DISINTEGRATING SLUDGE AS CARBON SOURCE FOR DENITRIFICATION

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Abstract

Within the UK and Europe the needs for removal of the nutrients nitrogen and phosphorus, is driven by the requirements of the EC Urban Wastewater Treatment Directive. The majority of UK treatment plants have an ammonia consent imposed by the Environment Agency which requires them to achieve nitrification. It is standard design practice in such circumstances to install a denitrification zone to reduce the effluent nitrate concentration which is known to aid the settleability of the sludge. Both biological and chemical phosphorus removal is practiced in the UK and whereas not common, the number of plants that must achieve biological phosphorus removal is quickly increasing. This presents a challenge in the UK where wet winters generate a weak sewage that cannot provide adequate carbon to drive both denitrification and biological phosphorus removal. Then, a successful degradation process requires an additional carbon supply to be provided for the denitrification stage and this is the circumstance where methanol or another external carbon source is bought and added to the process for this purpose. Disintegration of the excess sludge with ultrasound breaks down the biomass and releases the cell content -ideal carbon carriers- which are then available as an internal source of carbon in the denitrification stage. Biological nitrogen degradation in the wastewater treatment plant can therefore be maintained or even intensified. If part of the sonicated sludge is returned to the aerobic phase, the quantity of sludge to be disposed of is automatically reduced and bulking and foaming problems are complete eliminated. This is the application where Ultrawaves aims to optimise the biological reactor through the transformation of a waste into a resource and through other collateral benefits as well. This paper pretends to be descriptive and tries to show a systemic outlook regarding this efficient and innovative solution.

Keywords

Ultrasound, denitrification, biomass, carbon carriers, excess sludge, nitrogen degradation, bulking and foaming.

Introduction

Continuous research and development has created Ultrawaves ultrasound technology new and revolutionary applications in aerobic processes. There has been a big effort to understand the best way to optimise a biological reactor with ultrasound which has now been reached through different applications. It is now possible the complete elimination of associated problems with bulking and foaming through a selective sonication of a very tiny amount of Returned Activated Sludge (RAS). In addition it is also possible to enhance a dramatic excess sludge reduction when

a partial thickened waste activated sludge (TWAS) flow is disintegrated and returned back to the biological reactor whenever a cell lysis and cryptic growth process is induced. Sonication causes cell lysis with the consequent solubilisation of cellular constituents which become substrate available for further biodegradation which in turn results in an overall reduction of the excess sludge production (Hamer and Mason 1987; Canales *et al*., 1994). The most recent and interesting application has been carried out in the biological nitrogen removal due to sonicated TWAS performs a very useful and autochthonous readily biodegradable carbon source to denitrify. When TWAS is sonicated and recycled back to the anoxic zone of the biological reactor is used then as carbon source to support denitrification and the facility transforms a waste into a resource with a subsequent saving in carbon source purchase and sludge disposal cost.

It has been demonstrated that low frequency ultrasound waves generate the cavitation necessary to produce mechanical shear forces associated with sludge disintegration. Combined with high intensity ultrasound, the cell aggregates as well as single cells are destroyed and enzymatic and intracellular material is released into the medium resulting in a higher degree of substrate bio-availability for the remaining living microorganisms. In effect, the enzymatic biological hydrolysis, which is the initial and rate limiting of the biological food chain, is substituted and catalysed by this mechanical disintegration of the sludge (Tiehm *et al*., 2001).

Increasing its bioavailability with Ultrawaves technology, disintegrated sludge can be used then as an internal electron donor (energy source) to fuel denitrification stage. Indeed Biological Nutrient Removal (BNR), which is considered as the most sustainable and efficient process to remove nutrients from wastewater needs a sufficient carbon concentration (Abu-ghararah and Randal 1991) to be successful which causes a constant carbon sources demand. Hence the addition of chemicals such as methanol or acetate to enhance BNR process is sometimes necessary but the associated costs are significant and the need to have chemical storage facilities on the site decreases its attractiveness. However through excess sludge disintegration the release of suitable electron donors can be promoted and this by way sludges are re-used decreasing the overall sludge production in a facility while the BNR efficiency is assured.

Requirements for denitrification

The necessary conditions for the denitrification stage to develop in an activated sludge process can be summarised as follows.

Presence of nitrate (or nitrite)
The presence of nitrate normally implies nitrification as prerequisite. Through this biological process (nitrification) free and saline ammonia is oxidized to nitrite and nitrate by specific autotrophic organisms with behavioural characteristics that differ significantly from the heterotrophic ones. A good nitrification process is absolutely necessary in order to carry out an efficient denitrification. Although it is not the target of this paper to describe in depth the factors influencing nitrification, a number of conditions or elements affect the nitrification rate constants, efficiency of nitrification and sludge age. These conditions are wastewater source,

temperature, pH, unaerated zones, dissolved oxygen concentration (DO) and cyclic flow and load.

Absence of dissolved oxygen
The inhibitory effect of DO on denitrification has been extensively reported in the literature. At zero dissolved oxygen level the nitrate removed was 100%, while at 0.2 mg/l no significant denitrification was obtained (Carlson 1972). However, in a completely mixed anoxic reactor, even if no measurable DO is present, any oxygen entering such a reactor will be used preferentially by the microorganisms, thereby a stoichiometric reduction of the nitrate the reactor can denitrify has to be considered. Possible sources of DO can be high DO concentrations in the recycles from the aerobic zones to the anoxic zones and also the entrainment into the anoxic reactor via the air-wet interface due to unnecessarily high mixing intensities.

