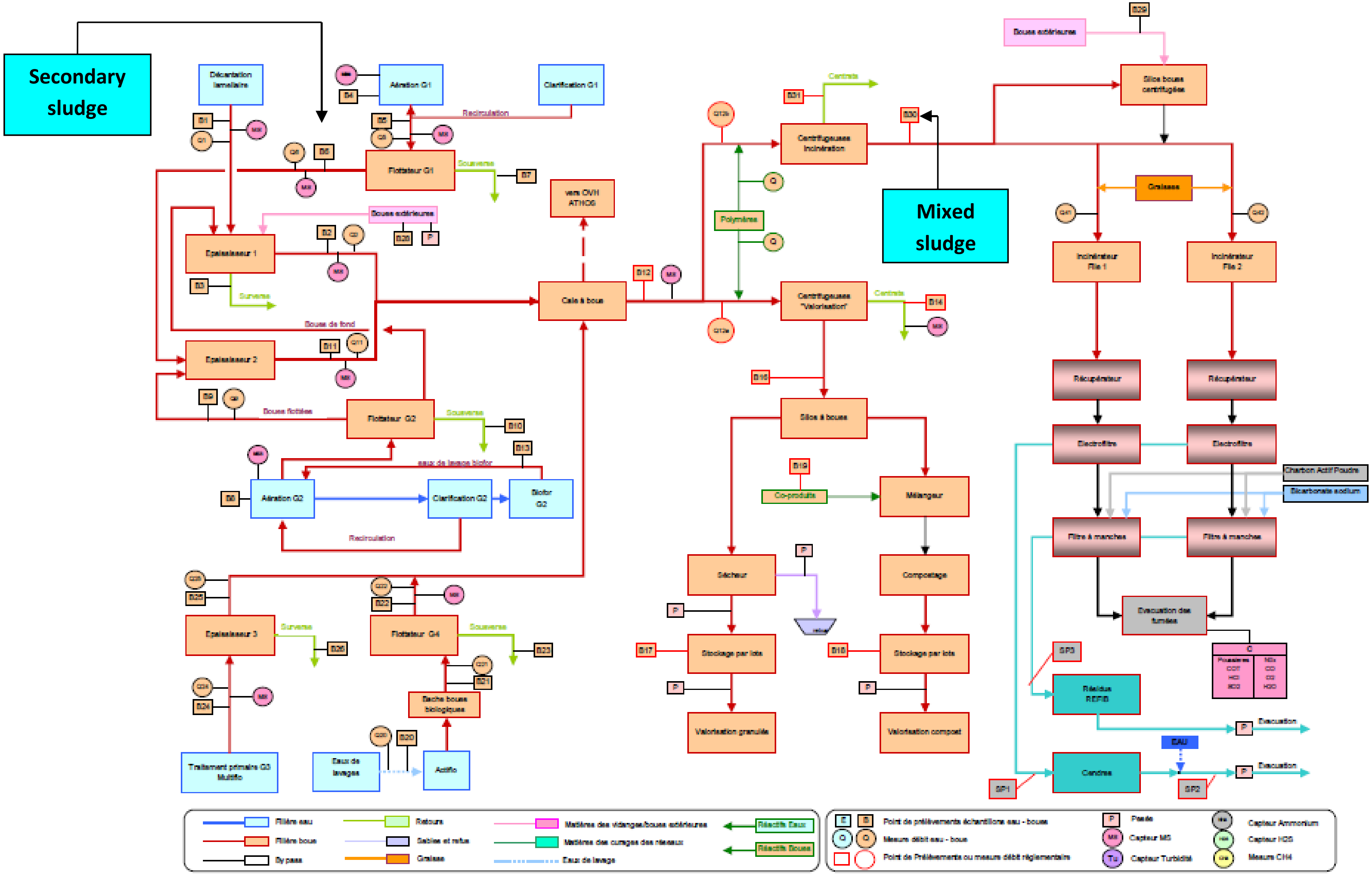
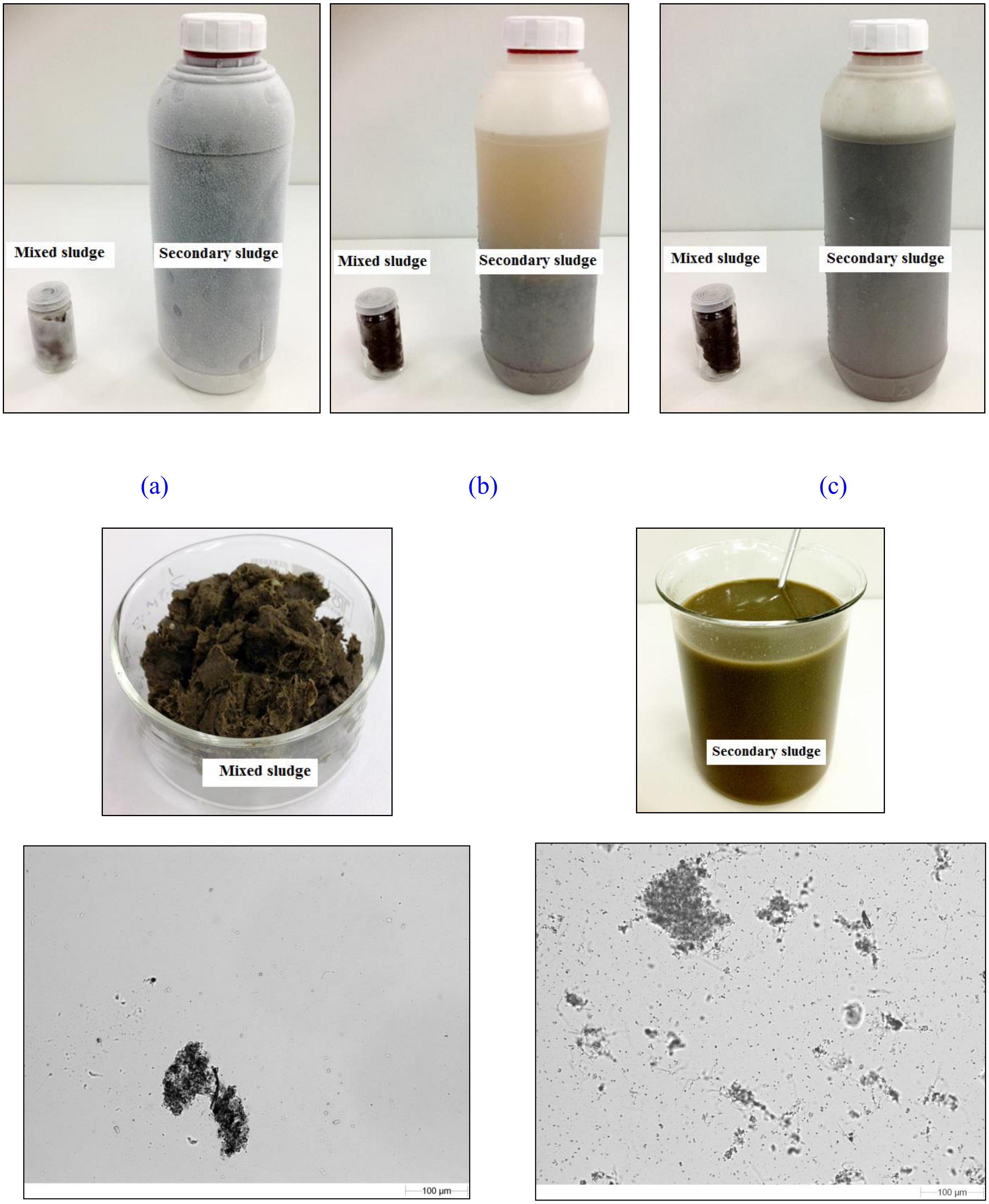


Fig 2.2: Sampling points at Ginestous *WWTP*



(a) (b) (c)

(d)

Fig 2.3: Photos of sludge samples:

(a) Frozen, (b) Defrosted, (c) Defrosted and homogenized, (d) Fresh sludge

Microscopic image of fresh secondary sludge shows the presence of many separate rounded microflocs, of less than 5 µm, along with a rather few filamentous species and large floc structures from 20 µm to 100 µm. Macroflocs of mixed sludge seem more compact (less fluffy) than those of secondary sludge.

2.3. SONICATION APPARATUS

The whole experimental set-up used for the study is depicted in Fig. 2.4. It consists in a high pressure *US* autoclave reactor, a gas feeding system and an electric control panel which includes all control electronic viewers and *PID* controllers. A few elements are detailed in the following section:

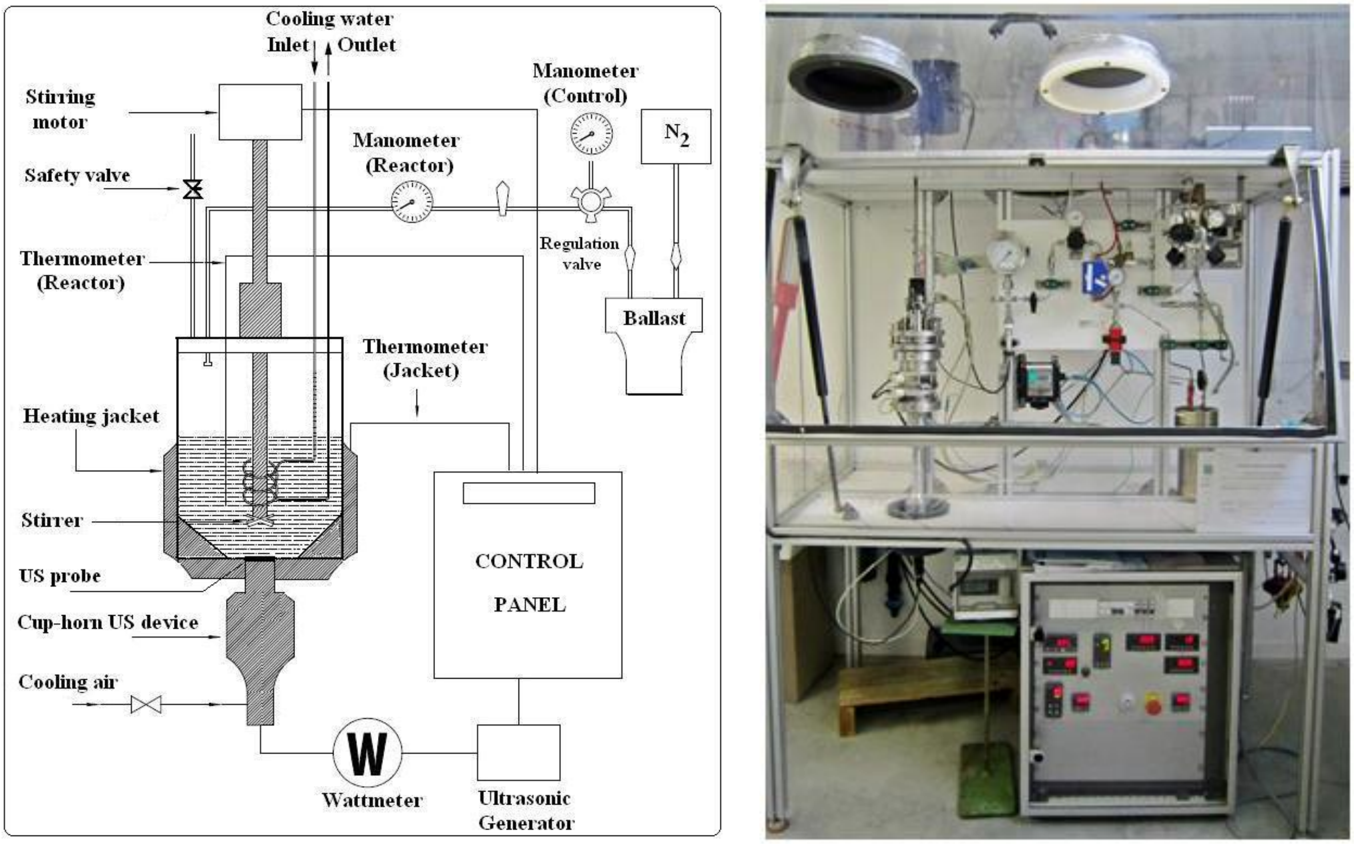


Fig 2.4: High pressure *US* reactor set-up

- High pressure reactor:

The reactor, shown in Fig. 2.5, and its internals are made of 316L stainless steel. The reactor internal diameter is 9 cm and its depth 18 cm, for a usable capacity of 1 L. A safety valve (*HOKE* 6500) limits overpressure to 19 bar. The solution is stirred by a Rushton type turbine of 32 mm diameter, with an adjustable speed up to 3000 rpm. It is equipped with a temperature probe and an internal coil in which a cooling water stream (5 bar, 15°C) is continuously circulated so that to remove the heat generated by sonication during the isothermal tests.


(a) (b)

Fig 2.5: (a) Closed and (b) opened cup-horn autoclave reactor

- Sonication devices:

The ultrasound emitting surface is situated at the bottom of the reactor (cup-horn configuration). All *US* devices have been supplied by Sinaptec.

The old *US* equipment works at 20 kHz only, with maximum P_{US} of 158 W and is provided with a 35 mm diameter probe. The new equipment consists in two generators working at 12 and 20 kHz, respectively, and for each two associated probes of 13 and 35 mm in diameter. Maximum P_{US} (transferred from the generator to the transducer) is 100 W and 400 W for 13 and 35 mm diameter probes, respectively. The 20 kHz device is composed of four elements: a piezoelectric transducer, a titanium booster, an aluminum flange ensuring a good mechanical connection, and an ultrasonic cup-horn placed at the bottom of the reactor. There is no booster for the 12 kHz device (Fig. 2.6). During operation, the transducer is cooled by compressed air.

(1) (2)

(3) (4)

Fig 2.6: Photos of the sonication devices: (1) 20 kHz, (2) 12 kHz, (3) 35 mm diameter probe, (4) 13 mm diameter probe.

The limitations of the equipment from preliminary tests at Sinaptec or LGC are presented in Table 2.5.

Table 2.5: Limitations of the equipment

	Max Applied Pressure (bar)	**Max Recommended Temperature (^{o}C)**
Old US generator 20 kHz		80
BP		
150 W	16.0	
New US generator 20 kHz		80
BP		
50 W	6.0	
150 W	6.0	
360 W	6.0	
SP		
50 W	2.0	
100 W	3.5	
New US generator 12 kHz		65
BP		
50 W	1.0	
150 W	3.0	
360 W	4.5	
SP		
50 W	5.5	
100 W	5.5	

- Thermoregulation:

The reactor may be heated by two 500 W annular heaters whose power can be adjusted thanks to an *ASCON X5 PID* controller to achieve experiments at selected temperature. As ultrasound energy is finally transformed in heat in the reactor, the temperature of the solution inside the reactor can be controlled (± 2°C) by using a *West* 8200 *PID* controller which regulates the flow rate of the cooling water circulating in the internal coil. The temperatures inside the reactor *(T1)* and of the jacket (*T2*) are measured by a *J*-type and a *K*-type thermocouple (Ø 1 mm), respectively. *T1* signal is recorded and displayed on a computer via an acquisition card (Analog *Device RTI* 800) and *DASYLab* software.

Two types of experiments will be carried out: thermo-regulated, by using the cooling coil, and at increasing temperature, without cooling.

It is noted that *T* of solution was not perfectly controlled by the cooling coil at the beginning of the process: a peak occurred when turning *US* on and disappeared after a few minutes. The higher P_{US}, the higher the peak, especially under pressure, but always less than 5°C, which may be considered convenient in usual *US* applications.

- Gas feeding and pressure regulation:

The reactor is fed with N_2 using a gas reservoir of 0.5 L (Burton Corblin 60101, max pressure of 270 bar) equipped with a safety valve set at 120 bar (Dorel R5200). The reactor pressure is set thanks to a pressure regulating valve (*TESCOM D44644-M-2-1-S*, max 60 bar at entry, max 19 bar at exit). There are two pressure transducers: *P1* (*KELLER PR33XEi*, 0-20 bar) measures the downstream pressure (pressure inside the reactor) and *P2* (*Huba Control* 2436, 0-250 bar) measures the upstream one. Pressure *P1* is measured with ± 0.05 bar precision.

2.4. ANALYTICAL METHODS

2.4.1 Total solids *(TS)* and Volatile solids *(VS)*

TS was determined by drying a well-mixed sample to constant weight at 105°C and *VS* was obtained from the loss on ignition of the residue at 550°C (*APHA*, 2005). A NABERTHERM 30- 3000 P330 furnace, presented in Fig. 2.7, was used for these measurements.

Fig 2.7: NABERTHERM 30-3000 P330 furnace

2.4.2 Chemical oxygen demand *(COD)* and the degree of sludge disintegration *(DD_{COD})*

Chemical oxygen demand *(COD)* is a standard method for indirect measurement of the amount of pollution (even the fraction that cannot be biologically oxidized) in a solution. The *COD* test is based on the chemical decomposition of (dissolved or suspended) organic and inorganic contaminants. The result of a *COD* test indicates the amount of water-dissolved oxygen consumed by the contaminants. It is expressed as mg of O_2 consumed per liter of sample under a given procedure.

A closed reflux colorimetric method (Hanna procedure adapted from EPA 410.4 approved method) was used for the measurement. In this procedure, the sample is heated for two hours at 150°C with a strong oxidizing agent, potassium dichromate, in a digestion reactor (Fig. 2.8a). Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). After cooling of the test tubes, the colorimetric analysis is performed.

Hanna Instruments *COD* test tubes in the range of 0-1500 mg_{O2}/L (reference HI 93754B-25 MR) were used, which contain ad-hoc amount of reagent in acidic medium corresponding to 2 mL of sample, as well as mercury sulfate to avoid chloride interferences. For this *COD* range, the amount of Cr^{3+} produced was analyzed by a spectrophotometer set at 620 nm (Fig. 2.8b), which was directly converted into *COD*. For each series, a reagent blank was also measured using organic free deionized water and its value was subtracted from the result of each sample.

The degree of sludge disintegration (DD_{COD}) was calculated by determining the soluble chemical oxygen demand after strong alkaline disintegration of sludge ($SCOD_{NaOH}$) and the chemical oxygen demand in the supernatant before and after treatment ($SCOD_0$ and $SCOD$, respectively):

$$DD_{COD} = (SCOD - SCOD_0) / (SCOD_{NaOH} - SCOD_0) * 100\ (\%)$$ (Nickel and Neis, 2007)

To measure $SCOD_{NaOH}$, used as a reference to evaluate the efficiency of organic matter solubilisation under *US*/chemical treatment, the sludge sample was mixed with 0.5 M *NaOH* at room temperature for 24 h (Li *et al.*, 2009). Besides, total chemical oxygen demand (*TCOD*) was also measured by potassium dichromate oxidation method (standard AFNOR NFT 90-101), so that the calculation of DD_{COD} based on *TCOD* instead of $SCOD_{NaOH}$ (see § 1.3.2.1) could be provided for comparison. Prior to *TCOD* measurement, the sludge sample was well homogenized by ultraturax before being diluted by a factor 50.

For *SCOD* determination, the supernatant liquid was filtered under vacuum using a cellulose nitrate membrane with 0.2 µm pore size. Besides, colloidal *COD* fraction -between 0.2 and 1 µm- was also measured in some cases. The filtered liquid was subjected to *COD* analysis as described above. The change in the *SCOD* indirectly represents the quantity of organic carbon which has been transferred from the cell content (disruption) and solid materials (solubilisation) into the external liquid phase of sludge. The errors in *COD* measurement were less than 5%.

Fig 2.8: Equipment for *COD* measurement: (a) *COD* reactor, (b) Hach spectrophotometer

2.4.3. Laser diffraction sizing analysis

The ***particle size distribution* (*PSD*)** of sludge before and after treatment was determined by using a Malvern particle size analyzer (Mastersizer 2000, Malvern Inc.), a laser diffraction-based system (measuring range from 0.02 to 2000 µm), presented in Fig. 2.9.

The principle of the particle size measurement by laser diffraction is based on the angles of diffraction generated when a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering.

All samples were preserved at room temperature more than 1 h before the measurement in order to get the same status regarding possible re-agglomeration. Each sample was diluted approximately 300-fold in osmosed water, before being pumped into the measurement cell (suction mode). The *PSD* was based on the average of five measurements (the first one being deleted because the operation is difficult at the beginning of the analysis) showing deviations of less than 5%. Optical properties of the material were set as default (refractive index 1.52, absorption 0.1) appropriate for the majority of naturally occurring substances (Minervini, 2008; Bieganowski *et al*., 2012). Only in the small particle range (*i.e.* for particle diameter smaller than 10 µm), the refractive index dependence becomes significant (Govoreanu *et al*., 2009). Moreover it was checked that these mean optical properties led to a weighted residual parameter of less than 2% as recommended by the manufacturer. Since the primary result from laser diffraction is a volume distribution, the volume moment mean diameter *D[4,3]* (or de Brouckere mean diameter) was used to reflect the mean particle size of sludge.

As abovementioned, the first measurement was deleted. The flow rate of the solution should be adjusted properly and maintained during the measurement. Besides, the samples should be added very regularly and slowly to maintain the level in the funnel, as well as to avoid the creation of bubbles that could be considered as particles.

Fig 2.9: Malvern particle size analyzer (Mastersizer 2000, Malvern Inc.)

2.4.4. Microscope examination

The Morphologi G3 particle characterization system from Malvern Instruments Ltd. (Malvern, UK) was used mainly to examine sludge floc structures. It also provides high quality, statistically significant particle size and shape information thanks to a high-resolution camera attached to the microscope (Fig. 2.10) and an image processing software. From successively photographed surfaces, images of the particles are separated by digital thresholding techniques and then recorded and analyzed individually. For a few experiments, the particle size distribution it provides was also examined in complement to *PSD* results obtained from laser diffraction

A few drops of sludge sample were placed on a carrying glass and covered with a lid before being examined with Morphologi G3 using 2.5× to 50× magnification (2.5× corresponds to a size range from 13 to 1000 µm, while 50× to 0.5-40 µm). Prior to analysis, sludge samples with about 30 g/L of TS content were diluted by a factor 10 to 50.

Fig 2.10: Morphologi *G3* equipment

2.4.5. Biochemical methane potential (*BMP*)

BMP tests are used to establish anaerobic biodegradability for the determination of ultimate methane potential and biodegradation rate. Methods based on measuring the gaseous end-products (biogas) have been developed and reported as standard protocols with variety of experimental set-ups. The normal procedure is to inoculate vials containing a small amount of substrate with an anaerobic inoculum, to place them in an incubator with controlled temperature, and to periodically and manually check for methane produced.

The measurements were performed by *CRIIT Génie des Procédés et Technologies Environnementales* at *INSA* Toulouse. The exact protocol was as follows: 100 mL of sludge sample, 20 mL of phosphate buffer (54 g/L of Na_2HPO_4, 18 g/L of KH_2PO_4), 50 mL of inoculum and 0.36 mL of a 1 g/L resazurin solution (color indicator to detect oxygen) were added in a Pyrex bottle. Then it was completed up to 400 mL with water and checked for pH (7-8). The headspace was swept with nitrogen before closing. There was also one vial containing no sludge sample, but only the inoculum.

Each flask was equipped with a rubber septum maintained by a screw cap. A Pharmed® type tubing (0.8 mm internal diameter) was inserted through the septum to insure a complete seal. The other extremity of the tube was equipped with a clamp and a Luer type fitting for sampling (Fig. 2.11a). These vials were placed in a Heraeus oven at 35°C (Fig. 2.11b).

Product volume was estimated from the measurement of the pressure in the vial. The concentrations of methane *(CH_4)*, hydrogen *(H_2)*, and carbon dioxide *(CO_2)* were measured by gas chromatography (Fig. 2.11c). After each measurement of concentration, a degassing to atmospheric pressure was performed. *BMP* tests were stopped when production plateau was obtained (after 80 days).

(a) (b) (c)

Fig 2.11: Equipment for *BMP* tests: (a) sealed Pyrex bottle with sampling tube, (b) Heraeus oven, (c) 5890 series II gas chromatograph

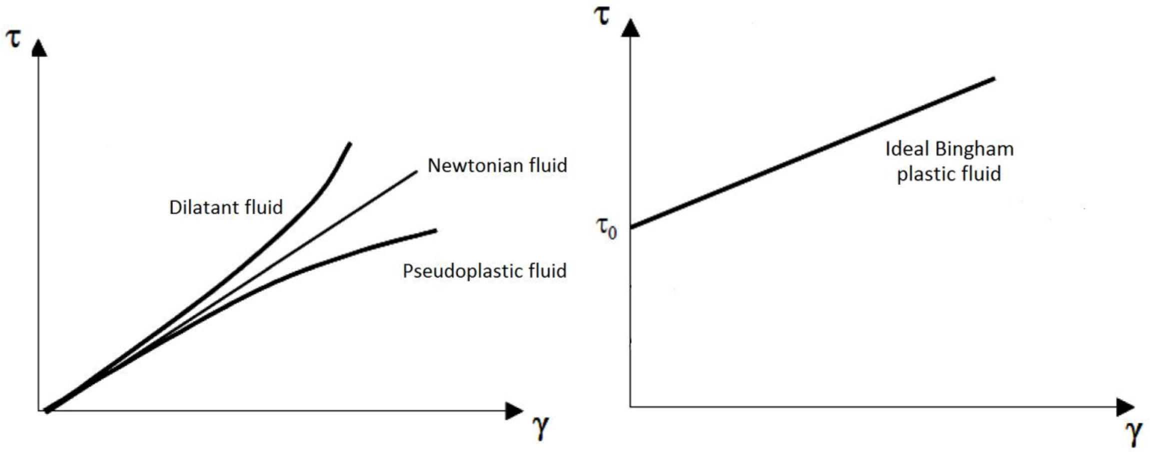
2.4.6. Rheology

Rheology is the study of flow and deformation of materials under applied forces and involves the measurement of shear stress τ in a fluid at various shear rates γ. Several mathematical models have been developed to describe the relationship between the two for substances which have a complex microstructure, such as sludge, suspensions, polymers, and other glass formers (*e.g.*, silicates), *etc.* and therefore exhibit a non-Newtonian behavior. Among them, the power law model is one of the most widely used, where:

$$\tau = K \cdot \gamma^{n}$$

and the apparent dynamic viscosity μ_{app} thus follows: $\mu_{app} = \frac{\tau}{\gamma} = K \cdot \gamma^{n-1}$

K is the consistency coefficient of the fluid (the greater the value of K the more viscous the fluid), and n is the flow behavior index, which is a measure of the degree of deviation from the Newtonian behavior: $n=1$ for Newtonian fluid, $n<1$ for pseudoplastic or shear-thinning material (effective viscosity decreases with shear rate), $n>1$ for dilatant or shear-thickening material (Fig. 2.12a). However some fluids, such as Bingham plastics (Fig. 2.12b), don't flow when a very small shear stress is applied, *i.e.* the shear stress must exceed a critical value known as yield stress (τ_0) for the fluid to flow.



(a) (b)

Fig 2.12: Flow curves of different fluids: (a) power law fluids, (b) Bingham plastic fluid

The Herschel–Bulkley model (1926) allows representing all the abovementioned behaviors and gives a better fit for many biological fluids than power law and Bingham fluid models, which it merges:

$$\tau = \tau_0 + K \cdot \gamma^n$$

The measurements were performed using an AR 2000 Rheometer (TA Instruments®) equipped with a cone (6 cm, 2°) and plate geometry (Fig. 2.13). The cone-plate geometry was recommended for sludge, due to the large size of sludge particles relative to the gap and the risk of centrifugation for coaxial cylinders and a less well defined velocity gradient for rotating blades (Spinosa and Wichmann, 2008). 2 mL of sludge sample were placed on the horizontal plate controlled at 25°C, and then the cone was rotated at a shear rate range of 0-1000 s^{-1}. Shear stress was measured and recorded corresponding to the investigated shear rates. Experiments were performed at increasing shear rates, then decreasing ones, to search for thixotropy. Fig. 2.14 shows a slight difference in between the two flow curves (closed and open red symbols) which might be due to a different organization of the sludge structure being exposed to high shear rates. This difference could be ignored as it was not more than that observed when changing measurement method (steady step *vs.* continuous ramp). Therefore model fitting was only performed on the increasing shear rate curve corresponding to equilibrium measurements. In most cases, Herschel–Bulkley model was found the most convenient and used thereafter to describe the rheological behavior of sludge. Fig. 2.14 shows an example of fitting by this model which has resulted in standard errors of less than 10%.

Fig 2.13: Rheometer *AR 2000* (*TA* Instruments)

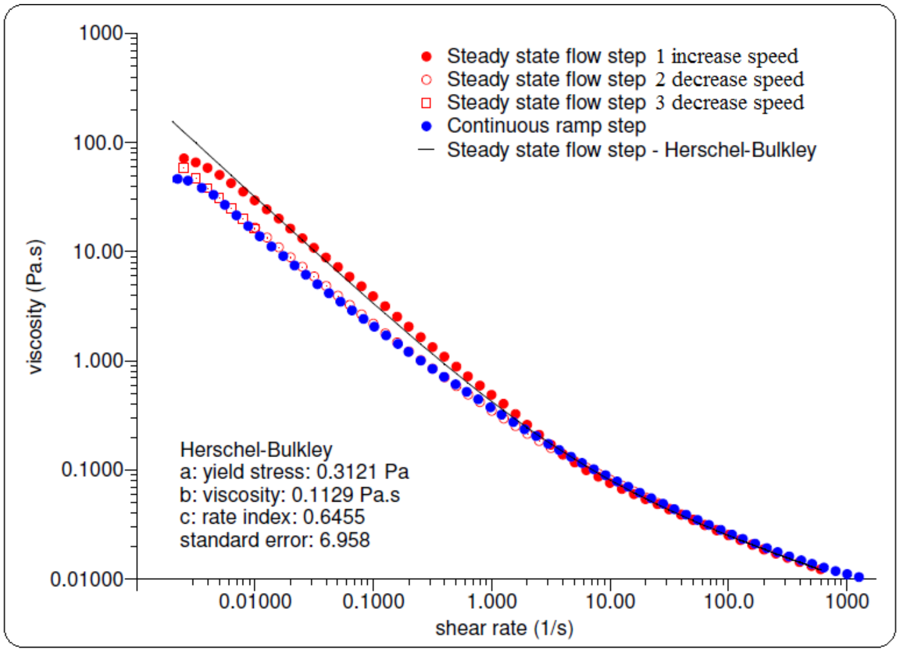


Fig 2.14: Rheological behavior of raw secondary sludge by Herschel–Bulkley model

---o0o---

Next chapters present the findings of sludge *US* pretreatment obtained from lab-scale experiments under a series of different conditions. The preliminary study of operation parameters is described first, then the effect of sonication parameters, followed by the discussion of the effect of external pressure on the efficiency of sludge *US* pretreatment. The last chapter is about the optimization of sludge *US* pretreatment.

CHAPTER 3

PRELIMINARY STUDY OF OPERATION PARAMETERS

HIGHLIGHTS

- Main operation parameters have been selected (*TS* of sludge, stirrer speed).

- Specific energy input *ES* plays a key role in sludge *US* disintegration.

- Sonication without cooling (―adiabatic”) is more efficient than isothermal sonication.

- The highest disintegration degree is found for secondary sludge.

- Mild alkalization of sludge before adiabatic sonication could be useful.

- Sludge particle size reduction is much faster than *COD* extraction.

INTRODUCTION

The objective of this preliminary section was to investigate the effects of some key operation parameters serving *US* process: total solid content of sludge *TS* (12-36 g/L), stirrer speed (250-1500 rpm), temperature conditions (adiabatic *vs.* isothermal), sludge type (mixed, secondary, and digested sludge), and prior sludge alkalization (using 22-77 mg_{NaOH}/g_{TS}). These parameters were varied separately or simultaneously. Most experiments were performed on mixed sludge with the initial 20 kHz equipment limited to P_{US} of 150 W and with a 35 mm diameter probe.

3.1. MATERIALS AND EXPERIMENTAL PROCEDURES

3.1.1. Sludge samples

In a first sampling (see Table 2.1, section 2.2), three types of sludge were collected from Ginestous *WWTP* or INSA (Toulouse, France) with a sufficient amount to test the operation parameters: mixed sludge (solid form, after centrifugation), secondary sludge (liquid form), and digested sludge (liquid form, after *AD* process of the secondary sludge).

From these samples, different suspensions were prepared whose properties are given in Table 3.1.

Table 3.1: Characteristics of prepared samples from 1st sludge collection

Parameter	**Value**				
Sludge samples	Defrosted mixed sludge		Fresh secondary sludge		Fresh digested sludge
Total solids (*TS*) (g/L)	28.0	14.0	28.0	14.0	14.0
Mean $SCOD_0$ (g/L)	2.7	1.5	4.5	1.9	0.4
$SCOD_{NaOH\ 0.5\ M}$ (g/L)	18.5	11.3	22.9	14.0	11.0
Total COD (TCOD) (g/L)	36.5	18.3	38.2	19.1	15.0
$SCOD_{NaOH}/TCOD$ (%)	50.7	61.7*	59.9	73.3*	73.3

*Higher ratios $SCOD_{NaOH}/TCOD$ at low *TS* might result from higher *NaOH/TS* ratios as same amount of *NaOH* was used.

A second mixed sludge sampling was conducted to investigate the effect of alkali addition prior to sonication (see Table 2.2, section 2.2). The properties of the corresponding suspension, prepared at 28 g/L *TS*, are displayed in Table 3.2 and show low difference with those of the previous mixed sludge sample (slightly higher organic content).

Table 3.2: Characteristics of prepared sample from 2nd sludge collection (mixed sludge)

Parameter	**Value**
Sludge sample	Defrosted mixed sludge
Total solids (*TS*) (g/L)	28.0
Mean $SCOD_0$ (g/L)	3.4
$SCOD_{NaOH\ 0.5\ M}$ (g/L)	19.6
Total *COD (TCOD)* (g/L)	38.9
$SCOD_{NaOH}/TCOD$ (%)	50.4

Additional experiments regarding the effect of *US* and temperature rise on DD_{COD} and evolution of sludge structures were performed with secondary sludge from the third sampling (see Table 2.3, section 2.2). Properties of the 28 g/L *TS* suspension are given in Table 3.3.

Table 3.3: Characteristics of prepared sample from 3rd sludge collection (secondary sludge)

Parameter		**Value**
Sludge sample		Defrosted secondary sludge
Total solids (*TS*)	(g/L)	28.0
Mean $SCOD_0$	(g/L)	2.8
$SCOD_{NaOH\ 0.5M}$	(g/L)	22.7
TCOD	(g/L)	36.3
$SCOD_{NaOH}/TCOD$	(%)	62.5

Finally, secondary sludge from the fourth sampling (see Table 2.3, section 2.2) was used to investigate the evolutions of the rheological behavior and of the soluble and colloidal *COD* fractions during *US* pretreatment. Properties of the sample prepared at 28 g/L *TS* is shown in Table 3.4.

Table 3.4: Characteristics of prepared sample from 4th sludge collection (secondary sludge)

Parameter		**Value**
Sludge sample		Defrosted secondary sludge
Total solids (*TS*)	(g/L)	28.0
Mean $SCOD_0$	(g/L)	4.1
$SCOD_{NaOH\ 0.5M}$	(g/L)	22.1
TCOD	(g/L)	39.1
$SCOD_{NaOH}/TCOD$	(%)	56.5

It can be noted that $SCOD_{NaOH}/TCOD$ ratio is higher for secondary and digested sludge samples than that of mixed sludge samples, which suggests that those sludge types are more readily disintegrated.

3.1.2. Experimental procedures

20 kHz *US* was emitted in a cup-horn autoclave reactor provided with a 35 mm diameter probe (labeled *BP*) and connected to a pressurized N_2 reservoir. Both the experimental set-up and operation mode are described in section 2.3.

For each experiment, a constant volume of synthetic sludge sample (0.5 L) was poured into the stainless steel reactor. Five different sonication times corresponding to five values of *ES* (7000, 12000, 35000, 50000, and 75000 kJ/kg_{TS}) were tested at P_{US} = 150 W.

$$ES = (P_{US} * t) / (V * TS)$$

with *ES*: specific energy input, energy per total solid weight (kJ/kg_{TS}), P_{US}: *US* power input (W), *t*: sonication duration (s), *V*: volume of sludge (L), and *TS*: total solid concentration (g/L).

First, mixed sludge was used to investigate the influence of *TS* content (12-36 g/L) and stirrer speed (250-1500 rpm), as well as separate and combined effects of ultrasound and temperature (which increases due to *US,* if uncontrolled) on sludge disintegration. Thereafter, the effect of sludge type was tested in both isothermal and adiabatic conditions.

For the effect of alkali addition, according to previous studies (Kim *et al.,* 2003; Jin *et al.,* 2009), NaOH was used for modifying the initial pH of sludge. Regarding the treatment sequence, –alkalisation followed by *US* pretreatment” was more effective than the reverse combination, as it allows the *US* treatment to benefit from the weakening of the sludge matrix. Conversely, the disrupted floc fragments could be re-aggregated into compact structures by the subsequent NaOH treatment (Jin *et al.,* 2009). Consequently, the former procedure was chosen for alkaline-*US* experiments.

3.2. RESULTS AND DISCUSSION

3.2.1. DD_{COD} evolution

It should be recalled here that DD_{COD} results were calculated based on chemical reference ($SCOD_{NaOH}$). When comparing the different types of sludge, efficiency in terms of *TCOD* is also discussed.

3.2.1.1. Effect of TS concentration

Five synthetic mixed sludge samples (S12, S24, S28, S32, and S36 corresponding to 12, 24, 28, 32, and 36 g/L of *TS*, respectively) were treated at atmospheric pressure, under adiabatic condition. The stirrer speed was set at 500 rpm. The results are presented in Fig. 3.1. The experiments at 28 g/L were triplicated and the coefficient of variation of DD_{COD} was about 5% (see error bars in Fig. 3.1). In the following studies, some experiments were repeated showing the same differences.

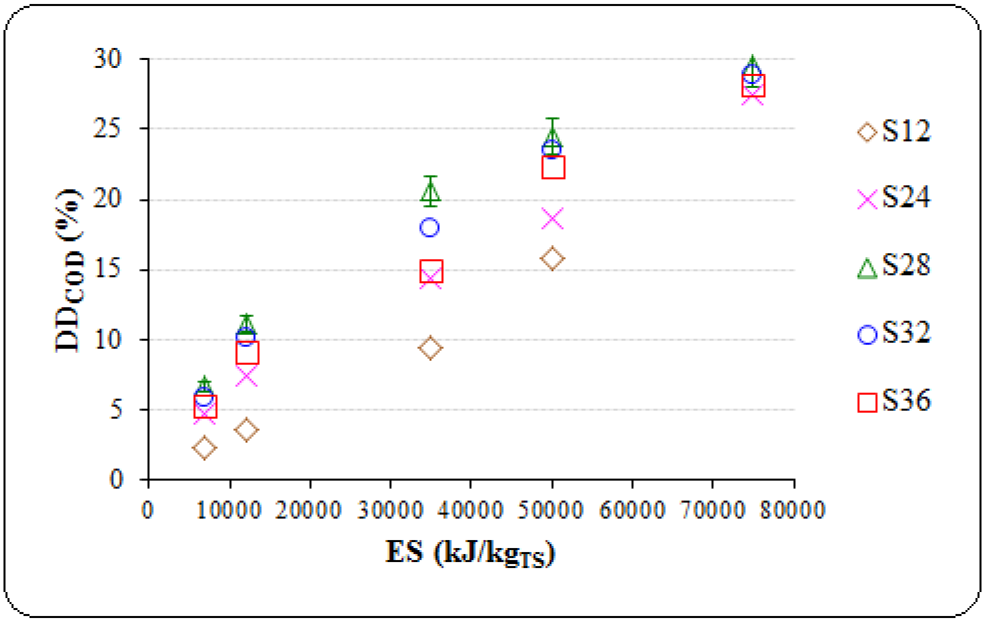


Fig 3.1: Effect of *TS* content on mixed sludge disintegration (DD_{COD}) *vs. ES*: P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.1), adiabatic condition, and atmospheric pressure

SCOD gradually increased with sonication time (0-150 min), but less and less. The relation between *SCOD* and *TS* content is not simple because the best DD_{COD} was not found at the maximum *TS*. For example, at *ES* of 7000 kJ/kg_{TS}, *SCOD* was improved by 2.4-fold when increasing *TS* from 12 to 24 g/L, but it did not significantly change for higher values. Fig. 3.1 actually exhibits a *TS* optimal value of 28 g/L in terms of DD_{COD} over the whole *ES* range. This behavior is in agreement with other studies (Mao *et al.*, 2004; Akin *et al.*, 2006; Show *et al.*, 2007; Zhang *et al.*, 2008b; Kidak *et al.*, 2009; Pilli *et al.*, 2011) and can be explained by opposite effects. The more *TS* of sludge, the more cells and aggregates are in contact with cavitation bubbles, thus the more efficiently P_{US} is consumed. On the other hand, the acoustic pressure field decreases faster from the emitter due to the poor propagation of the *US* wave in a higher *TS* suspension. Consequently, acoustic cavitation intensity is reduced. These two opposite effects lead to an optimum *TS* concentration that could slightly depend on sludge characteristics, operating conditions, and reactor design, *etc*. Some additional isothermal experiments on secondary sludge at lower frequency and higher pressure, presented in Appendix 2, seem to confirm this *TS* optimum not to depend on sludge type, frequency, nor pressure. For all the following experiments of this work (excepting those with digested sludge), synthetic samples were then prepared to match this 28 g/L *TS* concentration. It is interesting to note that this ―optimum" sludge concentration is close to the actual concentration of secondary sludge which could be treated directly.

3.2.1.2. Effect of stirrer speed

To know the effect of stirrer speed on DD_{COD} when *US* is applied, preliminary experiments at 250, 500, and 1500 rpm were carried out under ambient conditions (controlled *T* of 28±2°C, atmospheric pressure) with mixed sludge. Fig. 3.2 shows the resulting time-evolution of DD_{COD}.

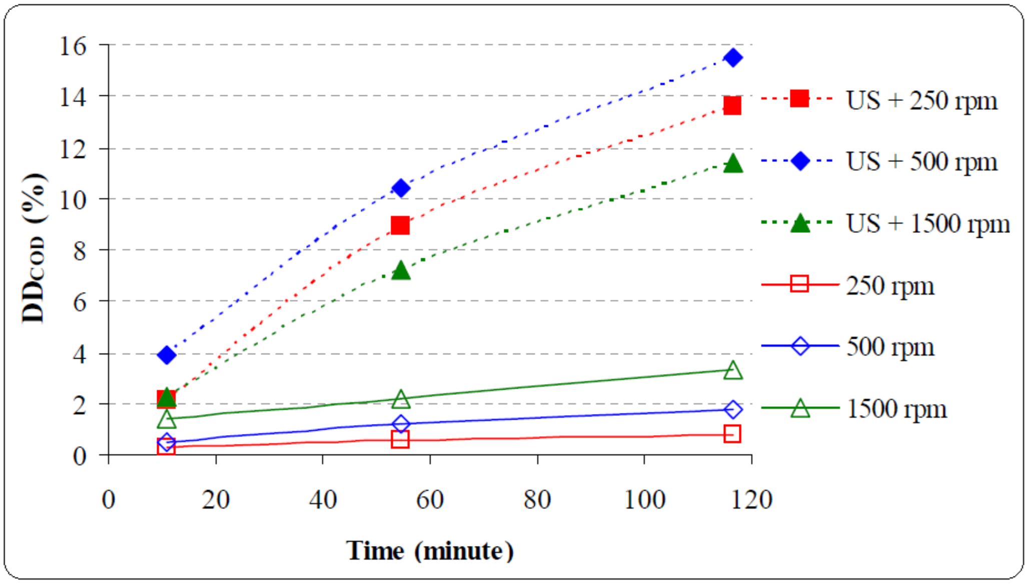


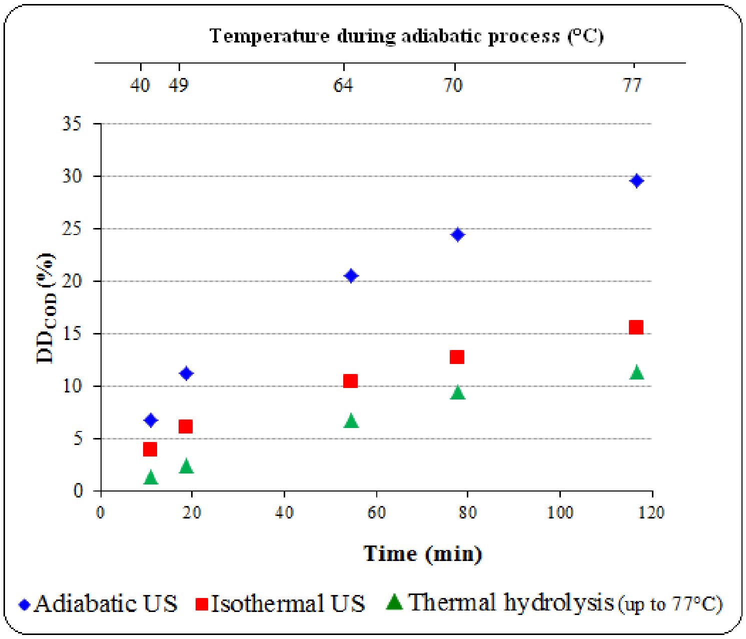
Fig 3.2: Effect of stirrer speed on time-evolution of mixed sludge disintegration P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.1), *T* = 28±2°C, and atmospheric pressure

As expected, for blank experiments (without *US*), the faster the stirring was, the higher the sludge disintegration was: after 2 h of stirring, DD_{COD} was 0.8, 1.8, and 3.3% for a stirrer speed of 250, 500, and 1500 rpm, respectively. However, these DD_{COD} values as well as the differences observed among the three corresponding series under *US* were rather low, which indicated that the main role of the stirrer was to make a homogeneous dispersion, rather than to efficiently enhance the transfer of organic matters from solid to aqueous phase.

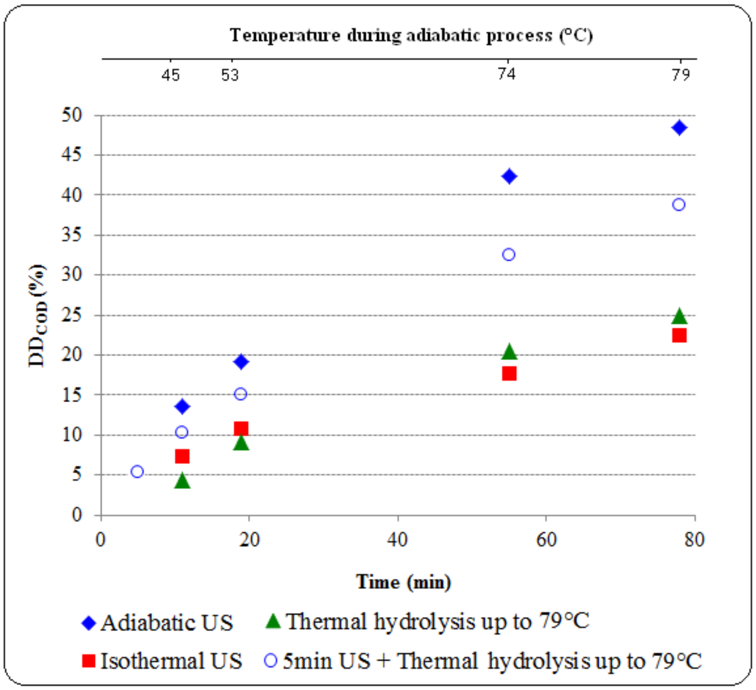
Under *US*, DD_{COD} increased when raising the stirrer speed from 250 rpm to 500 rpm, but decreased at 1500 rpm. The reactor was not equipped with baffles. Consequently high rotation speed of the whole liquid could result in the centrifugation of particles, leading to less particles present in the central zone where *US* is concentrated, then to a decrease of the sludge *US* pretreatment efficiency. In addition, aeration could occur and its main effect would be to severely damp the acoustic waves. Therefore, a stirrer speed of 500 rpm was applied in subsequent experiments of this work.

3.2.1.3. Effect of temperature rise under “adiabatic” conditions (without cooling)

The ultrasonic pretreatment has two simultaneous effects: (i) extreme macro and micro mixing caused by cavitation, and (ii) increase in the bulk temperature. To evaluate their individual contribution, different operating procedures were carried out for mixed (Fig. 3.3a) and secondary sludge (Fig. 3.3b): (1) *US* under isothermal conditions (cooling at 28±2°C), (2) *US* under ―adiabatic” conditions, (3) thermal hydrolysis: without *US* and with progressive increase of *T* as recorded in (2), and (4) 5 min of *US* and progressive increase of *T* afterwards (this series was conducted only on secondary sludge).



(a)



(b)

Fig 3.3: Effect of temperature profile* on time-evolution of sludge disintegration (DD_{COD}): P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L, and atmospheric pressure. (a) Synthetic mixed sludge (Table 3.1), (b) synthetic secondary sludge (Table 3.3).

