2

Ultrasound Pretreatment of Sludge for Anaerobic Digestion

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CONTENTS

Abstract Ultrasound pretreatment of sludge has been examined in an effort to improve the hydrolysis rate in anaerobic digestion. The reactions that resulted from the generation and collapse of cavitation bubbles produced under the acoustic condition can significantly modify the substances present in the sludge. The principles of ultrasound that encompass acoustic cavitation and bubble dynamics, the mechanisms of biological damage and effects, the industrial applications of ultrasound, and the specific applications of ultrasound in environmental engineering are presented.

1. INTRODUCTION

Sewage sludge is an unavoidable byproduct of wastewater treatment. Raw sludge is rich not only in organic carbon and pathogens but also in heavy metals and other environmental pollutants. Therefore, the sludge must be stabilized to enable an environmentally safe disposal or utilization. Anaerobic digestion is the most commonly applied process for the stabilization of sewage sludge.

There are many positive features of anaerobic treatment, for example, mass reduction, stable products, and improved dewatering properties of the fermented sludge. Anaerobic digestion is particularly unique among several sludge stabilization methods, because it has

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the ability to produce a net energy gain in the form of methane gas, leading to optimized cost effectiveness.

However, a main drawback of anaerobic digestion is its slow biological degradation rate, which results in a long fermentation period. A retention time of more than 20 days and the construction of huge digesters are usually necessary for degradation in an anaerobic process. Moreover, because of the low concentration of soluble organic matter contained in sludge, only 30–50% of the total COD or volatile solids (VS) can be degraded in very long time (1). The process of rapid industrialization and urbanization has dramatically increased the volume of sludge quantity generated. Hence, there is an urgent need to shorten the digestion period and enhance the degradation efficiency of anaerobic digestion.

The slow, rate-limiting hydrolysis process is the first step of anaerobic digestion. Extensive studies have explored ways to accelerate and enhance the performance of anaerobic digestion. The pretreatment process may include thermal pretreatment, high pressure homogenization, enzyme treatment, chemical solubilization by alkali, acid or base addition, mechanical disintegration, and ultrasound treatment. Among these processes, ultrasonication exhibits a greater potential of not being hazardous to the environment and is economically competitive.

Ultrasonic disintegration is a well-known method for breaking up microbial cells to release intracellular materials (2). Ultrasonic cavitation occurs more readily at a frequency of 20–40 kHz (3). During the sonication stage, some portion of the insoluble particulate organic matter can be transformed into a soluble state (1, 4). More than 100% increase of the maximum biological degradation rate had been achieved by ultrasonic transduction with an optimum intensity of 1.5 W/l at 25 kHz (5). The subsequent anaerobic digestion of the ultrasonically disrupted sludge may improve biogas production with a reduced sludge quantity that is vital to the economic consideration of a plant (6).

Various pretreatments of sludge have been studied in an effort to improve the hydrolysis rate. To enable a good understanding of the status of ultrasound treatment of sludge, Sect. 2 discusses other pretreatment methods including thermal, chemical, mechanical, enzyme, and irradiation.

Ultrasound generates high acoustic energy, and when this energy is applied to a liquid system, it is possible to generate physical and chemical reactions that can significantly modify the character of dissolved and particulate substances present in the liquid. These reactions result from the generation and collapse of cavitation bubbles produced under this acoustic condition. The principles of ultrasound encompass acoustic cavitation; bubble dynamics are presented in Sect. 3.

Section 4 focuses on the chemical and biological effects of ultrasound. The mechanisms of biological damage and effects are also described in this section.

Industrial applications of ultrasound are well established. With its many uses in automotive, electronic, optical, semiconductor, biomedical, and other industries, the use of ultrasound has become indispensable to modern manufacturing. Section 5 addresses the industrial applications of ultrasound, as well as its process parameters.

Section 6 discusses specific applications of ultrasound in environmental engineering with special emphasis on applications for wastewater treatment and anaerobic digestion.

2. PRETREATMENT OF SLUDGE FOR ANAEROBIC DIGESTION

2.1. Anaerobic Digestion

Anaerobic digestion is the most popular technique for wastewater sludge stabilization that results in the reduction of sludge volatile solids and the production of biogas. There are many positive features of anaerobic treatment: generated methane can be utilized as fuel; digestion has a low energy requirement; the pathogenic microorganisms in sludge are effectively killed; attention to operation is minimized; seasonal treatment is optimized; and the digested sludge is stable and may be disposed of harmlessly. However, since anaerobic stabilization is a very slow process, a long residence duration and large fermenter volumes are required.

Anaerobic fermentation converts organic materials biologically to methane and carbon dioxide in an environment devoid of oxygen. Anaerobic digestion of complex organic substances is usually considered to be a three-stage process consisting of hydrolysis, acidogenesis, and methanogenesis (Fig. 2.1).

Anaerobic digestion starts with the complex organic substances, which must initially be hydrolyzed to soluble organics of lower molecular weight. The first stage is the hydrolysis of long-chain complex organics, such as carbohydrates, proteins, and fats, to simpler molecules. Hydrolysis is a rather slow process and has been identified as the rate-limiting step. Complex organics are catalyzed by extracellular enzymes such as amylases, proteinases, lipases, and nucleases. Carbohydrates and proteins are hydrolyzed to simple sugars and amino acids, respectively. Fats are hydrolyzed to glycerol and long-chain fatty acids. These lower molecular weight organic compounds are then used by the acid formers to produce simple volatile fatty acids.

In the second stage, organic materials are converted into simple volatile fatty acids by a group of facultative and obligate anaerobes commonly termed as "acid formers". The products of this second-stage acidogenic conversion comprise predominantly organic fatty acids, and a small portion of biological cells. Although no waste stabilization is brought about during this stage of treatment, it is normally considered as an intermediate reaction to prepare the organic matter in a form amenable for the third stage of treatment. It is in the methanogenesis stage of treatment that actual waste stabilization occurs. The organic acids produced by the acid formers are converted by a unique group of microorganisms identified as "methane formers" into gaseous end products consisting of carbon dioxide, methane, and cells.

Even after some decades of optimization, a retention time of more than 20 days and the construction of huge digesters are usually necessary for efficient degradation in an anaerobic process. Nevertheless, the highest degree of degradation could be reached in an amount to about 40% for excess sludges (7).

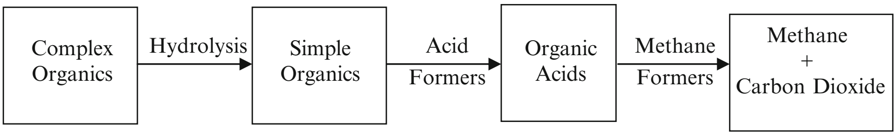

Fig. 2.1. Three-stage process of anaerobic digestion.

Hydrolysis is a slow stage that limits the speed of the entire process and leads to poor degradation results. Acceleration and better performance of the anaerobic process could be achieved by finding an alternative to the slow and rate-determining hydrolysis of the sludge. With increasing solubilization of the organic substances, more volatile solids become biodegradable. Thus, the efficiency of anaerobic digestion can be greatly enhanced by improving the rate of hydrolysis step by using physical and/or chemical pretreatment processes (8).

2.2. *Methods of Pretreatment*

Various pretreatments of sludge have been studied to improve the hydrolysis rate. These pretreatments led to rupture of the cell walls and membranes of bacteria in sludge, resulting in the release of organic substances outside of the cell. These organic substances can easily be hydrolyzed to their unit molecules by extracellular enzymes of anaerobic microbial origin, leading to an improved anaerobic digestion. The main methods of pretreatment are given below.

2.2.1. *Thermal Treatment*

Thermal treatment was first developed to improve the dewaterability of sewage sludge. The treatment is carried out through pasteurization by injecting steam at a temperature of 120–175°C with approximately 1×10^5 Pa pressure into a holding tank, mixing with the sludge, and raising the bulk suspension temperature to 70°C for 30 min. The thermal treatment at a temperature of 170–175°C breaks down the cells of microorganisms in the sludge into soluble organic matters, thereby improving the efficiency of anaerobic digestion and methane production (9).

Heating the sludge to above 150°C for 30 min would cause the breakdown of cell walls and the possible conversion of organics into more readily digestible forms. Experiments have indicated that a significant fraction of the volatile solids was liquefied following thermal treatment, and note an increase in gas production of approximately 34%. However, an acclimatization period was necessary for the digesters, and the quality of the supernatant liquors (in terms of the COD) was affected. Furthermore, this process requires more electrical energy than mechanical processes (10).

2.2.2. *Chemical Treatment*

The chemical treatment of sludge may be accomplished by using ozone, alkali, or acid treatment as discussed in the following sections.

2.2.2.1. OZONATION

The degree of biodegradability of the organic matter can be raised by partially oxidizing digested sludge with ozone (11). The objective is to apply additional treatment methods to these refractory sludge components, which cannot be disintegrated in either the one-stage or two-stage anaerobic degradation process. The refractory sludge components will then be partially oxidized either with ozone or with ozone in combination with hydrogen peroxide, which will lead to more complete degradation (12). Ozonation is not suitable for aerobic digestion due to nitrification and other problems.

2.2.2.2. ALKALI

The alkaline pretreatment may be used to hydrolyze and decompose lipids, hydrocarbon, and protein into smaller soluble substances such as aliphatic acids, polysaccharides, and amino acids (1).

The alkali treatment yields a significant reduction in microbial density and the release of COD from the sludge body, especially at pH ≥ 10. Lime and sodium hydroxide may be used for alkaline pretreatment of sludge to improve the solubilization efficiency of sludge. Lime treatment involves the addition of either CaO or $Ca(OH)_2$ in order to raise the pH to values of 11 or higher to kill off pathogens. However, the high pH environment may enhance the undesirable volatilization rate of ammonia, and the additional chemicals will increase the volume of the final product (1).

2.2.2.3. ACIDS

Acidification using low pH decreases the large floc size, resulting in better filterability. Nonalkaline chemicals, including either bactericides or oxidants, are seldom used because of their high cost.

Jean et al. (13) observed that adjustment of pH value for 2 h could disinfect the microorganisms in the sewage sludge by using total coliform bacteria as microbial indices. Microscopic observation revealed that in acidic conditions, the sludge floc retained its large shape and structure.

Chemical pretreatment methods have demonstrated the ability to improve the solubilization efficiency of sludge. However, the addition of inorganic chemicals has been shown to increase the volume of sludge, hence increasing the final waste volume. When acid or alkali is used, the salinity of the sludge will also be affected, thus possibly causing problems in sludge disposal (14).

2.2.3. Mechanical Treatment

Mechanical disintegration is a well-known process for obtaining intracellular products such as proteins or enzymes in biotechnological applications (15). Even for short grinding times, significant reduction of the mean particle size and an increase in surface area of the sludge was observed, because the floc structure of the sludge had been destroyed (12). The mechanical disintegration of sewage sludge destroys the floc structure of sludge and disrupts the cell walls of the microorganisms. Intracellular components are made immediately available for biological degradation, which leads to an acceleration of the process. Facultative anaerobic microorganisms are disrupted as well and become degradable, resulting in a higher degree of degradation.

However, mechanical disintegration needs high energy input. The investment for the disintegration aggregates has to be seen in relation to the reduction of digester volume and digestion time needed.

2.2.3.1. HIGH-PRESSURE HOMOGENIZATION

High-pressure treatment degrades sludge by utilizing the high shear stress produced when the sludge is released to the atmosphere. High-pressure homogenization is the most widely known method for large-scale operations. Sludge is compressed to approximately 60 MPa and then released from the compressor through a valve at a high speed, shooting onto an impaction ring. Cell disintegration of 85% can be achieved (16).