*The upper x-axis indicates the evolution of temperature during adiabatic *US* and thermal hydrolysis (note that higher temperature at same *ES* was achieved with the new equipment)

At all observations, DD_{COD} values under adiabatic sonication were the highest, followed by those under short time *US* + thermal hydrolysis, then under low temperature sonication and finally under thermal hydrolysis only**.** DD_{COD} values of sonicated samples under cooling (28°C) were about half those obtained under adiabatic conditions.

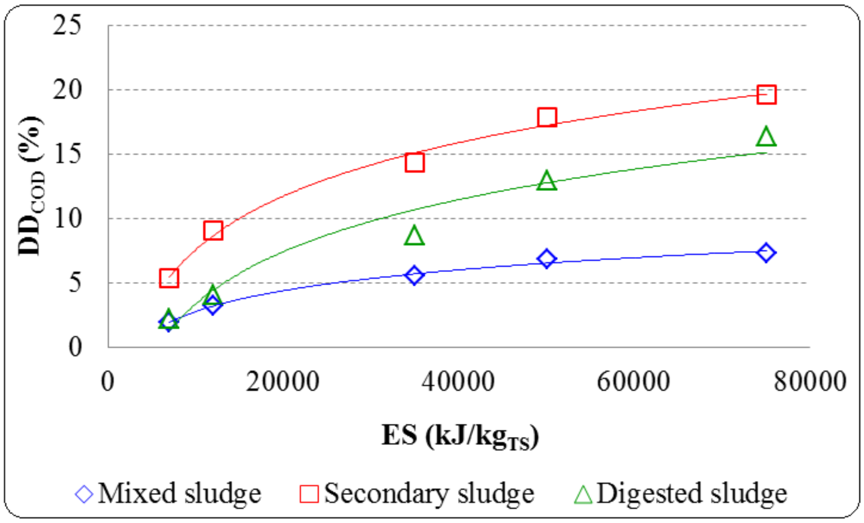
The main information brought by these experiments are as follows: (i) cavitation and thermal hydrolysis seem to show almost additional effects during adiabatic *US*, (ii) thermal hydrolysis of early disrupted sludge is faster than that of raw sludge (Fig. 3.3b); therefore the combined effect is actually more complex: cavitation acts mainly during the early stage of the adiabatic sonication, then *US* being progressively damped by the increasing temperature, thermal hydrolysis takes over, being ―boosted" by the initial work of *US*.

The resulting positive effect of combining *US* and temperature for sludge disintegration is in agreement with the conclusion of earlier works (Chu *et al.*, 2001; Kidak *et al.*, 2009; Li *et al.*, 2009) but opposite to most power *US* applications in which temperature only damps cavitation.

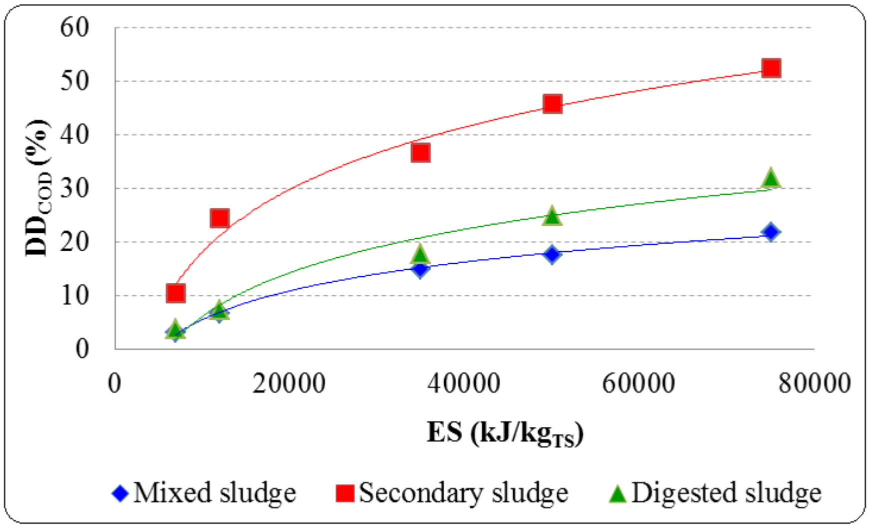
3.2.1.4. Effect of sludge type

Comparison of Fig. 3.3a and Fig. 3.3b shows secondary sludge (from 3rd sampling) to be better disintegrated than mixed sludge by *US* treatment, regardless of temperature control.

For further comprehension, the disintegration of different sludge types by both isothermal and adiabatic sonication was investigated with reduced *TS* of 14 g/L (as digested sludge was not available at 28 g/L). Fig. 3.4 and Fig. 3.5 depict disintegration degree of different sludge types calculated based on $SCOD_{NaOH}$ and *TCOD*, respectively. They once again indicate the predominance of adiabatic *US* as compared to isothermal *US* in terms of sludge disintegration. In addition, higher disintegration degrees (either based on *TCOD* or $SCOD_{NaOH}$) were found for secondary sludge, followed by digested sludge and mixed sludge, in all conditions. *AD* might have therefore consumed a fraction of *COD* which was the most readily solubilized. Note that *TCOD* based graphs slightly amplify the differences between mixed sludge and the others.

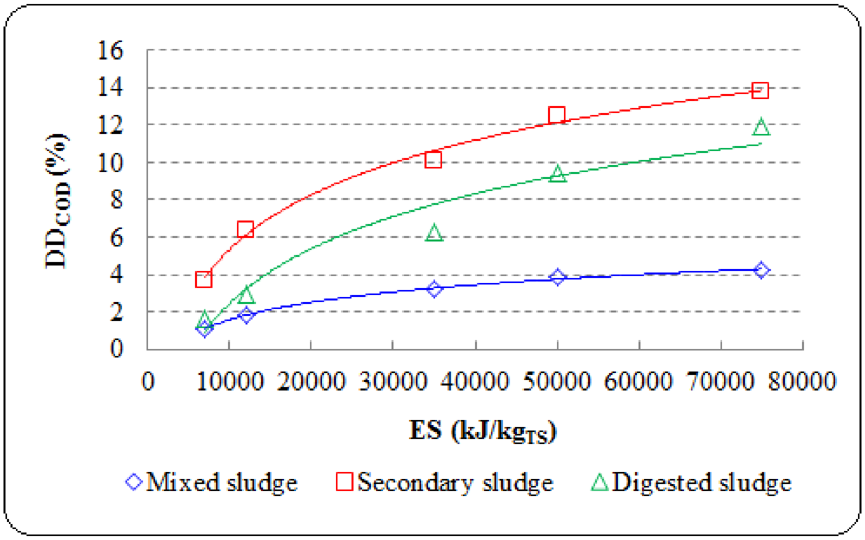


(a)

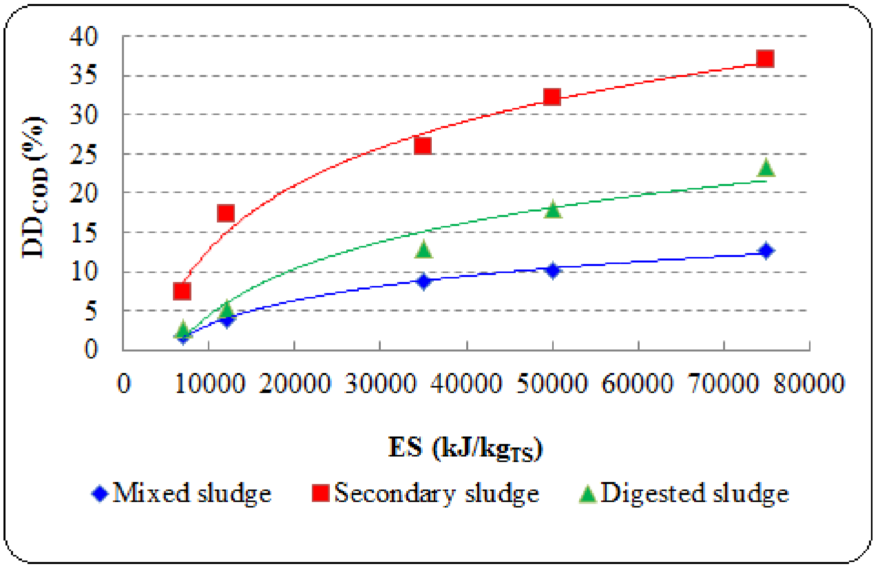


(b)

Fig 3.4: Effect of *ES* on *US* pretreatment efficacy of different sludge types (DD_{COD} based on $SCOD_{NaOH}$): P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 14 g/L (other properties in Table 3.1), and atmospheric pressure. (a) *T* = 28±2°C and (b) adiabatic condition



(a)



(b)

Fig 3.5: Effect of *ES* on *US* pretreatment efficacy of different sludge types with DD_{COD} based on *TCOD**: P_{US} = 150 W, *BP*, *FS* = 20 kHz, *TS* = 14 g/L (other properties in Table 3.1), and atmospheric pressure. (a) *T* = 28±2°C and (b) adiabatic condition.

* = $(SCOD_{US} – SCOD_0)/(TCOD-SCOD_0)*100$

3.2.1.5. Effect of alkaline addition prior to sonication

A given amount of NaOH was added into the fixed volume of mixed sludge to ensure the same condition of chemical application. The kinetics of sludge disintegration by NaOH was first investigated to select one convenient holding time corresponding to the most significant *COD* release. Sonication was then applied to alkalized sludge samples and the effects of *NaOH dose*, *ES* in the range of 0-75000 kJ/kg$_{TS}$, and *temperature profile* (isothermal/adiabatic conditions) were examined in order to improve sludge disintegration.

NaOH doses of 22, 40, 47, and 77 mg$_{NaOH}$/g$_{TS}$ were added to the mixed sludge solution, whose properties were given in Table 3.2, and let under stirring at room temperature for different time periods up to 2 h. Note for comparison that 714 mg$_{NaOH}$/g$_{TS}$ were used for the measurement of the reference $SCOD_{NaOH}$ with *TS* =28 g/L. These samples were labelled sol. 22, sol. 40, sol. 47, and sol. 77, respectively. The evolutions of pH and DD_{COD} of the samples as a function of time are shown in Table 3.5.

According to Kim *et al*. (2010), alkaline pretreatment usually acts faster than other methods. Indeed, in all cases, alkaline treatment resulted in a fast solubilisation of *COD*, more than 50% of the maximal observed yield being achieved within 10 min, followed by a quasi-plateau after 30 min. Therefore, a holding time of 30 min was selected for subsequent experiments combined with *US*. During this period, the pH of the sludge samples dropped about one unit as shown in Table 3.5. A comparison of sole alkaline and sole *US* pretreatment of sludge was also carried out and is presented in Appendix 3.

Table 3.5: Alkaline pretreatment of mixed sludge (Table 3.2) at room temperature

	Holding time (min)						
	0.5	10	20	30		40	117
	DD_{COD} (%)						
Sol. 22	*(pH 9.6)*	6.4	7.3	9.5	*(pH 8.6)*	10.7	12.3
Sol. 40	*(pH 10.2)*	11.5	13.3	17.0	*(pH 9.4)*	18.3	21.0
Sol. 47	*(pH 11.1)*	13.0	15.8	19.3	*(pH 10.1)*	21.0	22.5
Sol. 77	*(pH 12.2)*	24.4	26.3	29.0	*(pH 11.0)*	30.4	33.1

Subsequently, effect of *NaOH* addition prior to sonication was looked into. Different mixed sludge samples were prepared by adding increasing doses of *NaOH* (as per sol. 22 to sol. 77) and letting react for 30 min under stirring before applying *US* for 2 h.

Fig. 3.6 compares the final DD_{COD} values of the combined pretreatment to those of the *US* pretreatment, with and without cooling. As expected, alkali-*US* pretreatment was the most effective technique for sludge disintegration, and the resulting efficacy was nearly the sum of individual alkali and *US* pretreatments when sol. 22 or sol. 40 were kept under isothermal conditions (28°C). Jin *et al.* (2009) also observed such a result. Alkalisation also significantly reduced the differences observed between isothermal and adiabatic modes of *US* treatment. It is also worth noting that under *US*, the differences resulting from the addition of high NaOH amounts tended to vanish.

As shown in Table. 3.5, the higher the pH, the more easily the processes of natural shape losing of proteins, saponification of lipid, and hydrolysis of *RNA* occur (Li *et al.*, 2008; Carrère *et al.*, 2010). However, for overall process economy (related to chemicals used in pretreatment stage as well as in neutralisation step required for *AD*), NaOH addition should be limited. Moreover, high concentration of Na^+ was reported to cause the inhibition of *AD* (Carrère *et al.*, 2010). Thereby, selection of NaOH dose must be based on the pH of pretreated sludge which should comply with subsequent treatment - *AD* requiring a narrow pH range between 6.5 and 8 (Kim *et al.*, 2003). According to Fig. 3.6, pH of alkalized-sonicated mixed sludge solutions varied between 7.8 and 10.2 under cooling and between 7.1 and 9.2 under adiabatic condition. The upper pH values might be too high for a subsequent valorisation by *AD*. Therefore, addition of a small NaOH dose (as per sol. 22 or sol. 40) could be indeed a suitable option for the whole process. Nevertheless, no real synergy effect was observed as the best performance of the combined treatment was the sum of the individual ones, so this parameter was not systematically examined in the further studies.

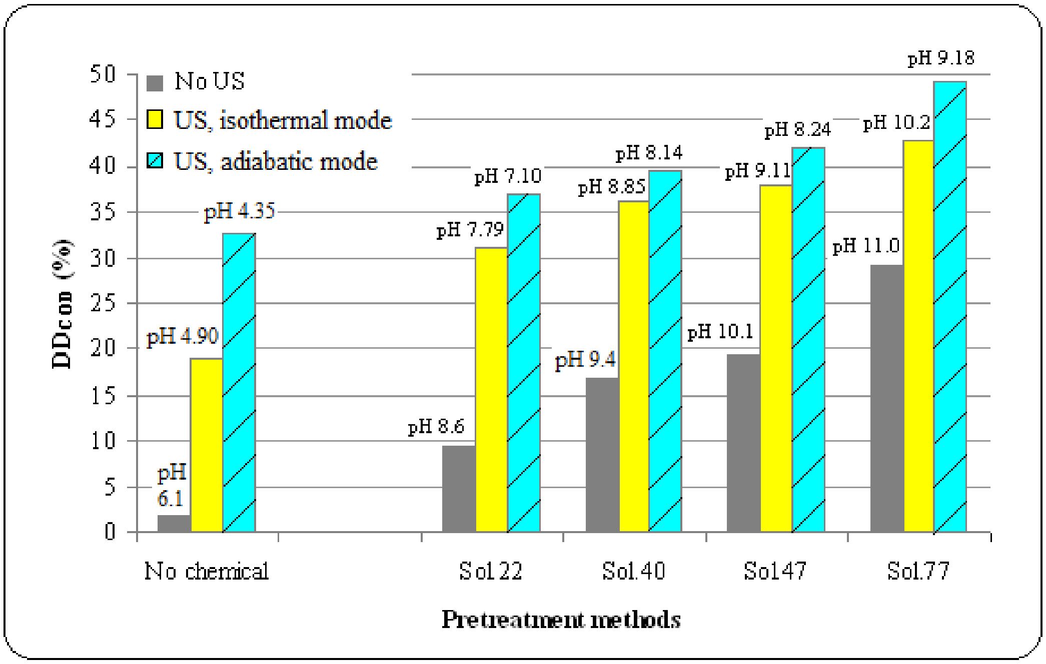


Fig 3.6: Comparison of different methods for mixed sludge disintegration (*TS* = 28 g/L, other properties in Table 3.2): F_S = 20 kHz, P_{US} = 150 W, *BP*, sonication duration = 117 min, NaOH dose = 0-77 mg_{NaOH}/g_{TS} (holding time = 30 min), and atmospheric pressure. Final pH value after treatment is also indicated on top of each corresponding bar

Only the combined effect of mild alkalization, temperature variations without cooling, and external pressure on mixed sludge *US* pretreatment was investigated and is presented in Appendix 3. The same conclusions were pointed out regarding the effect of *T* and alkalisation, but at 2 bar of external pressure, the overall process was still improved: up to about 46% of DD_{COD} after 2 h of adiabatic *US* for sol. 40. The final pH of 7.6 was also suitable for *AD*.

3.2.2. Particle size reduction and evolution of sludge structures

3.2.2.1 Analysis of laser diffraction measurements

Ultrasonic pretreatment is also very effective in reducing the particle size, which is sometimes used to assess the degree of sludge disintegration and commonly analyzed by laser diffraction as in this section. The reduction in particle size should accelerate the hydrolysis stage of sludge *AD* and enhance degradation of organic matters (Muller *et al*., 2004).

Fig. 3.7 describes the variation of the volume moment mean diameter (*D[4,3]*) of different sludge types (Table 3.1) as a function of *ES*. In accordance with Show *et al*. (2007), the mean particle sizes of secondary and digested sludge are lower than those of mixed sludge due to the aforementioned differences of properties.

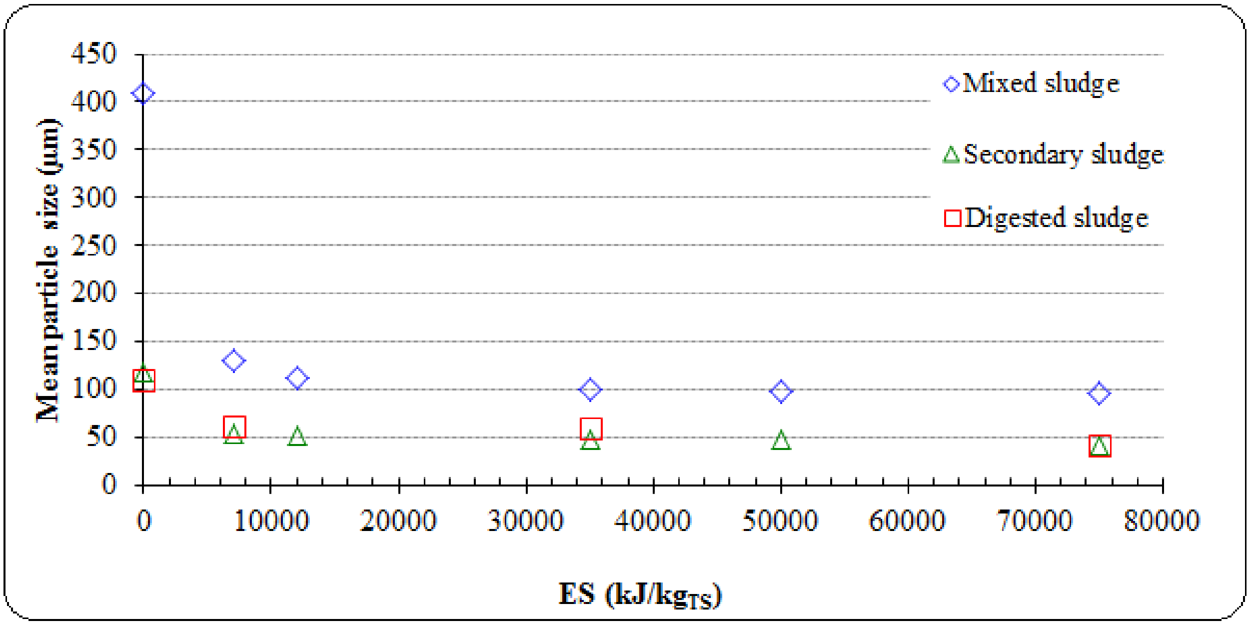


Fig 3.7: Mean particle (*D[4,3]*) size evolution of different types of sludge during *US* pretreatment: P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.1), and *T* = 28±2°C, atmospheric pressure

The highest particle size reduction was observed for mixed sludge, whose mean diameter was reduced by 68% to 77% when *ES* was increased from 7000 to 75000 kJ/kg$_{TS}$. Note that in this case, fresh sludge samples were used for secondary and digested sludge (no freezing). Suspensions prepared from defrosted secondary sludge exhibit a much higher initial size, probably due to a too gentle stirring during the preparation to break all agglomerates formed during freezing process. In addition, samples from different collections of same sludge type exhibit large discrepancies in mean particle size.

A fast particle size reduction was observed within a very short sonication duration, which is in agreement with Tiehm *et al.*, 1997 and Chu *et al.*, 2001. Additional *PSD* measurements for secondary sludge pretreated by adiabatic *US* at P_{US} of 150 W were also carried out. The same trend of fast particle size reduction was found and improvements of size reduction compared to isothermal *US* were insignificant. Under thermal hydrolysis only (with progressive temperature rise up to 78°C during 2 h), mean particle size slightly decreased within the first ten minutes about 14 % and kept almost unchanged afterwards.

In more details, Fig. 3.8 exhibits the evolution of mixed sludge *PSD* for different *ES* values: corresponding d_{90}, d_{50}, and d_{10} parameters decreased by 74%, 70% and 58%, respectively in the *ES* range of 7000 – 75000 kJ/kg_{TS}. This indicated that different particle sizes had slightly different reduction extents, in which large particles were disrupted more effectively by *US* than smaller ones (with a very fast reduction of particles of about 1000 µm). This point is similar to conclusions in previous works (Show *et al*., 2007; Pilli *et al.*, 2011)**.** It could be partly due to different consistency as large particles have been formed from the aggregation of smaller ones.

Remark: as shown in Fig. 3.8, the distribution of initial sludge was cut at 1950 µm which in fact corresponds to 99.86% of cumulative volume. Then the residual larger particles may be ignored.

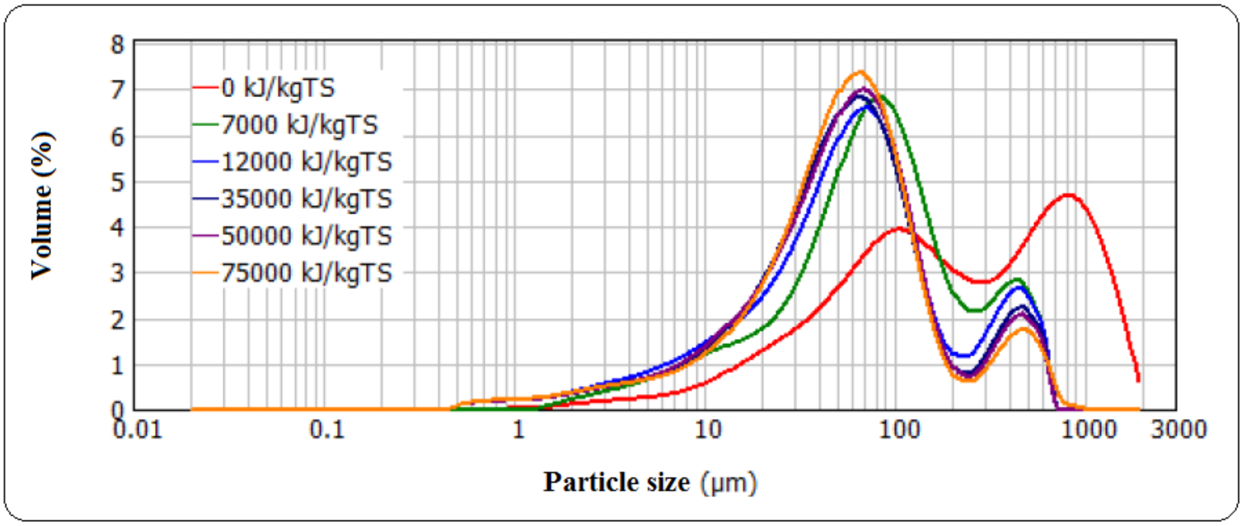


Fig 3.8: Evolution of particle size distribution of mixed sludge during *US* pretreatment: P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.1), *T* = 28±2°C, and atmospheric pressure

Gonze *et al.* (2003) found that particle size was decreased gradually with the increase in sonication time but that a reverse trend occurred after 10 min of sonication due to the re-flocculation of the particles. However, this phenomenon was not found in this work, probably due to higher ultrasound power. In order to better understand the effect of sonication on particle charges, zeta potential measurements were performed. First, zeta potential could not be measured with the actual suspension -due to too high particle size- but only with filtered suspension (<1 µm). Sonication was shown to have only marginal effect on zeta potential: -11.3 and -13.2 mV corresponding to pretreated sludge at 7000 kJ/kg$_{TS}$ and 50000 kJ/kg$_{TS}$, respectively, as compared to that of -6.94 mV for raw one. These small variations indicate a very low modification of surface charges by *US* treatment and the trend suggests even more stability. This result is then in agreement with the absence of re-flocculation.

Experiments were also carried out with sludge sampling at much shorter times of sonication, with and without prior alkalinisation. Mixed sludge sample corresponding to Table 3.2 was used for these tests. Fig. 3.9 shows that the particle size reduction occurs within the first 4 minutes of sonication. Moreover it indicates that if mild alkalinisation contributes to particle size reduction, its combination with *US* pretreatment leads to almost the same final *D[4,3]* value, of about 100 µm.

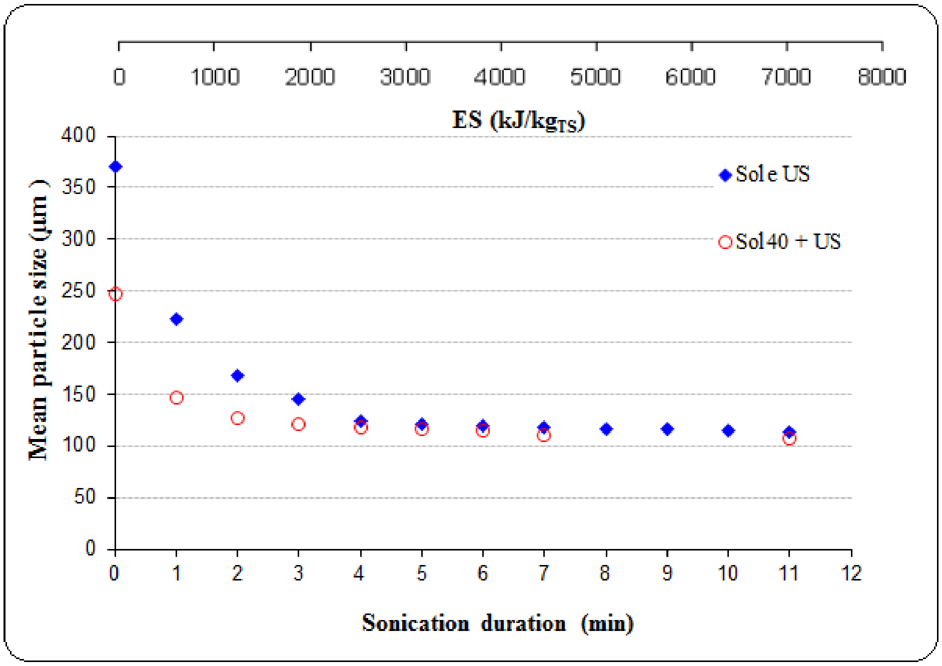


Fig 3.9: Mean particle size (*D[4,3]*) evolution of mixed sludge during the early stage of (alkali-) *US* pretreatment: P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.2), *T* = 28±2°C, and atmospheric pressure

Following the work of Gonze *et al.* (2003), the particle size distributions were deconvoluated into five populations, each corresponding to a log-normal distribution. The treatment was performed using OriginPro 8.6 (OriginLab). An example is given in Fig. 3.10 for the raw mixed sludge: a very small extra peak might be distinguished around 1 µm, but its contribution was always so low that it could not be adequately detected. Therefore, its contribution was neglected.

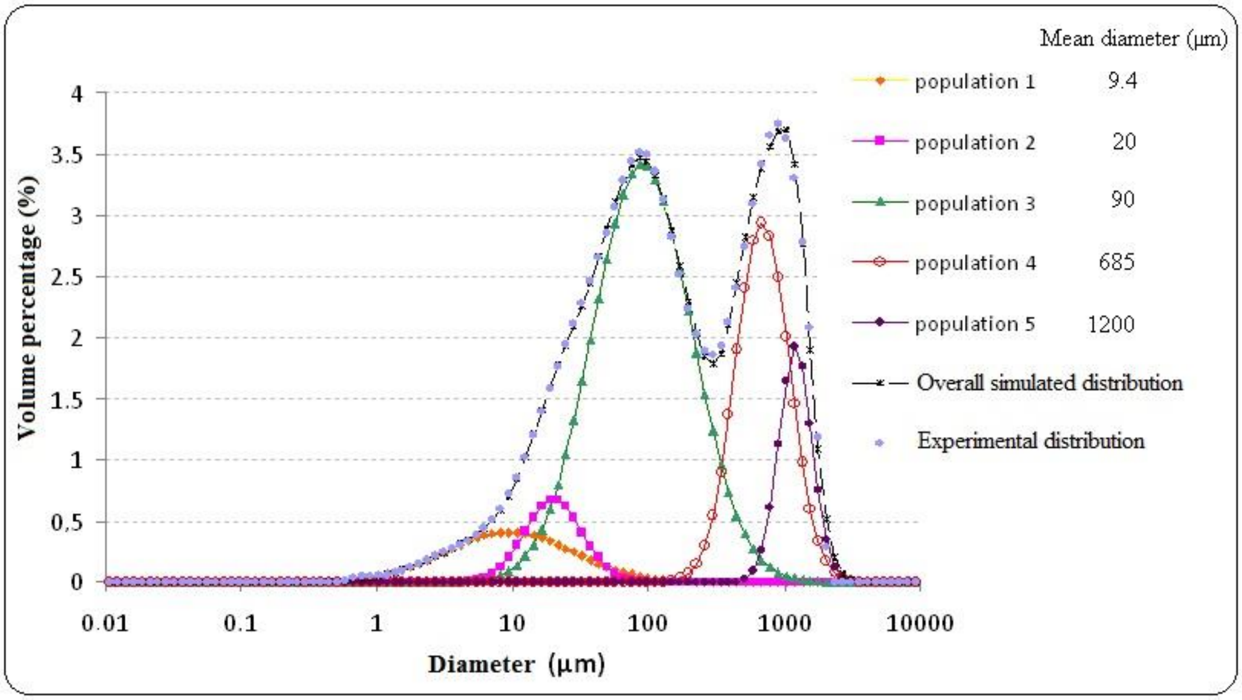
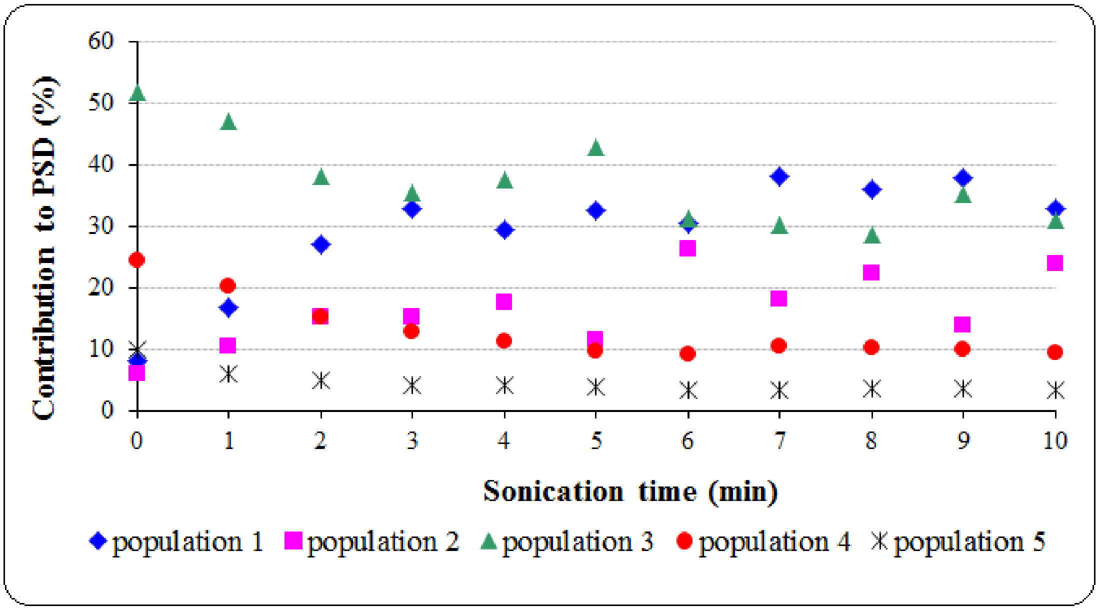


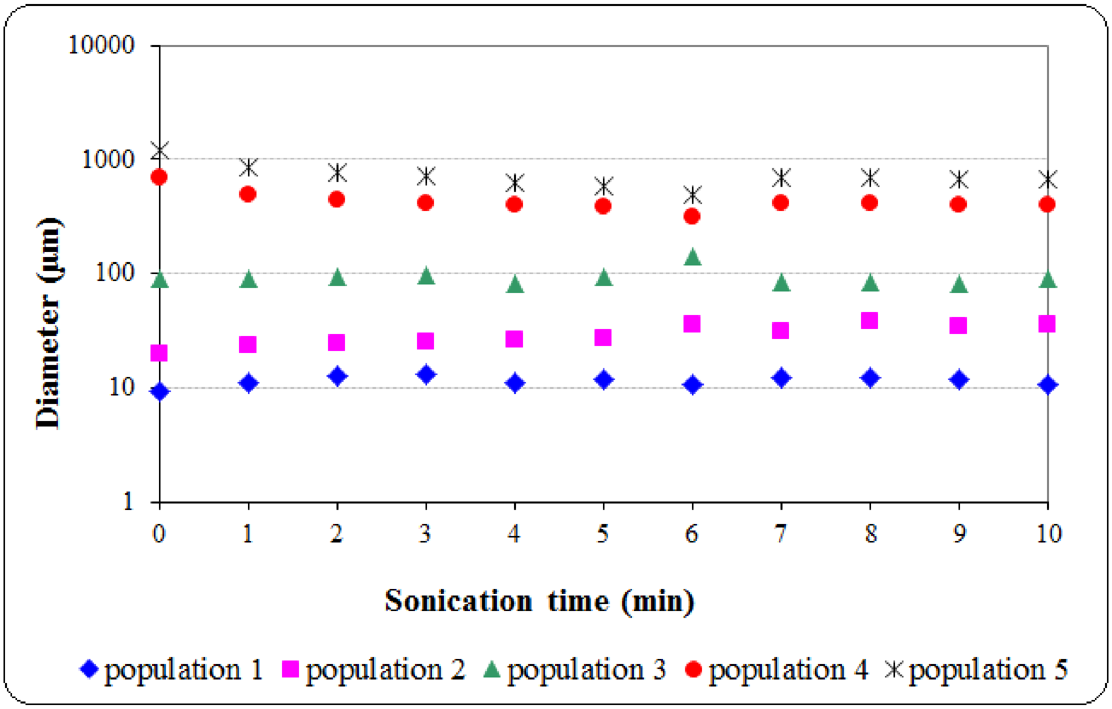
Fig 3.10: Deconvolution of *PSD* of raw mixed sludge (Table 3.2)

Fig. 3.11a shows the evolution of each population contribution during the *US* treatment: two macro-floc populations - population 4 and 5 of 685 µm and 1200 µm, respectively - could be distinguished in the mixed sludge, both their mean diameter and contribution significantly decreased during the first 4 min of sonication. Their diameter dropped to about 400 µm and 650 µm, respectively, while their contribution was divided by a factor 2.5 to 3 (Fig. 3.11b). Conversely, the size of populations 1 to 3 (about 10 µm, 20 µm, and 90 µm, respectively) remained almost constant during short *US* treatment. It seems thus that the decrease of the largest macro-flocs proceeded mainly according to erosion mechanism while population 3 was disrupted into micro-flocs (population 1).

After the 30 min of NaOH pretreatment (using 40 mg_{NaOH}/g_{TS}), the diameters of population 1 and 4 were reduced about 20% as compared to raw mixed sludge and the contributions of populations 4 and 5 were reduced by a factor 1.3 and 1.8, respectively (in favour of populations 2 and 3). However, their evolution under subsequent sonication, described in Fig. 3.12, remained similar as without NaOH addition. In this condition, mean diameter of population 4 and 5 dropped to 400 and 600 µm, respectively while that of populations 1 to 3 kept almost unchanged.

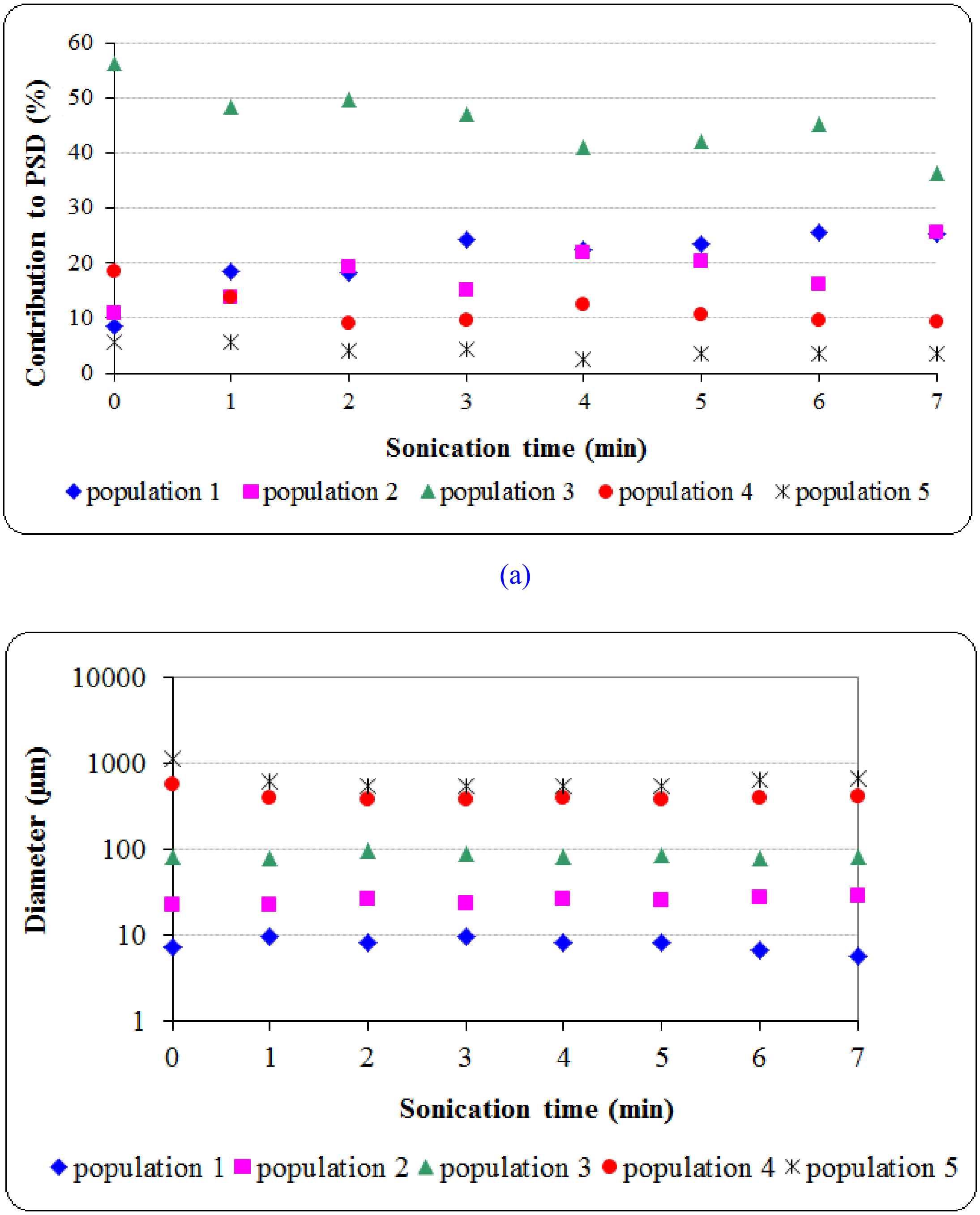


(a)



(b)

Fig 3.11: Evolution of *PSD* of mixed sludge during short sonication: (a) contribution of each population to *PSD*, (b) mean diameter of the populations (P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.2), *T* = 28±2°C, and atmospheric pressure)



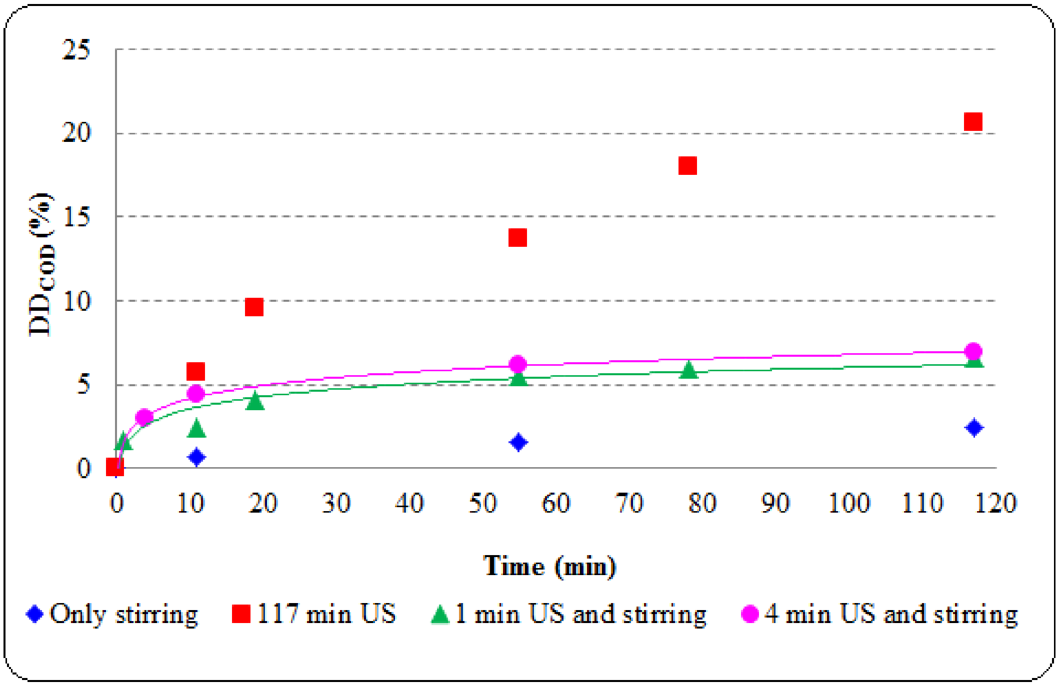
(a)

(b)

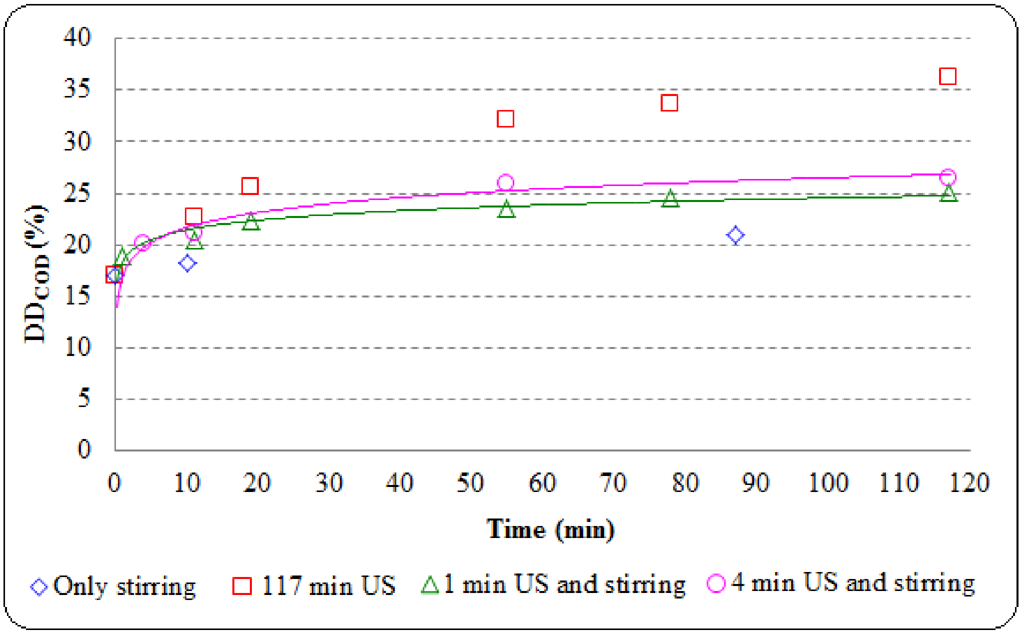
Fig 3.12: Evolution of *PSD* of mixed sludge during short sonication after NaOH addition (40 mg_{NaOH}/g_{TS}): (a) contribution of each population to *PSD*, (b) mean diameter of the populations (P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.2), *T* = 28±2°C, and atmospheric pressure)

For comprehension of the relationship between mean particle size reduction and *COD* solubilisation, additional isothermal experiments with and without pH modification (40 mg_{NaOH}/g_{TS}) were carried out in the following conditions: *US* were applied during the first minute or the first 4 min, and then only the stirrer was continuously operated under constant temperature (*T* = 28±2°C). Despite these two sonication durations resulted in distinct *D[4,3]*, especially under natural pH (Fig. 3.9), no differences were observed in terms of DD_{COD} afterwards (Fig. 3.13). These short *US* pretreatments provided first a small initial jump, then a slight enhancement of *COD* release. It is however much lower than observed in Fig. 3.3b when early disrupted sludge was subjected to a subsequent temperature rise.

Under room temperature conditions, the strong reduction of mean particle size achieved at low *ES* is not sufficient to affect *COD* solubilisation.



(a)



(b)

Fig 3.13: Effect of short sonication time on mixed sludge disintegration: P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.2), *T* = 28±2°C, and atmospheric pressure. (a) Without NaOH and (b) with addition of 40 mg_{NaOH}/g_{TS} (30 min of holding time)

3.2.2.2 Analysis of sludge particle images

Apart from analysis of Mastersizer 2000 *PSD*, effects of *US* and temperature rise on particle size and morphological parameters were examined by image processing of secondary sludge (Table 3.3) photographs from Morphologi G3 (some examples with lower magnifications than those used for image processing are shown in Fig. 3.14).

Morphologi G3 software captures 2D projection images of the particles (50000 to 100000 recorded particles), separates each 2D object and analyses its size and morphological characteristics, providing data on a number basis (a very small particle having the same weighting as a very large one). These number based distributions can be then transformed into volume distributions, as given by Mastersizer 2000.

Note that due to the difficulty in dealing with particles whose sizes are of different order of magnitude, the overlap parameter was modified to extend the range of the chosen objective (normally 3.5-400 μm for 10× and 0.5-40 μm for 50×), ensuring that larger particles were correctly measured.

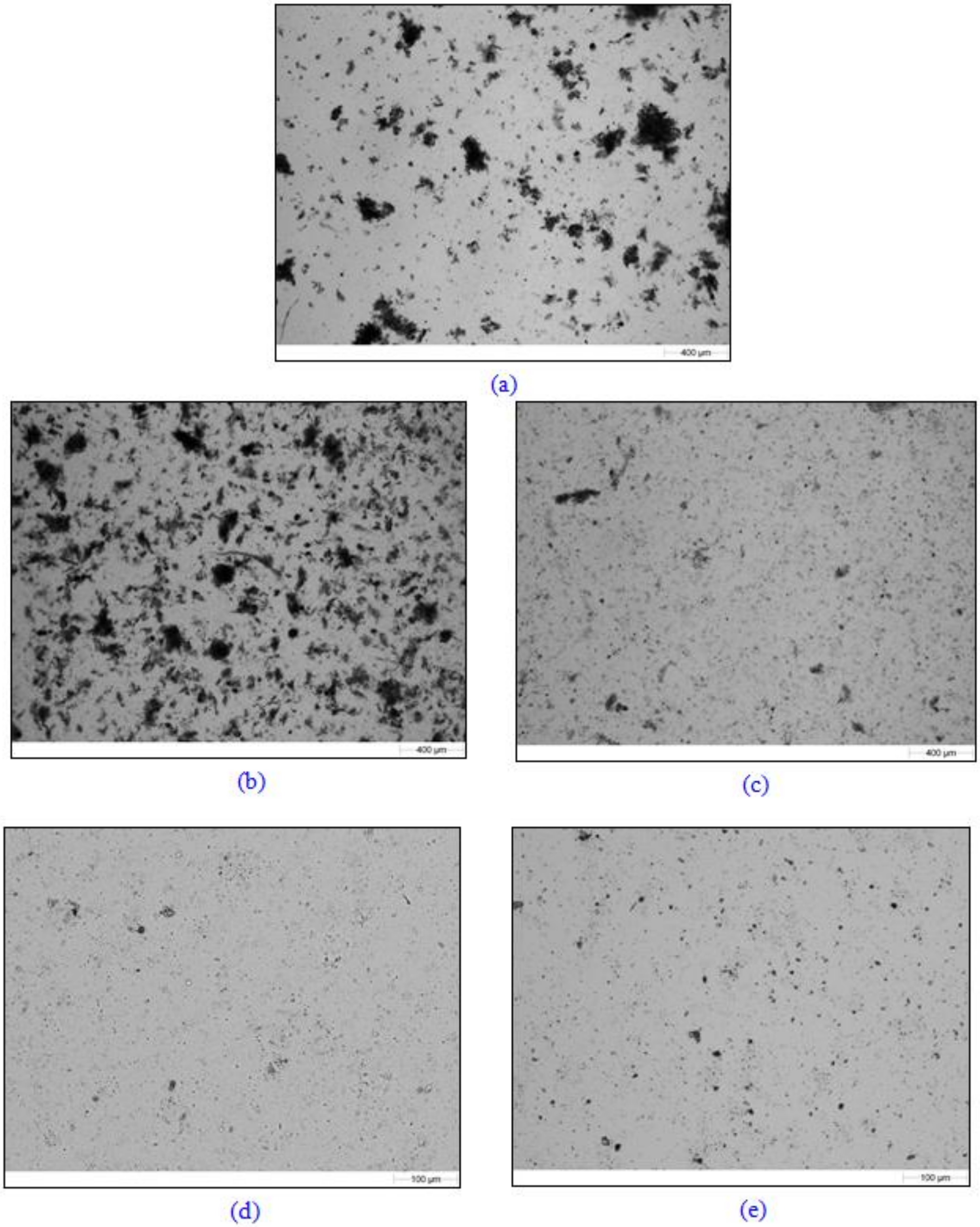


Fig 3.14: Photographs of raw and pretreated secondary sludge (Table 3.3, 20 kHz, 1 bar): (a) Raw sludge after defrosting (2.5×), (b) after 78 min of thermal hydrolysis up to 80^{o}C (2.5×), (c) after 5 min of *US* (150 W) + 73 min of thermal hydrolysis up to 80^{o}C (2.5×), (d) after 78 min of adiabatic *US* (150 W) + 162 min of stirring (10×), (e) after 117 min of isothermal *US* 150 W (10×)

Sludge particles, especially large ones, exhibit irregular shape, therefore the volume moment mean CE diameter (diameter of the circle of equivalent area to the 2D object), but also volume moment mean length and width (*L[4,3]* and *W[4,3]*, respectively) are given in Table 3.6.