2.2.3.2. STIRRED BALL MILLS

Ball-mills generate high shear stress by grinding beads to break the cell walls. The best result can be obtained when using the stirred ball mill for long grinding times, at high agitator speeds and with small particle sizes of the grinding beads (12).

2.2.4. Enzyme Treatment

The application of enzymes for the treatment of primary sludge with a high content of lignocellulosic material seems to be the most appropriate method. The use of enzymes can increase degradation; however, it is an expensive technique that produces a strong odor (17).

2.2.5. Irradiation Treatment

Irradiation can be generated directly by ionizing particles or indirectly by ionizing electromagnetic radiation obtained from radionuclide sources. Bacterial cells' structures are influenced by both the direct and indirect action of ionization products, disrupting the DNA and cell division. Viruses can be damaged by chain capture of the nucleic acid (18).

Irradiation treatment can substantially increase the concentrations of soluble organic matter. A significant improvement was seen in a 10-day-long biogas production study at a thermophilic temperature over the first 8 h (19).

However, the results of irradiation have not proven to be reproducible under the variety of conditions encountered in wastewater treatment plants, and energy costs have made it generally prohibitive.

3. FUNDAMENTAL OF ULTRASOUND

3.1. Introduction

Ultrasound is the term that is used to describe sound energy at frequencies above 20 kHz, i.e., above the range normally audible to human beings. Ultrasound is usually generated by a transducer, which converts mechanical or electrical energy into high-frequency vibrations. Ultrasound energy can be delivered into a fluid system via a horn or probe.

Sound is composed of longitudinal waves comprising rarefaction (negative pressures) and compressions (positive pressures). It is these alternating cycles of compression and rarefaction that, in high-power ultrasound applications, can produce a phenomenon known as cavitation. A broad range of frequencies and acoustic intensities can be generated by ultrasound. If high acoustic energy is applied to a liquid system, it is possible to generate physical and chemical reactions that can significantly modify the character of dissolved and particulate substances present in the liquid. These reactions result from the generation and collapse of cavitation bubbles, which are produced under this acoustic condition (20).

3.2. *Acoustic Cavitation*

3.2.1. Generation of Cavitation

Cavitation is the formation, growth, and collapse through implosion of microbubbles. These bubbles can be either gas or vapor filled and form in a wide variety of liquids under a wide range of conditions. Cavitation occurs in water, organic solvents, biological fluids, liquid helium, and molten metals, as well as many other fluids. Cavitation can be initiated by either setting up a tension in the liquid or by depositing energy into it (20).

The first type of cavitation observed was the formation of bubbles in liquids supersaturated with gas. The rise of cavitation as a topic for scientific research began with the development of high-powered and high-rpm steam turbines in the mid 1800s (21).

Tension appears in fluid flow, such as with ship propellers, hydrofoils, pipes, and pumps. The local deposition of energy is brought about by heat transfer in pipes or by dumping hot bodies into liquids (giving rise to eventually explosive bubble growth). It should be noted that this review is only relevant to the cavitation generated in sound fields (3).

Cavitation is accompanied by a number of effects having their origin in the dynamics of the bubbles generated. Cavitation bubbles tend to collapse extremely fast, emitting shock waves and even light (sonoluminescence). They erode solid surfaces and induce chemical reactions (21).

3.2.2. Two Types of Cavitation

Cavitation has been traditionally classified as one of two types: transient and stable. Transient cavitation involves large-scale variations in the bubble size (relative to its equilibrium size) over a time scale of a few acoustic cycles. This rapid growth usually terminates in a collapse of varying degrees of violence. Stable cavitation, on the other hand, usually involves small-amplitude (compared to the bubble radius) oscillations about an equilibrium radius. Stable cavitation in most instances results in little appreciable bubble growth over a time scale of thousands of acoustic cycles. This classification of cavitation is not strict, however. Stable cavitation can lead to transient cavitation, and the collapse of a transient cavity can produce smaller bubbles that undergo stable cavitation (3).

3.2.3. Acoustic Cavitation Conditions

When high acoustic intensities are applied, particularly in the low and mid frequency range, gas bubbles are generated that will grow by taking in gas and vapor from the liquid. These bubbles change in size in relation to the acoustic wave and can collapse in the compression cycle (implosion), with the final implosion in microseconds. This is called acoustic cavitation. At the implosion of the bubbles, extreme temperatures (5,000 K) and high pressures (500 bars) exist in the gaseous phase (22).

The bubble implosions produce short-lived (lasting micro-seconds) “hot spots” in the liquid, which can release sufficient energy to drive a variety of chemical reactions (23). The cavitation effect is influenced by a number of factors:

- Liquid temperature (it is likely to occur at higher temperatures)
- Viscosity

- Surface tension
- Ultrasonic intensity (often referred to as the acoustic energy density)
- Frequency of ultrasound vibration (usually set at 20–40 kHz)

The minimum amount of energy required to initiate cavitation is referred to as the cavitation threshold, and this varies for different fluids. Only the energy applied above the threshold will contribute to the formation of a cavitation bubble. In water, cavitation will generally occur once the ultrasonic energy rises above 1 W/cm^3 levels (23).

It is difficult to create cavitation beyond 1 MHz because the acoustic intensity that needs to be applied increases with increasing frequency. At frequencies greater than 1 MHz, the acoustic wave's impact on the liquid creates microcurrents together with stable, oscillating gas bubbles. These do not collapse, and may occasionally rise to the surface of the water body (22).

3.2.4. *Effects of Acoustic Cavitation*

Acoustic cavitation can affect a liquid through two possible avenues. The first is the bubble itself. The liquid is disrupted by the inhomogeneous presence of the bubbles. The second avenue through which cavitation affects a liquid interface continually changes shape and size; liquid molecules diffuse into and out of the bubble; the concentration of gas in the surrounding liquid varies; acoustic streaming occurs in the liquid in the vicinity of the bubble, often resulting in severe shear stresses; the interior pressure and temperature fluctuate rapidly; the bubble radiates acoustic energy as it oscillates; and thermal and viscous damping hinder the bubble oscillations (21).

3.3. *Bubble Dynamics*

3.3.1. *Formation of Bubbles*

Cavitation bubble collapse occurs when the expanding bubbles have reached their resonant radius. The resonant cavitation bubble radius is a function of the ultrasound frequency. In pure water and low surface tension, it can be calculated by the following equation:

$$\rho\omega_{\mathrm{r}}^{2}R_{\mathrm{r}}^{2} = 3\gamma P_{\mathrm{o}}, \tag{1}$$

where ρ is the density of water, ω_{r} is the resonance angular frequency, R_{r} is the resonant bubble radius, P_{o} is the pressure exerted on the liquid, and γ is the ratio of the specific heats of gases. γ correlates to the heat released upon gas compression (24) and varies from 1.66 to 1.4 and 1.33 for monoatomic, diatomic, and triatomic gases, respectively.

Taking the case of air bubbles in water at atmospheric pressure, the ultrasonic cavitation bubble radius can be approximated as

$$R_r \approx 3.28 f_{\mathrm{r}}^{-1}, \tag{2}$$

where the resonant bubble radius R_{r} is expressed in millimeters and f_{r} is the resonance frequency in kilohertz (25). The bubble radius is inversely proportional to the ultrasound frequency. The application of low frequencies creates larger cavitation bubbles. Upon bubble collapse, hard mechanical jet streams are produced that are responsible for many cavitation effects observed on solid surfaces.

3.3.2. *Jet Formation*

When a bubble is collapsing in a spherically asymmetric environment, the collapse changes in a remarkable way: a flat solid surface nearby causes the bubble to involute from the top (surface below the bubble) and develop a high-speed liquid jet towards the solid surface. When the jet hits the opposite bubble wall from inside, it pushes the bubble wall ahead, causing a funnel shaped protrusion (21).

3.3.3. *Sonoluminescence*

When a cavitation bubble field is observed in total darkness after allowing the eyes to adjust after 15–20 min, light can be seen emanating from the liquid, often in the form of filaments. Since the primary input is sound, the phenomenon is called sonoluminescence (21).

4. EFFECTS OF ULTRASOUND

4.1. Chemical Effects

As mentioned previously, acoustic cavitation generates extreme temperatures and high pressures in the gaseous phase. These dramatic conditions lead to pronounced chemical reactions with the application of ultrasound. These reactions are caused by the creation of highly reactive radicals ($H^\bullet$, $OH^\bullet$) and thermal breakdown of substances (pyrolysis), which mainly belong to the field of sonochemical reactions.

The principal products from the ultrasonic irradiation of water are H_2O_2 and H_2, and various data support the hypothesis of the intermediacy of hydroxyl radicals and hydrogen atoms, which was first reported by Neis (7).

$$2H_2O \xrightarrow{\text{Ultrasound}} 2OH^\bullet + 2H^\bullet \rightarrow H_2O_2 + H_2 \tag{3}$$

The wide range of oxidations and reductions that occurs with aqueous sonochemistry is often a consequence of secondary reactions of these high energy intermediates.

4.2. Biological Effects

4.2.1. *Mechanisms of Biological Damage*

Cavitation phenomena may cause damage to biological materials in several important ways. Transient cavitation generates very high pressures and temperatures, which theoretically can reach thousands of bars and degrees Kelvin, respectively, during the final stages of the collapse. The high-pressure shockwave that emanates from the location of the bubble is capable of causing mechanical damage to surrounding material. In cases where the bubble is adjacent to a solid surface, a high-velocity liquid jet may shoot through the bubble, impacting and damaging the cell walls. High temperatures can cause bond dissociations in molecules, producing free radicals that can react with biomolecular species in much the same way as those produced by ionizing radiations (26).

The inhomogeneous cyclic field established around stably oscillating bubbles can cause a steady flow of the fluid medium surrounding the bubble in a process known as microstreaming.

If streaming velocities are great enough, shear stresses resulting from the decreasing velocity with distance from the bubble can be sufficient to damage microbial cells (27).

It is quite clear that acoustic cavitation is the primary mechanism for the production of biological effects in most solutions, suspensions, plants, and insects. Some of these effects occur at levels lower than used clinically. It has also been demonstrated that cavitation nuclei exist in mammals and that 10-μm and larger bubbles are developed during sonication at low therapeutic levels (3).

4.2.2. *Bioeffects of Ultrasound*

If stabilized bodies of undissolved gas are present in tissues, ultrasound exposure may produce damage at relatively low values of acoustic intensity or pressure.

Carstensen et al. (28) found that exposure of plant roots to ultrasound caused reduction of growth. The reduction was most significant at a frequency of 1 and 2 MHz; subharmonic and noise signals were emitted from the tissue when the intensity was above $3\,\mathrm{W/cm^2}$. The growth reduction was much less when the tissue was under 20 atm hydrostatic pressure during exposure to ultrasound.

With the development of various aspects of acoustic cavitation, acoustic radiation forces, and acoustic streaming, ultrasound is a proven application in biological and medical techniques, such as sterilization, cell disruption, dental descaling, angioplasty, extracorporeal lithotripsy, fibrinolysis, sonoporation, and treatment of Meniere's disease (29).

5. INDUSTRIAL ULTRASOUND APPLICATIONS

Ultrasound is a widely applied technique with a brilliant future. As a form of mechanical energy, its application to matter under the right circumstances can result in permanent physical changes. Because energy is a product of power and time, for a given power, the length of ultrasound exposure determines the total energy input into the material treated, which normally bears some relationship to the desired result. By definition, ultrasound pertains to frequencies above human hearing (approximately 18 kHz). Most practical applications to date have been in the lower ultrasonic spectrum, between 20 and 60 kHz.