Table 3.6: Size parameters of raw and pretreated sludge samples (see legend of Fig. 3.14)

Sample (magnification)	***D[4,3]*** **based on CE diameter (µm)**	***L[4,3]*** **(µm)**	***W[4,3]*** **(µm)**
(a) (10×)	185.6	297.3	201.8
(b) (10×)	145.1	342.3	182.5
(c) (10×)	51.1	100.8	69.3
(d) (50×)	8.8	25.4	11.2
(e) (50×)	3.3	6.3	3.3

As previously found from laser granulometry, the size of the flocs is marginally affected by thermal hydrolysis (Fig. 3.14b and entry (b) of Table 3.6). Conversely, *US* pretreatment provokes a significant floc disruption. Their structural integrity is almost broken down after a short time of *US* (Fig. 3.14c) and a longer treatment seems to lead to a further reduction in size (entry d-e of Table 3.6). If the trends are consistent with those mentioned in the previous section (§ 3.2.2.1), this last observation is a little bit different from what was concluded from laser diffraction measurements where it seemed *D[4,3]* almost reached a plateau after 10 to 30 min (cf. Fig. 3.9). The mean diameters of sludge particles after *US* treatment calculated with Morphologi G3 are also smaller than those measured with Mastersizer 2000: 379 µm for a similar initial sample, 107.5 µm and 46.7 µm after 5 min and 78 min of similar *US* application, but under isothermal conditions. This might again result from the irregular shape of the remaining secondary particles (*cf. L[4,3] vs. D[4,3]*), and/or an overestimation of the microfloc size by laser diffraction due to the use of unoptimized optical properties.

The effect of *US* on sludge flocs can be also observed by the analysis of other morphological parameter variations. Floc form is characterized by their *elongation* (= 1-width / length), while their outline (rough/smooth) is described by *convexity* (= convex hull perimeter / actual perimeter) and *solidity* (= actual area / area enclosed by the convex hull) parameters. Normally, shapes with regular dimensions have an elongation of 0, while needles and rods have elongation approaching 1. For convexity, the value is 1 for a perfect smooth shape and below that for a very spiky or irregular object. Solidity can be seen as a measurement of compactness, thus a value approaching 1 indicates a more compact shape. In addition, combined defaults in particle form and outline with respect to a perfect smooth circle are given by *circularity* (= CE perimeter / actual perimeter). Table 3.7 exhibits the volume median values of these parameters after the different treatments. Very low solidity (< 0.4) is found for filamentous structures, while large flocs (> 100 μm) formed by agglomerates exhibit values between 0.4 and 0.75 and particles under 10 μm have a median solidity of 0.9. These small particles are also very smooth with a median convexity of 0.9. Table 3.7 confirms that the irregular and fluffy macroflocs are disrupted into smaller, smoother, and more compact structures by *US* which corresponds to an increase of median convexity and solidity (to values very close to 1), as well as of circularity (as elongation is conversely not much changed) with an increase of sonication time (or *ES*).

Table 3.7: Morphological parameters of raw and pretreated sludge samples (see legend of Fig. 3.14)

Sample (magnification)	**Vol. median circularity**	**Vol. median convexity**	**Vol. median elongation**	**Vol. median solidity**
(a) (10×)	0.40	0.53	0.32	0.71
(b) (10×)	0.31	0.45	0.35	0.65
(c) (10×)	0.39	0.54	0.33	0.69
(d) (50×)	0.67	0.88	0.37	0.84
(e) (50×)	0.83	0.95	0.30	0.94

3.2.3. Apparent viscosity and rheological behavior

Fig. 3.15 depicts the evolution of apparent viscosity *vs.* shear rate before and after isothermal *US* pretreatment in standard conditions: the sonicated sludge curves are lower than that of raw sludge, indicating a decrease in apparent sludge viscosity μ_{app} (for a given shear rate) as a function of *ES* (7000-50000 kJ/kg$_{TS}$). For instance, μ_{app} at $\gamma = 1$ s^{-1} is divided by 1.4 and 2.6 as compared to raw sludge for 7000 and 50000 kJ/kg$_{TS}$, respectively.μ_{app} values come somewhat closer at high shear rates, *e.g.* factor 1.2 and 2.0 at $\gamma = 100$ s^{-1}. Sludge viscosity is probably controlled by sludge floc structure and interaction (Trussell *et al.*, 2007); consequently, the disintegration of sludge flocs due to acoustic cavitation led to the decrease in viscosity of sonicated sludge (Trussell *et al.*, 2007; Pham *et al.*, 2009; Wang *et al.*, 2011).

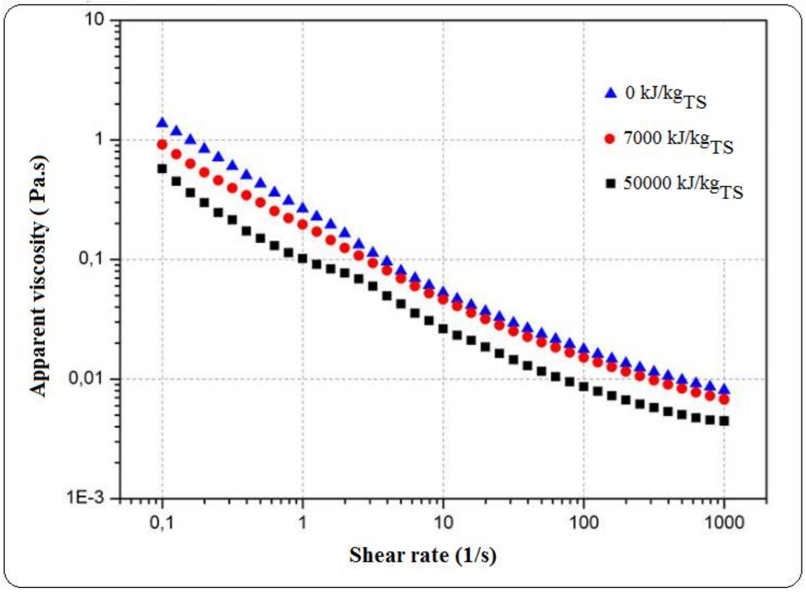


Fig 3.15: Apparent viscosity versus shear rate curves for raw and sonicated secondary sludge: P_{US} = 360 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (other properties in Table 3.4), *T* = 28±2°C, and atmospheric pressure

Herschel-Bulkley equation, $\tau = \tau_0 + K \cdot \gamma^n$, often used to model the rheological behavior of sludge has been selected in this work as fittings of sludge flow curves (τ *vs.* γ) resulted in standard errors of less than 10% (see section 2.4.6 of Chapter 2). Optimized values of model parameters are given in Table 3.8.

The consistency coefficient *K* which serves as a viscosity index of the system thus decreased. However, yield stress τ_0 and flow index *n* of sonicated sludge only showed relatively small changes with respect to raw sample, indicating that sonication under cooling decreased the apparent viscosity, but did not significantly affect the rheological behavior of the sludge.

Table 3.8: Apparent viscosity and parameters of Herschel-Bulkley model

	Yield stress τ_0 **(Pa)**	**Consistency** *K* **(Pa.s^n)**	**Flow index** *n* **(-)**	**Apparent viscosity** μ_{app} **(Pa.s)**	
				$\gamma = 1$ (s^{-1})	$\gamma = 100$ (s^{-1})
Isothermal US (28°C) at 20 kHz and 1 bar					
0 kJ/kg$_{TS}$	0.124	0.072	0.680	0.266	0.018
7000 kJ/kg$_{TS}$	0.093	0.066	0.667	0.196	0.015
50000 kJ/kg$_{TS}$	0.089	0.023	0.757	0.102	0.009

The rheological behavior of sludge treated at T = 28°C in different conditions of F_S (12 kHz *vs.* 20 kHz) and P_h (1 bar *vs.* 3.25 bar), as well as in the best conditions found in Chapter 6, was also looked into and is presented in Appendix 4, showing mainly an additional viscosity reduction by the moderate temperature rise in sequential *US*.

3.2.4 Solubilisation of organic fractions

To investigate the solubilisation of organic fractions under different pretreatment conditions, four secondary sludge samples (*TS* of 28 g/L, Table 3.1) were analyzed for proteins (organic N dosage) and sugars (anthrone test), *i.e.* total amounts and in solution after filtration on 1 µm pore size membrane (thus merging soluble and colloidal fractions). The total protein and sugar concentrations in these sludge samples were almost constant, suggesting negligible sonochemistry (Bougrier *et al.* 2008; Appels *et al* 2010).

(S1) Raw sludge

(S2) US_1 pretreated sludge: 150 W, 75000 kJ/kg$_{TS}$, 20 kHz, P_h = 2 bar and T = 28±2°C

(S3) US_2 pretreated sludge: 150 W, 75000 kJ/kg$_{TS}$, 20 kHz, P_h = 2 bar and adiabatic condition

(S4) Thermally pretreated sludge: constant temperature of 70°C for 2 hours (treatment resulting in almost same *SCOD* value as that of *S2*).

The release of organics is due to the disruption of chemical bonds in cell walls and membranes (Appels *et al.* 2010), the degradation of *EPS* (including saccharides, proteins, nucleic acids, and humic acids), and the release of intracellular matter from the cells where proteins are mainly located in (Bougrier *et al.* 2008). Results corresponding to the four samples are given in Table 3.9.

Table 3.9: Solubilisation of organic fractions

Sample	**Solubilisation yield (%)***	
	Protein	**Sugar**
S1	0	0
S2	61.3	28.0
S3	70.0	34.3
S4	42.0	29.1

** = (difference between the (soluble + colloidal) amounts in treated and raw samples) / (difference between the total amount and the initial (soluble + colloidal) amount) *100*

In accordance with previous *COD* results, solubilisation of proteins and sugars was higher under adiabatic *US* (*S3*) than under isothermal *US* (*S2*) or thermal hydrolysis (*S4*). Table 3.9 shows that proteins were released the most in all cases, but the different pretreatments resulted in different yields. For example, protein solubilisation of *S2* was about 46% higher than that of *S4* although almost same *SCOD* and solubilisation of sugars. The low solubilised amount of proteins in *S4* could be due to the fact that thermal treatment at temperatures lower than 95°C mainly affects *EPS* which are embedded in the sludge floc matrix, leading to solubilisation of carbohydrates and few proteins (Bougrier *et al.* 2008). Therefore, lower protein solubilisation of *S4* compared to those of *S2* and *S3* indicate *US* pretreatment to be more effective than low temperature thermal hydrolysis (70^{o}C) in terms of floc disruption and cell lysis.

Additional experiments were conducted to follow the effect of *ES* on the evolution of soluble (*SCOD*) and colloidal (*CCOD*) fractions of COD. Another secondary sludge sample (Table 3.4) was used for these tests. Fig 3.16 depicts evolutions of *SCOD/TCOD* and *CCOD/TCOD* during *US*. While *SCOD/TCOD* gradually increased, *CCOD/TCOD* increased quickly with *ES* up to 12000 kJ/kg$_{TS}$, then slowed down, and almost reached a plateau afterwards. Colloidal fraction was also much higher than soluble one over the investigated *ES* range (2 to 3-fold).

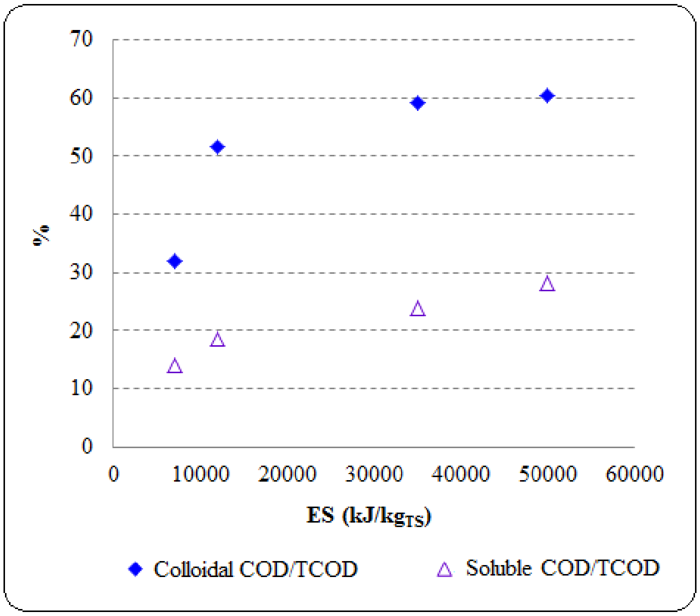


Fig 3.16: Effect of *ES* on *SCOD/TCOD* and *CCOD/TCOD* during *US: P$_{US}$* = 360 W, *BP, F$_S$* = 20 kHz, secondary sludge with *TS* = 28 g/L (other properties in Table 3.4), *T* = 28±2°C, and atmospheric pressure

3.3. CONCLUSIONS

First, it is confirmed specific energy input *ES* plays a key role in sludge *US* disintegration. For given external and *US* parameters, sludge disintegration degree increases nonlinearly with *ES*. Besides, main operation parameters were selected as follows.

Mixed sludge samples with different *TS* contents were pretreated using various sonication durations, exhibiting an optimal concentration of 28 g/L to get the highest *COD* release in the aqueous phase. Stirrer speed of 500 rpm was also found to be convenient for *US* pretreatment of sludge. These two values have then been applied in the following experiments of this work.

The contribution of temperature increase during *US* non isothermal treatment was evaluated. At any sonication time (or *ES*), DD_{COD} values were much higher under –adiabatic” sonication, while isothermal sonication was more efficient than thermal hydrolysis. The effect of *US* was clearly proved to be more important than that of sole thermal hydrolysis obtained with the same temperature-time profile.

Besides**,** the highest disintegration was found with secondary sludge, followed by digested and mixed sludge regardless of temperature control during sonication.

Additionally, pH adjustment -addition of low NaOH dose, between 22 and 40 mg_{NaOH}/g_{TS}- could be useful, that significantly improved *COD* release under subsequent *US* treatment while resulting in a final pH value suitable for subsequent *AD*.

Compared with the untreated sludge samples, particles were almost entirely disrupted down to their final size in the initial period of the ultrasonic process. The great difference in the kinetics of the two phenomena- fast size reduction and slower *COD* removal in liquid phase- should be emphasized and demonstrates that particle size is not the key parameter to follow *COD* solubilisation.

As a result of sludge floc disruption, apparent viscosity decreased as a function of *ES* during *US* pretreatment.

CHAPTER 4

EFFECT OF ULTRASOUND PARAMETERS ON SLUDGE PRETREATMENT BY ISOTHERMAL SONICATION

(POWER, INTENSITY, FREQUENCY)

HIGHLIGHTS

- Effect of acoustic frequency on sludge pretreatment was studied for the first time.
- High P_{US}-short time is preferred for sonication at atmospheric pressure and low temperature.
- At atmospheric pressure, effect of P_{US} appears more important than that of I_{US} when varied through emitter surface.
- Sludge disintegration is significantly improved by low frequency sonication.

INTRODUCTION

This part aims at investigating the key sonication parameters mostly at atmospheric pressure. Knowing that the reference economy parameter is the specific energy *ES*, it is important to check which way is the best to provide such energy for the best sludge disintegration (maximum DD_{COD}). What improvement can be expected when using higher power (P_{US}) during less time at same *ES* or higher intensity (I_{US}) at same power - by reducing the emitter surface in the same sono-reactor? Besides, it is commonly accepted that lower frequency improves *US* mechanical effects but frequencies below 20 kHz were hardly investigated. This part of our work provides a first approach of such issues. As it was rather difficult to separate mechanical (*US*) and thermal effects in non-isothermal conditions, it was decided in this section - devoted to *US* efficiency - to consider only isothermal treatment. Nevertheless, as adiabatic mode should probably provide better sludge disintegration due to combined effects, it will be investigated in the last chapter related to process optimization, assessed by DD_{COD}. Sequential sonication was also tested to know if this process improves sludge disintegration compared to continuous sonication.

4.1. MATERIALS AND EXPERIMENTAL PROCEDURES

4.1.1. Sludge samples

Secondary sludge from the third and fourth samplings (see Table 2.3 and 2.4, section 2.2) was used for this part. As mentioned, sludge sampling was performed at different periods in relation with the changes in *US* equipment along this work. The synthetic sludge samples were prepared with 28 g/L of *TS*, the optimum concentration for sludge disintegration found in Chapter 3.

Synthetic sludge sample, whose properties are recalled in Table 4.1, was used for investigating P_{US} and I_{US} effects. The effect of frequency was then looked into using the synthetic secondary sludge whose properties are recalled in Table 4.2.

Table 4.1: Characteristics of prepared sample from 3rd sludge collection (secondary sludge, recalled from Table 3.3)

Parameter		Value
Sludge sample		Defrosted secondary sludge
Total solids (*TS*)	(g/L)	28.0
Mean $SCOD_0$	(g/L)	2.8
$SCOD_{NaOH\ 0.5M}$	(g/L)	22.7
TCOD	(g/L)	36.3
$SCOD_{NaOH}/TCOD$	(%)	62.5

Table 4.2: Characteristics of prepared sample from 4th sludge collection (secondary sludge, recalled from Table 3.4)

Parameter		Value
Sludge sample		Defrosted secondary sludge
Total solids (*TS*)	(g/L)	28.0
Mean $SCOD_0$	(g/L)	4.1
$SCOD_{NaOH\ 0.5M}$	(g/L)	22.1
TCOD	(g/L)	39.1
$SCOD_{NaOH}/TCOD$	(%)	56.5

Reference experiments on these sludge samples at the same conditions and equipment, presented in Appendix 5, show significant difference in sludge *US* disintegration. Hence, comparisons to assess given parameter effect have always been carried out on the same substrate.

4.1.2. Experimental procedures

According to Chapter 3, a stirrer speed of 500 rpm was selected. A constant volume of synthetic sludge sample (0.5 L) was used for each experiment as in any other runs of this work.

For each frequency generator (12 and 20 kHz, supplied by Sinaptec), a 35 mm diameter probe (*BP*) and a 13 mm one (*SP*) were alternately set up at the bottom of the reactor with maximum P_{US} of 400 W and 100 W, respectively.

Due to effects of other operational conditions (*T*, pressure) and technical limitations of *US* systems, an I_{US} range of 5-75 W/cm^2 was investigated in the present work (Table 4.3). It is probably above the cavitation threshold for *WAS* at atmospheric pressure (according to the range for water with many impurities) even though it was suggested to be at 20–30 W/cm^2 by Zhang et al. (2008b). Note that a power ratio of 360/50 was applied between *BP* and *SP* as it corresponds to the surface ratio of the probes, allowing comparison at same $I_{US.}$

Table 4.3: Test parameters and levels

Combination	I_{US} **(W/cm^2)**	D_{US} **(W/L)**
SP 50W	37.7	100
SP 75W	56.5	150
SP 100W	75.3	200
BP 50W	5.2	100
BP 150W	15.6	300
BP 360W	37.4	720

The experiments listed in Table 4.3 allowed to investigate the effect of P_{US} first, then the effect of I_{US} resulting either from P_{US} or emitter surface variation. After that, F_S effect (12 and 20 kHz) was looked into using *BP*, varying P_{US} from 50 to 360 W.

Finally, the effect of sequential sonication was studied at 12 kHz, with a P_{US} range of 50-100 W for *SP* and 50-360 W for *BP*.

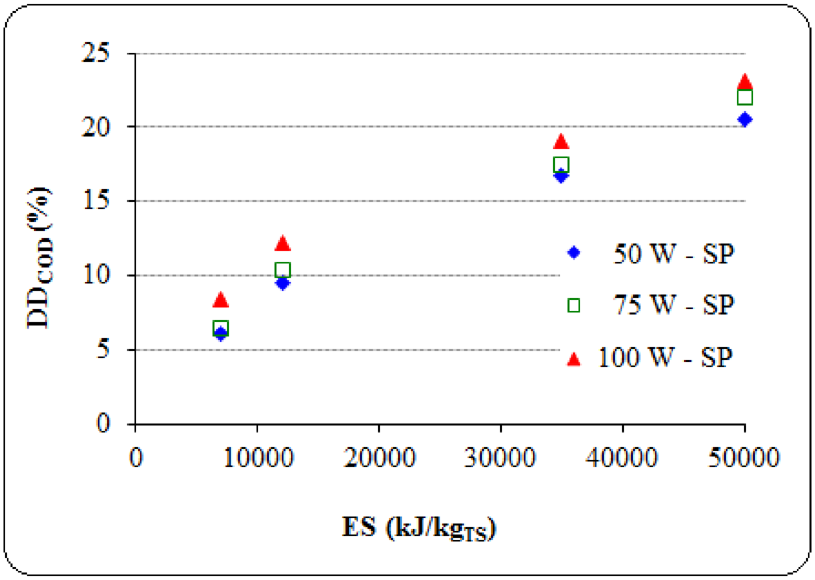
As abovementioned, almost all of the experiments of this chapter were performed at **atmospheric pressure** and in **isothermal mode**. The very few exceptions are mentioned otherwise.

4.2. RESULTS AND DISCUSSION

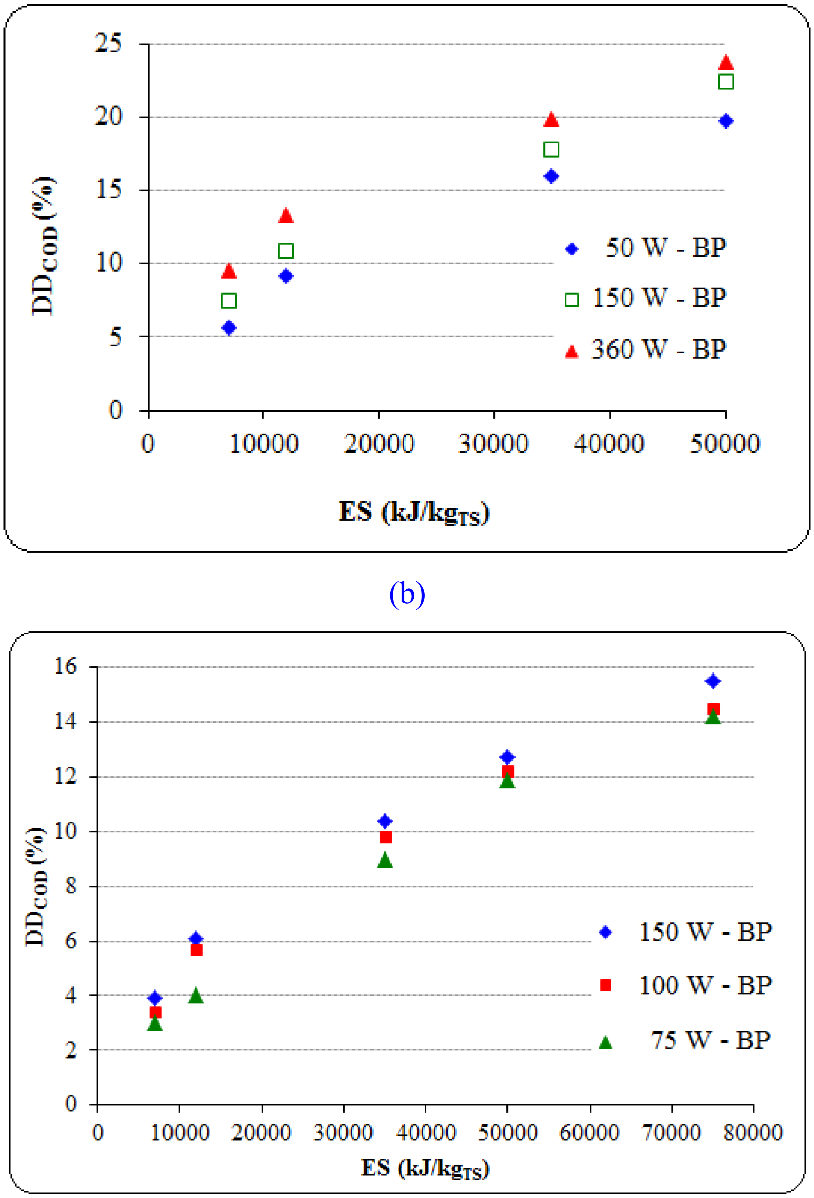
4.2.1. Effect of P_{US} on sludge disintegration

The effect of P_{US} on *WAS* disintegration was studied at 20 kHz for the two probes (13 and 35 mm diameter probes, labeled *SP* and *BP*, respectively) using their respective available range: 50-100 W for *SP* and 50-360 W for *BP*. Results are given in Fig. 4.1a and 4.1b. Besides, its effect on mixed sludge (whose properties are given in Table 3.1) was also clarified, presented in Fig. 4.2c, using the initial 20 kHz generator limited to 150 W. Actual operation shows the surface of the probe to be eroded by the time; therefore the performances of the old and new probes were compared in the same operating conditions and with the same sludge sample, showing a slight difference of sludge *US* pretreatment efficacy (less than 10%), that could be ignored (see Appendix 6).

The same conclusion was deduced from the experiments conducted on different sludge types, P_{US} ranges, and probe sizes. The higher P_{US}, the higher DD_{COD} was achieved at same energy consumption due to the increase in cavitation intensity. Despite higher uncertainty at low DD_{COD} (then low *ES*) the main effect was clearly observed at a low *ES* value of 7000 kJ/kg$_{TS}$, where DD_{COD} of secondary sludge sample was improved about 40% and 67% when increasing P_{US} from 50 to 100 W for *SP* (Fig. 4.1a) and from 50 to 360 W for *BP* (Fig. 4.1b), respectively. On the contrary at 50000 kJ/kg$_{TS}$, the corresponding gain was only 13% and 20%, respectively.



(a)



(b)

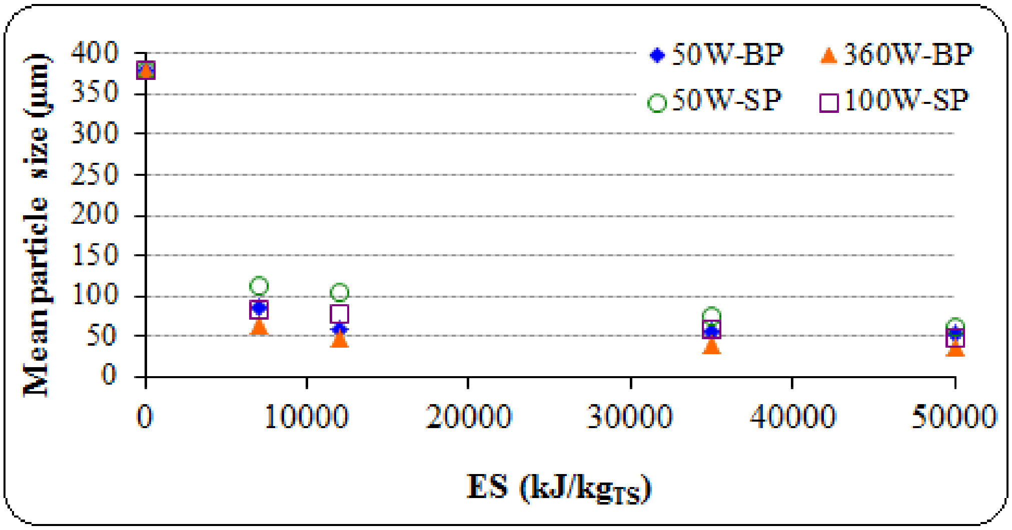
(c)

Fig 4.1: Effect of *ES* and P_{US} on DD_{COD}: 20 kHz, *TS* = 28 g/L, *T* = 28±2°C, and atmospheric pressure: (a) *SP*, secondary sludge (Table 4.1). (b) *BP*, secondary sludge (Table 4.1). (c) *BP*, mixed sludge (Table 3.1), ―limited P_{US}” generator (max.150 W)

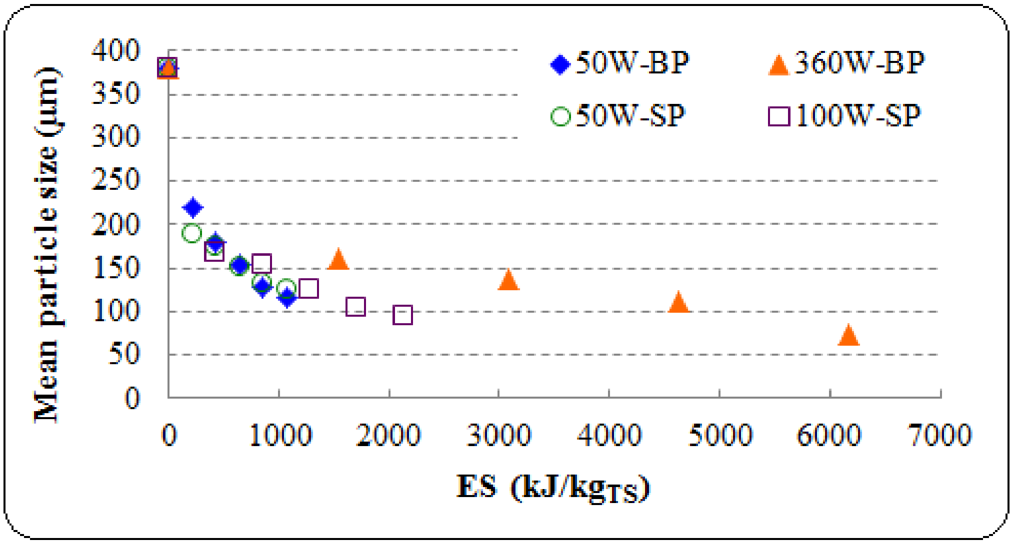
This limited but general positive effect of P_{US} on *WAS* disintegration proves that in the investigated range of I_{US} (< 75 W/cm^2) there is no significant ―saturation effect” due to a bubble cloud formation near the probe and then no severe damping of the *US* wave (Contamine *et al.*, 1994; Ratoarinoro *et al.*, 1995; Whillock and Harvey, 1997).

Apart from DD_{COD} increase, high P_{US} also showed a slight positive effect on sludge particle size reduction (see Fig. 4.2). In general, as found in section 3.2.2, the reduction rates of *D[4,3]* were very fast in the initial period of *US* corresponding to low *ES* then rather limited at higher *ES* (Fig. 4.2a).

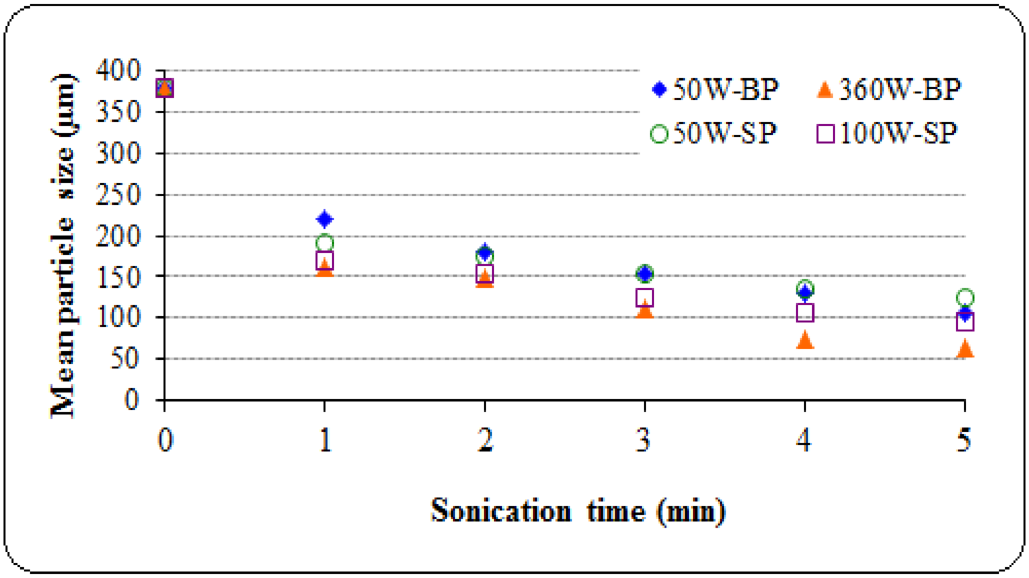
To better analyze this first step of fast reduction, additional experiments were conducted and presented on Fig. 4.2b-c. With respect to *US* duration, the higher P_{US}, the more and the faster particle sizes were decreased (Fig. 4.2c). However, surprisingly the opposite trend was observed in terms of *ES* (Fig. 4.2b). As particle size reduction was not relevant for *COD* solubilisation, this unexplained result was not more deeply investigated here but would deserve verification and further analysis if appropriate.



(a)



(b)



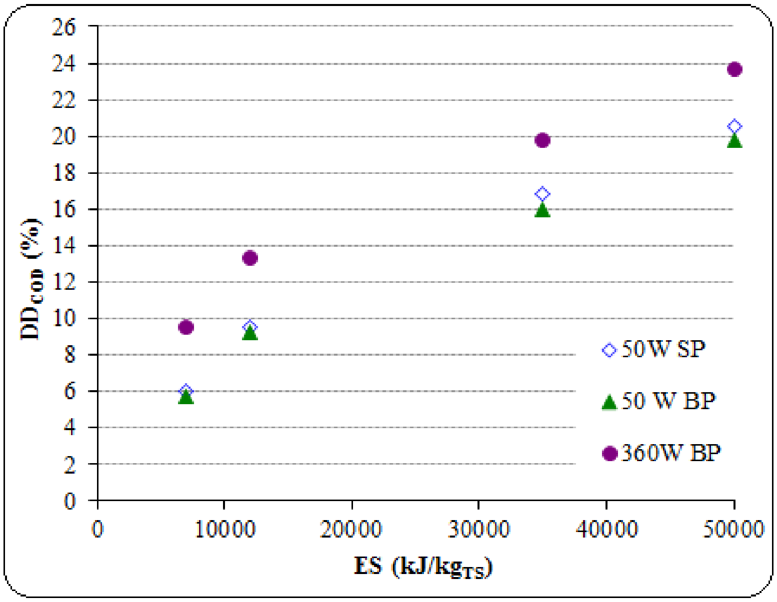
(c)

Fig 4.2: Evolution of secondary sludge mean particle size as a function of (a) high *ES*, (b) low *ES* and (c) sonication time using different P_{US} and probe sizes: 20 kHz, $T = 28\pm2$°C, and atmospheric pressure

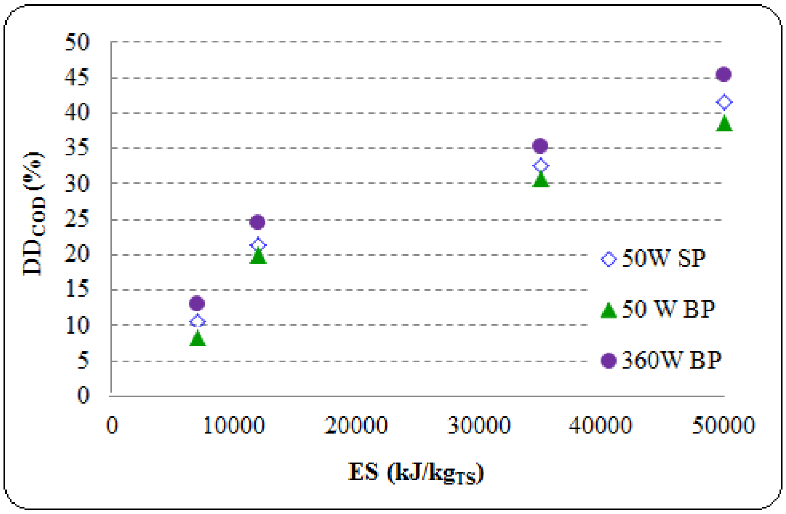
In agreement with other researchers (Chu *et al.*, 2001; Mao *et al.*, 2004; Gronroos *et al.*, 2005; Zhang *et al.*, 2008b; Kidak *et al.*, 2009), under isothermal mode (low *T*) and atmospheric pressure, the *highest* P_{US} – *shortest sonication time* mode was the most effective condition for sludge pretreatment in terms of DD_{COD} in the investigated range, which corresponds to the probable conditions of a scaled up process (as higher intensities would not be relevant).

4.2.2 Effect of I_{US} on sludge disintegration

Effects of I_{US} on sludge disintegration were investigated at same P_{US} (50 W) by changing the probe: *SP* (I_{US} of 37.7 W/cm^2) *vs. BP* (I_{US} of 5.2 W/cm^2). These experiments were conducted at both frequencies (12 and 20 kHz). Results are shown in Fig. 4.3 where additional experiments at an I_{US} value of 37.4 W/cm^2 but using a different P_{US}-probe combination (360 W-*BP*) are also reported for comparison of both effects.



(a)



(b)

Fig 4.3: Comparison of I_{US} (same P_{US} of 50W) and P_{US} (same probe) effects on DD_{COD} at different *ES*: *TS* = 28 g/L, *T* = 28±2°C, and atmospheric pressure. (a) 20 kHz, secondary sludge (Table 4.1). (b) 12 kHz, secondary sludge (Table 4.2)

First, experiments at the same P_{US} of 50 W showed only very little improvements of DD_{COD} (less than 10%) when increasing I_{US} from 5.2 to 37.7 W/cm^2. A similar but less significant observation could be deduced from Fig 4.1a and 4.1b for a higher P_{US} level: only about 10% of DD_{COD} improvement was achieved when increasing I_{US} by approximately 5 times, from 150W-*BP* (15.6 W/cm^2) to 100W-*SP* (75.3 W/cm^2) combination. This result may appear surprising as I_{US} is often claimed to be a significant parameter (Quarmby *et al*., 1999; Neis *et al*., 2000; Pilli *et al*., 2011). It should be recalled that in our experiments I_{US} was varied by varying probe size in the same reactor which involves an important modification of the ultrasonic field with a reduced irradiated volume. It could be therefore suggested that the expected gain due to higher cavitation at higher I_{US} would approximately be balanced by the reduced volume of the cavitation zone. Of course this result should no longer be expected when I_{US} is reduced down to the cavitation threshold where *US* have no more effects.

Another way of checking this parameter would consist of changing both the reactor volume and *US* power proportionally with the same probe. Obviously, changing reactor size would be much more complex to achieve, especially under pressure. Thus additional experiments on secondary sludge (Table 4.2) were carried out via changing P_{US} and sludge *V* proportionally with the same *BP* to keep the same D_{US} (300 W/L): 150W-500mL, 210W-700mL, and 270W-900mL. Note that sludge *V* of 500-900 mL is a convenient range corresponding to the reactor configuration used in this work. Results, presented in Fig. 4.4, show that DD_{COD} first increased following an increase in I_{US} from 16 to 22 W/cm^2 (corresponding to sludge *V* from 500 to 700 mL) due to an increase in cavitation intensity, then decreased at I_{US} of 28 W/cm^2 (sludge *V* of 900 mL) due to a poor propagation of *US* wave from the bottom to the top of the medium. The stirrer in this case was not able to well homogenize the whole suspension. Therefore, with this approach, an optimum of I_{US} could be found, *e.g.* 22 W/cm^2 from these tests.

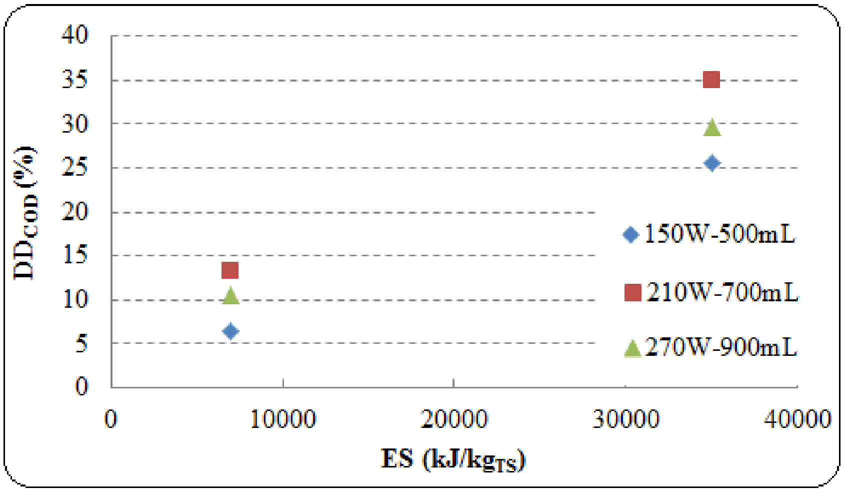


Fig 4.4: Effect of IUS (by changing PUS and sludge V proportionally with the same probe) on DDCOD at different ES: 20 kHz, BP, DUS = 300 W/L, TS = 28 g/L (Table 4.2), T = 28±2°C, and atmospheric pressure.

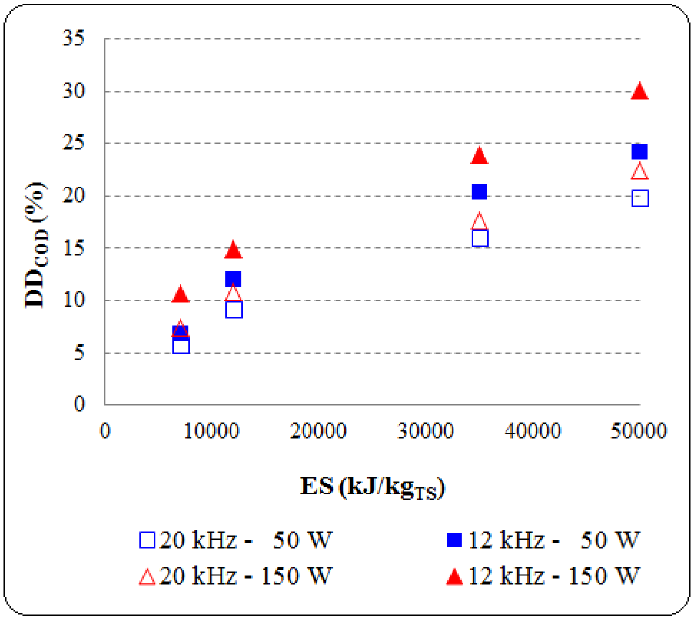
On the other hand, series at same I_{US} with different P_{US} indicated a larger effect of P_{US} than of I_{US} on DD_{COD} at both frequencies. For instance, at 20 kHz and in the *ES* range of 7000-50000 kJ/kg$_{TS}$,

DD_{COD} from 360W-*BP* were 58% to 16% higher than that from 50W-*SP* (at same I_{US}) (Fig. 4.3a) and even up to 13% higher than that from 100W-*SP* (at double I_{US}) (Fig 4.1a and 4.1b). At 12 kHz, P_{US} effect is slightly lower.

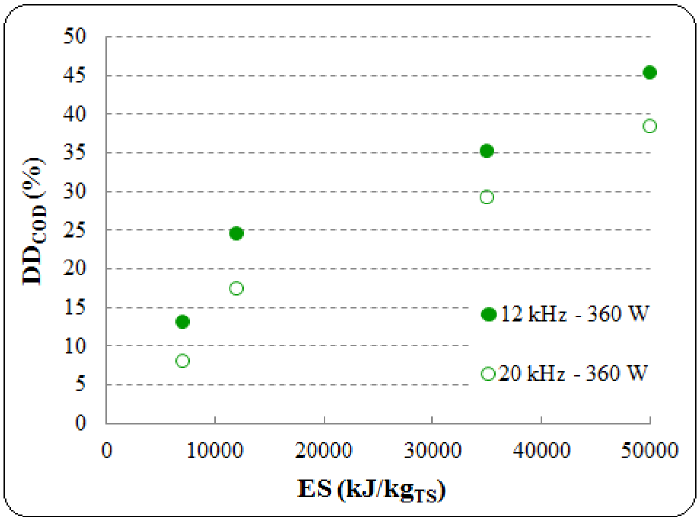
In both cases of frequency, high *US* power and low sonication time therefore should be preferred for sludge disintegration while increasing the I_{US} by reducing the emitter surface in the same reactor volume gives much less benefits.

4.2.3. Effect of frequency on the efficacy of sludge sonication

As mentioned in the introduction and literature review, even though most applications using mechanical effects of *US* power are improved when reducing *US* frequency, nearly no information is available under 20 kHz - the usual limit of commercial equipment corresponding also to the limit of human hearing. Effects of frequency -under this 20 kHz threshold- on the efficacy of sludge pretreatment were investigated using *BP*, and assessed by DD_{COD}. Most experiments were carried out at 360 W using secondary sludge sample given in Table 4.2. Besides, for P_{US} of 50 W and 150 W, additional experiments using sludge sample given in Table 4.1 were conducted. Results are shown in Fig. 4.5.



(a)



(b)

Fig 4.5: Effect of ES and sound frequency on sludge disintegration (DDCOD): BP, TS = 28 g/L, T = 28±2°C, and atmospheric pressure. (a) Secondary sludge given in Table 4.1. (b) Secondary sludge given in Table 4.2.

Fig. 4.5 shows that with the two different sludge samples, the lower the frequency, the more the sludge was disintegrated due to more violent cavitation. DD_{COD} were significantly improved at 12 kHz sonication as compared to 20 kHz *US*, by 21%, 45% and 64% for P_{US} of 50, 150 and 360 W, respectively, at an *ES* value of 7000 kJ/kg$_{TS}$. As previously found at 20 kHz, more sludge disintegration was achieved at higher P_{US} and the largest differences were noticed at low *ES*. According to Laborde *et al.* (1998), Thompson and Doraiswamy (1999), Zhang *et al.* (2008a), Pham *et al.* (2009), Carrère *et al.* (2010) and Pilli *et al.* (2011), the lower frequencies, the stronger shock waves and mechanical effects are favoured due to the resonance bubble size being inversely proportional to the acoustic frequency (Laborde *et al.* 1998). However, noting that at low frequency the maximum collapse time and the maximum size of the expanded cavity are increased, the optimum cavitation effect should occur at higher P_{US} (Whillock and Harvey, 1997).

Evolution of colloidal *COD* fraction of secondary sludge (Table 4.2) during sonication at different F_S was also measured and is presented in Appendix 7 (along with corresponding soluble *COD* fraction).

Besides, the lower the frequency, the faster the sludge particle size was reduced during the first two minutes. However, the differences in size thereafter were insignificant as depicted in Fig. 4.6.

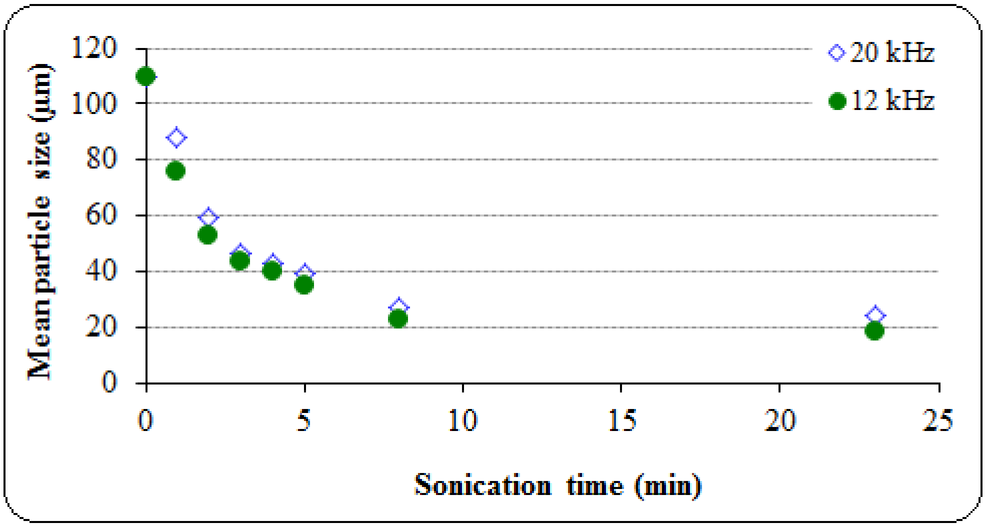


Fig 4. 6: Mean particle size reduction under sonication at different FS: PUS = 360 W, BP, TS = 28 g/L (Table 4.2), T = 28±2°C, and atmospheric pressure

4.2.4. Effect of sequential isothermal sonication on sludge disintegration

This part aims at investigating the performance of sequential sonication which could improve the efficiency of sludge disintegration as in other reported *US* applications (Casadonte *et al.*, 2005; Pham *et al.*, 2009). For this study, a few experiments were carried out under pressure, whose effect will be detailed in next chapter. Secondary sludge, presented in Table 4.2, 12 kHz generator, and both probes were used. Corresponding results, as final DD_{COD}, are presented in Fig. 4.7 and 4.8.