5.1. Process Parameters

In general, power ultrasound is characterized by an ability to transmit substantial amounts of mechanical power at small mechanical movements. Ultrasonic motional amplitude is limited by the allowable stress in the ultrasonic transducer material and is dependent on frequency. To demonstrate typical values, a 20-kHz transducer operating at peak displacement amplitude of 50 μm has a peak velocity of 6.28 m/s and a peak acceleration of 8×10^4 g. The power ultrasound is characterized by high vibrational frequencies, small displacements, moderate point velocities, and extremely high acceleration (21).

Most macrosonic applications depend on compound acoustic phenomena occurring in matter, which in turn are caused by primary vibratory inputs. Thus, acoustic pressure causes cavitation and microstreaming in liquids; vibratory stress causes heating and fatiguing in solids; and ultrasonic acceleration is responsible for surface instability occurring at liquid–liquid and liquid–gas interfaces (30).

5.2. Industrial Applications

The use of power ultrasound in industry has become well established. With its many uses in automotive, electronic, optical, semiconductor, biomedical, and other industries, power ultrasound has become indispensable to modern manufacturing.

5.2.1. Applications in Liquids

The applications of ultrasound in liquid include cleaning, soldering, deburring, erosion testing, cell disruption, extraction from plants, emulsification, dispersion of solids, sterilization, filtration, inhalation therapy, fuel atomization, drying of textiles, crystal growth, metal grain refinement, degassing, and medical surgery (21).

5.2.2. Applications in Solids

The aspects of ultrasound applications in solids include plastic welding, metal welding, metal forming, impact grinding, rotary abrasive, machining, metal cutting, fatigue testing, curing, trimming of composites, and dental descaling (21).

6. ULTRASONICATION FOR ENVIRONMENTAL ENGINEERING APPLICATIONS

While ultrasound has been used routinely for many years in fields such as medical diagnosis, cleaning, and others, the application of ultrasound technology in environmental engineering is still in its earliest phase, with only the first applications operational at a technical scale. While ultrasound shows great potential in environmental engineering, a number of scientific and technical questions exist, which include the influence of frequency, dissolved gases, and suspended solids on cavitation; optimal reactor design; economy, reliability, and life expectation of ultrasound equipment. Table 2.1 provides an overview of current ultrasound applications in water, wastewater, and sludge systems.

Table 2.1
Ultrasound applications in environmental engineering (7)

Domain	Objective
Potable water	Inactivate bacteria (disinfection) Improve separation of solids Remove encrustations in pipes and wells
Wastewater	Sonochemical pollutant degradation Improve biological degradation
Sludge	Disintegrate biosolids Decompose bulking-activated sludge flocs to allow sedimentation Improve dewatering

6.1. Ultrasonication on Wastewater Treatment

The biological treatment of wastewaters is usually preferred because of its low cost compared to chemical or physicochemical processes. This holds true unless bacteriotoxic or refractory pollutants inhibit biological activity, as happens in many industrial liquid wastes. If this occurs, more expensive chemical or physical methods must be used.

Ultrasound treatment shows some similarity to advanced oxidation processes (ozone, H_2O_2, UV), in which OH radicals are produced by the sonolysis of H_2O. Mechanisms involved in sonochemical transformations are still misidentified. However, acoustic cavitation appeared early as the main phenomenon responsible for chemical transformations (7).

6.1.1. Reactions of Ultrasound on Wastewater Treatment

Several modes of reactivity have been proposed: pyrolytic decomposition, hydroxyl radical oxidation, plasma chemistry, and supercritical water oxidation.

The first one, pyrolytic decomposition, takes place inside the cavities and affects the vapor from the liquid medium or dissolved organic compounds, which may penetrate into the bubbles. Indeed, energy concentrated in the bubbles is sufficient to break strong chemical bonds. In aqueous solutions, the main pyrolytic reaction is the dissociation of water. This thermal dissociation leads to the production of highly reactive radicals ($OH^\bullet$, $H^\bullet$) inside the bubbles (31).

It seems that the ratio between hydroxyl radical oxidation and pyrolysis depends on the localization of the solute (in the bulk solution, inside the bubble, or in the interfacial layer) and, therefore, on its physicochemical properties. Henglein (32) pointed out that the main property determining the entrance of a compound into the bubble was its hydrophobicity rather than its vapor pressure. Thus, hydrophilous organic compounds such as phenol and chlorophenols may undergo a hydroxyl radical attack in the bulk solution or in the interfacial film.

Other more hydrophobic compounds such as carbon tetrachloride, benzene, and chlorobenzenes may be mainly pyrolyzed inside the bubble. However, some other cases remain for which the localization of degradation is more difficult or for which there seems to be competition between mechanisms. In conclusion, hydrophobic and volatile organic compounds are destroyed very easily, whereas nonvolatile and hydrophilous compounds are more difficult to oxidize by ultrasound.

The third mode of reactivity proposed is that of plasma chemistry. Lepoint and Mullie (33, 34) observed some similarities between coronaluminescence and sonoluminescence as well as between coronachemistry and sonochemistry. This led them to assimilate the ultrasound effects to corona plasmas inside the bubbles.

6.1.2. Types of Pollutants Treated by Ultrasound

It has been shown that a variety of wastewater pollutant can be degraded using ultrasound. Different types of chemical pollutants have been investigated, for instance, chlorinated solvents and aromatics, hydrocarbons, pesticides, phenols, and polymers. Ultrasound cavitation generates pyrolytic reactions and hydromechanical forces. In many cases, these processes are the dominant factors in the ultrasound degradation of pollutants. It has been demonstrated that the reaction mechanisms vary depending on the different physicochemical properties of a particular pollutant:

- Volatile pollutants are degraded preferentially by pyrolytic reactions, which occur in the vapor phase of the cavitation bubble.
- Hydrophobic pollutants accumulate and react in the hydrophobic boundary layer of the cavitation bubble. Concentrations of OH radicals and H_2O_2 in the boundary layer are significantly higher than in the surrounding liquid. Pyrolysis and radical reactions contribute to the degradation.
- Hydrophilic pollutants in the bulk liquid are degraded by reaction with free radicals or H_2O_2.
- Macromolecules and particles are also degraded by hydromechanical forces triggered by the collapse of the cavitation bubbles.