Fig. 4.7 depicts the effect of sequential sonication on sludge disintegration at room conditions (atmospheric pressure, mean temperature of 28°C) using *SP* and an *ES* value of 35000 kJ/kg_{TS}. The following conditions were compared:

(*i*) 50 W continuous sonication (164 min)

(*ii*) 100 W continuous sonication (82 min)

(*iii*) 82 min of 100 W continuous sonication, as in (*ii*), but followed by stirring (no sonication) up to 164 min, to get the same treatment time as in *(i)* (marked as *100W + stirring*)

(*iv*) sequence made of 1 min sonication at 100 W followed by 1 min stirring (no sonication) and pursued for a total duration of 164 min (marked as *100W-1/1*)

(*v*) sequence made of 5 min sonication at 100 W followed by 5 min stirring (no sonication) and pursued up to 164 min of treatment (marked as *100W-5/5*).

Note that the *US* pulses of 1 min and 5 min were selected as particle size reduction was mainly achieved within these periods.

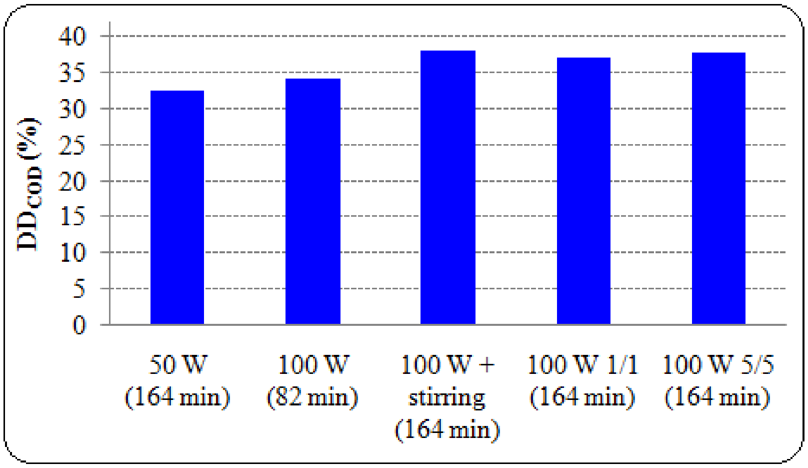


Fig 4.7: Effect of isothermal sequential sonication on sludge disintegration: SP, ES = 35000 kJ/kgTS, 12 kHz, T = 28±2°C, and atmospheric pressure

For continous sonication, as previously found, a highest efficiency of the *high* P_{US} *– short time US* mode was observed. When compared at same P_{US} (100 W), *ES* (35000 kJ/kg$_{TS}$) and treatment time (164 min), sludge disintegration degrees resulting from the continuous sonication and the two sequential procedures were almost the same. Thus there is no improvement by using sequential (or pulsed) sonication in these conditions but on the other hand, it is important to note that after sonication the process of disintegration goes on, slowly but significantly. So in other conditions, alternative sonication and silent periods might be beneficial.

Similar isothermal experiments using *BP* at atmospheric and under pressure (3.25 bar) were performed and presented in Fig. 4.8. There were two procedures for sequential sonication at 360 W under the pressure of 3.25 bar: 1 min sonication - 6 min stirring and 5 min sonication - 30 min stirring up to 164 min, marked as *360W-1/6-3.25bar* and *360W-5/30-3.25bar*, respectively. Again in continuous mode, DD_{COD} was appreciably improved by an increase in P_{US} (360 W *vs.* 50 W) and also external pressure (3.25 bar *vs.* 1 bar). In this condition of higher P_{US}, a significant improvement of DD_{COD} was observed when stirring after sonication and even better when using the sequential procedures. With the best sequential procedure 1/6, DD_{COD} was increased by 27% as compared to the reference continuous operation (P_{US} = 360W, 3.25 bar, and no stirring after 23 min of *US*).

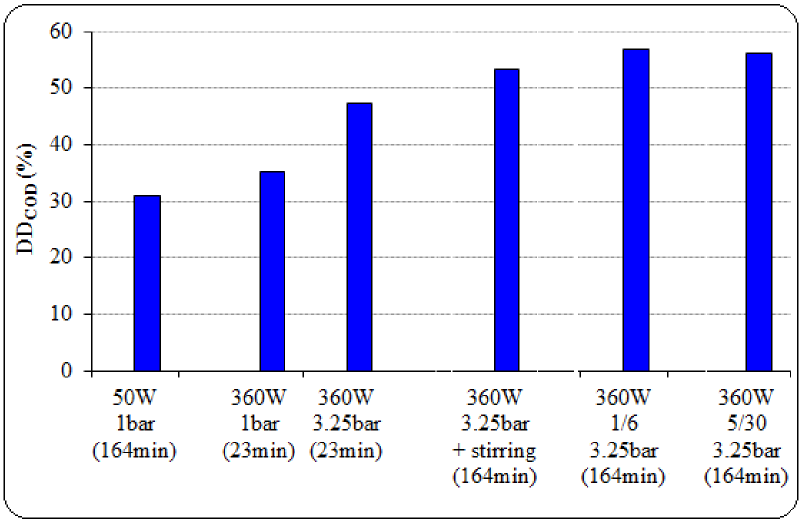


Fig 4.8: Effect of isothermal sequential sonication on sludge disintegration: BP, ES = 35000 kJ/kgTS, 12 kHz, 1 and 3.25 bar of pressure

To sum up, in isothermal mode and the same conditions of P_{US}, *ES*, pressure, and treatment time, some improvement in DD_{COD} was obtained in sequential mode in this special case of high P_{US} and high pressure.

4.3. CONCLUSIONS

This chapter aimed at investigating separately the main *US* parameters at same energy consumption (power, intensity, frequency, *etc.*) in a systematic approach, in order to get general information and trends to be used or checked in other potential applications of physical effects of acoustic cavitation.

The higher P_{US} for each size of probe, the higher sludge disintegration was achieved due to the increase in cavitation intensity involving maximum pressures and temperatures. In other words, *high* P_{US}*-short time sonication* procedure was the best option for sludge *US* pretreatment at atmospheric pressure.

At atmospheric pressure, increasing I_{US} by a reduction of emitter surface provided only very small improvement of sludge disintegration (less than 10%); meanwhile increasing P_{US} appeared much more efficient (up to 58% of DD_{COD} improvement).

Besides, sludge disintegration was significantly improved by low frequency sonication due to more violent cavitation: up to 64% of DD_{COD} from 12 kHz isothermal sonication as compared to 20 kHz at low *ES*. Sonication effects on sludge floc disruption and reduction of mean particle size were also somewhat improved at low frequency. Future works should investigate lower frequencies as there is no indication for any optimum frequency or for practical limitations at very low frequency.

Finally, sequential isothermal sonication was investigated, and due to consecutive disintegration after sonication, significant improvement of sludge disintegration was achieved in some cases. Such sequential mode should then be checked again when searching for the optimal non isothermal conditions (Chapter 6).

CHAPTER 5

EFFECT OF HYDROSTATIC PRESSURE ON SLUDGE PRETREATMENT BY ISOTHERMAL SONICATION

HIGHLIGHTS

- Effect of hydrostatic pressure was investigated for the first time.
- An optimum of pressure is observed above 1 bar in most configurations, whose exact location depends on P_{US} and I_{US}, but not on sludge type, *ES*, nor F_S.
- Sonication at optimal pressure significantly improves sludge disintegration.

INTRODUCTION

As presented in Chapter 2, at increasing hydrostatic pressure cavitation is more difficult to be achieved due to higher threshold, but it could produce more violent collapse due to the addition of both acoustic and hydrostatic pressure. Such higher temperature and pressure in the collapsed bubble lead to increase consequently the rate and yield of *US*-assisted reactions (Cum *et al*., 1988, 1990, 1992). However, most *US* experiments have been carried out at atmospheric pressure, and only a few studies have been focusing on how increasing hydrostatic pressure affects cavitation (Neppiras and Hughes, 1964; Chendke and Fogler, 1983a, 1983b; Whillock and Harvey, 1997; *etc*.), but nothing concerning sewage sludge.

This part aims at investigating the effect of external pressure on sludge sonication pretreatment for the first time. External pressure (up to 16 bar) was applied at different *ES* (7000-75000 kJ/kg_{TS}), P_{US} (50-360 W), probe sizes (13 and 35 mm diameter probes), sound frequencies (12 and 20 kHz), and sludge types (mixed and secondary sludge). The dependence of the pressure effect on these parameters will be indicated. As for the study of *US* parameters in the previous chapter, **the suspension temperature was controlled during sonication** (at 28±2°C) not to mix different effects. Combined effects of external pressure and temperature increase during sonication without cooling will be investigated in the last chapter for process optimization. The best conditions to obtain are expected to enhance sludge disintegration and then to save energy input as sludge pressurization needs only little energy.

5.1. MATERIALS AND EXPERIMENTAL PROCEDURES

5.1.1. Sludge samples

To investigate the dependence of the pressure effect on sludge type, mixed and secondary sludge samples from the first sampling (see Table 2.1, section 2.2) were used. The properties of corresponding synthetic samples prepared at the optimal concentration of 28 g/L *TS* are recalled in Table 5.1.

Table 5.1: Characteristics of prepared samples from 1st sludge collection (recalled from Table 3.1)

Parameter	**Value**	
Sludge samples	Defrosted mixed sludge	Fresh secondary sludge
Total solids (*TS*) (g/L)	28.0	28.0
Mean $SCOD_0$ (g/L)	2.7	4.5
$SCOD_{NaOH\ 0.5\ M}$ (g/L)	18.5	22.9
$TCOD$ (g/L)	36.5	38.2
$SCOD_{NaOH}/TCOD$ (%)	50.7	59.9

Secondary sludge from the third sampling (see Table 2.3, section 2.2) was used to study how the effect of external pressure on DD_{COD} is affected when varying I_{US}, through P_{US} and probe size. Thereby, a suspension with 28 g/L *TS* was prepared and its properties are given in Table 5.2 (recalled from Table 3.3).

Table 5.2: Characteristics of prepared sample from 3rd sludge collection (secondary sludge, recalled from Table 3.3)

Parameter	**Value**
Sludge sample	Defrosted secondary sludge
Total solids (*TS*) (g/L)	28.0
Mean $SCOD_0$ (g/L)	2.8
$SCOD_{NaOH\ 0.5M}$ (g/L)	22.7
$TCOD$ (g/L)	36.3
$SCOD_{NaOH}/TCOD$ (%)	62.5

Finally, the dependence of pressure effect on frequency was tested on secondary sludge from the fourth sampling (see Table 2.4, section 2.2). Table 5.3 (recalled from Table 3.4) shows the characteristics of the corresponding synthetic sample.

Table 5.3: Characteristics of prepared sample from 4th sludge collection (secondary sludge, recalled from Table 3.4)

Parameter		**Value**
Sludge sample		Defrosted secondary sludge
Total solids (*TS*)	(g/L)	28.0
Mean $SCOD_0$	(g/L)	4.1
$SCOD_{NaOH\ 0.5M}$	(g/L)	22.1
TCOD	(g/L)	39.1
$SCOD_{NaOH}/TCOD$	(%)	56.5

As presented and discussed in Appendix 5, a big difference in sludge *US* disintegration was observed from all these secondary sludge samples. Therefore, they were separately subjected to assess sludge *US* pretreatment efficiency.

5.1.2. Experimental procedures

Firstly, pressurized nitrogen (in the range of 1-16 bar) was applied during sonication of mixed and secondary sludge to investigate if hydrostatic pressure effects depend on *ES* value (7000-75000 kJ/kg_{TS}) and sludge type. Experimental conditions were: isothermal sonication (28±2°C), F_S of 20 kHz, P_{US} of 150 W, 35 mm diameter probe (*BP*), and *TS* of 28 g/L.

Secondly, effect of I_{US} (varied through P_{US} and probe size) on sludge sonication under pressure was looked into. Thereby, isothermal *US* was applied under various external pressures (1-6 bar) at given *ES* and P_{US} for each probe size. Operating conditions were: F_S of 20 kHz, P_{US} in the range of 50-360 W and 50-100 W for 35 mm *(BP)* and 13 mm *(SP)* diameter probe, respectively, *ES* of 50000 kJ/kg_{TS}, *T* of 28±2°C, and *TS* of 28 g/L.

Finally, experiments at 12 kHz were performed under 1 to 4 bar to study combined effects of low frequency and pressure on sludge disintegration. Other conditions were: *BP*, P_{US} of 150 and 360 W, *ES* of 35000 kJ/kg_{TS}, *T* of 28±2°C, and *TS* of 28 g/L.

The amplitude of acoustic pressure corresponding to each P_{US} and probe size, calculated form the following equation, is given in Table 5.4:

$$\boldsymbol{P_A = (2 * I_{US} * c * \rho)^{1/2}}$$

where P_A is the amplitude of acoustic pressure (Pa), I_{US} is ultrasonic intensity (W/m^2), c is the sound speed (m/s), and ρ is the density of the medium (kg/m^3).

The density of sludge suspension with *TS* = 28 g/L was measured at 25^{o}C and found almost equal to that of water: 996.7 kg/m^3. However, the speed of sound in sludge was neither measured in this work nor found in others. Values in different suspensions, *e.g.* kaolin clay slurries (Bamberger and Greenwood, 2004), clay sediments (Maa *et al.*, 1997; Ha, 2008), cornstarch (Johnson *et al.*, 2012), glass (Weser *et al.*, 2013), *etc.*, were therefore examined to find a convenient one. In the mass range of 1-5%, the differences in sound speed are insignificant and the values are almost equal to that in water (1496 m/s at 25^{o}C) which was therefore used for the calculation.

Table 5.4: Amplitude of acoustic pressure corresponding to each P_{US} and probe size

	P_{US} (W)	Amplitude of acoustic pressure (bar)
BP		
	360	10.6
	150	6.8
	50	3.9
SP		
	100	15.0
	50	10.6

5.2. RESULTS AND DISCUSSION

5.2.1. Effect of hydrostatic pressure on DD_{COD} for different *ES* values and sludge types

Mixed sludge (Table 5.1) was investigated first to evaluate the effect of static pressure on disintegration *vs.* sonication time. For these tests, 52 experiments were respectively conducted at various *ES* for different pressure values: 2 bar intervals were used first and then 1 bar intervals at *ES* of 35000 kJ/kg$_{TS}$. The results are presented in Fig. 5.1, where DD_{COD} is plotted as a function of pressure for different *ES* values.

All corresponding curves show the same trends of DD_{COD}: an initial increase up to 2 bar and a decrease thereafter, noticeably up to 6 bar, before a plateau from 6 to 10 bar approximately and a further decrease. The main result is that for this *US* equipment and application almost the same value of optimum pressure was found regardless of *ES*. It is also noteworthy that the absolute difference in DD_{COD} from 1 to 2 bar is approximately the same (2-3%) whatever *ES*. As a consequence, this effect appears relatively high at low *ES*, with a maximum improvement of 67% at 7000 kJ/kg$_{TS}$ and much lower at 75000 kJ/kg$_{TS}$ (23% gain). In addition, the positive effect of pressure up to 2 bar might lead to energy savings in sludge *US* pretreatment. For instance, at the optimum pressure, DD_{COD} obtained with *ES* of 7000, 35000, and 50000 kJ/kg$_{TS}$ were higher than those at atmospheric pressure with *ES* of 12000, 50000, and 75000 kJ/kg$_{TS}$, respectively. It is also interesting to note that the decrease of DD_{COD} beyond the optimal pressure was faster at higher *ES*. With the exception of the lowest *ES* values (7000 and 12000 kJ/kg$_{TS}$), all DD_{COD} values were lower at 6 bar than those at atmospheric pressure. The subsequent plateau is not easy to understand as a continuous decay would be expected. The amplitude of acoustic pressure of all these experiments performed at 150 W with *BP* is equal to 6.8 bar (Table 5.4) which should correspond to the upper limit of hydrostatic pressure to obtain cavitation. Sludge disintegration beyond this hydrostatic pressure might be expected much lower suggesting some *US* secondary effect out of cavitation.

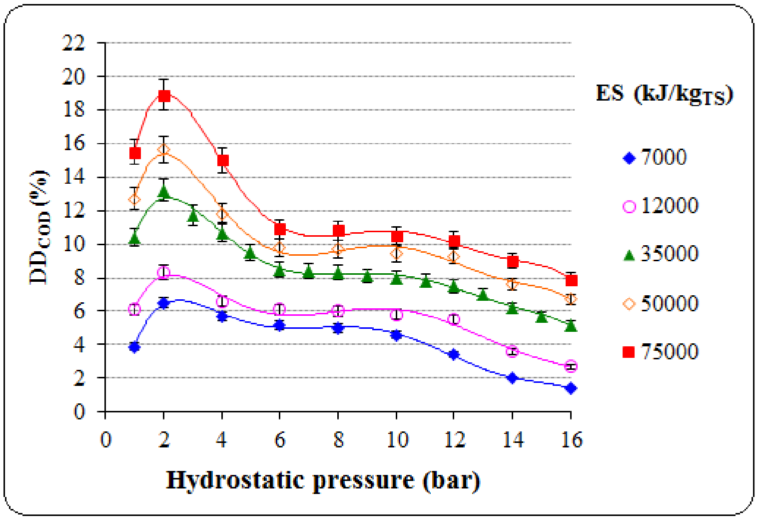


Fig 5.1: Effect of hydrostatic pressure on mixed sludge disintegration (DD_{COD}) for different final *ES* values: P_{US} = 150 W, *BP*, F_S = 20 kHz, *TS* = 28 g/L (Table 5.1), and *T* = 28±2°C.

Additional *US* experiments on secondary sludge (Table 5.1) were performed to check for the possible dependence of the pressure effect on sludge type. The results, shown in Fig. 5.2, indicated that the optimal pressure was again about 2 bar regardless of sludge type also.

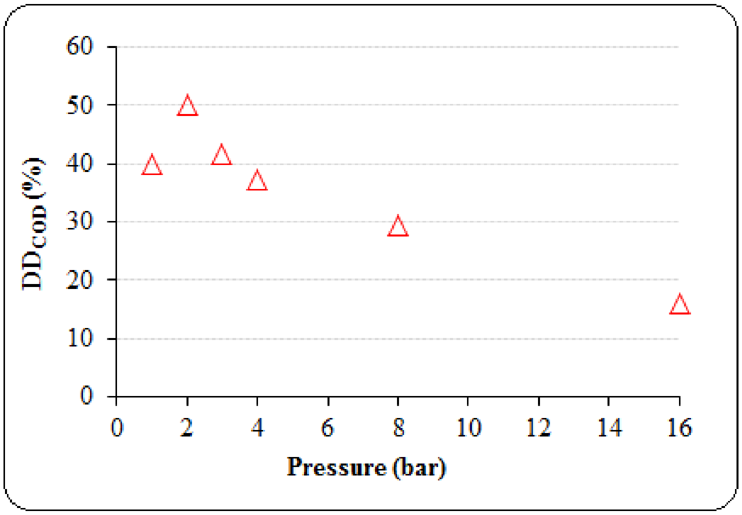


Fig 5.2: Effect of hydrostatic pressure on secondary sludge disintegration (DD_{COD}): P_{US} = 150 W, *BP*, *ES* = 75000 kJ/kg$_{TS}$, F_S = 20 kHz, *TS* = 28 g/L (Table 5.1), and *T* = 28±2°C

Alkali addition prior to sludge sonication was also investigated under optimum pressure and is presented in Appendix 3 showing same positive effect of pressurization.

Apart from enhancing DD_{COD}, sonication under convenient pressure makes the initial kinetics of particle disruption slightly faster, but the difference in final diameter compared to that at atmospheric pressure is negligible (Fig. 5.3). For instance, the reduction of the mean particle size of mixed sludge was 9.3% higher under 2 bar at 7000 kJ/kg$_{TS}$, but almost the same as at 1 bar beyond 35000 kJ/kg$_{TS}$.

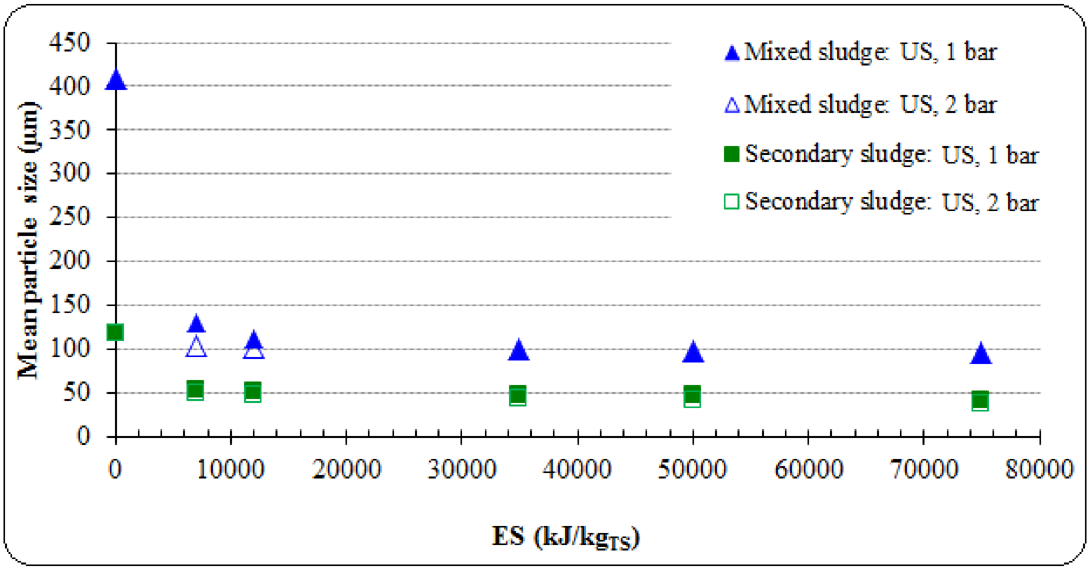
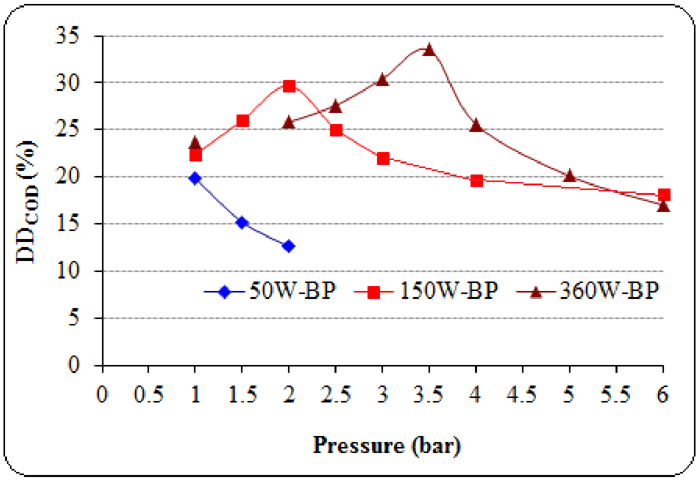


Fig 5.3: Mean particle size evolution of different sludge type during *US* pretreatment (based on *D[4,3]*): *BP*, P_{US} = 150 W, F_S = 20 kHz, *TS* = 28 g/L (Table 5.1), and *T* = 28±2°C

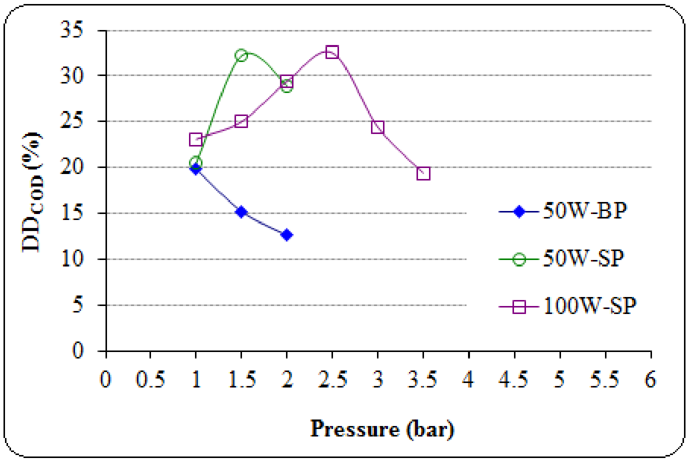
5.2.2. Effect of *US* power and intensity on the optimal pressure and subsequent DD_{COD}

This section presents the dependence of the optimal pressure on P_{US} and I_{US} when also varied by changing probe size at same P_{US}. As previously, this optimum is related to *US* solubilisation of organic matter quantified through DD_{COD}.

Sonication (20 kHz) was applied on secondary sludge (Table 5.2) at the same *ES* value of 50000 kJ/kg$_{TS}$ varying external pressure between 1 and 6 bar (with 0.5 bar intervals). Results are presented in Fig. 5.4. Note that the *US* system could not work at pressures higher than 2 bar for *SP* at 50 W.



(a)



(b)

Fig 5.4: Effect of hydrostatic pressure on DD_{COD} of secondary sludge for different P_{US} and probe sizes (F_S = 20 kHz, *ES* = 50000 kJ/kg$_{TS}$, *T* = 28°C, and *TS* = 28 g/L- Table 5.2): (a) 35 mm diameter probe (*BP*), (b) 13 mm diameter probe (*SP*) and *BP* at same P_{US}

Fig. 5.4 indicates that the optimum pressure value is a function of both P_{US} and probe size. First with the same probe (*BP)*, the optimum shifts toward higher pressure when increasing P_{US} (and thus I_{US} proportionally): 1 bar (or even lower) at 50 W, 2 bar at 150 W, and 3.5 bar at 360 W (Fig. 5.4a). At the much higher intensity delivered by *SP*, the optimum pressure was found at 1.5 bar at 50 W and 2.5 bar at 100 W (Fig. 5.4b). The decrease in DD_{COD} observed when raising pressure above atmosphere with *BP* at 50 W clearly shows that the expected positive effect of hydrostatic pressure only occurs at sufficient I_{US} (or acoustic pressure), unless cavitation intensity decreases. In other words, at same P_{US} (50 W), different effects of pressure resulting from different emitter surfaces indicate the dependence of optimum pressure on I_{US}. With the exception of *BP* at 50 W, sonication under convenient excess pressure significantly improves sludge disintegration efficiency compared to atmospheric sonication, especially at high I_{US} and at low *ES* as previously found in Fig 5.1*:* DD_{COD} improvements reach up to 95% for *SP* and 56% for *BP* (Fig. 5.5). Interestingly, at ―optimum” pressures, better sludge disintegration was found at 50 W (*SP*) than at 150 W (*BP*) which is very different from results obtained at atmospheric pressure in Chapter 4 (cf. Fig. 4.1).

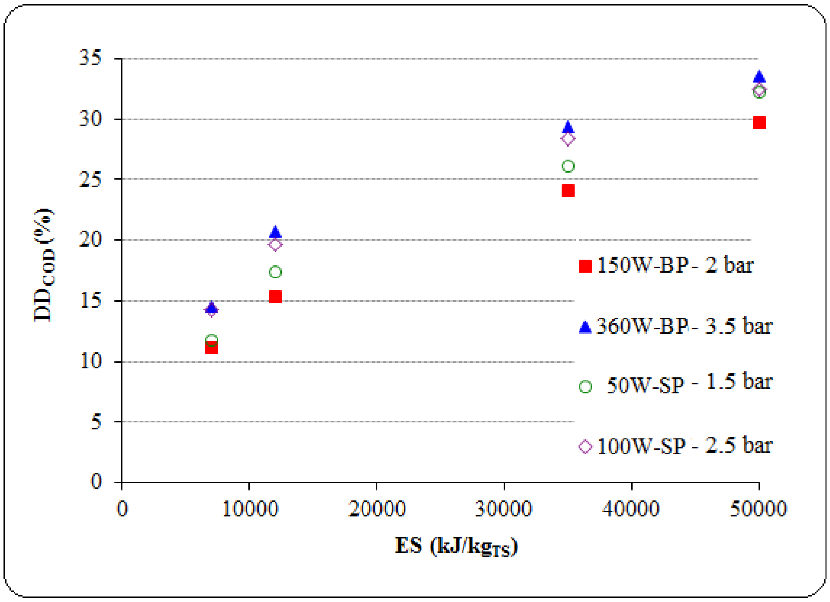


Fig 5.5: Disintegration degree of secondary sludge as a function of *ES* at the optimal pressures of each configuration (P_{US}, probe size): F_S = 20 kHz, *TS* = 28 g/L - Table 5.2, and *T* = 28±2°C

Fig. 5.6 depicts the effect of I_{US} under different pressures at same P_{US} (50 W) on secondary sludge disintegration. First, as found in Chapter 4, the role of I_{US} (at same P_{US} of 50 W with different probe sizes, corresponding to I_{US} of 5.2 and 37.7 W/cm^2) is insignificant at atmospheric pressure. However, its effect around the ―optimal” pressure becomes extremely high, *e.g.* at 50000 kJ/kg$_{TS}$, DD_{COD} obtained with *SP* is 2.1 and 2.3-fold higher than with *BP* at 1.5 and 2 bar, respectively. Such effect, much higher than that of P_{US} depicted in Chapter 4 at atmospheric pressure, highlights the complex interplay of the various parameters on cavitation efficiency.

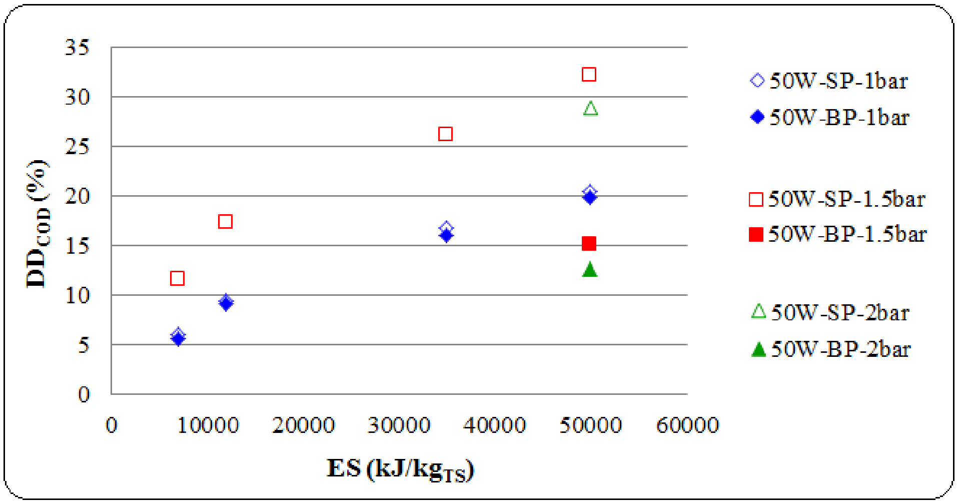


Fig 5.6: Effect of *ES*, *US* intensity (at same P_{US}) and pressure on secondary sludge disintegration: F_S = 20 kHz, *TS* = 28 g/L - Table 5.2, and *T* = 28±2°C

According to Lorimer and Mason (1987), increasing hydrostatic pressure leads to an increase in both the cavitation threshold and the intensity of cavity collapse, which can be explained as follows: when an acoustic field is applied to a liquid, the sonic vibrations create an acoustic pressure (P_a) which must be considered to be additional to the ambient hydrostatic pressure (P_h) already present in the medium. As mentioned in Chapter 1, theoretical calculations from Noltingk and Neppiras (1950), Flynn (1964), and Neppiras (1980), assuming an adiabatic collapse of the bubbles, allow estimating the temperature (T_{max}) and pressures (P_{max}) within the bubble at the moment of total collapse according to:

$$T_{\max} = T_o \left\{ \frac{P_m\,(\gamma - 1)}{P} \right\}$$

$$P_{\max} = P \left\{ \frac{P_m(\gamma - 1)}{P} \right\}^{\left(\frac{\gamma}{\gamma - 1}\right)}$$

where T_o is temperature of the bulk solution, γ is the ratio of specific heats of the gas (or gas vapour) mixture, P is the pressure in the bubble at its maximum size and usually assumed to be the vapour pressure of the liquid, P_m is the total solution pressure at the moment of transient collapse ($P_m \sim P_h + P_a$).

Thereby, increasing the hydrostatic pressure (P_h) leads to an increase in P_m, thus P_{max} and T_{max}, *i.e.* cavitation intensity. On the other hand, as abovementioned, increasing P_h also results in an increase in cavitation threshold, thus the amplitude of acoustic pressure (P_A directly depending on I_{US}) should be in excess as compared to hydrostatic pressure for cavitation bubbles to be generated: indeed it can be qualitatively assumed that if $P_h - P_A > 0$, there is no resultant negative pressure and cavitation cannot occur.

All these combined effects explain why different I_{US} values resulting either from a change of P_{US} or probe size lead to different optimal pressures (Fig. 5.4) and why I_{US} effect at given P_{US} becomes important when moderately raising the pressure, resulting in an inhibition of cavitation for the big probe and increased cavitation efficiency for the small one (Fig. 5.6).

In short, an optimum of pressure is achieved due to opposite effects of hydrostatic pressure: a reduction of the number of cavitation bubbles due to a higher cavitation threshold, but a more violent bubble collapse. This optimum pressure is both *US* power and intensity dependent.

5.2.3. Effect of very low frequency on the optimum pressure and subsequent DD_{COD}

Synthetic *WAS* samples with *TS* of 28 g/L were prepared for these tests (Table 5.3). The same *ES* of 35000 kJ/kg$_{TS}$ was applied using the 12 kHz sonicator with P_{US} of 150 and 360 W through the big probe under pressure. Based on results at 20 kHz, the pressure range 1-4 bar was more carefully investigated with closer intervals of pressure: 0.25 bar. Results are presented in Fig. 5.7.

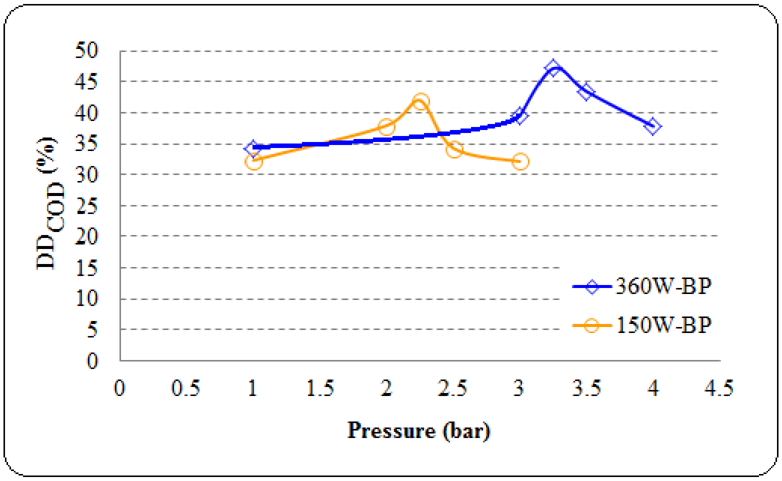


Fig 5.7: Effect of hydrostatic pressure on DD_{COD} of secondary sludge for different P_{US}: *BP*, *ES* = 35000 kJ/kg$_{TS}$, F_S = 12 kHz, *TS* = 28 g/L (Table 5.3), and *T* = 28°±2C

As previously found at 20 kHz (see § 5.2.2), the optimum pressure shifts when increasing I_{US}. Besides, the location of this optimum seems to be independent from sound frequency in the restricted investigated range: 2 bar at 150 W and 3.5 bar at 360 W (using 0.5 bar intervals) for 20 kHz as compared to 2.25 bar at 150 W and 3.25 bar at 360 W (0.25 bar intervals) for 12 kHz sonicator.

Additional isothermal experiments were performed to further understand the effect of frequency on sludge sonication under optimum pressure. Fig. 5.8 indicates that the lower the frequency, the more the sludge is disintegrated, which generalizes the results of Tiehm *et al.* (2001), Zhang *et al.* (2008a), Pham *et al.* (2009), and Carrère *et al.* (2010) to audible frequency. As compared to 20 kHz, 12 kHz isothermal sonication at the optimum pressure of 3.25 bar increases DD_{COD} by 23% and 10% for *ES* of 7000 and 50000 kJ/kg$_{TS}$, respectively. The frequency effect is therefore lower at the optimum pressure than at atmospheric pressure: DD_{COD} improvements by low frequency sonication at 1 bar were 64% and 18% for *ES* of 7000 and 50000 kJ/kg$_{TS}$, respectively (*cf.* Fig. 4.4).

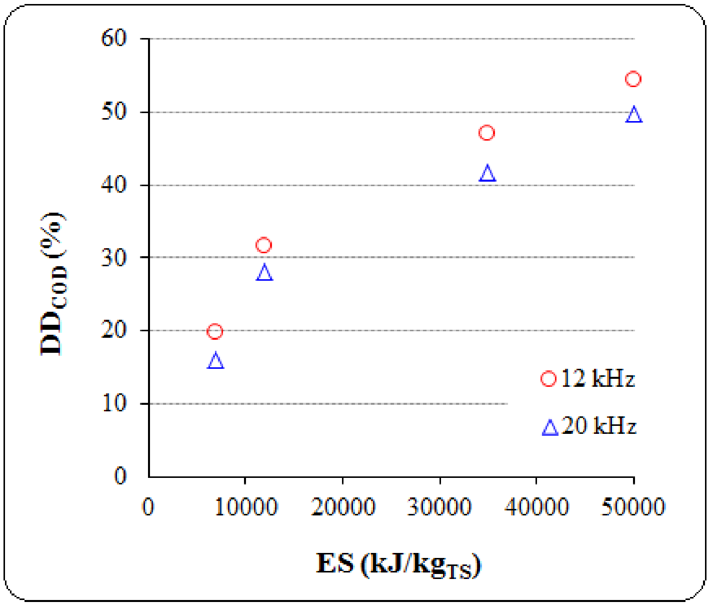


Fig 5.8: Effect of *ES* and frequency on secondary sludge disintegration under optimum pressure (3.25 bar): P_{US} = 360 W, *BP*, *TS* = 28 g/L (Table 5.3), and *T* = 28°±2C

5.3. CONCLUSIONS

The effect of hydrostatic pressure on sludge disintegration was studied for the first time using pressurized nitrogen (1-16 bar) in different operating conditions related to sludge type (mixed and secondary sludge), ES (7000-75000 kJ/kg$_{TS}$), P_{US} (50-360 W), probe size (13 and 35 mm diameter probes), and frequency (12 and 20 kHz).

The most effective isothermal sonication would be high P_{US}, low F_S, convenient excess pressure, and adequate TS concentration, *i.e.* according to our equipment possibilities 360 W (35 mm diameter probe), 12 kHz, 3.25 bar, and 28 g$_{TS}$/L, respectively.

As far as sufficient acoustic intensity was provided, an optimum pressure (> 1 bar) was found due to an increase in both cavitation threshold and cavitation intensity when increasing hydrostatic pressure.

Whereas Chapter 4 showed that effect of I_{US} on DD_{COD} was minor at atmospheric pressure, it was found to be much higher under convenient hydrostatic pressure.

The major result was that the location of the optimal pressure depends on P_{US} and I_{US} (or probe size), but not on ES, sound frequency, nor sludge type. Such an important result would have to be checked in other US applications.

In general, sludge disintegration efficacy was significantly improved by sonication at the optimum pressure as compared to that at atmospheric pressure, especially at low ES, leading to a potential of energy input savings in sludge sonication pretreatment, but also in most of ultrasound assisted processes (since the energy to pressurize the solution to the corresponding moderate pressure levels is much lower than the observed energy savings).

CHAPTER 6

OPTIMAL SONICATION FOR PRETREATMENT OF SLUDGE

HIGHLIGHT

- *US* pretreatment of sludge under ―adiabatic” conditions was optimized, regarding *US* parameters, pressure, and operation mode.

- Apart from P_{US} and probe size, optimal pressure is dependent on temperature.

- Adiabatic sequential sonication using 5 min *US*-on at 360 W, 12 kHz, and 3.25 bar and 30 min *US*-off is recommended.

- Methane production from sludge pretreated in optimal conditions is improved about 8% as compared to raw sludge.

INTRODUCTION

Preliminary investigations reported in Chapter 3 clearly showed that sonication without cooling (also called ―adiabatic” sonication though heat losses are important) gave much better results than isothermal treatment thanks to combined effects of cavitation and temperature rise due to the high *US* energy dissipated in the sludge. Nevertheless as these two effects are not easy to separate, it was decided to fully investigate both conditions: **isothermal**, as used in Chapters 4 and 5, to conveniently work on ultrasound parameters - with sludge disintegration as a significant mean of quantification in a fundamental sonochemical engineering approach - and **without cooling** to take advantage of the temperature raise in a more application driven approach. This last case - where *US* energy is optimized for sludge pretreatment as the specific *US* application - is detailed in this Chapter 6. As previously found with isothermal operation, *low frequency* and *high US power-short time* operation are supposed to be also more convenient in adiabatic condition, and here again *optimal hydrostatic pressure* is searched for optimal sludge pretreatment. Some of these parameters were separately investigated due to unavailable and limited equipment in the early stage of the research. This part thus aims at optimizing sonication process for sludge disintegration by simultaneous investigation of significant parameters, *i.e.* P_{US}, I_{US}, temperature rise, pressure, and operation mode (*continuous vs. sequential* sonication).

6.1. MATERIALS AND EXPERIMENTAL PROCEDURES

6.1.1. Sludge samples

Secondary sludge from the third sampling (see Table 2.3, section 2.2) was used for investigating the efficiency of adiabatic sonication (varying P_{US} and probe size) at atmospheric and under pressure. The properties of the corresponding synthetic sample are given in Table 6.1.

Synthetic samples of secondary sludge from the fourth sampling (see Table 2.4, section 2.2) were used for optimizing sonication process (continuous *vs*. sequential treatment). Their properties are given in Table 6.2

As already mentioned in previous chapters, investigation of a given parameter or parameter combination was performed with the same sludge sample to ensure a meaningful comparison, as the two secondary sludge samples resulted in different disintegration degrees (see Appendix 5).

Table 6.1: Characteristics of prepared sample from 3rd sludge collection (secondary sludge, recalled from Table 3.3)

Parameter	**Value**
Sludge sample	Defrosted secondary sludge
Total solids (*TS*) (g/L)	28.0
Mean $SCOD_0$ (g/L)	2.8
$SCOD_{NaOH\ 0.5M}$ (g/L)	22.7
TCOD (g/L)	36.3
$SCOD_{NaOH}/TCOD$ (%)	62.5

Table 6.2: Characteristics of prepared sample from 4th sludge collection (secondary sludge, recalled from Table 3.4)

Parameter	**Value**
Sludge sample	Defrosted secondary sludge
Total solids (*TS*) (g/L)	28.0
Mean $SCOD_0$ (g/L)	4.1
$SCOD_{NaOH\ 0.5M}$ (g/L)	22.1
TCOD (g/L)	39.1
$SCOD_{NaOH}/TCOD$ (%)	56.5

6.1.2. Experimental procedures

First, the effects of temperature rise under –adiabatic” *US*, which were preliminarily studied in Chapter 3 with mixed sludge under standard conditions - 20 kHz, atmospheric pressure (section 3.2.3) -, were further investigated with secondary sludge, varying P_{US} and probe size.

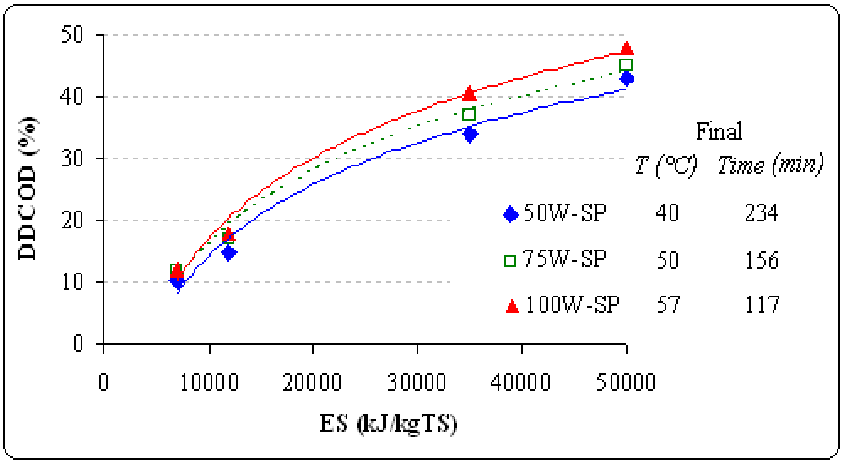
Thereafter, the dependence of the pressure optimum upon thermal profile and the subsequent effects on sludge *US* disintegration were looked into.

Adiabatic mode, low frequency (12 kHz), high power and convenient pressure excess were separately proved to be efficient conditions for sludge sonication. Thereby, final optimization of sludge *US* disintegration was performed in such conditions, varying P_{US}, hydrostatic pressure, as well as sonication mode (sequential vs. continuous *US*). In addition to the benefit of sequential mode observed under isothermal *US*, it was expected here to be also advantageous by limiting the temperature raise under high P_{US} which could be detrimental to cavitation and equipment. Biological methane potential (*BMP*) tests were finally carried out to assess the efficiency of sludge pretreatment on methane production.

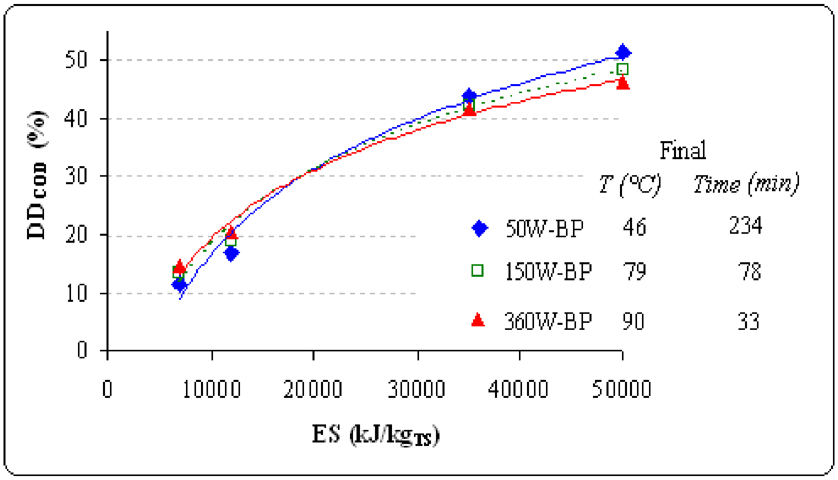
6.2. RESUTLS AND DISCUSSION

6.2.1. Adiabatic sonication at atmospheric pressure

Effect of P_{US} on DD_{COD} in adiabatic conditions was investigated using the following ranges: 50-100 W for *SP* and 50-360 W for *BP*. Experiments were conducted at 20 kHz and under atmospheric pressure. Results are given in Fig. 6.1.



(a)



(b)

Fig 6.1: Effect of *ES* and P_{US} on DD_{COD} under adiabatic sonication (F_S = 20 kHz, secondary sludge solutions with *TS* = 28 g/L - Table 6.1, atmospheric pressure): (a) *SP* and (b) *BP*. Final temperatures of adiabatic *US* are also given

As expected, evolution of sludge temperature was found to depend on P_{US}: higher P_{US} resulted in a more rapid increase of temperature and yielded a higher final value at given *ES* as the reactor was not fully insulated. In addition, and more surprisingly, different temperature profiles were also observed with same P_{US} but different probe sizes: at 50 W, final *T* increased from 40°C to 46°C when switching from *SP* to *BP*. This unexpected result means that the efficiency of ultrasound transmission to the sludge is significantly better with the big probe than with the small one, maybe due to limited wave propagation under intense cavitation. This effect (about 20%) cannot be precisely quantified as temperature in the laboratory may have changed.

Fig. 6.1a, corresponding to *SP*, proved again the *high* P_{US} *– short time* mode to be the most effective combination for sludge *US* pretreatment at atmospheric pressure, regardless of *T* control. Nevertheless, the positive effect of P_{US} in adiabatic mode was not better than in isothermal mode: for instance, at an *ES* value of 50000 kJ/kg$_{TS}$, DD_{COD} increased by 12% from 50 to 100 W, as compared to 13% for isothermal sonication. That means there was no positive effect of the slight temperature gain at 100 W as compared to 50 W (up to 17°C) despite the temperature level reached was still moderate.