For practical studies and experiments, the results of different chemical pollutants in wastewater after ultrasound treatment are listed in Table 2.2.

Two major mechanisms are responsible for the degradation of pollutant: radical reactions and pyrolytic decomposition. Among all the ultrasound applications, wastewater treatment

Table 2.2
Degradation of solutions of different compounds

Compounds	Sonication conditions	Intermediate products identified	Reference
Phenols	20 and 487 kHz, 30 W, air, 0.5 mM	Hydroquinone, catechol, 2,5-dioxohexen-3-dioic acid, muconic, maleic, succinic, formic, propanoic, oxalic, and acetic acids	(41)
2-chlorophenol	20 and 541 kHz, 30 W, air, 100 mg/l	Chlorohydroquinone, catechol, 3-chlorocatechol, chlorides	(53)
3-chlorophenol	20 kHz, 50 W, air, 0.05 mM	Chlorohydroquinone, 3- and 4-chlorocatechol,	(53)
4-chlorophenol	20 kHz, 50 W, air, 0.05 mM	Hydroquinone, 4-chlororesorcinol, 4-chlorocatechol, chlorides	(53)
Pentachlorophenol	500 kHz, air, 0.1 mM	Chlorides	(41)
Parathion	20 kHz, 84 W, air 0.1 mM	*p*-nitrophenol, sulfates, phosphates, formic, oxalic, and acetic acids	(54)
Benzenes	20 and 487 kHz, 30 W, air, 0.5 mM	Phenol, catechol, hydroquinone, 1,2,3-trihydroxybenzene, maleic and muconic acids, formaldehyde, acetylene	(55)
Chlorobenzene	20 and 487 kHz, 30 W, air, Air, O_2, 0.5 mM	4-chlorophenol, 4-chlorocatechol, hydroquinone, acetylene	(55)
Chloroform	20 kHz, 200 W, air	–	(55)
Carbon tetrachloride+phenol	20 and 500 kHz, 30 W, air, phenol: 0.5 mM, CCl_4: 3.8 mM	Chlorides, 2-chlorophenol, 2,4-dichlorophenol, chlorobenzoquinone	(55)

appears to be an original and expanding field of study. This process is convenient and simple in terms of temperature, pressure (ambient conditions), and reagents (no reagents). But the energy consumption for total pollutant mineralization is very high. The ultrasonication process is therefore considered a preoxidation step.

6.2. *Ultrasonication on Anaerobic Digestion*

As introduced in the first chapter, anaerobic digestion is the most popular technique for sewage sludge stabilization resulting in the reduction of sludge volatile solids and the production of biogas. Anaerobic digestion is a slow process, and the rate-limiting step is the hydrolysis of particulate organic matter to soluble substances (8). It has been postulated that the extreme conditions produced during sonication, if applied to sewage sludge, will cause cell disruption/lysis and release the intracellular organics, thus enhancing the digestion process. In addition, the physical action produced by the cavitation bubbles can reduce the sludge particle size distribution, which potentially increases the number of sites available for microbial action.

Neis et al. (22) investigated the effect of ultrasound pretreatment on sludge degradability by testing the increase of COD and size reduction of sludge solids (Table 2.3). Semi-continuous fermentation experiments with disintegrated and untreated sludge were conducted for 4 months on a half-technical scale. The results indicated that the fermentation of disintegrated sludge remained stable even at the shortest residence time of 8 days, with biogas production of 2.2 times that of the control fermenter. In a subsequent study (35), sonicated waste-activated sludge remained stable over a digestion time of 4 days. The effects of ultrasound frequency on the disintegration were examined by varying the frequency within a range from

Table 2.3
Technical specifications of the sonoreactors

References	(7)	(36)	(1)	(23)	(56)	(13)
Digester volume	2,000 l	1,500 l	1 l	10 l	400 ml	–
Sonicator volume, l	1.280	–	1.000	10.000	0.100	–
Frequency, kHz	31	31	20	20–35	23	–
Number of transducers	48	–	–	–	–	–
Hydraulic retention time in digester, day	4–16	8–22	–	12–15	8–12	0
Hydraulic retention time in sonicator, s	64	64	14–24/ml	<60	90	1,200–7,200
Power consumption, W	3,600	3,600	120	9,000	47	–
Acoustic intensity, $\mathrm{W/cm^2}$	5–18	–	–	–	–	–
Acoustic power density, $\mathrm{W/cm^3}$	2.2–7.9	–	–	–	–	0.11–0.33
Digestion temperature, °C	37	37	30–36	35	–	–
Duration, month	–	4	–	12	–	–

41 to 3,217 kHz, and the impact of different ultrasound intensities and treatment times on anaerobic digestion were also examined. Pilot-scale investigations conducted by Tiehm et al. (36) reported acceleration in anaerobic digestion of ultrasonically pretreated raw sludge.

Chiu et al. (1) investigated the use of alkaline treatment combined with ultrasound treatment for enhancing recovery of volatile fatty acid (VFA) from WAS digestion. They described the effects of ultrasound treatment on physical, chemical, and biological characteristics of waste-activated sludge. They also found a critical ultrasound power above which the floc structure was effectively disintegrated, microbial level acceptably disinfected, and particulate organic compounds sufficiently transformed into a soluble state. They also found that both ultrasonic vibration and bulk temperature rise contributed to the efficiency in treatment.