Conversely, the 50 W-sonication could have benefit from the temperature increase when switching from *SP* to *BP*, as in the latter case higher DD_{COD} were reached despite lower I_{US} (Fig. 6.1b). With *BP*, high power was only efficient in adiabatic conditions for *ES* values lower than 20000 kJ/kg$_{TS}$ (when the increase in sludge *T* and *US* duration were still small). The apparently surprising reverse trend at higher *ES*, then higher *T*, might be explained by the result of lower *US* efficiency at higher temperature: it is well known that cavitation bubbles accumulate higher fraction of water vapor during the growth phase at low acoustic pressure, which will cushion bubble collapse and make it much less violent. So in this range, the beneficial effect of *T* through thermal hydrolysis should be overpassed by the detrimental effect on cavitation efficiency.

To further understand the effect of *T* on cavitation efficiency, additional experiments were conducted on another secondary sludge (data was not shown) at 150W, atmospheric pressure, and isothermal conditions at constant *T* of 28, 55, 80^{o}C. Results, given in Fig. 6.2, show an increase in DD_{COD} when increasing *T* from 28 to 55^{o}C but a decrease at *T* of 80^{o}C. Moreover, there was only small differences in DD_{COD} between isothermal *US* and sole thermal hydrolysis at the same *T* of 80^{o}C. It is then clear that cavitation intensity is significantly dampened at too high *T* sonication and has much less effect than thermal hydrolysis.

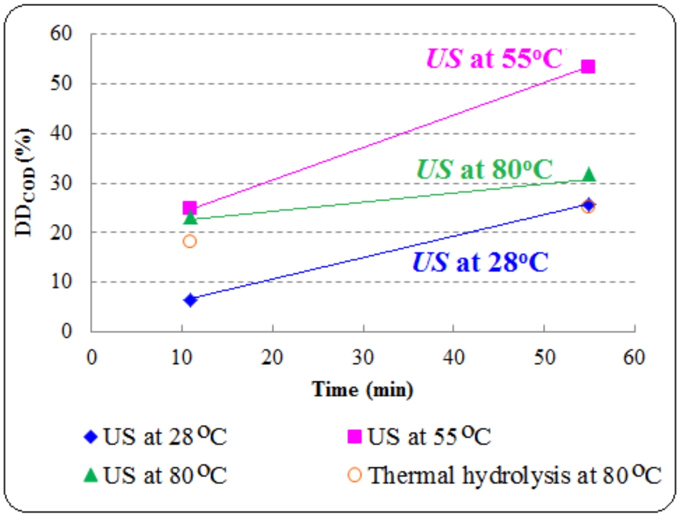


Fig 6.2: Effect of temperature on DDCOD by isothermal US (20 kHz, PUS = 150 W, BP, secondary sludge solutions with TS = 28 g/L – Table 6.2, and atmospheric pressure) and thermal hydrolysis.

Coming back to previous results presented in Fig.6.1, it should be mentioned that they were achieved on samples rapidly cooled at the end of sonication. In this case, the beneficial effect of high temperature for hydrolysis could not be fully recovered during the shortest treatments as thermal hydrolysis is a slower process than *US* solubilisation. Another comparison could then be made based on the **same treatment period,** including sonication plus maturation under stirring only. Thereby, additional experiments were conducted using *BP* at both same *ES* and treatment time (including *US* and –thermal hydrolysis” after *US*). At 50 W, adiabatic *US* was applied in the *ES* range of 7000-50000 kJ/kg_{TS} and the solutions were then cooled down immediately to 28°C. At 150

W and 360 W, *US* was turned off after same *ES* values were reached, but the stirrer was still working (no cooling) until the whole durations equaled those of 50 W experiments. Temperature evolutions (due to heat losses) corresponding to experiments at 50000 kJ/kg$_{TS}$ are depicted in Fig. 6.3. Results of DD_{COD}, given in Fig. 6.4, show again the *high* P_{US} – *short time* sonication to be the best mode for sludge disintegration at atmospheric pressure, thanks to thermal hydrolysis after *US* disintegration. Of course one may suggest that thermal insulation of our equipment would provide even better results by keeping higher temperature. Note that such energy saving by insulating the reactor could also save *US* energy for the same result in terms of DD_{COD}.

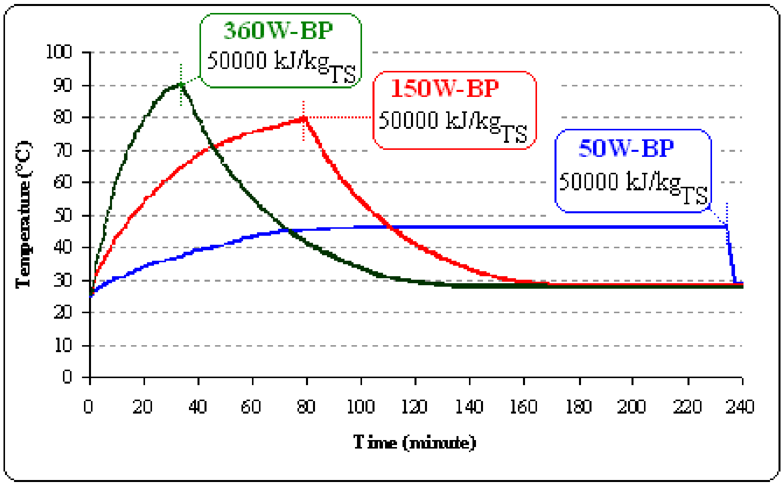


Fig 6.3 : Temperature evolutions for experiments with BP using ―adiabatic” US at ES = 50000 kJ/kgTS and stirring afterwards up to 240 min: FS = 20 kHz, secondary sludge solutions with TS = 28 g/L (Table 6.1), atmospheric pressure

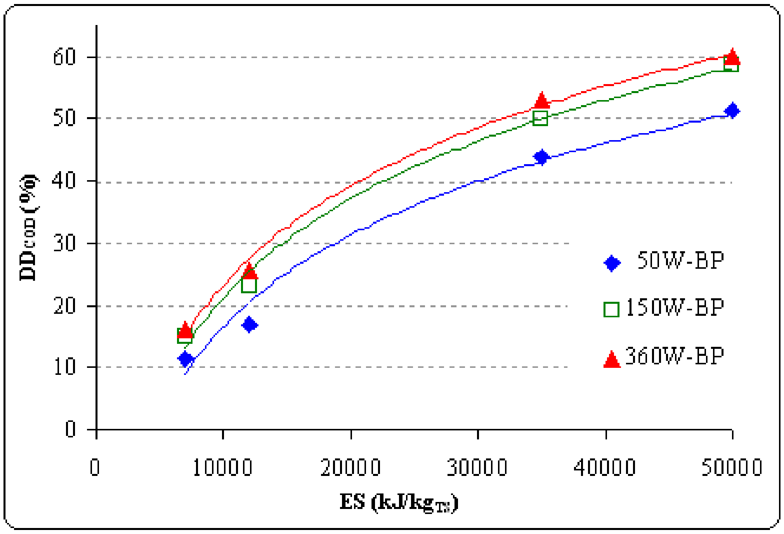


Fig 6.4: Effect of ES and PUS on DDCOD under adiabatic US followed by stirring up to 240 min (same conditions as in Fig. 6.3)

To sum up, the effect of *T* induced by sonication is rather complex and cannot be neglected. At atmospheric pressure, sludge disintegration still benefits from high P_{US} if enough time is let for thermal hydrolysis induced by *US* heating to operate.

6.2.2. Optimal pressure under adiabatic sonication

Based on isothermal results, optimal values of hydrostatic pressure under adiabatic *US* were searched in the 1-5 bar range at a given *ES* value, but for different P_{US} (100-360 W) and probe sizes. Results are shown in Fig. 6.5 where same *ES* (50000 kg/kg$_{TS}$) but different treatment durations were applied. This should however not much change the location of the optimum pressure, only the final corresponding DD_{COD} value (for instance increased from 60% to 66% at 360 W when after 33 min of *US*, the solution was let on stirring up to 78 min, to match the duration of the 150 W experiment).

Note also that data of Fig. 6.5 do not correspond to the same final temperature.

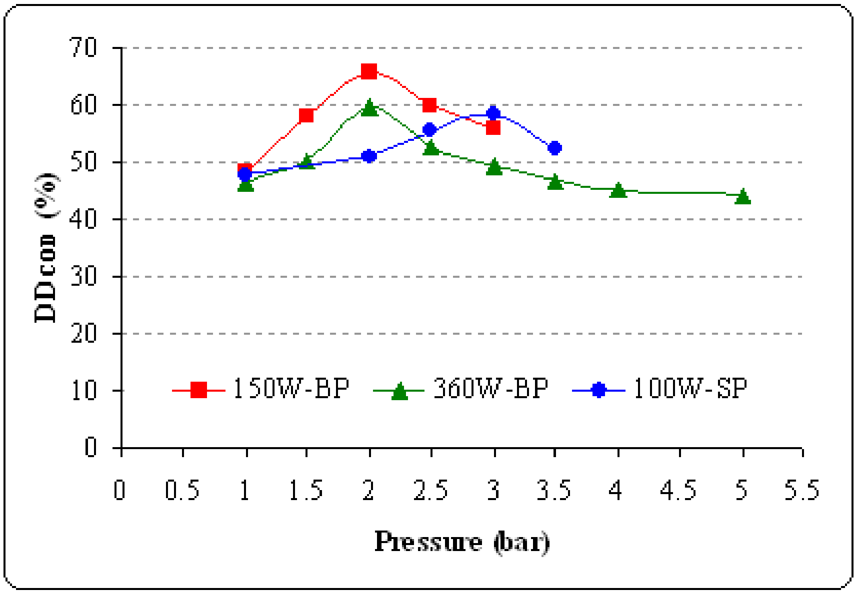


Fig 6.5 : Effect of pressure on DDCOD under adiabatic sonication for different combinations of PUS-probe sizes: ES = 50000 kJ/kgTS, FS = 20 kHz, secondary sludge solutions with TS = 28 g/L (Table 6.1)

Surprisingly, in adiabatic conditions, the same optimum pressure of 2 bar was obtained with the same probe (*BP*) at different P_{US} (150 and 360 W) while an increase would be expected at higher power according to isothermal data (section 5.2.2). The respective evolution of optimal pressure *vs.* P_{US} is complex in adiabatic condition and somewhat different with respect to isothermal case as the result of opposite effects of *T* on cavitation intensity and thermal hydrolysis. As observed, optimum pressures found under isothermal *US* were shifted differently depending on temperature profiles:

slight increase at the moderate *T* resulting from 100 W adiabatic *US* with *SP* (from 2.5 bar -Fig. 5.3b- to 3 bar -Fig. 6.5), but a decrease at extreme *T* found at 360 W with *BP* (from 3.5 bar -Fig. 5.3a- to 2 bar -Fig. 6.5). This result was not expected and would deserve more analysis based on single cavitation bubble dynamics at high pressure and high temperature.

6.2.3. Optimization of sludge sonication pretreatment

As previously found by investigation of separate effects of parameters, than a few convenient combinations, low frequency, high P_{US} and adiabatic condition should be preferred to improve *US* disintegration of sludge, while *TS* concentration and pressure give rise to optimal values. Moreover, the pressure optimum was found to depend upon *US* parameters, as well as thermal effects induced by cavitation. Then this last part of the work has been devoted to finalizing optimization of *US* sludge disintegration by searching for the optimal hydrostatic pressure while setting the other parameters at the most favorable conditions expected, *i.e.* 12 kHz, 360 W (*BP*), *TS* of 28 g/L (as found optimal in all investigated cases, *cf*. Chapter 3 and Appendix 2), and adiabatic conditions.

It was also noted that sonication at high P_{US} resulted in too high sludge temperature, more than 80°C, while the safety range recommended by the manufacturer is less than 65°C for the 12 kHz device. Extreme *T* might harm the transducer, lead to unstable P_{US} during sonication, and are not convenient to provide intense cavitation. In fact, several runs were interrupted due to the high *T*. Sequential sonication was therefore investigated to limit the *T* increase and possibly improve the process. The comparison of continuous and sequential modes contributed to the optimization of sludge sonication pretreatment.

Fig. 6.6 describes effects of continuous *vs*. sequential sonication on adiabatic sludge disintegration using same *ES* value of 35000 kJ/kg_{TS} and varying pressure in 1-3.25 bar range. Such *ES* value was chosen to have a relatively short treatment time in the most severe conditions (23 min at 360 W), not to harm the probe (erosion) nor the transducer (by limiting *T*). Corresponding temperature evolutions are given in Fig. 6.7. The following conditions were investigated:

(*i*) 50W continuous sonication (164 min)

(*ii*) 360W continuous sonication at 1, 2, and 3.25 bar (23 min)

(iii) 23 min of 360 W continuous sonication, as in (ii), but followed by stirring (no sonication) up to 164 min, to get the same treatment time as in (i) (marked as *360W-'xx' bar + stirring*) (*iv*) sequence made of 1 min sonication at 360 W followed by 6 min stirring (no sonication) and pursued for a total duration of 164 min (marked as *360W-1/6-'xx' bar*)

(*v*) sequence made of 5 min sonication at 360W followed by 30 min stirring (no sonication) and pursued up to 164 min of treatment (marked as *360W-5/30-'xx' bar*).

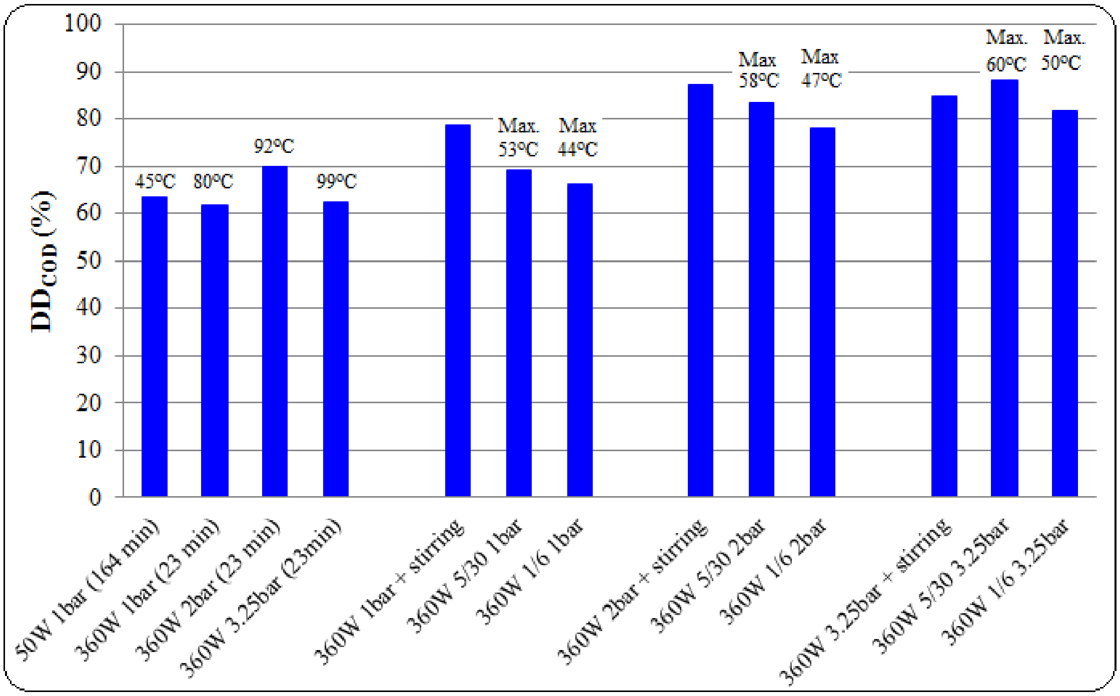


Fig 6.6: Comparison of continuous and sequential sludge US disintegration at different pressures under adiabatic conditions: BP, ES = 35000 kJ/kgTS, FS = 12 kHz, secondary sludge solutions with TS = 28 g/L (Table 6.2)

For the continuous process, adiabatic sonication at 360 W under 2 bar was found as the best condition, confirming the value of the optimum pressure found in Fig. 6.5 at this high P_{US}, regardless of the total treatment time. It is interesting to note that the final temperature under 360 W *US* increased from 80°C to 99°C with increasing hydrostatic pressure from 1 to 3.25 bar, proving a better energy transmission at high pressures. Then this better transmission does not mean better efficiency for sludge disintegration as abovementioned too high temperature is very detrimental for cavitation intensity. As discussed previously, such high temperatures could have additional positive effect due to thermal hydrolysis if the sludge is let under stirring. The comparison of all these runs was thus preformed at the same total time to let thermal hydrolysis go on after intense sonication. The corresponding three runs at 360 W showed much better DD_{COD} thanks to thermal hydrolysis and now 2 and 3.25 bar gave closer DD_{COD}, clearly higher than that at 1 bar. Again the benefit as compared to the 50 W-operation was only significant if the whole treatment period was kept unchanged. However, temperatures of solutions at the end of the 360 W-continuous-sonication were extremely high. Then its disadvantages as abovementioned could be avoided by sequential *US*.

For *sequential mode*, 360 W adiabatic *US* at 3.25 bar was the most efficient, followed by that at 2 bar and 1 bar. The pressure of 2 bar was thus no longer an optimum in the sequential process which provided a very similar temperature profile at 2 and 3.25 bar (Fig. 6.7). In other words, the surprising low optimum pressure found with 360 W continuous sonication (Fig. 6.5) was due to the negative effect of very high temperature (99°C at 3.25 bar *vs.* 92°C at 2 bar). Besides, the advantage of the 35 min period cycle (5/30) as compared to 7 min period cycle (1/6) at all applied pressures might be due again to temperature effect, as max sludge *T* of 5/30 mode were higher than those of 1/6 mode.

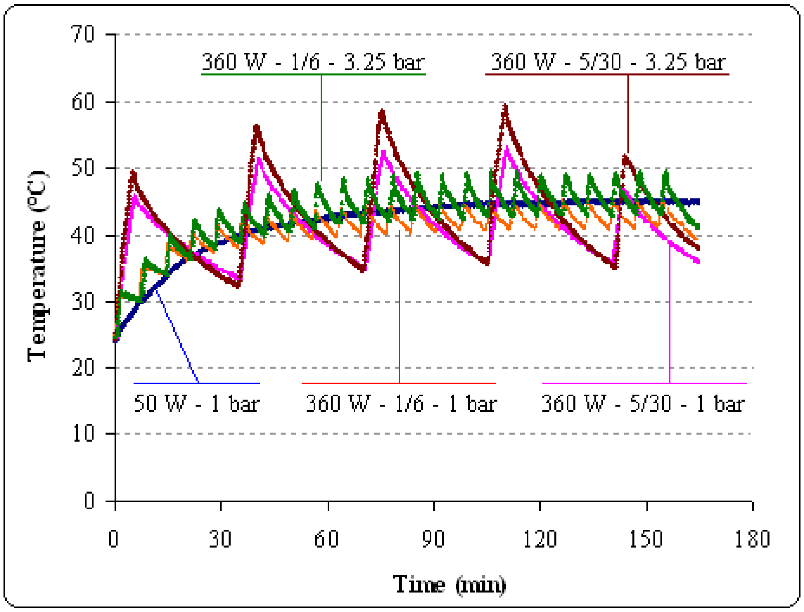


Fig 6.7: Temperature evolutions of sequential sonication (same conditions as in Fig. 6.6)

At the same *ES* of 35000 kJ/kg$_{TS}$ and treatment time of 164 min, DD_{COD} from optimal sequential sonication was about 39% higher than that from 50 W-continuous-sonication and almost equal to the best 360 W continuous operation, while yielding more reasonable temperatures.

In short, sequential sonication at 12 kHz and under 3.25 bar, with 5 min of adiabatic sonication at 360W and 30 min of stirring appears as the best combination to achieve a high sludge disintegration degree with the advantage of maintaining *T* in the recommended range. The sample pretreated by this procedure was then investigated for its methane production yield (*BMP* test) as compared to raw sludge.

6.2.4. Biochemical methane potential

To investigate the potential of methane production of pretreated sludge (using 12 kHz sonicator), four sludge samples (*TS* of 28 g/L, Table 6.2) were prepared for *BMP* tests:

(S1) Raw sludge (unpretreated sludge),

(S2) Sludge pretreated in optimal conditions (sequential 5 min 360 W *US*-on/30 min *US*-off pretreatment, *ES* = 35000 kJ/kg$_{TS}$, P_h = 3.25 bar, and adiabatic mode),

(S3) Shortly sonicated sludge (*ES* of 7000 kJ/kg$_{TS}$ at 360 W + stirring up to 164 min, P_h = 3.25 bar, and adiabatic mode), and

(S4) Mixture of raw and pretreated sludge (1/3 *S1* and 2/3 *S2*)

S3 was tested to see if even a short *US* pretreatment (much less expensive) could have a significant effect on *AD*, while *S4* (mixture of 1/3 raw and 2/3 sonicated sludge) was checked to try to avoid the initial delay observed in a preliminary test (see Appendix 8) and attributed to the destruction of the sludge bacteria by sonication.

The cumulative volumes of methane produced by those samples are compared in Fig. 6.8. Their rheology was also examined and is presented in Appendix 4.

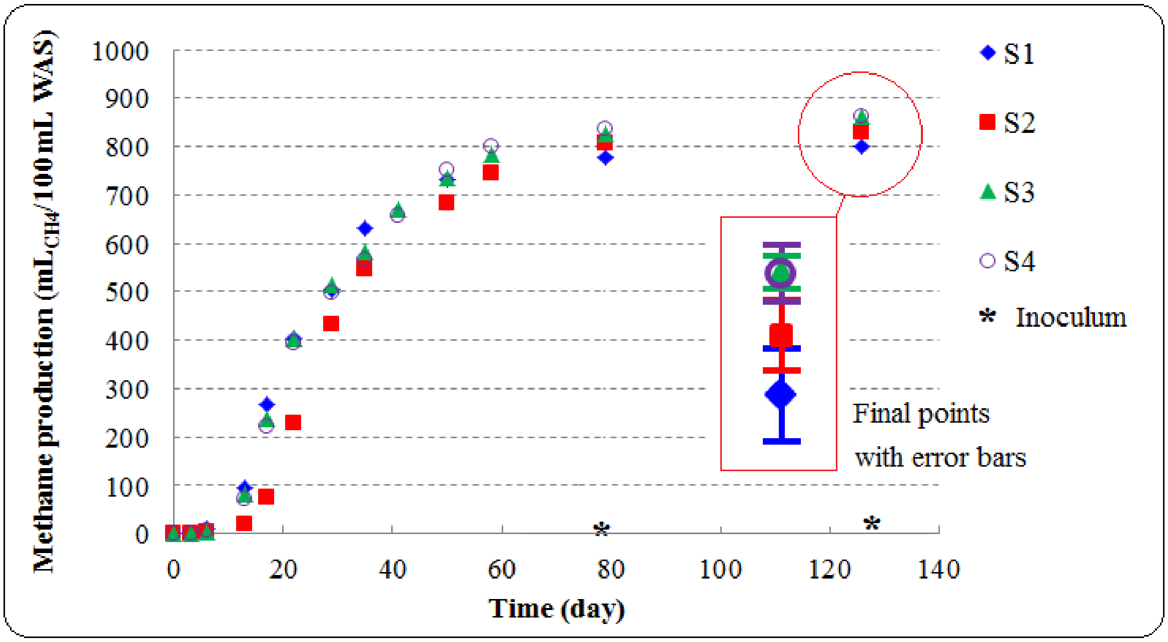


Fig 6.8: BMP of pretreated sludge samples

In the first six days, the methane production rate was low for all samples due to the lag phase of anaerobic digestion. Then the rate increased significantly till the 40th day and slowed down afterwards due to substrate limitation. It can be noticed that *S2* exhibited a longer initial delay in methane production as compared to the other samples (as observed in preliminary tests detailed in Appendix 8). It could be due to the degradation of bacteria and enzymes under *US*. Within 80 days, the cumulative methane production almost reached its maximum value. The final results showed that all *US* pretreatment led to higher methane volume production than the raw sample, with improvements of 8% for *S3* and *S4* and 4% for *S2* as compared to *S1,* just above the measurement uncertainty. The small differences of methane production measured by *BMP* tests make it hard to choose any condition (*ES* value or fraction of the stream to go through the sonicator) for continuous *AD*. Further investigations via continuous operation could be conducted, but probably with much lower energy consumption as suggested below.

In short, *US* pretreatment conditions found in this work are good for sludge disintegration, *i.e.* rupturing cell walls and facilitating the release of intracellular matters into the aqueous phase as measured through DD_{COD}. Nevertheless it could be concluded from this work that DD_{COD} is not a convenient parameter for subsequent *AD*. In terms of CH_4 production, very few gains were achieved despite huge energy consumption and then much lower *US* energy should be tried. Finally, for the main purpose of pretreatment, *i.e.* acceleration of hydrolysis stage and then enhancement of anaerobic digestion, very important questions remain: why do several works claim *US* pretreatment to be efficient for better *AD*? Might it be due to different sludge quality and/or to *BMP* test conditions? As mentioned, large differences in DD_{COD} were already observed depending on sludge samples. Pretreatment effect could be more visible on sludge with longer age. Besides, *BMP* protocol used in this work mainly focused on CH_4 production yield (with a small volume of inoculum as compared to sludge volume) and did not give information on possible benefit regarding *AD* kinetics.

6.3. CONCLUSIONS

This part aimed at obtaining with the available equipment the best conditions of sonication for sludge disintegration by simultaneous investigation of low frequency, high power, hydrostatic pressure, adiabatic mode, and continuous *vs*. sequential process.

First, the effect of *T* increase during sonication without cooling cannot be neglected both during and after the process, as thermo hydrolysis is a rather slow process As a result, at same final time more efficiency of sludge disintegration was achieved from high P_{US} and adiabatic *US*.

Besides, positive effect of pressure associated with high power adiabatic *US* was also found. Interestingly, apart from its dependence on P_{US} and probe size, the optimum pressure could be affected by *T*. Concerning disintegration, a slight increase was obtained at moderate *T,* mainly due to higher numbers of cavitation bubbles, then a decrease at extreme *T* (>80°C) due to the less violent collapse of cavitation bubbles containing too much vapor.

For comparison of continuous and sequential modes, sequential adiabatic sonication using 5 min *US*-on at 360 W, 12 kHz, and 3.25 bar and 30 min *US*-off showed the best efficiency of sludge disintegration and the advantage of maintaining *T* in the recommended range.

Finally, *US* pretreatment only led to a slight improvement in methane production, always less than 10% with respect to raw sludge. This result is extremely disappointing as compared to several other works, meaning that *US* pretreatment which proved to be efficient in solubilizing sludge organic compounds has no significant effect on their subsequent *AD*. Nevertheless, it should be noted that in better adiabatic process, with improved reactor insulation, higher temperature increase would be obtained at same energy consumption and then same DD_{COD} would probably require much lower *US* energy.

CONCLUSIONS

This research aimed at optimizing ultrasonic pretreatment of sludge to obtain the most suitable conditions concerning sludge disintegration effectiveness prior to anaerobic digestion. The specific objectives of this work were (i) investigation of main operation parameters including thermal effects (ii) separate quantification of sonication parameter effects on isothermal sludge disintegration, (iii) study of sludge *US* pretreatment under pressure and audible frequency for the first time, and (iv) optimization of the whole set of parameters of *US* process which was hardly performed before.

Though having achieved very advanced *COD* solubilisation in optimal conditions, consecutive tests of biochemical methane production (*BMP*) gave very disappointing results showing only marginal effects. This result raises important questions: why did several authors claim that *US* increases either kinetics and/or yield of methane production? Are such discrepancies due to different sludge characteristics and/or to *BMP* test conditions? Did these works conveniently separate *US* effects from other ones which would have performed the efficient pretreatment? Further studies dedicated to *AD* kinetics and using different types of sludge would be required to answer these questions.

If the results of this work are still to be analyzed concerning the selected application of sludge pretreatment towards *AD*, they are of major interests for a more general sonochemical engineering approach.

New general knowledge on ultrasound processing may be outlined from this work as similar trends were observed on different kind of physico-chemical quantities: *COD*, particle size, morphology, viscosity.

First it has been confirmed that acoustic energy per unit solid weight is the most significant parameter and that –high power - short time” procedure makes the most efficient use of this acoustic energy, while sequential operation could bring a slight improvement. When investigating the effects of acoustic intensity, again pressure and temperature conditions played a major role.

In addition, the two new major contributions pointed out in this work concern the significant improvements always obtained at the optimum of hydrostatic pressure and at audible frequency (12 kHz) as compared to the standard atmospheric pressure and 20 kHz.

Concerning low frequency, rather simple explanation may be given according to cavitation bubble dynamics. The promising results presented here suggest to continue investigations of lower frequency and to search an eventual optimum, having in mind the possible limitations due to noise excess.

Much more complex features were observed concerning pressure as the optimum depended not only on ultrasonic intensity, but also on the selected temperature profile (*i.e.* constant by cooling or increasing in pseudo adiabatic mode). In the specific case of sludge solubilisation, temperature has simultaneous effects on thermal hydrolysis and on cavitation. The latter effect is very complex according to cavitation bubble dynamics dampened by vapor content and the dependence of the cavitation threshold on temperature and pressure. It can be concluded that optimal pressure and temperature should be investigated (or at least verified) for each specific application.

REFERENCES

A

Abramov, O.V. High-Intensity Ultrasonics: Theory and Industrial Applications. Golden and Breach Science Publishers, Amesterdam, Netherlands, (1998) 80–82.

Achu N. I. and Liu J., Enhancement of anaerobic digestion of dewatered-sewage sludge through anaerobic pretreatment. 11th IWA World Congress on Anaerobic Digestion, 23-27 September, 2007, Brisbane, Australia.

Akin B., Khanal S.K., Sung S., Grewell D., Van-Leeuwen J., Ultrasound pre-treatment of waste activated sludge, Water Sci. Technol. 6 (2006) 35–42.

Akin B., Waste activated sludge disintegration in an ultrasonic batch reactor, Clean – Soil, Air, Water 36 (2008) 360–365.

Aldin S., Elbeshbishy S., Tu F., Nakhla G., Ray M., (2008), Pre-treatment of Primary Sludge Prior to Anaerobic Digestion. http://www.nt.ntnu.no/users/skoge/prost/proceedings/aiche-2008/data/papers/P137267.pdf, 28/11/2012

APHA, AWWA, and WEF, 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, D.C.

Appels L., Degrève J., Bruggen B.V., Impe J.V., Dewil R., Influence of low temperature thermal pre-treatment on sludge solubilisation, heavy metal release and anaerobic digestion, Bioresource Technology 101 (2010) 5743–5748

Apul O.G. 2009. Municipal sludge minimization: evaluation of ultrasonic and acidic pretreatment methods and their subsequent effects on anaerobic digestion. Thesis of Master Degree - Middle East Technical University (Turkey). http://etd.lib.metu.edu.tr/upload/12610366/index.pdf (accessed 28 July 2012).

Asakura Y., Nishida T., Matsuoka T., Koda S., Effects of ultrasonic frequency and liquid height on sonochemical efficiency of large-scale sonochemical reactors, Ultrasonics Sonochemistry 15 (2008) 244–250

B

Bader K. B., Raymond J. L., Mobley J., Church C.C. The effect of static pressure on the inertial cavitation threshold, J. Acoust. Soc. Am. 132 (2) (2012a) 728-737

Bader K. B., Mobley J., Church C. C. The effect of static pressure on the strength of inertial cavitation events, Journal of the Acoustical Society of America, 132 (4) (2012b) 2286-2291

Bamberger J.A. and Greenwood M.S. Measuring fluid and slurry density and solids concentration non-invasively. Ultrasonics 42 (2004) 563–567

Banu J.R., Uan D.K. and Yeom I.T. Effect of alum on nitrification during simultaneous phosphorus removal in anoxic/oxic reactor. Biotechnol. Bioprocess Eng., 14 (2009) 543-548.

Barber W.P. The effects of ultrasound on sludge digestion, J. Chart. Inst. Water Environ. Manage. 19 (2005) 2–7

Baroutian S., Eshtiaghi N., Gapes D. Rheology of a primary and secondary sewage sludge mixture: Dependency on temperature and solid concentration, Bioresource Technology, 140 (2013) 227-233.

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. <http://www.dep.state.pa.us/DEP/DEPutate/Watermgt/WSM/WSM_TAO/InnovTech/ProjReviews/Ultrasound-Disintegr.htm>

Bieganowski A., Lagod G., Ryzak M., Montusiewicz A., Chomczynska M. and Sochan A. Measurement of activated sludge particle diameters using laser diffraction method. Ecol. Chem. Eng. S. 19 (4) (2012) 567–608.

Bishnoi P., 2012, Effect of thermal hydrolysis pretreatment on anaerobic digestion of sludge. Thesis of Master Degree – Faculty of the Virginia Polytechnic Institute and State University, Blacksburg, VA. http://scholar.lib.vt.edu/theses/available/etd-08142012-145531/unrestricted/Bishnoi_Pallavi_T_2012.pdf (assessed 3 July 2013)

Bougrier C., Albasi C., Delgenes J.P., Carrere H., Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. Chemical Engineering and Processing 45 (2006) 711–718

Bougrier C., Delgenès J.P., Carrère H. Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. Chem. Eng. J. 139 (2) (2008) 236–244.

Braguglia C. M., Mininni G., Gianico A., Is sonication effective to improve biogas production and solids reduction in excess sludge digestion? Water Sci. Technol. 57 (4) (2008) 479–483.

Brett H. W. W. and Jellinek H. H. G. Degradation of long-chain molecules by ultrasonic waves. Part VI. Effect of pressure. J. Polym. Sci. 21 (1956) 535–545.

Bunrith S. 2008 Anaerobic digestibility of ultrasound and chemically pretreated waste activated sludge, thesis of Master Degree, Asian Institute of Technology (Thailand). www.faculty.ait.ac.th/visu/Data/AIT-Thesis/Master Thesis Final/Bunrith.pdf (accessed 28 July 2012)

C

Carrère H., Dumas C., Battimelli A., Batstone D.J., Delgenès J.P., Steyer J.P., Ferrer I., Pretreatment methods to improve sludge anaerobic degradability: A review, Journal of Hazardous Materials 183 (2010) 1–15

Casadonte D.J., Flores M., and Petrier C. Enhancing sonochemical activity in aqueous media using power-modulated pulsed ultrasound: an initial study. Ultrasonics Sonochemistry, 12 (2005) 147–152.

Chang T-C, You S-J, Damodar R-A., Chen Y-Y. Ultrasound pretreatment step for performance enhancement in an aerobic sludge digestion process. Journal of the Taiwan Institute of Chemical Engineers 42 (2011) 801–808

Chen Y., Yang H. Effect of acid and surfactant treatment on activated sludge dewatering and settling, Water Res. 35 (2001) 2615–2620.

Chendke P. K. and Fogler H. S., Sonoluminescence and Sonochemical Reactions of Aqueous Carbon Tetrachloride Solutions, J. Phys. Chem. 87 (1983a) 1362-1369

Chendke P. K. and Fogler H. S., Effect of Static Pressure on the Intensity and Spectral Distribution of the Sonoluminescence of Water, J. Phys. Chem, 87 (1983b) 1644-1648

Chiu. Y.C, Chang. C.N, Lin. J.G and Huang. S.J. Alkaline and ultrasonic pretreatment of sludge before anaerobic digestion. Water Science and Technology, 36 (11) (1997) 155-162

Chokshi A. H., Mukherjee A. K., Duba A. G., Durham W. B., Handin J. W. and Wang H. F. (eds.), The Brittle-Ductile Transition in Rocks, Geophysical Monograph, Vol. 56, The American Geophysical Union, Washington, DC (1990) p. 83.

Chokshi A. H. and Mukherjee A. K., The influence of hydrostatic pressure on grain boundary sliding in superplasticity: implications for cavitation, Materials Science and Engineering

A-Structural Materials Properties Microstructure and Processing, 171 (1-2) (1993) 47-54

Chu C.P., Chang B.V., Liao G.S., Jean D.S., Lee D.J., Observations on changes in ultrasonically treated waste-activated sludge, Water Res. 35 (2001) 1038–1046

Chu C.P., Lee D.J., You C.S., Tay J.H., ‗Weak" ultrasonic pretreatment on anaerobic digestion of flocculated activated biosolids, Water Res. 36 (2002) 2681–2688.

Colin F., Gazbar S., Distribution of water in sludges in relation to their mechanical dewatering, Water Res. 29 (8) (1995) 2000–2005.

Contamine F., Faid F., Wilhelm A. M., Berlan J., Delmas H. Chemical Reactions Under Ultrasound: Discrimination of Chemical and Physical Effects. Chem. Eng. Sci. 49 (24B) (1994) 5865-5873.

Crum L. A. Comments on the Evolving Field of Sonochemistry by a Cavitation Physicist. Ultrason. Sonochem. 2 (2) (1995) 147-152.

Cum G., Galli G., Gallo R., Spadaro A. Role of frequency in the ultrasonic activation of chemical reactions, Ultrasonics. 30 (4) (1992) 267-270

Cum G., Gallo R., Spadaro A. Effect of Static Pressure on the Ultrasonic Activation of Chemical Reactions. Selective Oxidation at Benzylic Carbon in the Liquid Phase. J. Chem. Soc. Perkin Trans. 2 (1988) 375–383.

Cum G., R. Gallo, Spadaro A. Temperature Effects in Ultrasonically Activated Chemical Reactions, IL Nuovo Cimento. 12 D (10) 1990

D

Deojay D.M., Sostaric J.Z., Weavers L.K. Exploring the effects of pulsed ultrasound at 205 and 616 kHz on the sonochemical degradation of octylbenzene sulfonate, Ultrasonics Sonochemistry. 18 (2011) 801–809

Dewil R., Baeyens J., Goutvrind R. Ultrasonic treatment of waste activated sludge, Environ. Prog. 25 (2006) 121–128.

Dezhkunov N., Lernetti G., Francescutto A., Reali M., Ciuti P., Cavitation Erosion and Sonoluminescence at High Hydrostatic Pressures, ACUSTICA 83 (1) (1997) 19-24

Doche M-L., Hihn J-Y., Mandroyan A., Viennet R., Touyeras F. Influence of ultrasound power and frequency upon corrosion kinetics of zinc in saline media, Ultrasonics Sonochemistry, 10 (2003) 357–362

Drijvers D., de Baets R., de Visscher A., Van Langenhove H. Sonolysis of Trichloroethylene in Aqueous Solution: Volatile Organic Intermediates. Ultrason. Sonochem. 3 (1996) 83-90.

E

El-Hadj T.B., Dosta J., Marquez-Serrano R., Mata-Alvarez J. Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene removal, Water Res. 41 (2007) 87–94.

Entezari M. H. and Kruus P. Effect of Frequency on Sonochemical Reactions. II: Temperature and intensity effects. Ultrason. Sonochem. 3 (1996) 19-24.

Entezari M. H., Kruus P., Otson R. The Effect of Frequency on Sonochemical Reactions. III: Dissociation of Carbon Disulfide. Ultrason. Sonochem. 4 (1997) 49-54.

Erden G. and Filibeli A. Ultrasonic pre-treatment of biological sludge: consequences for disintegration, anaerobic biodegradability, and filterability, Journal of Chemical Technology & Biotechnology 85 (1) (2009) 145-150.

F

Feng X., Lei H.Y., Deng J.C., Yu Q., Li H.L. Physical and chemical characteristics of waste activated sludge treated ultrasonically, Chem. Eng. Process. 48 (2009a) 187–194 (Process Intensification).

Feng X., Deng J., Lei H., Bai T., Fan Q., Zhaoxu L. Dewaterability of waste activated sludge with ultrasound conditioning, Bioresour. Technol. 100 (2009b) 1074–1081.

Finch R.D. The dependence of sonoluminescence on static pressure. Brit J Appl Phys. 16 (1965) 1543-1553

Flynn HG. Physics of acoustic cavitation in liquids. In: Physical Acoustics, Vol. 1 (Mason WP ed.). Academic Press, New York, 1964, Part B, 57-172

Francony A., Petrier C. Sonochemical Degradation of Carbon Tetrachloride in Aqueous Solution at Two Frequencies: 20 kHz and 500 kHz. Ultrason. Sonochem. 3 (1996) 77-82.

G

Gaitan D. F., Tessien R. A., Hiller R. A., Gutierrez J., Scott C., Tardif H., Callahan B., Matula T. J., Crum L. A., Holt R. G., Church C.C., Raymond J. L, Transient cavitation in high-quality-factor resonators at high static pressures, Journal of the Acoustical Society of America. 127 (6) (2010) 3456-3465.

Gonze E., Pillot S., Valette E., Gonthier Y. and Bernis A. Ultrasonic treatment of an aerobic sludge in batch reactor. Chemical Engineering and Processing, 42 (2003) 965–975.

Govoreanu R., Saveyn H., Van der Meeren P., Nopens I., Vanrolleghem P. A. A methodological approach for direct quantification of the activated sludge floc size distribution by using different techniques. Water Sci. Technol. 60 (7) (2009) 1857-1867.

Gronroos A., Kyllonen H., Korpijarvi K., Pirkonen P., Paavola T., Jokela J., Rintala J., Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion, Ultrason. Sonochem. 12 (2005) 115–120

Gutierrez M., Henglein A. Chemical Action of Pulsed Ultrasound: Observation of an Unprecedented Intensity Effect. J. Phys. Chem. 94 (9) (1990) 3625-3628.

H

Ha H. K., 2008. Acoustic measurements of cohesive sediment transport: suspension to consolidation. PhD thesis. The Faculty of the School of Marine Science, The College of William and Mary in Virginia. http://web.vims.edu/library/theses/Ha08.pdf?svr=www (assessed 29 Oct 2013)

Houghton J.L., Stephenson T. Effect of influent organic content on digested sludge extracellular polymer content and dewaterability, Water Res. 36 (2002) 3620–3628

Hogan F., Mormede S., Clark P., Crane M., Ultrasonic sludge treatment for enhanced anaerobic digestion, Water Sci. Technol. 50 (2004) 25–32.

J

Jin Y., Li H., Mahar R.B, Wang Z., Nie Y. Combined alkaline and ultrasonic pre-treatment of sludge before aerobic digestion. Journal of Environmental Sciences, 21 (2009) 279–284

Johnson B.L, Holland M.R, Miller J.G, Katz J.I. Ultrasonic Attenuation and Speed of Sound of Cornstarch Suspensions. J. Acoust. Soc. Am. 133(3) (2013)1399-1403

Jorand F., Zartarian F., Thomas F., Block J. C., Bottero J. Y. Chemical and structural linkage between bacteria within activated sludge flocs. Water Res., 29 (6) (1995) 1639–1647.

K

Keles C., Icemer. G. T., Ozen S. Inactivation of Salmonella spp. by Low-Frequency Electric Fields in Sewage Sludge. International Journal of Civil & Environmental Engineering IJCEE-IJENS 10 (06) (2010) 13-18

Khanal K., Isik H., Sung S., Avan Leeuwen J., Ultrasonic conditioning of waste activated sludge for enhanced aerobic digestion, Proceedings of IWA Specialized Conference – Sustainable Sludge Management: State of the Art,Challenges and Perspectives, May 29–31, Moscow, Russia, 2006.

Khanal S.K., Grewell D., Sung S., Van Leeuwen J., Ultrasound applications in wastewater sludge pretreatment: A review, Crit. Rev. Environ. Sci. Technol. 37 (2007) 277–313

Kidak R., Wilhelm A-M, Delmas H. Effect of process parameters on the energy requirement in ultrasonical treatment of waste sludge, Chemical Engineering and Processing 48 (2009) 1346–1352

Kim D.H, Jeong E., Oh S.E., Shin H.S. Combined (alkaline + ultrasonic) pretreatment effect on sewage sludge disintegration Water Research, 44 (2010) 3093 – 3100

Kim J., Park C., Kim T.H., Lee M., Kim S., Kim S.W. and Lee J. Effects of various pre-treatments for enhanced anaerobic digestion with waste activated sludge. Journal of Bioscience and Bioengineering, 95 (3) (2003) 271–275

Kobayashi D., Honma C., Suzuki A., Takahashi T., Matsumoto H., Kuroda C., Otake K., Shono A. Comparison of ultrasonic degradation rates constants of methylene blue at 22.8 kHz, 127 kHz, and 490 kHz, Ultrasonics Sonochemistry 19 (2012) 745–749

Kopp J. and Dichtl N., Influence of the free water content on the dewaterability of sewage sludges, Water Science & Technology, 44 (10) (2001) 177–183, IWA Publishing

Kopplow O, Barjenbruch M, Heinz V. Sludge pre-treatment with pulsed electric fields. Water Sci Technol. 49(10) (2004) 123-129.

Kunz P. and Wagner St. (1994) Results and outlooks of investigations of sewage sludge disintegration - Ergebnisse und Perspektiven aus Untersuchungen zur KlaÈrschlammdesintegration, awt-abwassertechnik,Heft 1.

L

Laborde, J.-L., Bouyer, C., Caltagirone, J.-P., Gerard, A. Acoustic bubble cavitation at low frequencies. Ultrasonics 36 (1–5) (1998) 589–594.

Leighton, Review : What is ultrasound?, Progress in Biophysics and Molecular Biology 93 (2007) 3–83

Leighton, T.G., 1994. The Acoustic Bubble. Academic Press, London.

Leighton, T.G., 1998. Fundamentals of underwater acoustics and ultrasound. In: Fahy, F.J., Walker, J.G. (Eds.), Noise and Vibration, Vol. 1. E & F Spon, Routledge, London, pp. 373–

444 (Chapter 7).

Li C., Liu G., Jin R., Zhou J., Wang J. Kinetics model for combined (alkaline + ultrasonic) sludge disintegration. Bioresource Technology 101 (2010) 8555–8557

Li H., Jin. Y., Mahar R.B., Wang Z., Nie Y., Effects of ultrasonic disintegration on sludge microbial activity and dewaterability, J. Hazard. Mater. 161 (2009) 1421–1426.

Li H., Jin Y., Mahar R.B, Wang Z., Nie Y., Effects and model of alkaline waste activated sludge treatment. Bioresour. Technol. 99 (2008) 5140–5144.

Lin. J.G, Ma. Y.S, Chao. A.C and Huang. C.L. BMP test on chemically pretreated sludge. Bioresource Technology, 68 (1999) 187-192.

Liu C., Xiao B., Dauta A., Peng G., Liu S., Hu Z. Effect of low power ultrasonic radiation on anaerobic biodegradability of sewage sludge. Bioresource Technology, 100 (2009) 6217–6222

Liu X., Liu H., Chen J., Du G., Chen J. Enhancement of solubilisation and acidification of waste activated sludge by pre-treatment, Waste Management, 28 (2008) 2614–2622

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.

Lorimer J. P. and Mason T. J., Sonochemistry: Part 1-The Physical Aspects , Chem. Soc. Rev., 16 (1987) 239-274

M

Maa JP-Y, Sun K-J, He Q. Ultrasonic characterization of marine sediments: a preliminary study. Mar Geol 141 (1997) 183–192

Mahmoud A., Olivier J., Vaxelaire J., Hoadley A.F.A. Electrical field: A historical review of its application and contributions in wastewater sludge dewatering. Water Research. 44 (8) (2010) 2381–2407

Mao T., Hong S.Y., Show K.Y., Tay J.H., Lee D.J. A comparison of ultrasound treatment on primary and secondary sludges. Water Sci. Technol. 50 (2004) 91–97.

Minervini D., 2008. The potential of ultrasound treatment for sludge reduction, PhD thesis, Cranfield university (UK). https://dspace.lib.cranfield.ac.uk/bitstream/1826/4085/1/Minervini_Thesis_2008.pdf (accessed 24 April 2013).

Minnaert M. On musical air-bubbles and the sound of running water, Philosophical Magazine 16 (104) (1933) 235–248

Muller J., 1996. Mechanical disintegration of sewage sludge – Mechanischer Klärschlammaufschluß-, Schriftenereihe ”Berichte aus der Verfahrenstechnik” der Fakultät für Maschinenbau und Elektrotechnik der Universität Braunschweig. Shaker Verlag, Aachen, Germany.

Muller J., Winter A., Strunkmann G., Investigation and assessment of sludge pre-treatment processes, Water Sci. Technol. 49 (10) (2004) 97–104.

N

Na S., Kim Y.U., Khim J., Physiochemical properties of digested sewage sludge with ultrasonic treatment, Ultrason. Sonochem. 14 (2007) 281–285

Neis U., Nickel K., Tiehm A., Enhancement of anaerobic sludge digestion by ultrasonic disintegration, Water Sci. Technol. 42 (2000) 73–80

Neppiras E. A. and Hughes D. E. Some Experiments on the Disintegration of Yeast by High Intensity Ultrasound, Biotechnology And Bioengineering, 6 (1964) 247-270

Neppiras E. A. Acoustic cavitation. Phys. Rep. 61 (1980) 160-251

Neyens E., Baeyens J., Dewil R., De Heyder B. Advanced sludge treatment affects extracellular polymericsubstances to improve activated sludge dewatering, Journal of Hazardous Materials 106B (2004) 83–92

Neyens E., Baeyens J., Weemas M., De Heyder B. Hot Acid Hydrolysis as a Potential Treatment of Thickened Sewage Sludge. Journal of Hazardous Materials, 98 (1-3) (2003) 275–293.

Nickel K., Neis U. Ultrasonic disintegration of biosolids for improved biodegradation, Ultrason. Sonochem. 14 (2007) 450–455

Noltingk B. E., Neppiras E. A. Cavitation Produced by Ultrasound. Proc. Phys. Soc., London, 63B (1950) 674-685

Nowak Q. Optimizing the use of sludge treatment facilities at municipal WWTPs. J. Environ. Sci. Hlth. A., 41 (2006) 1807-1817

O

Onyeche T.I., Schlafer O., Bormann H., Schroder C., Sievers M., Ultrasonic cell disruption of stabilised sludge with subsequent anaerobic digestion, Ultrasonics 40 (2002) 31–35

P

Pham A.T., 2011. SEWAGE SLUDGE ELECTRO-DEWATERING. A PhD Thesis. Mikkeli University Consortium, Mikkeli, Finland. http://www.doria.fi/bitstream/handle/10024/72598/isbn%209789522651693.pdf?sequence=2 (assessed 29 Oct. 2013)

Pham T. D., Shrestha R. A., Virkutyte J., Sillanpaa M. Recent studies in environmental applications of ultrasound, Can. J. Civ. Eng. 36 (2009) 1849–1858

Pham T.T.H., Brar S.K., Tyagi R.D., Surampalli R.Y., Ultrasonication of waste water sludge – Consequences on biodegradability and flowability. Journal of Hazardous Materials 163 (2009) 891-898.

Pilli S., Bhunia P., Yan S., LeBlanc R.J., Tyagi R.D., Surampalli R.Y. Ultrasonic pretreatment of sludge: A review. Ultrasonics Sonochemistry. 18 (2011) 1–18

Pilling J. and Ridley N. Effect of hydrostatic pressure on cavitation in superplastic aluminum-alloys, Acta Metallurgica, 34 (4) (1986) 669-679

Q

Quarmby J., Scott J.R., Mason A.K., Davies G., Parsons S.A., The application of ultrasound as a pre-treatment for anaerobic digestion, Environ. Technol. 20 (1999) 1155–1161.

R

Rai C.L., Struenkmann G., Mueller J., Rao P.G. Influence of ultrasonic disintegration on sludge growth and its estimation by respirometry, Environ. Sci. Technol. 38 (2004) 5779–5785.

Ratoarinoro N., Contamine F., Wilhelm A.M., Berlan J., Delmas H. Power Measurement in Sonochemistry. Ultrason. Sonochem. 2 (1) (1995) 43-47.

Rayleigh L. On the pressure developed in a liquid during the collapse of a spherical cavity. Philosophical Magazine, 34 (1917) 94-98

Rittmann B.E, Lee H-S, Zhang H., Alder J., Banaszak J.E, Lopez R. Full-scale application of focused-pulsed pre-treatment for improving biosolids digestion and conversion to methane. Water Science & Technology—WST. 58.10 (2008) 1895-1901

Rochebrochard S., Suptil J., Blais J-F., Naffrechoux E. Sonochemical efficiency dependence on liquid height and frequency in an improved sonochemical reactor, Ultrasonics Sonochemistry 19 (2012) 280–285

Rooze J., Rebrov E. V., Schouten J. C., Keurentjes J. T. F. Effect of resonance frequency, power input, and saturation gas type on the oxidation efficiency of an ultrasound horn, Ultrasonics Sonochemistry 18 (2011) 209–215

Rossier, Membrez, Mottet (2007). Comparaison des technologies de prétraitement des boues d'épuration pour l'augmentation de la production de biogas. Département de l'environnement, des transports, de l'énergie et de la communication DETEC. http://www.bfe.admin.ch/php/modules/publikationen/stream.php?extlang=fr&name=fr_897865446.pdf.

Roxburgh R., Sieger R., Johnson B., Rabinowitz B., Goodwin S., Crawford G., Daigger G., Sludge minimization technologies- doing more to get less. WEFTEC®.06 - Water Environment Foundation, (2006) 506-525 http://www.environmental-expert.com/Files%5C5306%5Carticles%5C8538%5C040.pdf

Rynkiewicz M. Application of constant electric field in simultaneous intensification of dewatering of wastewater sludge and filtrate purification. Environ. Prot. Eng. 37 (3) (2011) 93-100.

S

Salerno M.B, Lee H-S, Parameswaran P., Rittmann B.E. Using a Pulsed Electric Field as a Pretreatment for Improved Biosolids Digestion and Methanogenesis. Water Environ. Res., 81 (2009) 831-839

Salsabil M.R., Prorot A., Casellas M., Dagot C. Pretreatment of activated sludge: effect of sonication on aerobic and anaerobic digestibility, Chem. Eng. J. 148 (2009) 327–335

Sauter M., Emin A., Schuchmann H. P., Tavman S. Influence of hydrostatic pressure and sound amplitude on the ultrasound induced dispersion and de-agglomeration of nanoparticles, Ultrason. Sonochem. 15 (2008) 517–523.

Schmitz U., Berger C.R., Orth H. Protein analysis as a simple method for the quantitative assessment of sewage sludge disintegration. Water Res. 34 (2000) 3682–3685.

Shimizu T., Kudo K., Nasu Y., Anaerobic waste-activated sludge digestion – a bioconversion mechanism and kinetic model, Biotechnol. Bioeng. 41 (1993) 1082–1091.

Show K.Y., Mao T., Lee D.J., Optimization of sludge disruption by sonication, Water Res. 41 (2007) 4741–4747.

T

Thompson L. H. and Doraiswamy L. K., REVIEWS - Sonochemistry: Science and Engineering, Ind. Eng. Chem. Res. 38 (1999) 1215-1249

Tiehm A., Nickel K., Zellhorn M.M., Neis U., Ultrasound waste activated sludge disintegration for improving anaerobic stabilization, Water Res. 35 (2001) 2003–2009

Tiehm A., Nickel K., Neis U., The use of ultrasound to accelerate the anaerobic digestion of sewage sludge, Water Sci. Technol. 36 (1997) 121–128

Trussell R.S., Merlob P., Hermanowiczc S. W., Jenkins D. Influence of mixed liquor properties and aeration intensity on membrane fouling in a submerged membrane bioreactor at high mixed liquor suspended solids concentration. Water Research, 41 (2007) 947-958.

U

Ultrawaves GmbH - Water & Environmental Technologies. Waste water treatment plants – Intensified sludge treatment by ultrasound. www.ultrawaves.de

Ultrawaves – Royce Water Technologies – Biosolids treatment innovation. www.roycewater.com.au

V

Valo A., Carrère H., Delgenès J.P. Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion. Journal of Chemical Technology and Biotechnology, 79 (11) (2004) 1197–1203

Vesilind P.A., Hsu C.C., Limits of sludge dewaterability, Water Sci. Technol. 36 (11) (1997) 87–91.

W

Wang F., Ji M., Lu S. Influence of ultrasonic disintegration on the dewater-ability of waste activated sludge, Environ. Prog. 25 (2006b) 257-260.

Wang F., Lu S., Ji M., Components of released liquid from ultrasonic waste activated sludge disintegration, Ultrason. Sonochem. 13 (2006a) 334–338.

Wang F., Wang Y., Ji M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. J. Hazardous Materials B123 (2005) 145-150

Wang Q., Kuninobu M., Kakimoto K., Ogawa H.I., Kato Y. Upgrading of anaerobic digestion of waste activated sludge by ultrasonic pre-treatment, Bioresour. Technol. 68 (1999) 309–313

Wang Y., Li M., Gong C., Effect of on-line ultrasound on the properties of activated sludge mixed liquor in a membrane bioreactor. 2011 International Conference on Agricultural and biosysystem engineering. Advances in biomedical engineering Vols. 1-2

Weser R., Wöckel S., Hempel U., Wessely B., Auge J. Particle characterization in highly concentrated suspensions by ultrasoundscattering method. Sensors and Actuators A 202 (2013) 30-36

Whillock G.O.H, Harvey B.F. Ultrasonically enhanced corrosion of 304L stainless steel I: The effect of temperature and hydrostatic pressure, Ultrasonics Sonochemistry 4 (1997a) 23-31

Whillock G.O.H., Harvey B.F., Ultrasonically enhanced corrosion of 304L stainless steel II: The effect of frequency, acoustic power and horn to specimen distance, Ultrasonics Sonochemistry 4 (1997b) 33-38

Woodard S.E. and Wukash R.F. A hydrolysis/thickening/filtration process for the treatment of waste activated sludge. Water Science and Technology, 30 (3) (1994) 29–38.

X

Xie R., Xing Y., Ghani Y.A., Ooi K., Ng S., 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 (2007) 533–541.

Y

Yasui K., Towata A., Tuziuti T., Kozuka T., Kato K., Effect of static pressure on acoustic energy radiated by cavitation bubbles in viscous liquids under ultrasound, Journal of the Acoustical Society of America, 130 (5) Special Issue (2011) 3233-3242

Yin X., Han P., Lu X., Wang Y. A review on the dewaterability of bio-sludge and ultrasound pre-treatment, Ultrasonics Sonochemistry 11 (2004) 337–348

Young G.C. Performance of anaerobic filters under transient loading and operating conditions. In: Proceedings of the Seminar/Workshop on Anaerobic Filters: An Energy Plus for Wastewater Treatment, Orlando, FL, January, 1980, 159–170.

Z

Zhang G., Zhang P., Gao J., Chen Y. Using acoustic cavitation to improve the bio-activity of activated sludge, Bioresource Technology 99 (2008a) 1497–1502

Zhang G., Zhang P., Yang J., Liu H. Energy-efficient sludge sonication: Power and sludge characteristics. Bioresource Technology 99 (2008b) 9029–9031

Zhang P., Zhang G., Wang W., Ultrasonic treatment of biologic sludge: floc disintegration, cell lysis and inactivation, Bioresour. Technol. 98 (2007) 207– 210.

APPENDICES

APPENDIX 1

SONICATION DEVICES

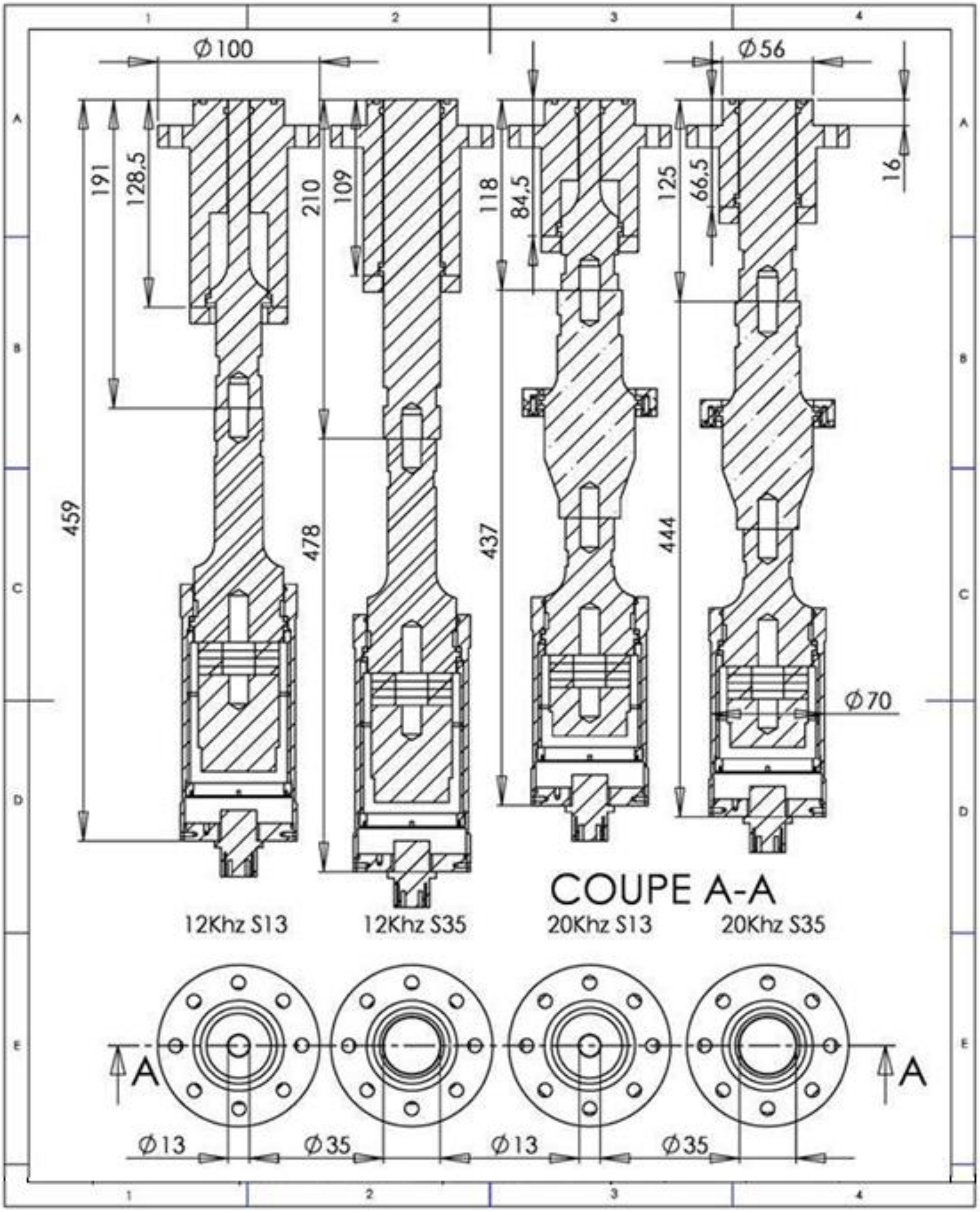


Fig. A1.1: Schemes of the sonication devices:

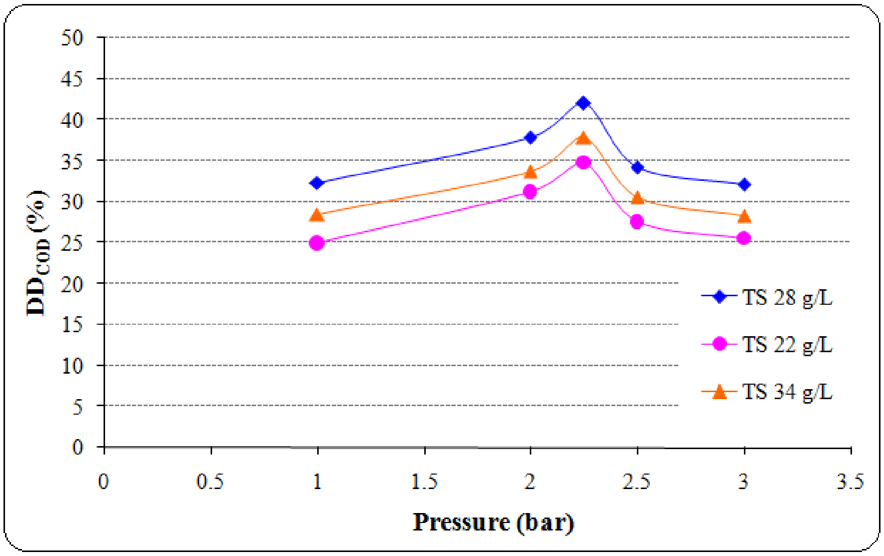
(1) 12 kHz – *SP*; (2) 12 kHz – *BP*; (3) 20 kHz – *SP*; (4) 20 kHz - *BP*

APPENDIX 2

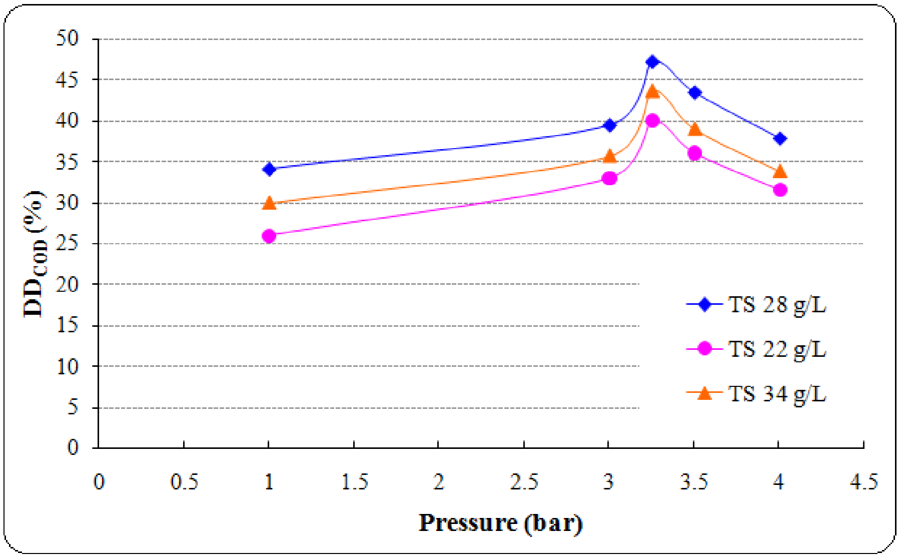
OPTIMUM TOTAL SOLIDS FOR SLUDGE ULTRASONIC PRETREATMENT AT LOW FREQUENCY, HIGH POWER INPUT, AND HIGH PRESSURE

Preliminary tests (section 3.2.1.1), conducted at a given P_{US} (150 W), 20 kHz, adiabatic mode, atmospheric pressure, and on mixed sludge, showed an optimum *TS* of 28 g/L for sludge *US* pretreatment. In this part, the optimum *TS* was checked again at lower frequency (12 kHz), higher pressure (1-4 bar), different P_{US} (150 and 360 W - *BP*), isothermal mode, and *ES* of 35000 kJ/kg$_{TS}$. Thereby, three synthetic secondary sludge samples from 4th sampling (see Table 2.4, section 2.2) with *TS* of 22, 28, and 34 g/L were prepared for these tests.

Results, presented in Fig. A2.1, show the optimum *TS* for secondary sludge *US* disintegration to be also about 28 g/L at any pressure, low frequency and low temperature. Moreover, the same optimum pressure found from different synthetic samples indicated optimum pressure not to depend on *TS* concentration.



(a)



(b)

Fig. A2.1: Effect of P_h, *TS*, and P_{US} on sludge *US* pretreatment: *BP*, *ES* = 35000 kJ/kg$_{TS,}$ 12 kHz, secondary sludge (Table 2.4), and T = 28±2°C. (a) P_{US} = 150 W, (b) P_{US} = 360 W

APPENDIX 3

EFFECT OF ALKALI ADDITION ON THE EFFICIENCY OF SLUDGE ULTRASONIC PRETREATMENT UNDER PRESSURE

INTRODUCTION

According to Wang *et al.* (2005), pH adjustment to a suitable value prior to *US* pretreatment is an important step. However, sludge acidification was detrimental to *US* pretreatment performance, especially at low pH values (Apul, 2009). Meanwhile, alkaline pretreatment enhanced sludge solubilisation, anaerobic biodegradability, and methane production (Kim *et al.*, 2003; Valo *et al.*, 2004). Therefore, the combined alkaline-*US* pretreatment, based on different mechanisms of sludge disintegration (modification of structural properties and intense mechanical shear force), is expected to take advantage of both and achieve a better efficiency of sludge pretreatment.

Sludge disintegration by *US* under optimum pressure was proved to be very efficient in Chapter 5 (isothermal mode) and confirmed in Chapter 6 (adiabatic mode). For given P_{US} of 150 W, *BP*, and 20 kHz, it was found an optimum pressure of 2 bar in both isothermal and adiabatic sonication.

This part aimed at investigating the combined effect of alkaline, external pressure, on sludge *US* pretreatment with and without cooling (isothermal and –adiabatic” modes). Mixed sludge was used and DD_{COD} was the main parameter to assess the pretreatment efficiency.

1. Effect of alkaline pretreatment on DD_{COD}

As presented in Chapter 3, NaOH was used to increase the pH of sludge (Kim *et al.*, 2003; Jin *et al.*, 2009). The effect of alkaline pretreatment on DD_{COD} was investigated by adding a given amount of NaOH into the fixed volume of synthetic mixed sludge (Table 3.2) to ensure the same condition of alkaline application: 22, 40, 47, and 77 mg_{NaOH}/g_{TS} (for comparison, 714 mg_{NaOH}/g_{TS} were used for the measurement of the reference $SCOD_{NaOH}$ with TS = 28 g/L). These samples were labelled sol. 22, sol. 40, sol. 47, and sol. 77, respectively.

Fig. A3.1 recalls the effect of alkaline pretreatment on DD_{COD} investigated by varying both alkaline dose and holding time.

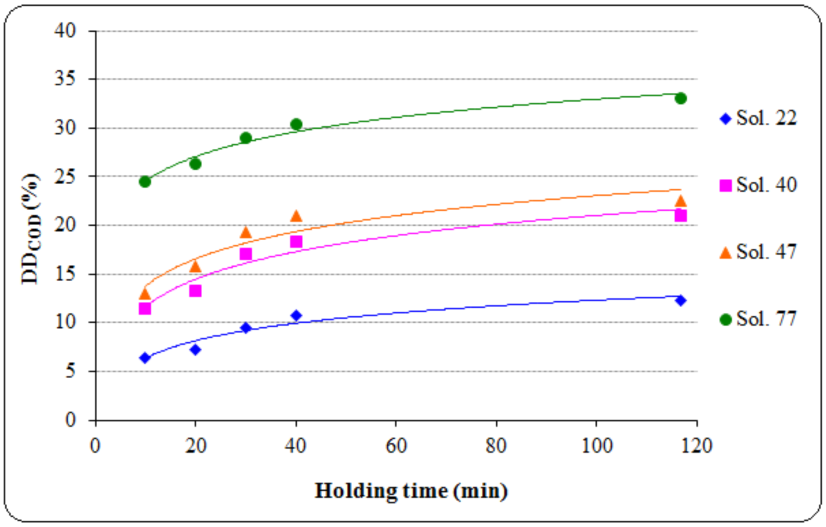


Fig. A3.1: Effect of NaOH addition on mixed sludge disintegration at ambient *T*

DD_{COD} increased continuously with NaOH dose in the investigated range. Recommended values for NaOH dose vary between 50 and 200 mg_{NaOH}/g_{TS} to ensure that NaOH is in excess and achieves a significant enhancement of DD_{COD} (Kim *et al.*, 2003; Bunrith, 2008; Jin *et al.*, 2009). However, after 30 min, DD_{COD} value from sol.40 was almost double of that from sol.22, but close to that from sol.47. In other words, an increase of the NaOH amount from 40 to 47 mg_{NaOH}/g_{TS} resulted in a pH jump of nearly one unit, without significant effect on *COD* solubilisation. Considering this pH transition (and its final value, shown in Table 3.5), a dose of 40 mg_{NaOH}/g_{TS} could be selected as a critical NaOH dose for chemical disintegration of sludge.

2. Comparison of sole ultrasonic and sole chemical pretreatment of sludge

Fig. A3.2 depicts the main results of *US* treatment carried out on the mixed sludge using the old generator, P_{US} of 150W, *BP*, 20 kHz, with various thermal conditions (isothermal/adiabatic) and external pressures (atmospheric/optimal value of 2 bar).

Conversely to chemical treatment which showed a fast *COD* solubilisation (after 30 min as abovementioned), DD_{COD} gradually increased during 2 h of sonication. The efficiency of *US* resulted nearly equally from mechanical and thermal effects induced by cavitation as DD_{COD} obtained dropped from 32.8% under adiabatic mode to 19.1% under isothermal mode after 2 h of sonication. When applying optimum pressure of 2 bar, DD_{COD} was improved, up to 24% in isothermal and 10% in adiabatic conditions.

After 30 min under NaOH treatment, the volume mean diameter *D[4,3]* of mixed sludge was 288, 247, 203, and 133 µm for sol. 22, sol. 40, sol. 47, and sol. 77, respectively, compared to 370 µm for the untreated sample. For the same time under isothermal sonication, *D [4,3]* dropped to about 100 µm. However, with the exception of sol. 22, a much higher DD_{COD} was achieved by chemical treatment. This could be explained that apart from causing the disintegration of floc structures and cell walls, hydroxyl anions also resulted in extensive swelling and subsequent solubilisation of gels in sludge (Kim *et al.*, 2003). The higher the pH, the more easily the processes of natural shape losing of proteins, saponification of lipid, and hydrolysis of RNA occur (Li *et al.*, 2008; Carrère *et al.*, 2010).

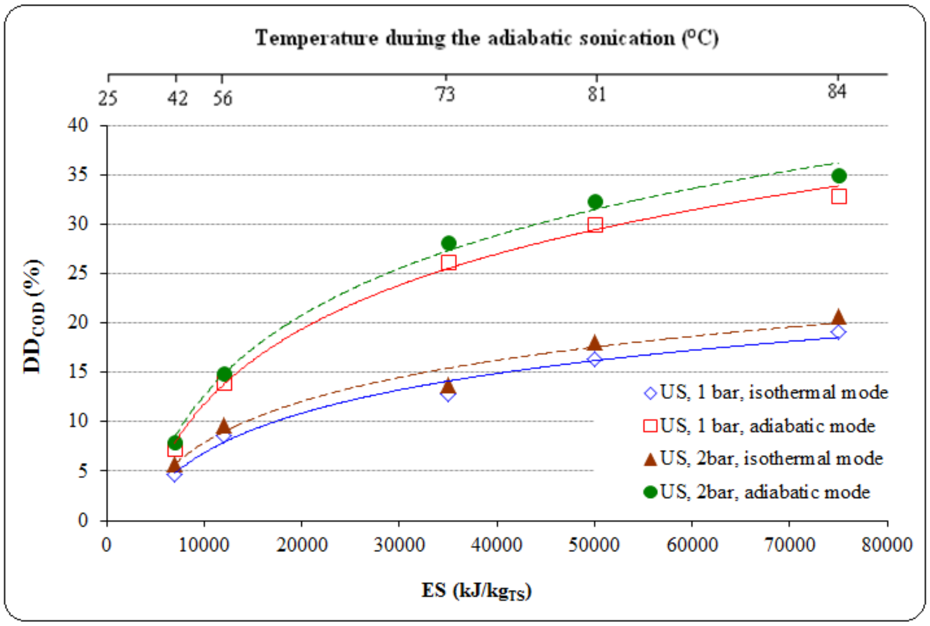


Fig. A3.2: Mixed sludge disintegration under *US* pretreatment: evolution of *COD* solubilisation as a function of *ES* (P_{US} = 150 W, *BP*, 20 kHz, *TS* = 28 g/L,). The upper y-axis indicates the evolution of temperature during the adiabatic sonication (final *T* for each corresponding *ES* value).

3. Effect of *NaOH* addition prior to sonication under pressure

The *alkalisation followed by US pretreatment* procedure was chosen for alkaline-*US* experiments (Jin *et al.*, 2009). The effects of *NaOH dose*, *ES* (0-75000 kJ/kg$_{TS}$), *temperature profile* (isothermal/adiabatic conditions), and *external pressure* (atmospheric pressure/optimal pressure of 2 bar for this *US* system, found in Chapter 5 and 6) were examined in order to improve sludge disintegration.

According to previous results in this work, an alkaline dose of 40 mg_{NaOH}/g_{TS} and a holding time of 30 min (section 3.2.1.5) were applied prior to *US* application. Besides, some positive effects of external pressure were also observed, with an optimal of about 2 bar corresponding to *US* system of 150 W, *BP*, and 20 kHz. Therefore, subsequent *US* experiments at different *ES* (or sonication duration) combining all parameters (pH adjustment, isothermal / adiabatic modes, and external pressure application) were conducted for sol.40. The results are shown in Fig. A3.3.

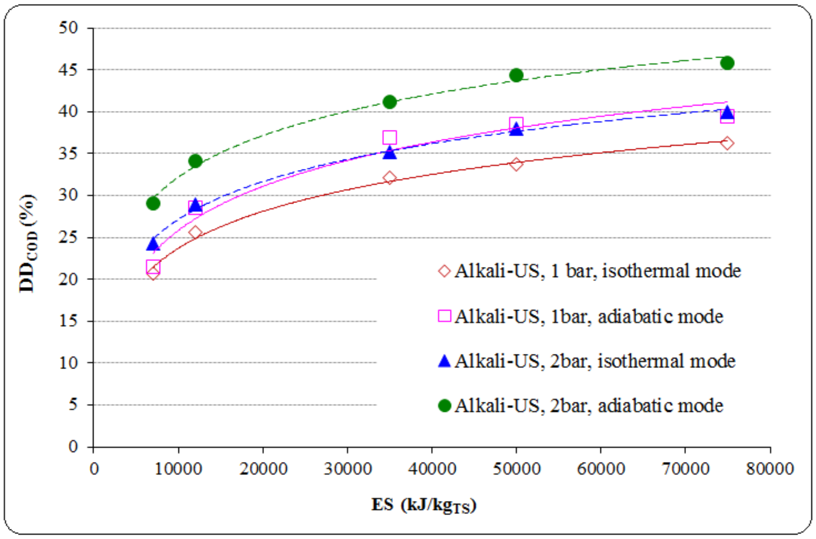


Fig. A3.3: Mixed sludge disintegration under alkali-*US* pretreatment: evolution of *COD* solubilisation as a function of *ES* (P_{US} = 150 W, *BP*, 20 kHz, *TS* = 28 g/L, NaOH dose = 40mg_{NaOH}/g_{TS}, holding time of 30 min).

The same conclusions prevailed regarding the effect of temperature and alkalisation, but at 2 bar of external pressure, the overall process was still improved: up to about 46% of DD_{COD} after 2 h of sonication of sol. 40. The final pH of 7.6 was also suitable for *AD*. The solubilisation performance depicted in Fig. A3.3 was somewhat lower than that reported by Jin *et al.* (2009) (about 45% with 99 mg_{NaOH}/g_{TS} and *ES* 12000 kJ/kg_{TS}) and Kim *et al.* (2010) (50-60% for pH 9-10 and *ES* < 30000 kJ/kg_{TS}). Apart from the higher NaOH doses applied, it could be due to different experimental conditions as compared to the present work: substrates (WAS (Jin *et al.*, 2009; Kim *et al.*, 2010) *vs.* mixed sludge), *US* apparatus (probe system (Jin *et al.*, 2009; Kim *et al.*, 2010) *vs.* cup-horn system), *US* intensity and *US* density reflected by P_{US}, probe diameter, and volume of sludge per experiment (300W (Kim *et al.*, 2010) *vs.* 150W; 6mm (Jin *et al.*, 2009) *vs.* 35mm of probe diameter; 0.1 L (Jin *et al.*, 2009; Kim *et al.*, 2010) *vs.* 0.5 L of sludge).

CONCLUSIONS

This part proved that *US* pretreatment of sewage sludge benefits from the combined effects of generated heat, mild alkalisation, and also external pressure application, which was not investigated in earlier works. It was confirmed that under controlled *T* condition, *US* and alkali pretreatments have distinct mechanisms of action on sludge, resulting in different kinetics of *COD* release and additive effects for low NaOH dose. Conversely, the chemical pretreatment hided the positive effect of the heat generated by *US* under adiabatic condition.

Addition of low NaOH dose (between 22 and 40 mg_{NaOH}/g_{TS}) could be useful, that significantly improved *COD* release under subsequent *US* treatment while resulting in a final pH value suitable for subsequent *AD*. In the later condition, DD_{COD} yield reached up to 46% at 75000 kJ/kg_{TS} as compared to 35% for sole *US*.

APPENDIX 4

RHEOLOGICAL BEHAVIOR OF SONICATED SLUDGE

The rheological behavior of sludge treated in the best conditions found in Chapter 6 was looked into. Three sludge samples (*TS* of 28 g/L, Table 3.4) were prepared for this test:

(S1) Raw sludge (unpretreated sludge),

(S2) Sludge pretreated in optimal conditions (sequential 5 min 360 W *US*-on/30 min *US*-off pretreatment, $ES = 35000$ kJ/kg_{TS}, 12 kHz, $P_h = 3.25$ bar, and adiabatic mode), and

(S3) Shortly sonicated sludge (*ES* of 7000 kJ/kg_{TS} at 360 W and 12 kHz + stirring up to 164 min, $P_h = 3.25$ bar, and adiabatic mode).

Apparent viscosity and Herschel-Bulkley parameters of these three samples and other samples treated at $T = 28°C$, in different conditions of pressure (1/3.25 bar) and frequency (12/20 kHz), are given in Table A4.1 for comparison purpose.

In Chapter 3 it was found that isothermal *US* ($T = 28°C$) at 20 kHz and atmospheric pressure did not significantly affect the rheological behavior of sludge. Table A4.1 shows that this result can be generalized to other pressures or frequencies accounting for the discrepancies in between raw samples. A larger reduction of yield stress may be however attributed to the 12 kHz treatment.

In addition, it could be inferred from Table A4.1 that sludge viscosity reduction by mechanical effect of *US* is enhanced thanks to the effect of temperature, *e.g.* μ_{app} at $\gamma = 1\ s^{-1}$ is divided by 4.0 and 7.5 as compared to raw sludge for isothermal and adiabatic *US* (360 W, 35000 kJ/kg_{TS} 12 kHz, 3.25 bar), respectively. In this condition, the flow index comes close to 1, but the yield stress is still significant.

Table A4.1: Apparent viscosity and parameters of Herschel-Bulkley model for different sonicated samples of secondary sludge (*TS* = 28 g/L, Table 6.2) (P_{US} = 360 W)

	Yield stress τ_0 **(Pa)**	**Consistency** *K* **(Pa.s^n)**	**Flow index** *n* **(-)**	**Apparent viscosity** μ_{app} **(Pa.s)**	
				γ = 1 (s^{-1})	γ = 100 (s^{-1})
Isothermal US (28°C) at 20 kHz and 1 bar					
0 kJ/kg$_{TS}$	0.124	0.072	0.680	0.266	0.018
7000 kJ/kg$_{TS}$	0.093	0.066	0.667	0.196	0.015
Isothermal US (28°C) at 20 kHz and 3.25 bar					
0 kJ/kg$_{TS}$	0.124	0.072	0.680	0.266	0.018
7000 kJ/kg$_{TS}$	0.109	0.041	0.712	0.138	0.012
Isothermal US (28°C) at 12 kHz and 1 bar					
0 kJ/kg$_{TS}$	0.246	0.057	0.731	0.399	0.019
7000 kJ/kg$_{TS}$	0.123	0.053	0.684	0.196	0.014
Isothermal US (28°C) at 12 kHz and 3.25 bar					
0 kJ/kg$_{TS}$	0.246	0.057	0.731	0.399	0.019
7000 kJ/kg$_{TS}$	0.087	0.051	0.683	0.163	0.013
35000 kJ/kg$_{TS}$	0.079	0.029	0.724	0.099	0.009
Conditions of Fig. A4.1 (Sequential adiabatic US at 12 kHz and 3.25 bar)					
S1 (0 kJ/kg$_{TS}$)	0.312	0.113	0.646	0.486	0.025
S3 (7000 kJ/kg$_{TS}$)	0.117	0.017	0.853	0.115	0.012
S2 (35000 kJ/kg$_{TS}$)	0.069	0.007	0.947	0.065	0.008

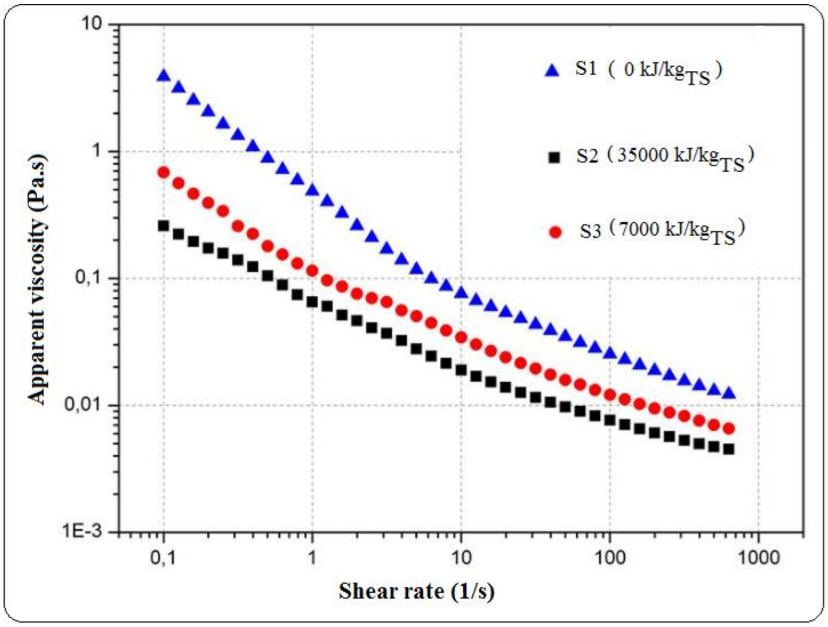


Fig. A4.1: Apparent viscosity versus shear rate of secondary sludge under *US* pretreatment: 360 W, 12 kHz, *TS* = 28 g/L (Table 3.4), adiabatic sonication, and 3.25 bar

APPENDIX 5

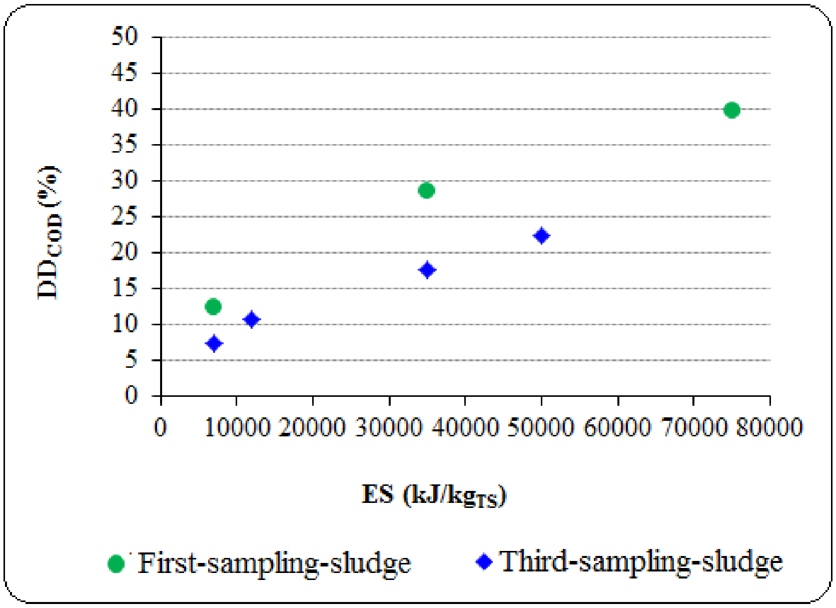
DISINTEGRATION DEGREE OF DIFFERENT SLUDGE SAMPLES (SAME TYPE OF SLUDGE)

As mentioned, different sludge collections were conducted during the thesis following the variations of *US* equipment along this work. This appendix compares these different samples for the same sludge type (*e.g.* secondary sludge) when treated at the same *US* conditions.

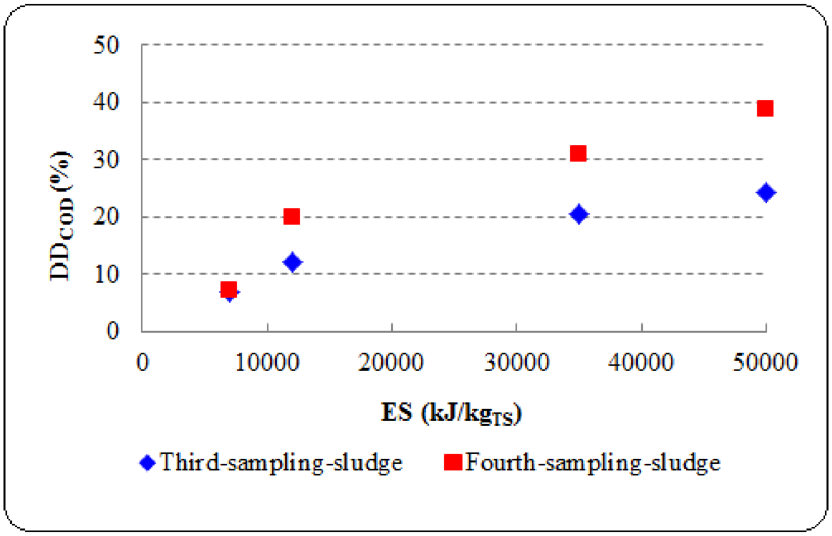
Thereby, synthetic secondary sludge samples from the first and third collections (given in Table 3.1 and Table 3.3, respectively) were treated at 20 kHz, P_{US} of 150 W (*BP*), isothermal mode (*T* = 28°C), and atmospheric pressure.

In addition, synthetic secondary sludge samples from the third and fourth collections (Table 3.4) which were also treated in standard conditions (28°C, 1 bar), but at 12 kHz and 50 W (*BP*) were compared.

Results depicted in Fig. A5.1 show that these secondary sludge samples collected at different times of the work resulted in different *US* disintegration degrees. Obviously, comparisons to assess sludge *US* efficiency were then always done on the same substrate.



(a)



(b)

Fig. A5.1: Disintegration degree (DD_{COD} *vs.* ES) of different secondary sludge samples

(a): P_{US} = 150 W, *BP*, F_S = 20 kHz, T = 28±2°C, and atmospheric pressure

(b): P_{US} = 50 W, *BP*, F_S = 12 kHz, T = 28±2°C, and atmospheric pressure

APPENDIX 6

EFFECT OF THE PROBE SURFACE STATUS ON SLUDGE ULTRASONIC PRETREAMENT EFFICACY

The probe surface has been progressively eroded along the operation time as shown in Fig. A6.1. Its effect on sludge *US* efficiency was investigated using the 20 kHz equipment, P_{US} of 150W, *ES* range of 7000-75000 kJ/kg$_{TS}$, *BP*, isothermal mode, atmospheric pressure, and synthetic secondary sludge sample given in Table 4.1. Results, depicted in Fig. A6.2, show a slight decrease in sludge *US* pretreatment efficacy due to the erosion of the probe surface: about 10% at *ES* of 7000 kJ/kg$_{TS}$ but less than 5% at higher *ES* values, which could be ignored.

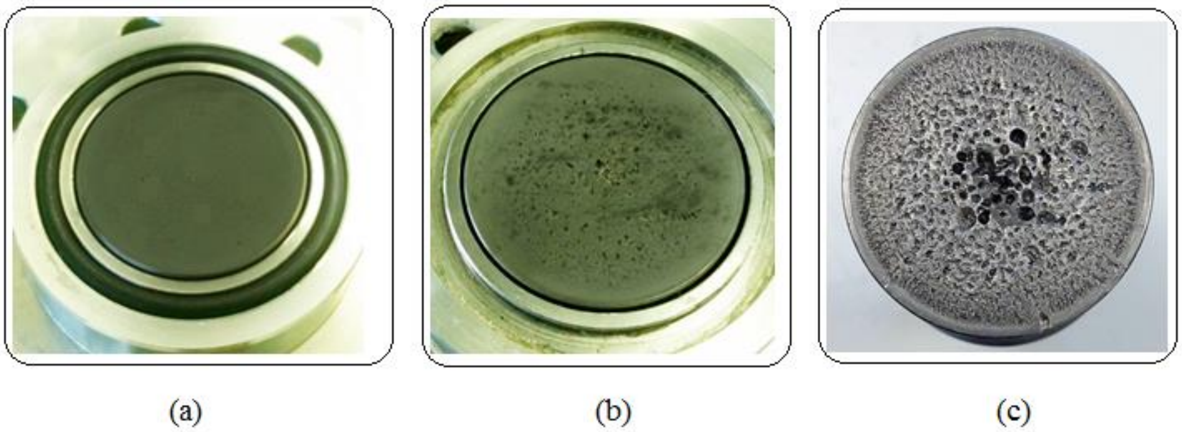

(a) (b) (c)

Fig. A6.1: The surface of (a) the brand-new probe, (b) eroded probe, and (c) extremely eroded probe

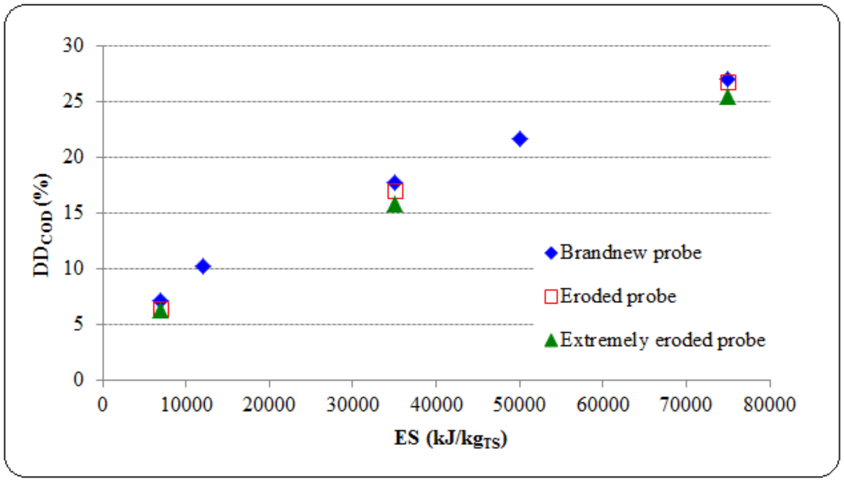


Fig. A6.2: Effect of the probe status on sludge *US* disintegration: P_{US} = 150 W, *BP*, F_S = 20 kHz, synthetic secondary sludge given in Table 4.1, $T = 28\pm2^{o}$C, and atmospheric pressure

APPENDIX 7

EFFECT OF FREQUENCY ON THE EVOLUTION OF COLLOIDAL COD FRACTION DURING SONICATION

Fig. A7.1 depicts evolutions of colloidal *COD* fraction of secondary sludge (Table 4.2) during *US* at different F_S. Unlike *SCOD/TCOD* which gradually increased following an increase in *ES*, *CCOD/TCOD* increased quickly up to *ES* of 12000 kJ/kg_{TS}, then slowed down, and almost reached a plateau with *ES* more than 35000 kJ/kg_{TS}. Regardless of F_S, *CCOD/TCOD* values were much higher than *SCOD/TCOD* in the investigated *ES* range. In addition, both soluble and colloidal fractions were increased under lower frequency sonication (12 kHz *vs*. 20 kHz) although the improvements were rather low.

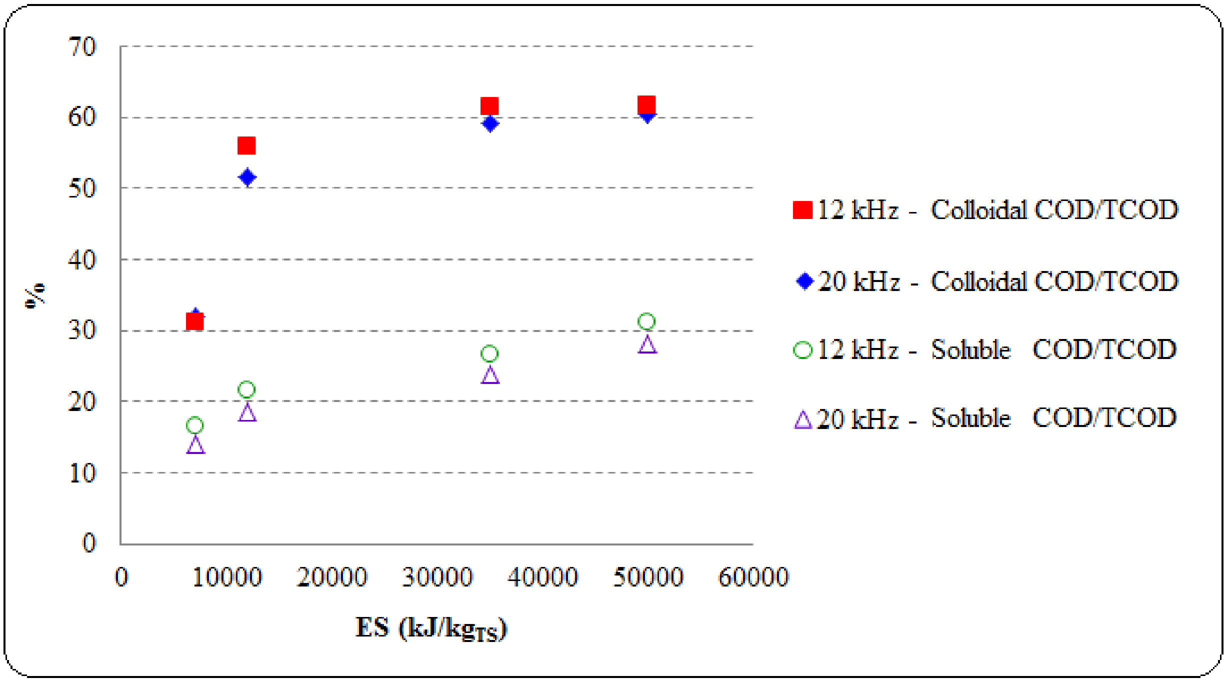


Fig. A7.1: Effect of frequency on *SCOD/TCOD* and *CCOD/TCOD* during *US*: *BP*, P_{US} = 360 W, *TS* = 28 g/L, secondary sludge given in Table 4.2, *T* = 28±2°C, and atmospheric pressure

APPENDIX 8

PRILIMINARY TESTS OF BIOCHEMICAL METHANE POTENTIAL

To preliminarily investigate the potential of methane production of pretreated sludge (using 20 kHz sonicator), four synthetic secondary sludge samples (*TS* of 28 g/L, Table 3.1) were prepared: *(S1) raw sludge* (unpretreated sludge), *(S2) US pretreated sludge I* (150 W, 75000 kJ/kg_{TS}, 2 bar, and *T* = 28±2°C), *(S3) US pretreated sludge II* (150 W, 75000 kJ/kg_{TS}, 2 bar, and adiabatic mode), and *(S4) thermal pretreated sludge* (*T* = 70±2°C for 2 h to get *SCOD* almost equal to that of *S2*). *BMP* tests were performed during 75 days and the results are displayed in Fig. A8.1.