Clark and Nujjoo (23) studied the cell lysis and particle size reduction after ultrasound pretreatment. A series of laboratory-scale anaerobic digesters were operated, and following ultrasonication, significant increases in biogas yield were noted. The experiments utilized a variety of ultrasonic devices (of different geometries and construction materials) and sludge types.

Jean et al. (13) investigated the effects of ultrasound and pH values on the microbial density level in sewage sludge by using total coliform and heterotropic-plate-count (HPC) bacteria. It was observed that sonication at a higher intensity produces a smaller floc size in a shorter time. A high pH was observed to break up large flocs into smaller aggregates.

Suslick (37) reported that ultrasound of high acoustic intensities causes cavitation in water bodies when the energy forces applied exceeded the binding energy of the molecular attractive forces.

Bien and Wolny (38) observed that the effect of ultrasonic treatment on sewage sludge depends on the kind of sludge and chemical compounds used in the dewatering process. The sludge was dewatered on a vacuum filter after conditioning with polyelectrolytes and the ultrasound field.

6.2.1. Reactions of Ultrasound Pretreatment

Based on the previous studies, several factors are thought to be responsible for the disintegration of sludge with ultrasound treatment. These factors may be summarized as follows:

1. Sonochemical effects
2. High mechanical forces
3. Thermal breakdown of volatile hydrophobic substances

Through these processes, bacterial cells are disunited by pressure waves and cavitation generated from an ultrasonic generator, leading to elution of intracellular organic substances (39). The floc structure in sewage sludge is destroyed, and this increases the accessibility of hydrolytic bacteria to the released intracellular organic substances. This situation leads to greater efficiency during subsequent anaerobic digestion (40).

Inside the collapsing cavitation bubbles, the temperature and pressure can rise up to about 5,000 K and several hundred atmospheres. These extreme conditions can generate very reactive hydroxyl radicals ($H^\bullet$, $OH^\bullet$) (25, 30). In this way, sonochemical reactions can degrade volatile pollutants by pyrolytic processes inside the cavitation bubbles and nonvolatile pollutants by hydroxyl radical reactions in the bulk liquid (41, 42). While sonochemical degradation processes can occur in a broad ultrasound frequency ranging from 20 kHz to about 1 MHz, the highest efficiency of sonochemical reactions was observed at more than 100 kHz (24, 41).

Many studies show that mechanical forces are the key contributing factor to the ultrasonic disintegration of sewage sludge. As described by Neis (7), at the first impact of the acoustic wave, sludge flocs are separated and a large number of single cells are formed. While sonication continues, single bacteria cells may act as nuclei for the formation of bubbles. This might mean they are captured and ruptured in the cavitation bubbles that, during the rarefaction cycle, can grow up to 175 μm in diameter before collapsing. The violent collapse produces very powerful hydromechanical shear forces in the bulk liquid surrounding the bubble.

Mechanical forces are most effective at frequencies below 100 kHz, which is the same frequency range of the optimal disintegration achieved. It had been shown that macromolecules with a molar mass above 40,000 are disrupted by hydromechanical shear forces produced by ultrasonic cavitation (43). On the other hand, sonochemical processes, i.e., production of hydroxyl radicals, were most significant at frequencies between 200 and 1,000 kHz (44). Therefore, hydromechanical forces produced by ultrasonic cavitation are more important for sewage sludge disintegration than sonochemical processes.

6.2.2. Influencing Parameters

6.2.2.1. FREQUENCY

Sludge disintegration was most significant at low frequencies. Low-frequency ultrasound creates large cavitation bubbles that upon collapse initiate powerful jet streams exerting strong shear forces in the liquid. A decreased efficiency in sludge disintegration observed at higher frequencies was attributed to smaller cavitation bubbles that do not allow the initiation of such strong shear forces (35).

Theoretical considerations are useful for understanding the decrease in disintegration efficacy as ultrasound frequency increases. As depicted in Eq. (2) discussed previously, the resonant cavitation bubble radius is a function of ultrasound frequency. The bubble radius is inversely proportional to the ultrasound frequency. The application of low frequencies creates larger cavitation bubbles. Upon bubble collapse, hard mechanical jet streams are produced that are responsible for many cavitation effects observed on solid surfaces. A valid assumption might be that the energy released by a jet stream is a function of the bubble size at the moment of collapse. The number and size of cavitation bubbles in a sludge media may certainly be different to a pure water system due to the presence of a high number of solids, different density of the liquid, and the presence of dissolved gases. However, the degree of sludge disintegration could be related to the theoretical bubble size calculated by using this equation. Starting at a point where R is about 4 μm, the degree of cell disintegration increases proportionally to the logarithm of the bubble radius (35).

Comparing sonochemical efficiency at different frequencies is a complex problem because sonochemistry is associated with the bubble of cavitation. Formation and behavior of the bubble is closely linked to the sound pressure field, which depends on the reactor (design) and on the ultrasonic source (frequency, surface emitting area, intensity). In a reactor with a well-defined configuration, a modification of the ultrasonic frequency will change the local bubble population and may affect the yield of the reaction (45).

6.2.2.2. DURATION/TREATMENT TIME

Concentrations of organic substances in the supernatant, such as protein, carbohydrate, and COD, have been observed to increase proportionally with ultrasonic pretreatment time (40). Short sonication times resulted in sludge floc deagglomeration without the destruction of bacteria cells. Longer sonication brought about the breakup of cell walls, disintegration of sludge solids, and release of dissolved organic compounds to the liquid phase (35).