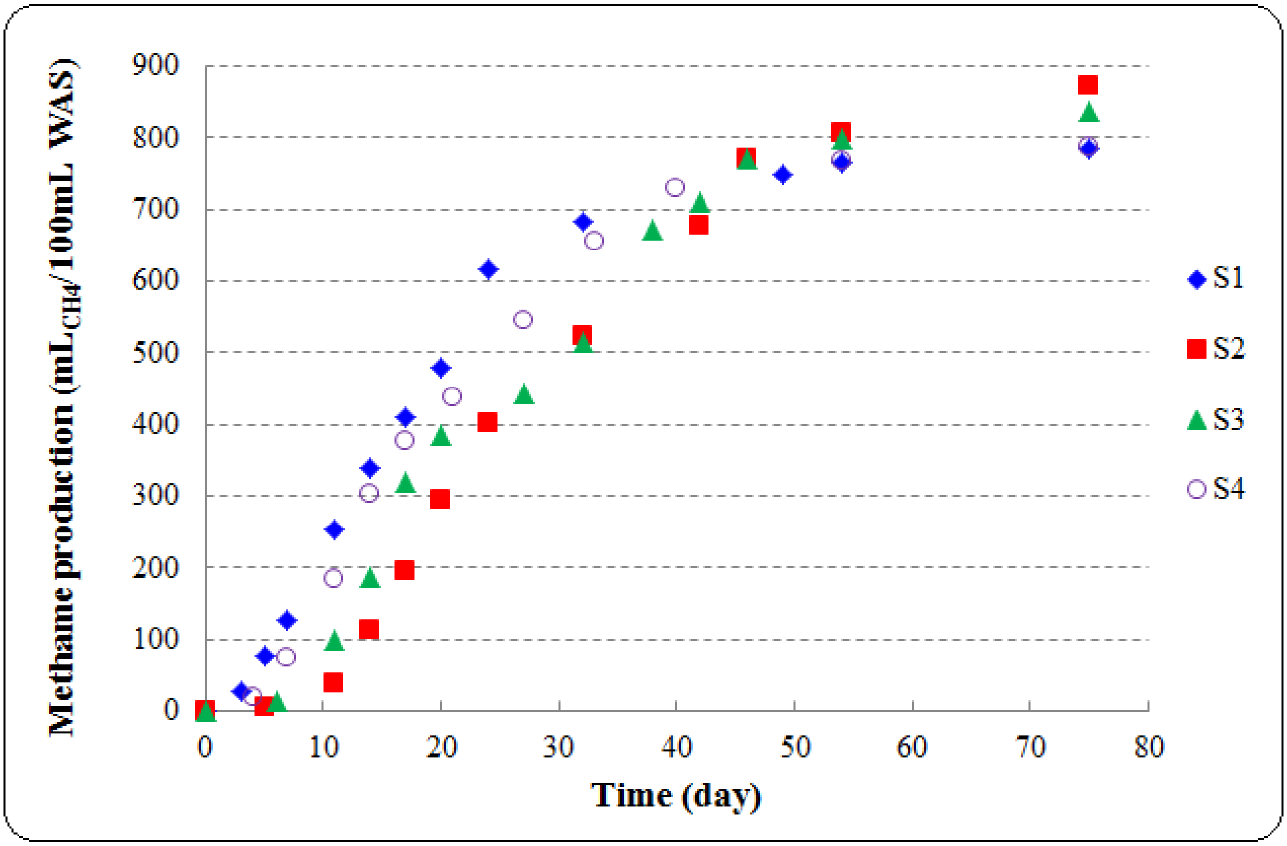


Fig. A8.1: *BMP* of pretreated sludge samples

During the first month of the test, the CH_4 production rates of *S1* and *S4* almost linearly increased while an initial delay (during the first week) was observed for sonicated sludge samples (*S2* and *S3*) which could likely be due to the degradation of bacteria and enzymes under *US*. The production rates for *S1* and *S4* were then retarded and the accumulated CH_4 almost reached the maximum steady value after 50 days of the test due to substrate limitation. For *S2* and *S3,* after the initial delay, the production rates significantly increased during the next 6 weeks and slowed down thereafter. As compared to raw sludge (*S1*), the final results showed no improvement in CH_4 production from thermal pretreated sludge (*S4*) while about 6% and 11% of improvement could be achieved from *S3* and *S2*, respectively.

PUBLICATIONS


Volume 20, issue 5
September 2013
ISSN 1350-4177
ELSEVIER
Ultrasonics
SONOCHEMISTRY
Available online at www.sciencedirect.com
SciVerse ScienceDirect
http://www.elsevier.com/locate/ultsonch

Ultrasonics Sonochemistry 20 (2013) 1203–1210

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Ultrasonic sludge pretreatment under pressure

Ngoc Tuan Le *, Carine Julcour-Lebigue, Henri Delmas

Université de Toulouse, Laboratoire de Génie Chimique, INP-ENSIACET, 31030 Toulouse, France

ARTICLE INFO

Article history:
Received 12 November 2012
Received in revised form 19 March 2013
Accepted 19 March 2013
Available online 29 March 2013

Keywords:
Digested sludge
Mixed sludge
Pressure effect
Secondary sludge
Sludge disintegration
Ultrasonic pretreatment

ABSTRACT

The objective of this work was to optimize the *ultrasound (US) pretreatment of sludge*. Three types of sewage sludge were examined: mixed, secondary and secondary after partial methanisation (“digested” sludge). Thereby, several main process parameters were varied separately or simultaneously: stirrer speed, total solid content of sludge *(TS)*, thermal operating conditions (adiabatic vs. isothermal), ultrasonic power input (P_{US}), specific energy input *(ES)*, and for the first time external pressure. This parametric study was mainly performed for the mixed sludge. Five different *TS* concentrations of sludge (12–36 g/L) were tested for different values of *ES* (7000–75,000 kJ/kg_{TS}) and 28 g/L was found as the optimum value according to the solubilized chemical oxygen demand in the liquid phase (*SCOD*). P_{US} of 75–150 W was investigated under controlled temperature and the “*high power input – short duration*” procedure was the most effective at a given *ES*. The temperature increase in adiabatic *US* application significantly improved *SCOD* compared to isothermal conditions. With P_{US} of 150 W, the effect of external pressure was investigated in the range of 1–16 bar under isothermal and adiabatic conditions for two types of sludge: an optimum pressure of about 2 bar was found regardless of temperature conditions and *ES* values. Under isothermal conditions, the resulting improvement of sludge disintegration efficacy as compared to atmospheric pressure was by 22–67% and 26–37% for mixed and secondary sludge, respectively. Besides, mean particle diameter (*D[4,3]*) of the three sludge types decreased respectively from 408, 117, and 110 µm to about 94–97, 37–42, and 36–40 µm regardless of sonication conditions, and the size reduction process was much faster than *COD* extraction.

1. Introduction

Due to economic reasons and/or negative impacts on environment, incineration, composting, ocean discharge, and land spreading, known as the most common sludge disposal options used over the years, are no longer sustainable. Meanwhile, anaerobic digestion (*AD*) of sludge is an efficient and sustainable technology for sludge treatment. However, a pretreatment of sludge, which ruptures the cell wall and facilitates the release of intracellular matters into the aqueous phase, is required to enhance the *AD* as hydrolysis is the rate-limiting step of microbial conversion.

Ultrasound (*US*) irradiation has been reported as a promising mechanical disruption technique, resulting in improved biodegradability and bio-solid quality [1], increased methane production [1–3], sludge reduction [3,4], and less sludge retention time [5].

Despite ultrasonic sludge treatment reached commercial developments and gave rise to many works, none of them was carried out to investigate the effect of pressure. Changing the hydrostatic pressure will change the resonance condition of cavitation bubbles via their equilibrium radius and then may drive the system toward resonance conditions [6]. At resonance conditions, the rate and yield of reactions will increase [7–9]. More probably, both the cavitation threshold and the intensity of cavity collapse increase following an increase in external pressure [10], suggesting a possible optimum pressure. Brett and Jellinek [11] stated that bubbles could be visible for gas-applied pressure as high as 16 atm. Nevertheless, nearly all the *US* experiments have been carried out at atmospheric pressure. Only a few studies have been focusing on how increasing static pressure affects cavitation.

Most works on pressure effects concern sonoluminescence, and no consensus emerges about an optimum value as reported by Chendke and Fogler [11,12]. The early works of Finch (1955) cited by the authors indicated that the greatest sonoluminescence intensity was observed in water at a static pressure of about 1.5 atm (over an investigated range of 1–8 atm), but Chendke and Fogler recommended a value of 6 atm to promote sonoluminescence in nitrogen-saturated water [11]. In aqueous carbon tetrachloride solutions, the intensity of the sonoluminescence did not show any monotonous behavior: it first went up to 6 atm, then reached a minimum at 8 atm, got a new maximum at 12 atm, and was finally almost inhibited above 18 atm [12]. Whillock and Harvey [13] investigated the effects of hydrostatic pressure on the corrosion of 304L stainless steel in an ultrasonic field. An increase in pressure

---

* Corresponding author. Tel.: +33 (0) 5 34 32 36 96; fax: +33 (0) 5 34 32 36 97.
E-mail address: ngoctuan.le@ensiacet.fr (N.T. Le).

1350-4177/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ultsonch.2013.03.005

Table 1
Characteristics of the sludge samples.

Parameter	Value				
	Mixed sludge		Secondary sludge		Digested sludge
Raw sludge samples					
Total solids (*TS*)	285 mg/g		37.5 g/L		14.0 g/L
Volatile solids (*VS*)	238 mg/g		32.2 g/L		11.9 g/L
VS/*TS*	83.5%		85.8%		84.7%
Synthetic sludge samples					
Total solids (*TS*)	28.0 g/L	28.0 g/L	28.0 g/L	14.0 g/L	14.0 g/L
$SCOD_{\mathrm{NaOH\ 0.5\ M}}$	18.5 g/L	11.3 g/L	22.9 g/L	14.0 g/L	11.0 g/L
TCOD	36.5 g/L	18.3 g/L	38.2 g/L	19.1 g/L	15.0 g/L

up to 4 bar at a constant temperature caused a strong increase in corrosion rate. Closer to the present subject, Neppiras and Hughes [14] investigated the influence of pressure (up to 5.8 atm) on the disintegration of yeast cells and found an optimum value of 4 atm.

Following these researches, static pressure seems to be an important parameter, but it has been marginally investigated due to the complex equipments required. In case of sludge pretreatment, external pressure should be varied simultaneously with other related parameters, including total solid content of sludge (*TS*), *US* power input (P_{US}), specific energy input (*ES*), thermal operating conditions, etc., in order to select optimal conditions for actual application. The effect of ultrasound will be presented in terms of disintegration degree (organic matters solubilized in liquid phase) and particle size reduction. The objective of this work is to optimize high-power low-frequency ultrasonic pretreatment of sludge, and especially to emphasize on static pressure for the first time, which is expected to enhance sludge disintegration, to increase methane production, and to facilitate the *AD*.

2. Materials and methods

2.1. Sludge samples

Three types of sludge were collected from Ginestous wastewater treatment plant (Toulouse, France) with a sufficient amount for all experiments in this study: mixed sludge (solid form, after centrifugation), secondary sludge (liquid form), and digested sludge

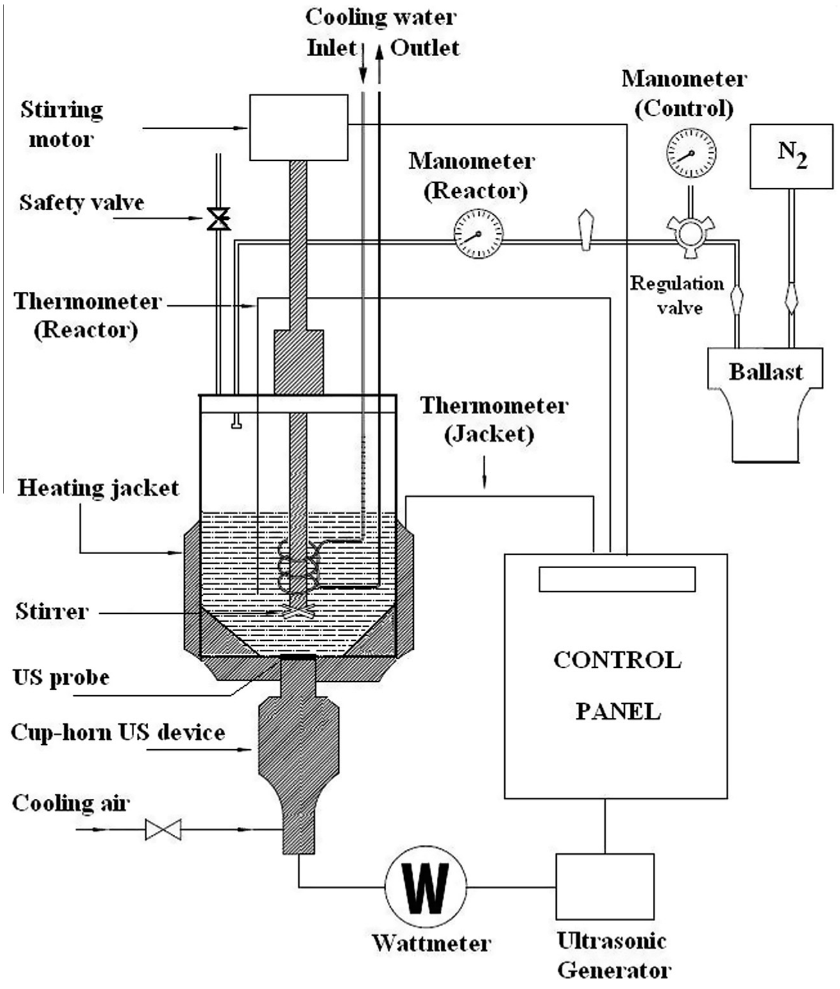


Fig. 1. Ultrasonic autoclave set-up.

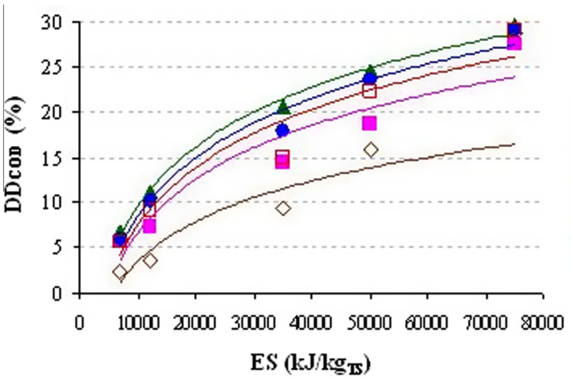


Fig. 2. Effect of *TS* content on mixed sludge disintegration (DD_{COD}): P_{US} = 150 W, adiabatic condition and atmospheric pressure.

(liquid form, after anaerobic digestion process of the secondary sludge). Their properties, given in Table 1, were evaluated according to standard analytical methods (see Section 2.3).

For mixed sludge, it was sampled in 100 g plastic boxes and preserved in a freezer. Kidak et al. [15] reported that this preliminary maintaining step might change some physical characteristics of the sludge, but it should not significantly affect *COD* solubilisation results. It was confirmed in the present study, the difference in sludge disintegration between fresh sludge (without freezing) and frozen sludge was less than 5% on the whole *ES* range (7000–75,000 kJ/kg_{TS}).

Secondary and digested sludge lots were sampled in 1L plastic boxes and stored at a constant temperature of 3–4 °C.

When performing experiments, the required amount of sludge was defrosted (for frozen sludge) and diluted with distilled water to prepare synthetic sludge samples with a given *TS* content.

2.2. Ultrasound application

Ultrasonic irradiation was emitted by a cup-horn ultrasound unit (see Fig. 1) included in an autoclave reactor which was connected to a pressurized N_2 bottle.

The reactor and its internals were made of 316L stainless steel. The reactor internal diameter was 9 cm and its depth 18 cm, for a usable capacity of 1 L. A safety valve (HOKE 6500) limited overpressure to 19 bar. The solution was stirred by a Rushton type turbine of 32 mm diameter, with an adjustable speed up to 3000 rpm. A cooling water stream (15 °C) was continuously circulated in an internal coil to maintain a constant temperature (*T*) of the solution at 28 ± 2 °C during sonication.

The ultrasound system had a fixed frequency of 20 kHz and a maximum total power of 200 W corresponding to P_{US} of 158 W. The *US* device, supplied by Sinaptec, was composed of four elements: a piezoelectric transducer (M202045), a titanium booster (B20B), an aluminum flange (AU4G) ensuring a good mechanical connection, and an ultrasonic cup horn (PLANUS P2035041, 35 mm diameter probe) placed at the bottom of the reactor. The transducer was cooled by compressed air during operation.

Prior to the application of external pressure to *US* pretreatment, some process parameters were examined separately to identify adequate values. For each experiment, a constant volume of synthetic sludge sample (0.5 L) was poured into the stainless steel reactor. Five different sonication times corresponding to five values of *ES* (7000, 12,000, 35,000, 50,000, and 75,000 kJ/kg_{TS}) were tested.

$$\mathbf{ES} = (\mathbf{P_{US}} * \mathbf{t})/(\mathbf{V} * \mathbf{TS})$$

with *ES*: specific energy input, energy per total solid weight (kJ/kg_{TS}), P_{US}: *US* power input (W), *t*: sonication duration (s), *V*: volume of sludge (L), and *TS*: total solid concentration (g/L).

First, the influence of *TS* content (12–36 g/L), stirrer speed (250–1500 rpm), and P_{US} (75–150 W) along with ultrasonic duration was investigated for mixed sludge disintegration. Afterwards, separate and combined effects of ultrasound and temperature (which increased due to *US*) were examined for mixed and secondary sludge. The effect of external pressure (in the range 1–16 bar) was then evaluated for these two types of sludge. Finally, the best combination of process parameters was subsequently tested for all the sludge samples.

2.3. Analytical methods

Total and volatile solids contents (*TS* and *VS*, respectively) were measured according to the following procedure (APHA, 2005). *TS* was determined by drying a well-mixed sample to constant weight at 105 °C. *VS* was obtained from the weight loss on ignition of the residue at 550 °C.

The *degree of sludge disintegration* (DD_{COD}) was calculated by determining the soluble chemical oxygen demand after strong alkaline disintegration of sludge ($SCOD_{NaOH}$) and the chemical oxygen demand in the supernatant before and after treatment ($SCOD_0$ and *SCOD*, respectively) [16]:

$$\mathbf{DD_{COD}} = (\mathbf{SCOD} - \mathbf{SCOD_0})/(\mathbf{SCOD_{NaOH}} - \mathbf{SCOD_0}) * \mathbf{100}(\%);$$

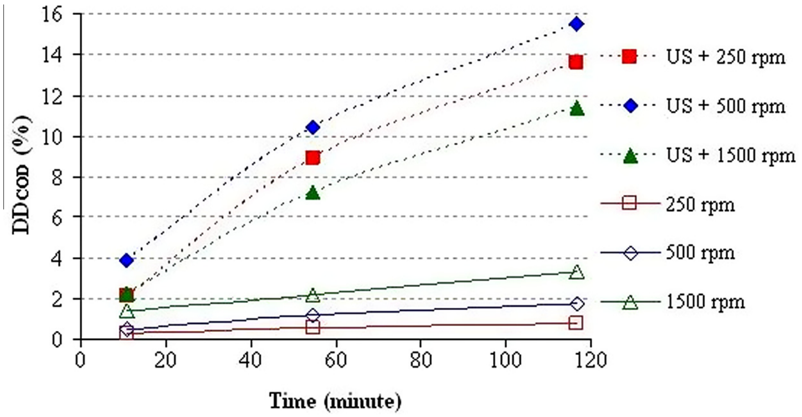


Fig. 3. Effect of the stirrer speed on mixed sludge disintegration (DD_{COD}): P_{US} = 150 W, (when under *US*), controlled *T* (28 ± 2 °C), and atmospheric pressure.

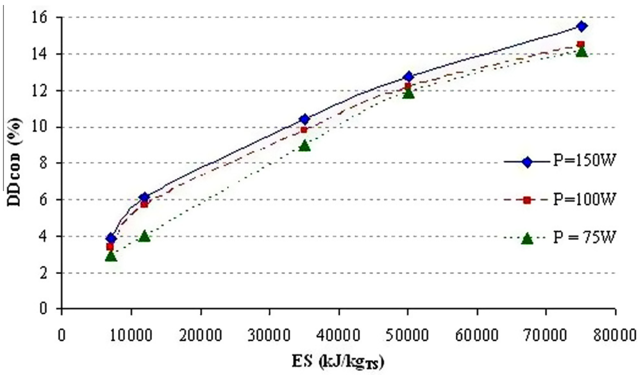


Fig. 4. Effect of specific energy input *ES* with three P_{US} on mixed sludge disintegration (DD_{COD}): t = 0–233 min, controlled *T* (28 ± 2 °C), and atmospheric pressure.

To measure the $SCOD_{NaOH}$ value, used as reference to evaluate the efficiency of organic matter solubilization under *US*, the sludge sample was mixed with 0.5 M NaOH at room temperature for 24 h [17]. Besides, total chemical oxygen demand (*TCOD*) was also measured by potassium dichromate oxidation method (standard AFNOR NFT 90-101).

Prior to *SCOD* determination, the supernatant liquid was filtered under vacuum using a cellulose nitrate membrane with 0.2 μm pore size. *COD* of the filtered liquid was measured as per Hach spectrophotometric method. The change in the *SCOD* indirectly represents the quantity of organic carbon that has been transferred from the cell content (disruption) and solid materials (solubilisation) into the external liquid phase of sludge. The experiments were triplicated and the coefficients of variation (*CV*) were about 5%.

The *particle size distribution* (*PSD*) of sludge before and after treatment was determined by using Malvern particle size analyzer (Mastersizer 2000, Malvern Inc.), a laser diffraction-based system (measuring range from 0.02 to 2000 μm). Each sample was diluted approximately 300-fold in osmosed water, before being pumped into the measurement cell (suction mode). The *PSD* was based on the average of five measurements showing deviations of less than 3%. Optical properties of the material were set as default (refractive index 1.52, absorption 0.1) appropriate for the majority of naturally occurring substances. Since the primary result from laser diffraction is a volume distribution, the volume mean diameter *D[4,3]* (or de Brouckere mean diameter) was used to illustrate the mean particle size of sludge.

3. Results and discussion

3.1. Effect of TS concentration on DD_{COD}

Five synthetic mixed sludge samples (S12, S24, S28, S32, and S36 corresponding to 12, 24, 28, 32, and 36 g/L of *TS*, respectively) were treated at atmospheric pressure, under adiabatic condition, and at a constant P_{US} of 150 W – close to the maximum, because "high power and short time" of *US* should be preferred for a given *ES* [15]. The respective *ES* was varied (7000, 12,000, 35,000, 50,000, and 75,000 kJ/kg_{TS}) via the sonication time. The stirrer speed was adjusted to 500 rpm. The results are presented in Fig. 2.

SCOD gradually increased with sonication time (0–150 min) but less and less and the relation between *SCOD* and *TS* content was not simple because the best DD_{COD} was not found at the maximum *TS*. For example, at *ES* of 7000 kJ/kg_{TS}, *SCOD* was improved by 2.4-fold when increasing *TS* from 12 to 24 g/L, but did not significantly change for higher values. Fig. 2 actually exhibited a *TS* optimal value of 28 g/L in terms of DD_{COD} over the whole ES range. This behavior is in agreement with other studies [4,15,18–21] and can be explained by explained by opposite effects. The increase in *TS* provides more cells and aggregates to be in contact with cavitation bubbles; thereby, the *US* power input, which is required to generate cavitation, is more efficiently consumed. Nevertheless, at higher sludge loading, the acoustic pressure field decreases faster from the emitter due to the degraded propagation of the ultrasonic wave in a denser suspension. Consequently, acoustic cavitation intensity will be reduced. These two opposite effects lead to an optimum *TS* concentration that could slightly depend on sludge characteristics, operating conditions, reactor design, *US* power, and *US* frequency, etc.

For all the following experiments of this work (excepting those with digested sludge), synthetic samples were prepared to match this 28 g/L *TS* concentration corresponding to values of *TCOD* and $SCOD_{NaOH}$ given in Table 1.

3.2. Effect of stirrer speed on DD_{COD}

To decorrelate the effect of stirrer speed on DD_{COD} when *US* is applied, preliminary experiments at 250, 500, and 1500 rpm were carried out under ambient conditions (controlled *T* of 28 ± 2 °C,

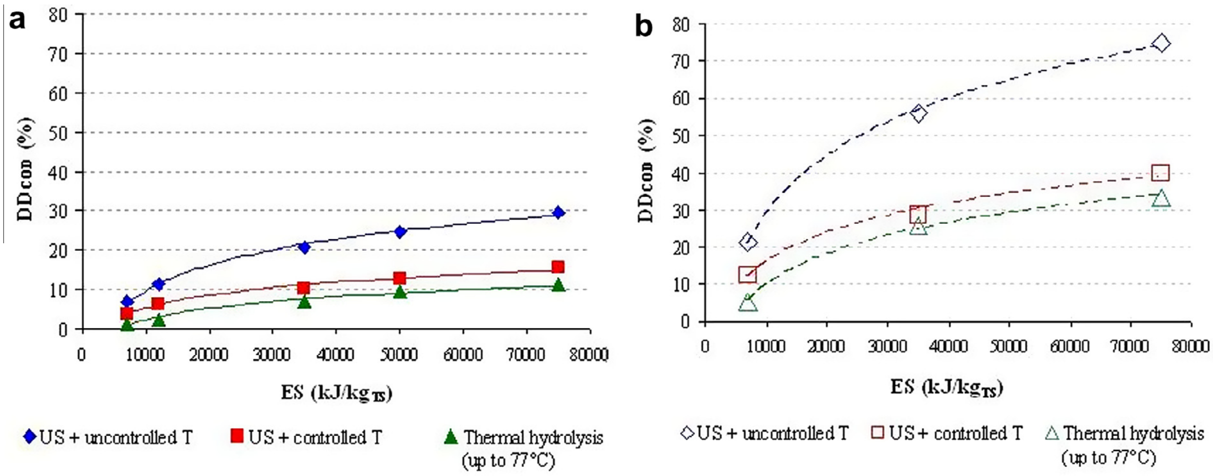


Fig. 5. Effect of temperature on (a) mixed sludge and (b) secondary sludge disintegration (DD_{COD}): P_{US} = 150 W (0 W for thermal hydrolysis), *TS* = 28 g/L, and atmospheric pressure.

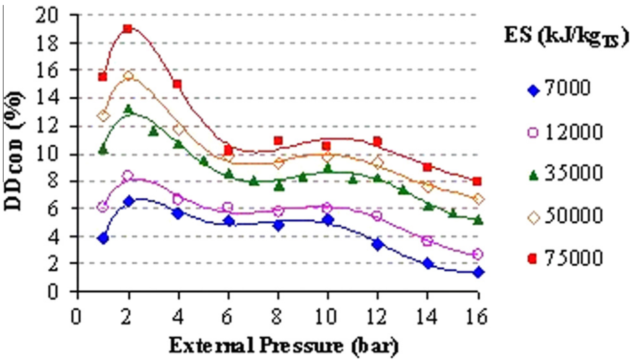


Fig. 6. Effect of external pressure on mixed sludge disintegration (DD_{COD}): P_{US} = 150 W, controlled T (28 °C), and TS = 28 g/L.

atmospheric pressure) with mixed sludge. Fig. 3 exhibits the resulting time-evolution of DD_{COD}.

As expected, for blank experiments (without *US*), the faster the stirring was, the higher the sludge disintegration was: after 2 h of stirring, DD_{COD} was 0.8%, 1.8%, and 3.3% for a stirrer speed of 250, 500, and 1500 rpm, respectively. However, these DD_{COD} values as well as the differences observed among the three corresponding series under *US* were rather low, which indicated that the main role of the stirrer was to make a homogeneous solution, rather than to significantly enhance the transfer of organic matters from solid to aqueous phase.

Under *US*, DD_{COD} increased when raising the stirrer speed from 250 rpm to 500 rpm, but decreased at 1500 rpm. The reactor was not equipped with baffles. Consequently high rotation speed of the whole liquid resulted in the centrifugation of particles, leading to less particles present in the central zone where *US* is concentrated, then to a decrease of the sludge *US* pretreatment efficiency. In addition, aeration could occur and its main effect would be to severely damp the acoustic waves. Therefore, a stirrer speed of 500 rpm was applied in subsequent experiments of this work.

3.3. Effect of US power input along with sonication duration

Three different P_{US} (75, 100, and 150 W) were tested under a controlled *T* of 28 °C and at atmospheric pressure. In each case, *ES* values of 7000, 12,000, 35,000, 50,000, and 75,000 kJ/kg$_{TS}$ were applied by varying the sonication duration. The corresponding performance reflected by DD_{COD} is illustrated in Fig. 4.

For all P_{US}, the disintegration of sludge increased gradually with sonication time *t*. A quasi-linear increase of DD_{COD} was observed in the *ES* range of 0–50000 kJ/kg$_{TS}$ (up to about 12–13%), followed by a slower increase until the end of the process (about 14–16% at *ES* of 75,000 kJ/kg$_{TS}$). This complies with recent researches [5,19,21].

For a given *ES* value, DD_{COD} was the highest in 150 W experiments, followed by 100 W and 75 W experiments. This effect was best observed in the first stage of the process (ES < 50000 kJ/kg$_{TS}$). Afterwards ($ES \geqslant$ 50000 kJ/kg$_{TS}$), DD_{COD} values did not exhibit notable discrepancies for most combinations of P_{US} and *t*. For instance, the highest differences were observed at *ES* of 12,000 kJ/kg$_{TS}$: DD_{COD} of [75 W–37 min] and [100 W–28 min] experiments represented respectively, 66% and 93% of that measured after applying 150 W during 19 min. At *ES* of 75,000 kJ/kg$_{TS}$, DD_{COD} values obtained for all P_{US} differed by less than 10%.

Although it did not result in a significant enhancement of DD_{COD}, the *"high power input – short duration"* sonication procedure proved, again, to be the most effective combination for sludge pretreatment in isothermal conditions, as already reported by other researchers [4,15,18,22,23]. The reason could be attributed to the relative resistance of municipal sludge particles to ultrasonic disruption (especially fibrous particles), requiring high values of P_{US} [15]. A *US* power input of 150 W was applied in all following experiments.

3.4. Effect of temperature and of sludge type on DD_{COD}

The ultrasonic pretreatment has two simultaneous effects: (i) extreme macro and micro mixing caused by the cavitation, and (ii) increase in the bulk temperature. To evaluate their individual contribution, three operating procedures were carried out for mixed and secondary sludge: (1) *US* under isothermal conditions (cooling at 28 °C), (2) *US* under adiabatic conditions, (3) thermal hydrolysis: without *US*, progressive increase of *T* up to 77 °C as found in (2).

Results, illustrated in Fig. 5a and b, show the disintegration (ultrasonic or thermal pretreatments) of secondary sludge to be about 3-fold higher than that of mixed sludge. As confirmed by Show et al. [21], secondary sludge, mainly composed of biological substances (derived from activated processes), is readily disrupted, while mixed sludge (mixture of primary and secondary sludge) contains many non-degradable materials from primary sludge (plastic, textile, fibrous, born, sand…) that cannot be easily disintegrated.

At all observed times and with both types of sludge, DD_{COD} values under adiabatic sonication were the highest, followed by those at low temperature sonication and thermal hydrolysis. DD_{COD} values of sonicated samples under cooling (28 °C) were about half those obtained under adiabatic conditions (uncontrolled *T*).

In accordance with recent works [15,17,22], the higher the temperature, the higher the ultrasonic disintegration efficiency. This is

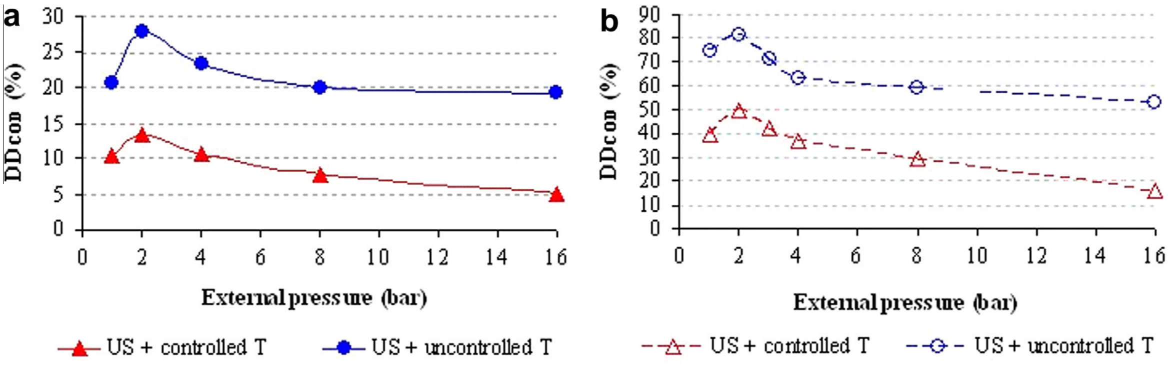


Fig. 7. Effect of external pressure on (a) mixed sludge and (b) secondary sludge disintegration (DD_{COD}): under different temperature conditions: P_{US} = 150 W, TS = 28 g/L. (a) ES = 35,000 kJ/kg$_{TS}$. The final temperature in adiabatic mode was about 75 °C. (b) ES = 75,000 kJ/kg$_{TS}$. The final temperature in adiabatic mode was about 85 °C.

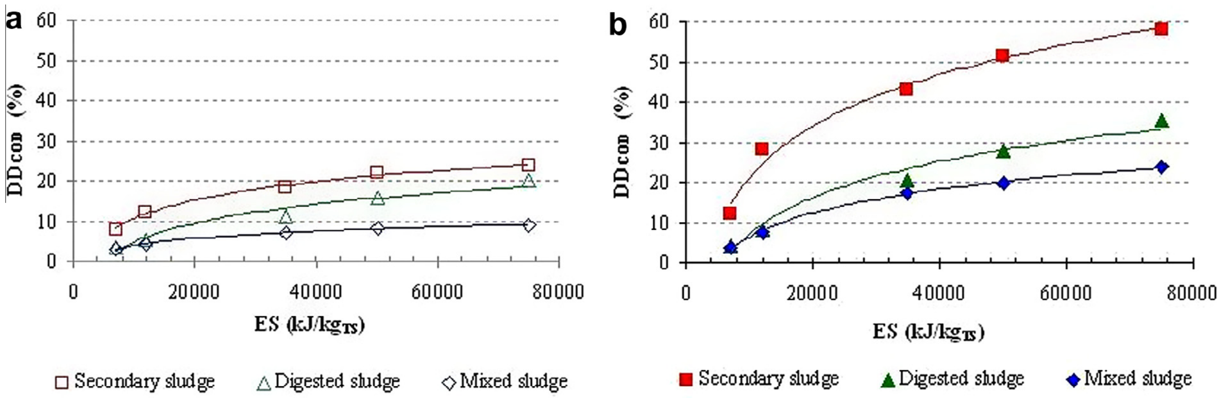


Fig. 8. Effect of specific energy input *ES* on ultarsonic pretreatment efficacy of different sludge types at optimum pressure and different temperature conditions: P_{US} = 150 W and *TS* = 14 g/L (a) isothermal condition (28 °C) and (b) adiabatic condition.

opposite to most power *US* applications as cavitation intensity is higher at low temperature. In short, it is clear that ultrasonic disintegration of sludge is the result of two different effects: the specific cavitation effect and the thermal effect. Despite lower performances, next experiments were conducted under isothermal condition to have a clear understanding of *US* effect under different values of static pressure.

3.5. Effect of external pressure on DD_{COD}

Experiments to investigate the effect of the external pressure (1–16 bar) on the efficacy of ultrasonic pretreatment of sludge were carried out for mixed sludge in the following conditions: optimum *TS* of 28 g/L, isothermal mode, P_{US} of 150 W, and *ES* in the range of 0–75,000 kJ/kg$_{TS}$. Results are presented in Fig. 6.

All curves corresponding to different *ES* values show the same trends of DD_{COD}: an initial increase up to 2 bar and a decrease thereafter, noticeably at pressures over 4 bar. Compared with experiments at atmospheric pressure, sludge disintegration efficacy was significantly improved at the optimum pressure of 2 bar and this effect was relatively high at low *ES*, with a maximum improvement of 67% at 7000 kJ/kg$_{TS}$ (Fig. 6). It is interesting to note that beyond the optimum pressure (about 2 bar), the decrease of DD_{COD} was faster at higher *ES*. With the exception of the lowest *ES* (7000 and 12,000 kJ/kg$_{TS}$), all DD_{COD} values were lower at 6 bar than those at atmospheric pressure. Nevertheless, the positive pressure effect up to 2 bar might lead to energy savings in sludge pretreatment applications with ultrasound. For instance, at the optimum pressure, DD_{COD} obtained with ES of 7000, 35,000, and 50,000 kJ/kg$_{TS}$ were higher than those at atmospheric pressure with *ES* of 12,000, 50,000, and 75,000 kJ/kg$_{TS}$, respectively.

To examine the effect of pressure (1–16 bar) along with temperature during sonication, further experiments were performed under adiabatic condition. The results, shown in Fig. 7a and b, once again confirmed the optimum pressure found in this work to be about 2 bar regardless of temperature and sludge type.

According to Thompson and Doraiswamy [6], increasing the external pressure increases the cavitation intensity and consequently results in an overall improvement of the *US* efficiency. Conversely, increasing the external pressure also leads to an increase in the cavitation threshold [10]. Thereby, to produce cavitation at higher static pressures, the acoustic pressure must be increased via an increase in *US* intensity. However, at a given *US* intensity, a too high static pressure prevents bubble formations, cavitation, and then sludge ultrasonic disintegration. To sum up, as suggested by a simple analysis, an optimum pressure was expected due to opposite effects of external pressure: a reduction of the number of cavitation bubbles due to a higher acoustic cavitation threshold, but a more violent bubble collapse. The major result is that the optimum pressure seems to depend neither on the energy input, nor on the sludge type, nor on temperature that might be surprising.

Although mixed and secondary sludge led to very different DD_{COD}, the same order of sludge disintegration effectiveness was observed regardless of sludge type: (i) *US* + uncontrolled *T* + optimum pressure of 2 bar > (ii) *US* + uncontrolled *T* + atmospheric pressure > (iii) *US* + controlled *T* (28 °C) + optimum pressure of 2 bar > (iv) *US* + controlled *T* + atmospheric pressure. These conditions (ii) and (iii) showed the effect of pressure to be less than that of the temperature increase due to *US*.

The disintegration of different sludge types (mixed, secondary, and digested sludge) was investigated for a reduced *TS* of 14 g/L (as digested sludge was not available at 28 g/L), the optimum pressure of 2 bar, and both isothermal and adiabatic modes. Results are given in Fig. 8a and b. As previously found, adiabatic *US* was more efficient than isothermal *US* in terms of sludge disintegration, with an improvement of 22–82%, 39–88%, and 33–86% for mixed, secondary, and digested sludge, respectively. The results indicated the highest disintegration of secondary sludge, followed by digested sludge and mixed sludge regardless of temperature control.

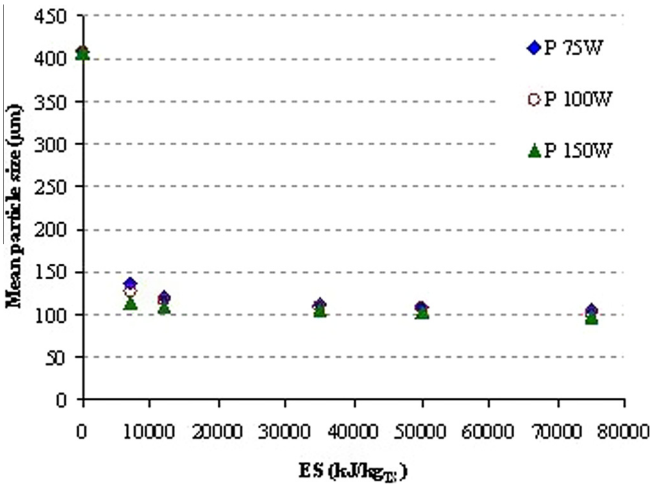


Fig. 9. Mean particle size evolution of mixed sludge (based on *D[4,3]*) during *US* pretreatment with different P_{US} values: controlled *T* (28 ± 2 °C) and atmospheric pressure.

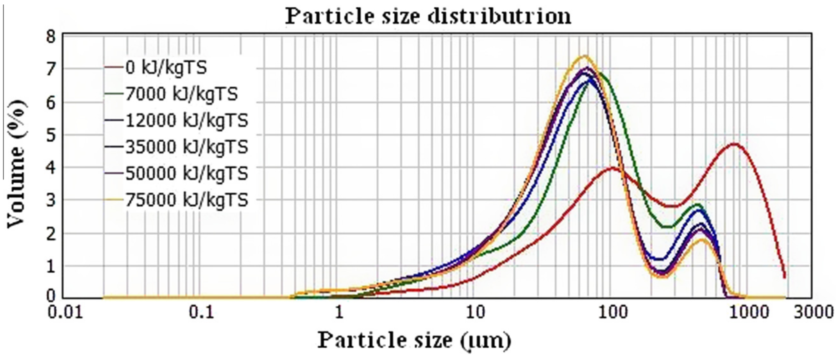


Fig. 10. Evolution of particle size distribution of mixed sludge during *US* pretreatment: P_{US} = 150 W, controlled *T* (28 °C), *TS* = 28 g/L, and atmospheric pressure.

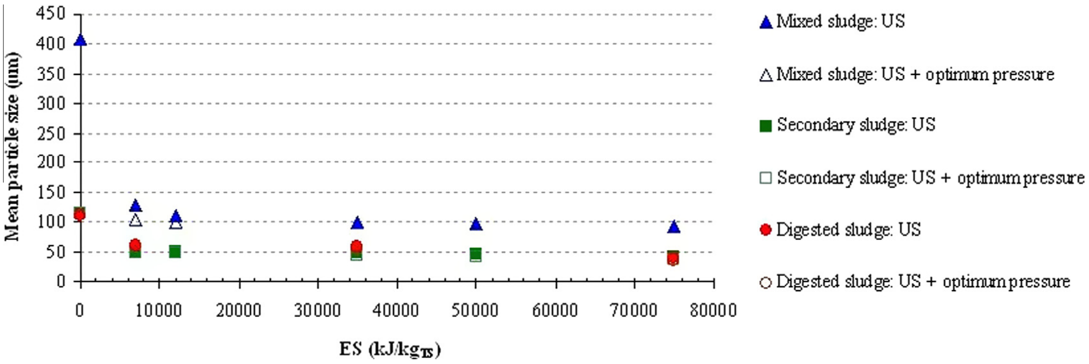


Fig. 11. Mean particle size evolution of different types of sludge during *US* pretreatment (based on *D[4,3]*): P_{US} = 150 W and controlled *T* (28 °C).

3.6. Particle size reduction

Ultrasonic pretreatment is also very effective in reducing the particle size, which is sometimes used to assess the degree of sludge disintegration and commonly analyzed by laser diffraction. The reduction in particle size should accelerate the hydrolysis stage of sludge *AD* and enhance degradation of organic matters. However, this parameter was not advised for process optimization [24].

Fig. 9 describes *D[4,3]* evolution of mixed sludge samples as a function of *ES* for the three investigated P_{US} at atmospheric pressure. Gonze et al. [25] found that particle size was decreased gradually with the increase in sonication time and a reverse trend occurred after 10 min of sonication due to the re-flocculation of the particles. However, this phenomenon was not found in this work, probably due to higher ultrasound power. In order to better understand the effect of sonication on particle charges, zeta potential measurements were performed. First, zeta potential could not be measured with the actual suspension -due to too high particle size- but only with filtered suspension (<1 μm). Sonication was shown to have only marginal effect on zeta potential: −11.3 and −13.2 mV corresponding to pretreated sludge at 7000 kJ/kg$_{TS}$ and 50,000 kJ/kg$_{TS}$, respectively, as compared to that of −6.94 mV for unpretreated one. These small variations indicate a very low modification of surface charges leading to even more stability. This result is then in agreement with the absence of re-flocculation.

Compared with the untreated sludge, particle size was reduced by 68–77% following the subsequent increase in *ES* of 7000–75,000 kJ/kg$_{TS}$. Main reduction of *D[4,3]* was observed within a much shorter duration compared to the time required for a significant *COD* release in the aqueous phase: after 10–20 min of sonication, a quasi-plateau was reached to about 100 μm regardless of P_{US}. Other works [5,22] came to the same conclusion of a fast particle size reduction within a very short sonication time.

In the *ES* range of 7000–75,000 kJ/kg$_{TS}$, d_{90}, d_{50}, and d_{10} values of mixed sludge decreased by 74%, 70% and 58%, respectively. This indicated that different particle sizes had slightly different reduction extents, in which large particles were disrupted more effectively by *US* than smaller ones due to their larger surface exposed to sonication or to different consistency. This point, also illustrated in Fig. 10 showing a very fast reduction of the class of large particles (about 1000 μm), is similar to conclusions in previous works [19,21]. As shown on Fig. 10, the distribution of initial sludge was cut at 1950 μm corresponding to 99.86% of cumulative volume. Then the residual larger particles may be ignored.

When *US* experiments were conducted at optimum pressure, although the kinetics of disruption was slightly faster, the difference in final particle diameter compared to that at atmospheric pressure was negligible (Fig. 11). For instance, the enhancement of particle size reduction of mixed sludge dropped from 9.3% at 7000 kJ/kg$_{TS}$ to less than 1% at 35,000–75,000 kJ/kg$_{TS}$. In accordance with Show et al. [21], the mean particle size of secondary and digested sludge was lower after *US* treatment than that of mixed sludge due to the aforementioned differences of properties.

4. Conclusions

Mixed sludge samples with different *TS* contents were pretreated with various sonication durations. An initial value of 28 g/L always yielded the highest *COD* release in the aqueous phase (DD_{COD}).

Different *US*/temperature combinations were then investigated to evaluate the effect of *US*. At any sonication time (or *US* specific energy *ES*), DD_{COD} values were the highest under adiabatic sonication, followed by those obtained by sonication under cooling, and then thermal hydrolysis ones regardless of sludge type. The effect of *US* was clearly more important than that of sole thermal hydrolysis obtained with the same temperature–time profile. The effect of external pressure on *US* sludge pretreatment was studied for the first time on mixed and secondary sludge using pressurized nitrogen in the range of 1–16 bar. At 150 W of P_{US}, DD_{COD} exhibited an optimum with respect to applied pressure at about 2 bar for all applied *ES* values. At the optimum pressure and low *ES* (7000 kJ/kg_{TS}), disintegration efficacies of secondary and mixed sludge were improved up to 37% and 67%, respectively, compared to those at atmospheric pressure.

Compared with the untreated sludge samples, mean particle size of mixed, secondary, and digested sludge was decreased by 68–77%, 55–68%, and 44–67%, respectively and particles were almost entirely disrupted in the initial period of the ultrasonic process. At 2 bar, the final size was nearly obtained at the first sampling time. The great difference in the kinetics of the two phenomena- fast size reduction and slower *COD* removal in liquid phase- should be emphasized and demonstrate that particle size is not the key parameter to follow *COD* solubilization.

All these data suggest that the best energy efficiency would correspond to short *US* exposure at the optimal pressure and under adiabatic condition. The under pressure ultrasonic pretreatment of sludge might offer a significant potential of energy savings in sludge pretreatment applications with ultrasound.

Acknowledgments

The authors acknowledge the financial support from the Ministry of Education and Training of Vietnam and Institut National Polytechnique of Toulouse (France). They also thank Alexandrine BARTHE (Ginestous), Berthe RATSIMBA, Ignace COGHE, Jean-Louis LABAT, Jean-Louis NADALIN, Lahcen FARHI (LGC), Christine REY-ROUCH (SAP, LGC), Xavier LEFEBVRE, and Anil SHEWANI (INSA) for technical and analytical support.

References

[1] S.K. Khanal, D. Grewell, S. Sung, J. Van Leeuwen, Ultrasound applications in wastewater sludge pretreatment: a review, Crit. Rev. Environ. Sci. Technol. 37 (2007) 277–313.
[2] W.P. Barber, The effects of ultrasound on sludge digestion, J. Chart. Inst. Water Environ. Manage. 19 (2005) 2–7.
[3] T.I. Onyeche, O. Schlafer, H. Bormann, C. Schroder, M. Sievers, Ultrasonic cell disruption of stabilised sludge with subsequent anaerobic digestion, Ultrasonics 40 (2002) 31–35.
[4] T. Mao, S.Y. Hong, K.Y. Show, J.H. Tay, D.J. Lee, A comparison of ultrasound treatment on primary and secondary sludges, Water Sci. Technol. 50 (2004) 91–97.
[5] A. Tiehm, K. Nickel, U. Neis, The use of ultrasound to accelerate the anaerobic digestion of sewage sludge, Water Sci. Technol. 36 (1997) 121–128.
[6] L.H. Thompson, L.K. Doraiswamy, REVIEWS – sonochemistry: science and engineering, Ind. Eng. Chem. Res. 38 (1999) 1215–1249.
[7] G. Cum, R. Gallo, A. Spadaro, Effect of static pressure on the ultrasonic activation of chemical reactions. Selective oxidation at benzylic carbon in the liquid phase, J. Chem. Soc., Perkin Trans. 2 (1988) 375–383.
[8] G. Cum, R. Gallo, A. Spadaro, Temperature effects in ultrasonically activated chemical reactions, Il Nuovo Cimento 12 (10) (1990).
[9] G. Cum, G. Galli, R. Gallo, A. Spadaro, Role of frequency in the ultrasonic activation of chemical reactions, Ultrasonics 30 (4) (1992).
[10] J.P. Lorimer, T.J. Mason, Sonochemistry: part 1-the physical aspects, Chem. Soc. Rev. 16 (1987) 239–274.
[11] P.K. Chendke, H.S. Fogler, Effect of static pressure on the intensity and spectral distribution of the sonoluminescence of water, J. Phys. Chem 87 (1983) 1644–1648.
[12] P.K. Chendke, H.S. Fogler, Sonoluminescence and sonochemical reactions of aqueous carbon tetrachloride solutions, J. Phys. Chem. 87 (1983) 1362–1369.
[13] G.O.H. Whillock, B.F. Harvey, Ultrasonically enhanced corrosion of 304L stainless steel I: the effect of temperature and hydrostatic pressure, Ultrason. Sonochem. 4 (1997) 23–31.
[14] E.A. Neppiras, D.E. Hughes, Some experiments on the disintegration of yeast by high intensity ultrasound, Biotechnol. Bioeng. VI (1964) 247–270.
[15] R. Kidak, A.-M. Wilhelm, H. Delmas, Effect of process parameters on the energy requirement in ultrasonical treatment of waste sludge, Chem. Eng. Process. 48 (2009) 1346–1352.
[16] U. Schmitz, C.R. Berger, H. Orth, Protein analysis as a simple method for the quantitative assessment of sewage sludge disintegration, Water Res. 34 (2000) 3682–3685.
[17] H. Li, J. Yiying, R.B. Mahar, W. Zhiyu, N. Yongfeng, Effects of ultrasonic disintegration on sludge microbial activity and dewaterability, J. Hazard. Mater. 161 (2009) 1421–1426.
[18] G. Zhang, P. Zhang, J. Yang, H. Liu, Energy-efficient sludge sonication: power and sludge characteristics, Biores. Technol. 99 (2008) 9029–9031.
[19] S. Pilli, P. Bhunia, S. Yan, R.J. LeBlanc, R.D. Tyagi, R.Y. Surampalli, Ultrasonic pretreatment of sludge: a review, Ultrason. Sonochem. 18 (2011) 1–18.
[20] B. Akin, S.K. Khanal, S. Sung, D. Grewell, J. Van-Leeuwen, Ultrasound pretreatment of waste activated sludge, Water Sci. Technol. 6 (2006) 35–42.
[21] K.Y. Show, T. Mao, D.J. Lee, Optimization of sludge disruption by sonication, Water Res. 41 (2007) 4741–4747.
[22] C.P. Chu, B.V. Chang, G.S. Liao, D.S. Jean, D.J. Lee, Observations on changes in ultrasonically treated waste-activated sludge, Water Res. 35 (2001) 1038–1046.
[23] A. Grönroos, H. Kyllonen, K. Korpijarvi, P. Pirkonen, T. Paavola, J. Jokela, J. Rintala, Ultrasound assisted method to increase soluble chemical oxygen demand (*SCOD*) of sewage sludge for digestion, Ultrason. Sonochem. 12 (2005) 115–120.
[24] I. Dogan, Combination of Alkaline solubilisation with microwave digestion as a sludge disintegration method: effect on gas production and quantity and dewater-ability of anaerobically digested sludge, [MSc/MA Dissertation], 2008.
[25] E. Gonze, S. Pillot, E. Valette, Y. Gonthier, A. Bernis, Ultrasonic treatment of an aerobic sludge in batch reactor, Chem. Eng. Process. 42 (2003) 965–975.


ELSEVIER
Journal of
Environmental
Management

Journal of Environmental Management 128 (2013) 548–554

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Improving sewage sludge ultrasonic pretreatment under pressure by changing initial pH

Ngoc Tuan Le, Carine Julcour, Berthe Ratsimba, Henri Delmas*

Université de Toulouse, Laboratoire de Génie Chimique, INP-ENSIACET, 31030 Toulouse, France

A R T I C L E   I N F O

Article history:
Received 14 February 2013
Received in revised form
28 May 2013
Accepted 5 June 2013
Available online

Keywords:
Alkalization
Sonication
Sludge disintegration
Chemical oxygen demand
Particle size distribution
Mixed sludge

A B S T R A C T

This work aimed at understanding the combined effect of sludge pH, temperature, and external pressure on the efficiency of sewage sludge ultrasound (US) pretreatment. Based on the evolution of both the degree of sludge disintegration (DD_{COD}) and pH, application of 40 mg_{NaOH}/g_{TS} during 30 min was selected for chemical pretreatment. Mechanical and thermal effects induced by cavitation contributed in similar proportion to sludge disruption, but the role of the latter effect tended to be weakened after mild alkalisation of sludge. When applying external pressure, DD_{COD} was always improved, by about 10% at the optimal value of 2 bar. The optimal combination was an addition of 40 mg_{NaOH}/g_{TS} prior to adiabatic sonication at 2 bar, resulting in a DD_{COD} value of about 46% at 75,000 kJ/kg_{TS} (as compared to 35% for sole US) for the investigated mixed sludge. Very short time US application yielded a drastic reduction of the volume mean particle size, mainly due to the erosion and disruption of large flocs (>90 μm), yet this was not sufficient to initiate significant subsequent COD solubilisation under stirring.

1. Introduction

The first objective of sewage sludge treatment is to remove organic matters and water, which reduces the volume and mass of sludge and also cuts down toxic materials and pathogens. Biological, mechanical, chemical methods and thermal hydrolysis have been listed as popular techniques for sludge pretreatment (Carrère et al., 2010). Among these techniques, anaerobic digestion (AD) is the most traditional one. However, this process is limited by long sludge retention time and rather low overall degradation efficiency. Sludge mainly consists of microbial cells that limit the biodegradability of intracellular organic matters by their walls (Kim et al., 2010). Therefore, sludge disintegration pretreatment, which disrupts sludge flocs, breaks cell walls, and facilitates the release of intracellular matters into the aqueous phase, can be considered as a simple approach for improving rate and/or extent of degradation.

Ultrasonication (US) is a promising applicable mechanical disruption technique for sludge disintegration and microorganism lyses. However, US requires high energy input, generally referred as the specific energy input (ES) in kJ/kg of dried sludge, and causes great discussions due to economic issues in practical application. This high cost could be reduced by the combination with other pretreatment methods, the adjustment of sludge properties (total solid content (TS), pH, and volume of sludge, etc.), and/or the optimisation of ultrasonic parameters (frequency, specific energy input, intensity, density, etc.), and external pressure, etc.

According to Pilli et al. (2011), the effects of sonication parameters and sludge properties on solubilisation of the chemical oxygen demand (COD) can be rated as follows: sludge pH > sludge concentration > ultrasonic intensity > ultrasonic density. This suggests that pH adjustment to a suitable value prior to US pretreatment is an important step.

Sludge cells were proved to be disintegrated and dissolved by acidic treatment. Only the acid dose significantly affected the solubilisation of sludge (Woodard and Wukash, 1994). The optimal pH values for reducing volatile suspended solids and excess sludge subsequently varied between 1.5 (Woodard and Wukash, 1994) and 3 (Neyens et al., 2003). However, acidic pretreatment alone exhibited a very low performance as compared to US pretreatment for releasing organic matters into the liquid phase. Moreover, sludge acidification was detrimental to US pretreatment performance, especially at low pH values (Apul, 2009).

On the other hand, alkaline pretreatment enhanced sludge solubilisation, anaerobic biodegradability, and methane production (Kim et al., 2003; Valo et al., 2004). Besides, the combination of alkaline and US gave better performances of TS solubilisation as compared to both thermo-acidic and US-acidic pretreatments (Liu et al., 2008). Moreover, Chu et al. (2001) showed that

---

* Corresponding author. Tel.: +33 (0) 5 34 32 36 78; fax: +33 (0) 5 34 32 36 97.
E-mail address: henri.delmas@ensiacet.fr (H. Delmas).

0301-4797/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jenvman.2013.06.001

extracellular polymeric substances (EPS) and gels surrounding cells limit the efficiency of ultrasonic treatment on sludge disintegration. Adjusting the pH of sludge to alkali value promotes EPS hydrolysis and gel solubilisation. After that, cell walls cannot maintain an appropriate turgor pressure (Jin et al., 2009) and easily disrupt. Therefore, the combined alkaline-US pretreatment, based on different mechanisms of sludge disintegration (modification of structural properties and intense mechanical shear force), is expected to take advantage of both and achieve a better efficiency of sludge pretreatment. Some synergetic effects were even noticed (Kim et al., 2010). In near-neutral pH conditions (pH 7–8), waste activated sludge (WAS) solubilisation obtained from combined, chemical, and US (1.9 W/mL, 60 s) pretreatments was 18, 13.5, and 13%, respectively (Bunrith, 2008). At higher pH values (pH 11–13), the solubilisation reached 60–70% with the combined method (ES 7500–30,000 kJ/kg_{TS}) while it never exceeded 50% in individual pretreatments (Jin et al., 2009; Kim et al., 2010). Methane production yield derived from full stream combined-pretreated sludge (pH 9, ES 7500 kJ/kg_{TS}) was also 55% higher than that from the control (Kim et al., 2010).

The chemicals used for increasing the pH of sludge also affect WAS solubilisation efficacy: NaOH > KOH > $Mg(OH)_2$ and $Ca(OH)_2$ (Kim et al., 2003; Jin et al., 2009). Ca^{2+} and Mg^{2+} are key substances binding cells with EPS. As a result, their presence may enhance the reflocculation of dissolved organic polymers (Jin et al., 2009), leading to a decrease in soluble COD. On the other hand, overconcentration of Na^+ (or K^+) was reported to cause subsequent inhibition of AD (Carrère et al., 2010).

For ambient conditions of US process, modification of external pressure was proved to change cavitation intensity (Thompson and Doraiswamy, 1999), and to improve the rate and yield of US-assisted reactions (Cum et al., 1988). However, most US experiments have been carried out at atmospheric pressure; only a few studies have been focussing on how increasing static pressure affects cavitation but they almost concern sonoluminescence. To our knowledge, we have conducted the first study about the effect of pressure (1–16 bar) on sludge US pretreatment (Le et al., 2013). We found an optimum pressure of 2 bar for sludge disintegration regardless of ES (P_{US} of 150 W), temperature, and sludge type. At this optimum pressure and over the ES range of 7000–75000 kJ/kg_{TS}, adiabatic US was more efficient than isothermal US (with an improvement of 22–82%, 39–88%, and 33–86% for mixed, secondary, and digested sludge, respectively). These conditions were therefore applied in the present work for the mixed sludge. Solubilisation of COD, evolution of pH, and evolution of particle size distribution were examined for separate, then combined, US and alkaline pretreatments.

2. Materials and methods

2.1. Sludge samples

Mixed sludge was collected after centrifugation from Ginestous wastewater treatment plant (Toulouse, France) with a sufficient amount for all experiments in this work. Its properties, given in Table 1, were evaluated according to standard analytical methods (see § 2.3).

It was sampled in 100 g plastic boxes and preserved in a freezer. Kidak et al. (2009) reported that this preliminary maintaining step might change some physical characteristics of the sludge, but it should not significantly affect COD solubilisation results. It was confirmed in this work, the difference in sludge disintegration between fresh sludge (without freezing) and frozen sludge was less than 5% on the whole ES range (7000–75,000 kJ/kg_{TS}).

When performing experiments, the required amount of sludge was defrosted and diluted with distilled water up to 500 mL per experiment. According to our previous results (Le et al., 2013), the optimum TS concentration for sludge ultrasonic disintegration was 28 g/L.

Table 1
Characteristics of the sludge sample.

Parameter	Value
Raw sludge	
pH	6.3
Total solids (TS)	270 mg/g
Volatile solids (VS)	233 mg/g
VS/TS	86.2%
Synthetic sample	
Total solids (TS)	28.0 g/L
$SCOD_{NaOH\ 0.5\ M}$	19.6 g/L
Total COD (TCOD)	38.9 g/L

2.2. Ultrasound application to original or alkalized sludge

The US stainless steal reactor (9 cm internal diameter and 18 cm height) consisted of a cup-horn type transducer (35 mm diameter probe) and was connected to a pressurized N_2 bottle (Fig. 1). The sludge solution was stirred by a Rushton type turbine of 32 mm diameter, with an adjustable speed up to 3000 rpm. Cooling water was allowed to circulate in an internal coil to maintain a constant temperature ($T = 28 \pm 2$ °C) during isothermal sonication tests.

The US system had a fixed frequency of 20 kHz, and a maximum total power of 200 W corresponding to an ultrasonic power input (P_{US}) of 158 W. The transducer was cooled by compressed air during operation.

US tests were performed at the highest P_{US} (150 W) as it proved to be the most effective in isothermal conditions. A convenient stirrer speed of 500 rpm, as also found in previous work, was applied in all tests.

For each experiment, a constant volume of synthetic sludge sample (0.5 L) was poured into the stainless steel reactor. Five different sonication times corresponding to five values of ES (7000, 12,000, 35,000, 50,000, and 75,000 kJ/kg_{TS}) were tested.

$$ES = (P_{US}*t)/(V*TS)$$

with ES: specific energy input, energy per total solid weight (kJ/kg_{TS}), P_{US}: US power input (W), t: sonication duration (s), V: volume of sludge (L), and TS: total solid concentration (g/L).

According to previous studies (Kim et al., 2003; Jin et al., 2009), NaOH was used for adjusting the pH of sludge. Regarding the treatment sequence, "alkalisation followed by ultrasonic pretreatment" was more effective than the reverse combination, as it allows the US treatment to benefit from the weakening of the sludge matrix. Conversely, the disrupted floc fragments could be re-aggregated into compact structures by the subsequent NaOH treatment (Jin et al., 2009). Consequently, the former procedure was chosen for alkaline-US experiments.

A given amount of NaOH was added into the fixed volume of sludge to ensure the same condition of chemical application. The kinetics of sludge disintegration by NaOH was first investigated to select a convenient a holding time corresponding to the most significant COD release (cf. § 3.1.1). Sonication was then applied to alkalized sludge samples and the effects of *NaOH dose*, ES in the range of 0–75,000 kJ/kg_{TS}, *temperature profile* (isothermal/adiabatic conditions), and *external pressure* (atmospheric pressure/optimal pressure of 2 bar in accordance with previous results) were examined in order to improve sludge disintegration.

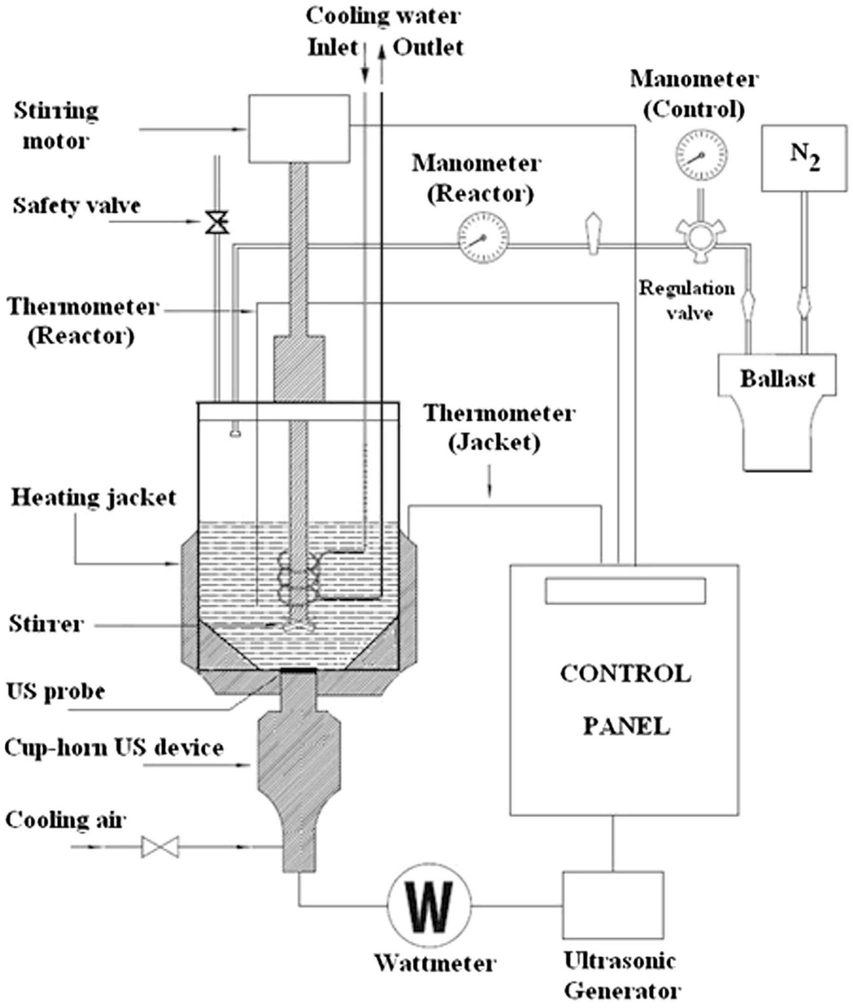


Fig. 1. Ultrasonic autoclave set-up.

2.3. Analytical methods

Total and volatile solid contents (TS and VS, respectively) were measured according to the following procedure (APHA, 2005): TS was determined by drying a well-mixed sample to constant weight at 105 °C and VS was obtained from the loss on ignition of the residue at 550 °C.

The ***degree of sludge disintegration*** (DD_{COD}) was calculated by determining the soluble chemical oxygen demand after strong alkaline disintegration of sludge ($SCOD_{NaOH}$) and the chemical oxygen demand in the supernatant before and after treatment ($SCOD_0$ and SCOD, respectively):

$$DD_{COD} = (SCOD - SCOD_0)/(SCOD_{NaOH} - SCOD_0)*100(\%)$$

(Nickel and Neis, 2007).

To measure the $SCOD_{NaOH}$, used as a reference to evaluate the efficiency of organic matter solubilisation under US/chemical treatment, the sludge sample was mixed with 0.5 M NaOH at room temperature for 24 h (Li et al., 2009). Besides, total chemical oxygen demand (TCOD) was also measured by potassium dichromate oxidation method (standard AFNOR NFT 90–101).

Prior to SCOD determination, the supernatant liquid obtained after sedimentation was filtered under vacuum using a cellulose nitrate membrane with 0.2 μm pore size. The filtered liquid was subjected to COD analysis as per Hach spectrophotometric method. The change in the SCOD indirectly represents the quantity of organic carbon that has been transferred from the cell content (disruption) and solid materials (solubilisation) into the external liquid phase of sludge. The experiments were triplicated and the coefficients of variation (CV) were about 5%.

The ***particle size distribution*** **(PSD)** of sludge before and after treatment was determined by using a Malvern particle size analyzer (Mastersizer, 2000; Malvern Inc.), a laser diffraction-based system (measuring range from 0.02 to 2000 μm). Each sample was diluted approximately 300-fold in osmosed water, before being pumped into the measurement cell (suction mode). The PSD was based on the average of five measurements showing deviations of less than 3%. Optical properties of the material were set as default (refractive index 1.52, absorption 0.1) appropriate for the majority of naturally occurring substances (Minervini, 2008; Bieganowski et al., 2012). Only in the small particle range (i.e. for particle diameter smaller than 10 μm), the refractive index dependence becomes significant (Govoreanu et al., 2009). Moreover it was checked that these mean optical properties led to a weighted residual parameter of less than 2% as recommended by the manufacturer.

Since the primary result from laser diffraction is a volume distribution, the volume mean diameter *D*[4,3] (or de Brouckere mean diameter) was used to illustrate the mean particle size of sludge.

3. Results and discussion

3.1. Effect of chemical pretreatment on DD_{COD}

The effect of chemical pretreatment on DD_{COD} was investigated by adding NaOH doses of 22, 40, 47, and 77 mg_{NaOH}/g_{TS} to the mixed sludge solution (for comparison, 714 mg_{NaOH}/g_{TS} were used for the measurement of the reference $SCOD_{NaOH}$). These samples were labelled sol. 22, sol. 40, sol. 47, and sol. 77, respectively. The evolution of pH and DD_{COD} of the samples, measured at room temperature, is shown in Table 2.

3.1.1. Kinetics of alkaline sludge disintegration and effect of NaOH dose

According to Kim et al. (2010), chemical pretreatment usually acts faster than other methods. Indeed, in all cases, alkaline treatment resulted in a fast solubilisation of COD, more than 50% of the maximal observed yield being achieved within 10 min, followed by a quasi-plateau after 30 min. Therefore, a holding time of 30 min was selected for subsequent experiments combined with US. During this period, the pH of the sludge samples dropped by about one pH unit as shown in Table 2.

DD_{COD} increased continuously with NaOH dose in the investigated range. However, for overall process economy (related to chemicals used in pretreatment stage as well as in subsequent neutralisation required for AD), NaOH addition should be limited. Moreover, high concentrations of Na^+ were reported to cause subsequent inhibition of AD (Carrère et al., 2010). Recommended values for NaOH dose vary between 50 and 200 mg_{NaOH}/g_{TS} to ensure that NaOH is in excess and achieves a significant enhancement of DD_{COD} (Kim et al., 2003; Bunrith, 2008; Jin et al., 2009). However, after 30 min, DD_{COD} value from sol. 40 was almost double of that from sol. 22, but close to that from sol. 47. In other words, an increase of the NaOH amount from 40 to 47 mg_{NaOH}/g_{TS} resulted in a pH jump of nearly one unit, without significant effect on COD solubilisation. Considering this pH transition (and its final value), a dose of 40 mg_{NaOH}/g_{TS} could be selected as a critical NaOH dose for chemical disintegration of sludge.

3.1.2. Comparison of sole ultrasonic and sole chemical pretreatment of sludge

Fig. 2 recalls the main results of US treatment carried out on the mixed sludge using P_{US} of 150 W, with various thermal conditions (isothermal/adiabatic) and external pressures (atmospheric/optimal value of 2 bar) (Le et al., 2013).

Conversely to chemical treatment which showed a fast COD solubilisation (after 30 min as abovementioned), DD_{COD} gradually increased during the 2 h of sonication.

The efficiency of US resulted nearly equally from mechanical and thermal effects induced by cavitation as DD_{COD} of mixed sludge obtained dropped from 32.8% under adiabatic conditions to 19.1% at a controlled temperature of 28 °C after 2 h of sonication. When applying external pressure, the degree of sludge disintegration was slightly improved, by about 10% at the optimal value of 2 bar.

Table 2
Chemical pretreatment of mixed sludge (room temperature).

	Holding time (min)						
	0.5	10	20	30		40	117
	pH	DD_{COD} (%)	DD_{COD} (%)	pH	DD_{COD} (%)	DD_{COD} (%)	DD_{COD} (%)
Sol. 22	9.6	6.4	7.3	8.6	9.5	10.7	12.3
Sol. 40	10.2	11.5	13.3	9.4	17.0	18.3	21.0
Sol. 47	11.1	13.0	15.8	10.1	19.3	21.0	22.5
Sol. 77	12.2	24.4	26.3	11.0	29.0	30.4	33.1

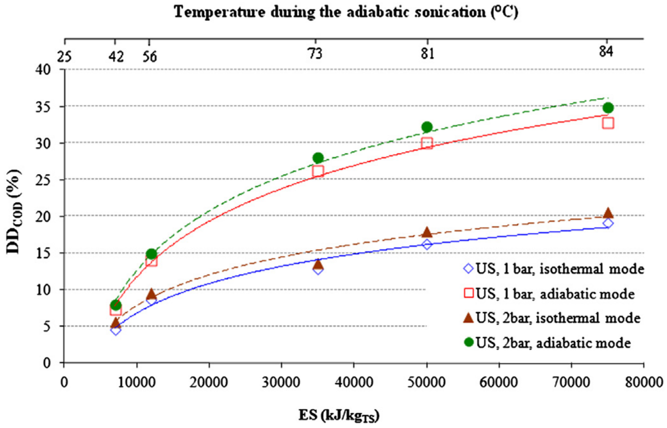


Fig. 2. Mixed sludge disintegration under US pretreatment: evolution of COD solubilisation as a function of applied specific energy (TS = 28 g/L, P_{US} = 150 W). The upper y-axis indicates the evolution of temperature during the adiabatic sonication (final T for each corresponding ES value).

After 30 min under NaOH treatment, the volume mean diameter D[4,3] of mixed sludge was 288, 247, 203, and 133 μm for sol. 22, sol. 40, sol. 47, and sol. 77, respectively, compared to 370 μm for the untreated sample. For the same time under controlled temperature sonication, D[4,3] dropped to about 100 μm. However, with the exception of sol. 22, a much higher DD_{COD} was achieved by chemical treatment. This could be explained that apart from causing the disintegration of floc structures and cell walls, hydroxyl anions also resulted in extensive swelling and subsequent solubilisation of gels in sludge (Kim et al., 2003). The higher the pH, the more easily the processes of natural shape losing of proteins, saponification of lipid, and hydrolysis of RNA occur (Li et al., 2008; Carrère et al., 2010). Obviously, selection of NaOH dose must also be based on the pH of sludge after chemical pretreatment that should comply with subsequent treatment – methanisation requiring a narrow range between 6.5 and 8 (Kim et al., 2003).

3.2. Effect of NaOH addition prior to sonication

3.2.1. Combined chemical – ultrasonic pretreatment of sludge at atmospheric pressure

Different mixed sludge samples were prepared by adding increasing doses of NaOH (as per sol. 22 to sol. 77) and letting react for 30 min under stirring before applying US for 2 h.

Fig. 3 compares the final DD_{COD} values of the combined pretreatment to those of the US pretreatment, with and without cooling. As expected, alkali-ultrasonic pretreatment was the most effective technique for sludge disintegration, and the resulting efficacy was nearly the sum of individual alkali and US pretreatments when sol. 22 or sol. 40 were kept under isothermal conditions (28 °C). Jin et al. (2009) also observed such a result. Alkalisation significantly reduced the differences observed between the controlled and uncontrolled temperature modes of US treatment. It is also worth noting that under US, the differences resulting from the addition of different NaOH amounts tended to vanish. Therefore, addition of a small NaOH dose (as per sol. 22 or sol. 40) should be indeed the best option for the whole process.

3.2.2. Combined chemical – ultrasonic pretreatment of sludge under pressure

Some positive effect of external pressure was observed in our previous work, with an optimal pressure of about 2 bar. Hence, some experiments were also carried out under this external pressure value. In the previous experiments (cf. § 3.2.1), after 2 h of

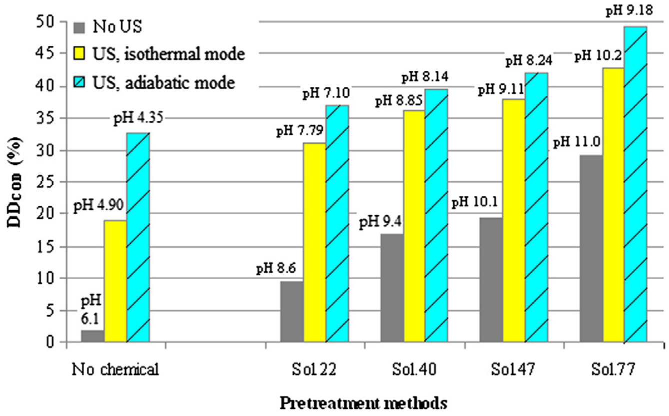


Fig. 3. Comparison of different methods for mixed sludge disintegration (TS = 28 g/L): P_{US} = 150 W, sonication duration = 117 min, NaOH dose = 0–77 mg_{NaOH}/g_{TS} (holding time = 30 min), and atmospheric pressure. Final pH value after treatment is also indicated on top of each corresponding bar.

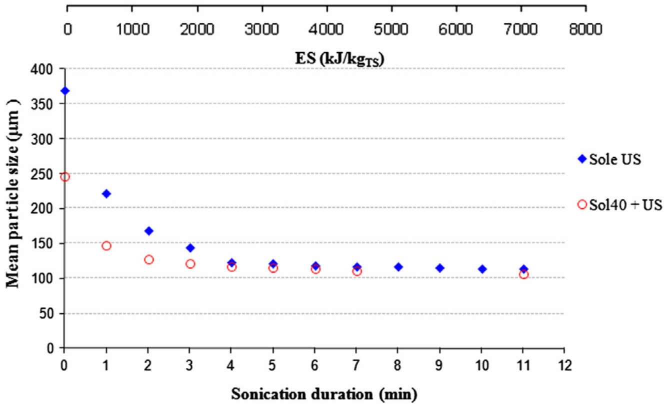


Fig. 5. Mean particle size evolution of mixed sludge (based on $D[4,3]$) during the early stage of (alkali-)US pretreatment: P_{US} = 150 W, controlled T (28 °C), and atmospheric pressure.

sonication, the pH of the different alkalized mixed sludge solutions varied between 7.8 and 10.2 under cooling and between 7.1 and 9.2 under adiabatic condition. The upper values are too high for a subsequent valorisation by methanisation according to the abovementioned pH range of AD. Therefore, subsequent US experiments at different ES (or sonication duration) combining all parameters (pH adjustment, isothermal/adiabatic modes, and external pressure application) were conducted for sol. 40 only. The results are shown in Fig. 4.

The same conclusions prevailed regarding the effect of temperature and alkalisation, but at 2 bar of external pressure, the overall process was still improved: up to about 46% of DD_{COD} after 2 h of sonication of sol. 40. The final pH of 7.6 was also suitable for AD. The solubilisation performance depicted in Fig. 4 was somewhat lower than that reported by Jin et al. (2009) (about 45% with 99 mg_{NaOH}/g_{TS} and ES 12000 kJ/kg_{TS}) and Kim et al. (2010) (50–60% for pH 9–10 and ES < 30,000 kJ/kg_{TS}). Apart from the higher NaOH doses applied, it could be due to different experimental conditions as compared to the present work: substrates (WAS (Jin et al., 2009; Kim et al., 2010) vs. mixed sludge), US apparatus (probe system (Jin et al., 2009; Kim et al., 2010) vs. cup-horn system), US intensity and US density reflected by P_{US}, probe diameter, and volume of sludge per experiment (300 W (Kim et al., 2010) vs. 150 W; 6 mm (Jin et al., 2009) vs. 35 mm of probe diameter; 0.1 L (Jin et al., 2009; Kim et al., 2010) vs. 0.5 L of sludge).

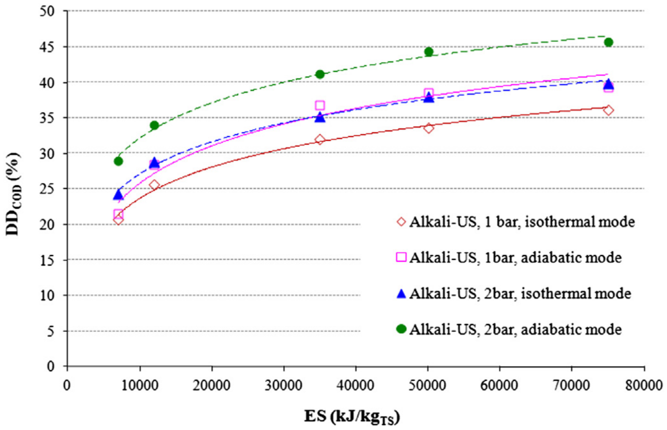


Fig. 4. Mixed sludge disintegration under alkali-US pretreatment: evolution of COD solubilisation as a function of applied specific energy (TS = 28 g/L, P_{US} = 150 W, NaOH dose = 40 mg_{NaOH}/g_{TS}).

3.3. Particle size reduction

As abovementioned in § 3.1.2, US pretreatment is very effective in reducing the sludge particle size, which accelerates the hydrolysis stage of AD and enhances the degradation of organic matters. Main reduction of $D[4,3]$ was observed within a much shorter duration compared to the time required for a significant COD release in the aqueous phase. Other works (Chu et al., 2001; Gonze et al., 2003; Show et al., 2007) came to the same conclusion.

In order to observe more precisely the particle size reduction, experiments were carried out with particle size sampling at much shorter time of sonication. The results (Fig. 5) show that the combination of US and chemical treatment accelerated the size reduction, but the final $D[4,3]$ value was almost the same, about 100 μm.

According to the work of Gonze et al. (2003), the particle size distributions were deconvoluated into five populations, each following a log-normal distribution. The treatment was performed using OriginPro 8.6 (OriginLab). An example is given in Fig. 6 for the raw mixed sludge: a very small extra peak might be distinguished around 1 μm, but its contribution was always so low that it could not be adequately detected. Therefore, its contribution was neglected.

Fig. 7a shows the evolution of each population contribution during the US treatment: two macro-floc populations – population

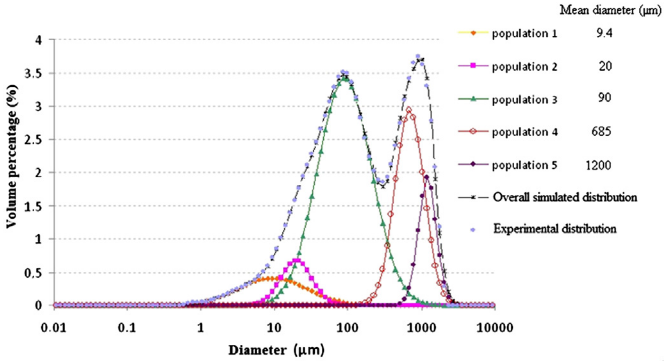


Fig. 6. Deconvolution of PSD of raw mixed sludge.

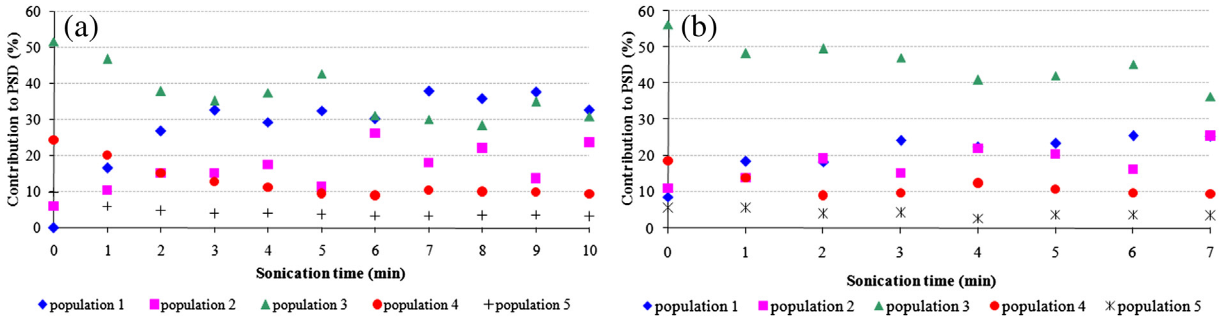


Fig. 7. Contribution of each population to PSD of mixed sludge during short sonication: (a) without addition of NaOH and (b) using 40 mg_{NaOH}/g_{TS} (P_{US} = 150 W, controlled T at 28 °C, and atmospheric pressure).

4 and 5 of 685 μm and 1200 μm, respectively – could be distinguished in the mixed sludge, both their mean diameter and contribution significantly decreased during the first 4 min of sonication. Their diameter dropped to about 400 μm and 650 μm, respectively, while their contribution was divided by a factor 2.5 to 3. Conversely, the size of populations 1 to 3 (about 10 μm, 20 μm, and 90 μm, respectively) remained almost constant during short US treatment. It seems thus that the decrease of the largest macro-flocs proceeded mainly according to erosion mechanism, while population 3 was disrupted into micro-flocs (population 1).

After the 30 min NaOH pretreatment (using 40 mg_{NaOH}/g_{TS}), the diameters of population 1 and 4 were reduced by about 20% as compared to raw mixed sludge and the contributions of populations 4 and 5 were reduced by a factor 1.3 and 1.8, respectively (in favour of population 2) (Fig. 7b). However, their evolution under subsequent sonication remained similar as without NaOH addition. In this condition, mean diameter of population 4 and 5 dropped to 400 and 600 μm, respectively, while that of populations 1 to 3 kept almost unchanged.

For a further comprehension of the relationship between mean particle size reduction and COD solubilisation, additional experiments with and without pH adjustment (40 mg_{NaOH}/g_{TS}) were carried out in the following conditions: US were applied during the first minute or the first 4 min, and then only the stirrer was continuously operated under cooling. Despite these two sonication durations resulted in distinct $D[4,3]$, especially under natural pH (Fig. 5), no differences were observed in terms of DD_{COD} afterwards (Fig. 8). These short US pretreatments only provided a small initial jump of COD release, but did not modify its evolution. Therefore, it proves that the strong reduction of mean particle size observed at low ES was not sufficient to affect COD solubilisation as expected by the different process dynamics.

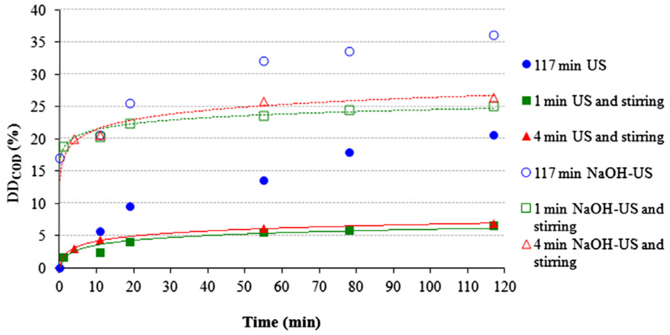


Fig. 8. Effect of short sonication time on mixed sludge disintegration with and without addition of NaOH (40 mg_{NaOH}/g_{TS}): P_{US} = 150 W, controlled T (28°C), and atmospheric pressure.

4. Conclusions

This work proved that US pretreatment of sewage sludge benefits from the combined effects of generated heat, mild alkalisation, and also external pressure application, which was not investigated in earlier works. It was confirmed that under controlled temperature condition, US and alkali pretreatments have distinct **mechanisms of** action **on sludge**, resulting in different kinetics of COD release and additive effects for low NaOH dose. Conversely, the chemical pretreatment hided the positive effect of the heat generated by US under adiabatic condition. It was also shown that the fast reduction of sludge mean particle size observed at low ES is not sufficient to explain the effect of US on COD solubilisation.

Addition of low NaOH dose, between 22 and 40 mg_{NaOH}/g_{TS}, is recommended, that significantly improved COD release under subsequent US treatment while resulting in a final pH value suitable for subsequent methanisation. In the later condition, DD_{COD} yield reached up to 46% at 75,000 kJ/kg_{TS} as compared to 35% for sole US.

Acknowledgements

The authors acknowledge the financial support from the Ministry of Education and Training of Vietnam and Institut National Polytechnique of Toulouse (France). They also thank Alexandrine BARTHE (Ginestous WWTP), Ignace COGHE, Jean-Louis LABAT, Jean-Louis NADALIN, Lahcen FARHI (LGC), Christine REY-ROUCH (SAP, LGC), Xavier LEFEBVRE, Anil SHEWANI (INSA, LISBP, Toulouse), and SINAPTEC company for technical and analytical support.

References

APHA, AWWA, WEF, 2005. Standard Methods for the Examination of Water and Wastewater, twenty-first ed. American Public Health Association, Washington, D.C.

Apul, O.G., 2009. Municipal Sludge Minimization: Evaluation of Ultrasonic and Acidic Pretreatment Methods and Their Subsequent Effects on Anaerobic Digestion. Thesis of Master Degree. Middle East Technical University, Turkey. http://etd.lib.metu.edu.tr/upload/12610366/index.pdf (accessed 28.07.12.).

Bieganowski, A., Lagod, G., Ryzak, M., Montusiewicz, A., Chomczynska, M., Sochan, A., 2012. Measurement of activated sludge particle diameters using laser diffraction method. Ecol. Chem. Eng. S 19 (4), 567–608.

Bunrith, S., 2008. Anaerobic Digestibility of Ultrasound and Chemically Pretreated Waste Activated Sludge. Thesis of Master Degree. Asian Institute of Technology, Thailand. www.faculty.ait.ac.th/visu/Data/AIT-Thesis/Master Thesis Final/Bunrith.pdf (accessed 28.07.12.).

Carrère, H., Dumas, C., Battimelli, A., Batstone, D.J., Delgenès, J.P., Steyer, Ferrer, I., 2010. Pretreatment methods to improve sludge anaerobic degradability: a review. J. Hazard. Mater. 183, 1–15.

Chu, C.P., Chang, B.V., Liao, G.S., Jean, D.S., Lee, D.J., 2001. Observations on changes in ultrasonically treated waste-activated sludge. Water Res. 35, 1038–1046.

Cum, G., Gallo, R., Spadaro, A., 1988. Effect of static pressure on the ultrasonic Activation of chemical reactions. Selective oxidation at benzylic carbon in the liquid phase. J. Chem. Soc. Perkin Trans. 2, 375–383.

Govoreanu, R., Saveyn, H., Van der Meeren, P., Nopens, I., Vanrolleghem, P.A., 2009. A methodological approach for direct quantification of the activated sludge floc size distribution by using different techniques. Water Sci. Technol. 60 (7), 1857–1867.

Gonze, E., Pillot, S., Valette, E., Gonthier, Y., Bernis, A., 2003. Ultrasonic treatment of an aerobic sludge in batch reactor. Chem. Eng. Process 42, 965–975.

Jin, Y., Li, H., Mahar, R.B., Wang, Z., Nie, Y., 2009. Combined alkaline and ultrasonic pre-treatment of sludge before aerobic digestion. J. Environ. Sci. (China) 21, 279–284.

Kidak, R., Wilhelm, A.M., Delmas, H., 2009. Effect of process parameters on the energy requirement in ultrasonical treatment of waste sludge. Chem. Eng. Process 48, 1346–1352.

Kim, D.H., Jeong, E., Oh, S.E., Shin, H.S., 2010. Combined (alkaline + ultrasonic) pretreatment effect on sewage sludge disintegration. Water Res. 44, 3093–3100.

Kim, J., Park, C., Kim, T.H., Lee, M., Kim, S., Kim, S.W., Lee, J., 2003. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. J. Biosci. Bioeng. 95 (3), 271–275.

Le, N.T., Julcour-Lebigue, C., Delmas, H., 2013. Ultrasonic sludge pretreatment under pressure. Ultrason. Sonochem. 20, 1203–1210.

Li, H., Jin, Y., Mahar, R., Wang, Z., Nie, Y., 2008. Effects and model of alkaline waste activated sludge treatment. Bioresour. Technol. 99, 5140–5144.

Li, H., Jin, Y., Mahar, R., Wang, Z., Nie, Y., 2009. Effects of ultrasonic disintegration on sludge microbial activity and dewaterability. J. Hazard. Mater. 161, 1421–1426.

Liu, X., Liu, H., Chen, J., Du, G., Chen, J., 2008. Enhancement of solubilisation and acidification of waste activated sludge by pre-treatment. Waste Manage. 28, 2614–2622.

Minervini, D., 2008. The Potential of Ultrasound Treatment for Sludge Reduction. PhD thesis. Cranfield University, UK. https://dspace.lib.cranfield.ac.uk/bitstream/1826/4085/1/Minervini_Thesis_2008.pdf (accessed 24.04.13.).

Neyens, E., Baeyens, J., Weemas, M., De Heyder, B., 2003. Hot acid hydrolysis as a potential treatment of thickened sewage sludge. J. Hazard. Mater. 98 (1–3), 275–293.

Nickel, K., Neis, U., 2007. Ultrasonic disintegration of biosolids for improved biodegradation. Ultrason. Sonochem. 14, 450–455.

Pilli, S., Bhunia, P., Yan, S., LeBlanc, R.J., Tyagi, R.D., Surampalli, R.Y., 2011. Ultrasonic pretreatment of sludge: a review. Ultrason. Sonochem. 18, 1–18.

Show, K.Y., Mao, T., Lee, D.J., 2007. Optimization of sludge disruption by sonication. Water Res. 41, 4741–4747.

Thompson, L.H., Doraiswamy, L.K., 1999. Sonochemistry: science and engineering. Ind. Eng. Chem. Res. 38, 1215–1249.

Valo, A., Carrère, H., Delgenès, J.P., 2004. Thermal, chemical and thermo-chemical pretreatment of waste activated sludge for anaerobic digestion. J. Chem. Technol. Biotechnol. 79 (11), 1197–1203.

Woodard, S.E., Wukash, R.F., 1994. A hydrolysis/thickening/filtration process for the treatment of waste activated sludge. Water Sci. Technol. 30 (3), 29–38.

ABSTRACT

The objective of this work is to optimize high-power low-frequency sonication (*US*) pretreatment of sludge, and especially to investigate for the first time possible improvements by higher pressure and audible frequency. After a preliminary examination of regular process conditions (sludge conditioning, sludge type, prior alkalization, temperature control, *etc.*), effects of US parameters (power -P_{US}, intensity -I_{US}, specific energy input -*ES*, frequency -*FS*, *etc.*) and of hydrostatic pressure (P_h) were specifically looked into, separately and in combination, first under cooling at constant temperature (28°C), then under the progressive temperature rise provoked by sonication.

First, it was confirmed that specific energy input (*ES*) plays a key role in sludge *US* disintegration (*i.e.* solubilisation of organic matter) and that temperature rise during adiabatic-like sonication is beneficial through additional effects of thermal hydrolysis and cavitation. At a given *ES* value, low *FS* (12 kHz *vs.* 20 kHz) and high P_{US} enhance soluble chemical oxygen demand (*SCOD*) due to more violent cavitation, while hydrostatic pressure gives rise to an optimum value due to its opposite effects on cavitation threshold and intensity. One major result is that optimal pressure depends on I_{US} (P_{US}) as well as temperature profile, but not on *ES*, F_S, nor sludge type.

Setting the other parameters at the most favorable conditions expected, *i.e.* 12 kHz, 360 W, 28 g_{TS}/L, and adiabatic conditions, final optimization was achieved by searching for this pressure optimum and examining sequential procedure to avoid too high temperature dampening cavitation intensity and damaging the transducer. Such conditions with sequential mode and P_h of 3.25 bar being selected succeeded in achieving very high *SCOD*, but only marginally improved subsequent methanization yield.

Keywords : Ultrasonic pretreatment; Audible frequency; Hydrostatic pressure; Municipal sludge disintegration; Soluble chemical oxygen demand; Particle size distribution

RESUME

L'objectif de ce travail est d'optimiser le prétraitement de boues par des ultrasons de puissance (*US*) à basses fréquences, et en particulier d'étudier pour la première fois des améliorations possibles en modifiant la pression hydrostatique, et la fréquence jusqu'à l'audible. Après un examen préliminaire des conditions du procédé (conditionnement des boues, type de boues, alcalinisation préalable, contrôle de la température), les effets des paramètres ultrasonores (puissance, intensité, énergie spécifique, fréquence) et de la pression hydrostatique ont été spécifiquement étudiés, séparément et simultanément, d'abord à température constante (28°C), puis sans refroidissement.

On a ainsi vérifié que l'énergie spécifique joue un rôle clé dans la désintégration des boues sous *US* (*i.e.* solubilisation de la matière organique) et que l'élévation de température pendant la sonication adiabatique est bénéfique grâce aux effets combinés d'hydrolyse thermique et de cavitation. Pour une énergie spécifique donnée, une faible fréquence (12 kHz contre 20 kHz) et une haute puissance améliorent la solubilisation de la matière organique grâce à une cavitation plus violente, tandis qu'on observe un optimum de pression hydrostatique en raison de ses effets opposés sur le seuil et l'intensité de la cavitation. Un résultat important est que la pression optimale dépend de l'intensité ultrasonore et du profil de température, mais pas de l'énergie spécifique, ni de la fréquence, ni du type de boues.

Après avoir fixé les conditions les plus favorables (soit 12 kHz, 360 W, 28 gTS/L et conditions adiabatiques), l'optimisation finale a fourni la pression de travail (3,25 bar) et les paramètres du mode séquentiel (*US* ON/OFF, permettant d'éviter de hautes températures qui amortissement l'intensité de la cavitation et peuvent endommager le transducteur). Ces conditions ont permis d'atteindre un rendement d'extraction de la *DCO* très élevé, mais n'améliorent que faiblement le rendement ultérieur de méthanisation.

Mots-clés : Prétraitement ultrasons ; Fréquence audible ; Pression hydrostatique; Désintégration des boues municipales; DCO dissoute ; Distribution de taille des particules