An optimum pretreatment time should exist in terms of efficiency and energy cost. Chu et al. (46) concluded that the ultrasonic treatment consists of several stages. At the first stage of sonication (0–20 min) at a power input exceeding the critical level, the porous floc could be readily deteriorated into compact flocculi, while the dewaterability of sludge was markedly deteriorated. In the second stage (20–60 min), although the floc size remained almost unchanged, both heterotrophic bacteria and total coliform were effectively disinfected. The soluble COD value increased, accompanied by a reduction in microbial density levels. In the final stage (60–120 min), if the bulk temperature was controlled, ultrasonic treatment had essentially no effect on the sludge characteristics. However, the raised bulk temperature of sludge could induce continuous transformation of solid-state organic compounds into a soluble form (46). Pretreatment longer than 30 min did not lead to continued extensive increases in methane generation (40).

6.2.2.3. ENERGY LEVEL (INTENSITY/DENSITY)

The degree of disintegration is amplified by an increased acoustic intensity in an applied range, which can be increased by more than twofold by an increase of the sound energy from 6 to 8 $\mathrm{W/cm^2}$ intensity. This is due to the higher mechanical shear forces produced at higher intensities, rupturing more microorganisms (7). Tests at 0.11 W/ml had almost no effects on the floc size. Only when the power level had exceeded 0.22 W/ml would the particle size apparently decrease (46). The cavitation threshold for water was reported to be about 0.4 $\mathrm{W/cm^2}$ by Lorimer (47). But Tiehm et al. (35) observed disintegration at a rather low intensity of 0.1 $\mathrm{W/cm^2}$. A lower cavitation threshold for sludge seems reasonable due to the presence of a high number of small particles and gas bubbles acting as cavitation nuclei.

Jean et al. (13) reported that the soluble COD increased by 12 times at the high-intensity level, but was almost unchanged at the low-intensity level. At a low ultrasonic intensity, the floc size and the heterotrophic-plate-count (HPC) bacteria level only mildly decreased, but the total coliform level markedly reduced after 40-min sonication. At a high intensity level, the total coliform and HPC density levels as well as the floc size were sufficiently reduced.

Neis (7) conducted a study to optimize the reduction of ultrasound energy input/degree of cell disintegration and anaerobic digestion time. Generating ultrasound waves with optimized pulsed signals reduced the power consumption considerably. While there may be other cases requiring longer treatment times, typically energy doses between 4 and 10 $\mathrm{kWh/m^3}$ should be sufficient.

6.2.3. *Ultrasonic Sludge Disintegration*

6.2.3.1. STRUCTURAL CHANGES

Gorczyca's floc formation model (48) consists of primary particles ($\approx 2\,\mu m$), compact flocculi and microflocs ($\approx 13\,\mu m$), and highly porous flocs ($\approx 100\,\mu m$). The mechanical forces generated by ultrasonic waves at 0.44 W/ml could disintegrate the highly porous floc into microflocs or flocculi and release some extracellular polymers (4). At a low intensity, the floc size decreased gradually from 31 to 20 μm in 60 min, that was 35% reduction in size, while in the high intensity test, the floc size reduced to its plateau value (14 μm) in less than 20 min (13).

Ultrasonic treatment has no effects on the surface charge of the suspended particles. However, as floc breakage occurs, the concentrations of Ca^{2+} and Mg^{2+} ions in the supernatant markedly increase. Calcium and magnesium ions are generally accepted as the essential components to bridge the constituent particles in a sludge floc (46, 49, 50).

6.2.3.2. COD/SCOD CHANGE

Ultrasound treatment of sewage sludge leads to a breakup of microbial cell walls. Intracellular compounds are released, resulting in an increase of COD in the aqueous phase (51). The quantity of bioavailable dissolved organic substrate measured as soluble COD is significantly increased and considerably accelerates the subsequent sludge degradation. Soluble COD was chosen as the marker analysis by a number of researchers to measure organic availability in sludge. The relationship between SCOD rise and sonication time has been reported to be linear (31).

Clark (23) observed that a significant increase in SCOD was also found in primary sludges after ultrasound pretreatment. When compared with secondary sludges, primary sludges contain relatively low levels of microbial biomass, i.e., cells. Thus, an increased SCOD is due to cavitation-induced cell lysis; otherwise, a small increase in SCOD would be expected.

6.2.3.3. BIOGAS

Enhanced degradation rates result in a significant increase of biogas production. Neis (7) found that the percent of methane in the biogas was always slightly higher in the fermenters operated with disintegrated sludge than in the control fermenters. Chemostat-fed sonicated sludges had 5–10% greater methane content than the untreated samples. The increase in specific methane production appears to be dependent upon the hydraulic retention time (HRT). At longer HRTs, the percentage increase in specific methane production was reduced (23). Different sludge samples have different characteristics that cause different gas production capacities. Adequate stirring of the reactor content and the maintenance of digestion temperature may ensure better digestion (6).

6.2.4. *Methods to Enhance Ultrasound Efficiency*

Ultrasound is a pressure wave that propagates through a medium with a vast amount of energy dissipation. Thus, reducing energy consumption and enhancing efficiency are critical for the application of ultrasound at full-scale wastewater treatment plants. It has been reported that the reduction of high concentrations of persistent organic pollutants, viz. hexachlorobenzene and phenanthrene, can be achieved through ultrasonication on contaminated soil slurry with moisture ratio in the range of 2:1–3:1 (57).

Using simultaneous ultrasonic and alkaline treatments, the pretreatment time for municipal waste-activated sludge can be greatly shortened, resulting in a high amount of SCOD released (1). Since the two methods rely on different mechanisms to solubilize particulate organic substances, a combination of the methods will take advantage of two mechanisms and achieve better efficiency.

It has been found that the joint activity of polyelectrolytes and ultrasound are particularly favorable for the reduction of sludge volume. The mechanism of this method may be explained by a partial dehydration, i.e., the removal of the water dipoles from some part of the particle surfaces in the solid phase. This gives rise to disturbances in the stability of the hydration layer, which is replaced by an orientation of polyelectrolyte macroparticles with long chains that simultaneously "bridge" several particles. As a result, this leads to an increased number of adsorbed molecules of the reagent at the particle surface and the flocculation of minute particles present in the suspension (52).

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