Facultative bacterial mass
Facultative bacteria are characterised by the fact that they can use both oxygen and nitrate as an oxidant for organic matter. A large fraction of the bacterial mass that develops in an activated sludge process is facultative. Activated sludge generated under aerobic conditions will use nitrate immediately when it is placed in an anoxic environment. The rate of nitrate utilisation continues without change, as long as the anoxic condition and the availability of organic matter persist. The propensity to denitrify is widespread among facultative bacteria biomass. Dissimilative denitrification with end products N_2, NO and NO_2 has been established in many cases. The bulk of the bacterial mass in wastewater treatment is facultative and a significant fraction is capable to carry out a dissimilative denitrification. Recent studies on denitrification tend to support the view that there is little difference between the bacterial masses in processes where nitrification only or nitrification-denitrification takes place. There is little merit therefore in attempting to analyse the bacterial composition of the sludge detail. A sludge generated under aerobic condition when subjected to the appropriate environmental conditions, will show a denitrifying capability immediately and will continue to do so, subsequently without apparent change in reactivity.

Electron donor
The oxidation of carbonaceous compounds with nitrate as electron acceptor (denitrification) provides the energy required by the facultative heterotrophs bacteria for synthesis of new mass and endogenous respiration. The electron donor constitutes the source of the energy and this is precisely the axis where all biological denitrification researches revolve. Indeed the energy source which serves as the electron donor in the denitrification process has been deeply studied for a variety of substances as carbonaceous energy sources. They can be categorised as follows.

- Energy sources not present in the wastewater, i.e. an external carbon source (methanol, acetic acid, etc.) which is added to the denitrification stage.
- Energy sources present in the influent wastewater, i.e. an internal carbon source entering the system with the wastewater.

- Energy sources which are self-generated within the system by the release of nutrient by the organisms in the death phase. This is the point where the ultrasonic disintegration takes place due to the tremendous increase reached of the fraction readily biodegradable after the sludge disintegration.

The need to add a supplementary carbon source

A variety of denitrification and pre-denitrification processes have been developed through a modification of the conventional activated sludge process (anaerobic-aerobic-oxic, 4-stage Bardenpho, etc.). In these processes, the total nitrogen (TN) removal efficiency depends basically on the carbon/nitrogen ratio in the influent wastewater as well as the internal recycle ratio from the aerobic to anoxic zone. Recirculation practical limits cannot assure the TN elimination and an insufficient carbon/nitrogen ratio increases more the problem. Carbon-nitrogen ratio is specially damaged in wastewater treatment facilities with primary settlement due to this unitary process can remove up to 40% of the chemical oxygen demand (COD) but around 10 to 15% of nitrogen. This nitrogen is known as Total Kjeldahl Nitrogen (TKN) and represents the combination of organically bound nitrogen and free and saline ammonia.

The addition of external carbon sources for denitrification has become absolutely necessary for wastewater treatment plants to meet stringent effluent nitrogen limits. However the concerns regarding safety issues as well as the each time higher external carbon sources costs have motivated Ultrawaves to invest a lot of resources in order to bring an alternative to this practice.

In practice, it is possible to determine the supplementary carbon source to be added in many ways. First to consider is a nitrogen balance equation in order to obtain the nitrate to be removed:

$$S_{NO3,D} = C_{N,BRi} - S_{Norg,SSo} - S_{NH4,SSo} - S_{NO3,SSo} - X_{Norg,ES}$$

Each of the terms is defined in figure1.

Term	Symbol	Unit
Nitrate to be denitrified	$S_{NO3,D}$	mg/l
Total nitrogen at the entrance of the biological reactor	$C_{N,BRi}$	mg/l
Organic nitrogen after the secondary sedimentation	$S_{Norg,SSo}$	mg/l
Ammonia nitrogen after the secondary sedimentation	$S_{NH4,SSo}$	mg/l
Nitrate after the secondary sedimentation	$S_{NO3,SSo}$	mg/l
Nitrogen incorporated into the excess sludge	$X_{Norg,ES}$	mg/l

Figure 1: *Nitrogen balance terms, symbols and units.*

Next stage is to calculate the denitrification capacity which is referred to the BOD_5 (biological oxygen demand of the wastewater during decomposition occurring over a 5 day period) at the

entrance of the biological reactor and the nitrate to be denitrified. The rate between both is known as denitrification capacity

$$\text{Denitrification capacity} = \frac{S_{NO3,D}}{C_{BOD5,BR}}$$

Where $C_{BOD5,BR}$ is the concentration of BOD_5 at the entrance of the biological reactor. For models based in calculations in terms of the COD instead of the BOD_5, the relation is the same but considering $COD/BOD_5 = 2$ (Cortacans 2010). This is linked with the the denitrification fraction which is the volume of denitrification related to the volume of the biological reactor (V_D/V_R).

V_D/V_R	$S_{NO3,D}/C_{BOD5,BR}$ for pre-connected denitrification	$S_{NO3,D}/C_{BOD5,BR}$ for simultaneous and intermittent denitrification
0.2	0.11	0.06
0.3	0.13	0.09
0.4	0.14	0.12
0.5	0.15	0.15

Figure 2: *Dimensioning values for denitrification at Temperature of 10 to 12 degrees (ATV-131).*

Considering for instance a V_D/V_R of 0.5 that would allow a theoretical denitrification capacity of 0.15 kg of nitrate denitrified per kg of BOD_5 introduced in the biological reactor. If the denitrification capacity calculated in practice is higher than the theoretical, as often happens, an alternative carbon source has to be considered due to there are more nitrates to denitrify than BOD_5 allows. The difference between theoretical and practical denitrification capacities is the nitrates to denitrify with an external carbon source addition.

Suitable carbon sources to support denitrification

A variety of carbon sources can support denitrification step. The online fermentation of wastewater is able to increase the suitable carbon source, mainly in the form of volatile fatty acids (VFAs) by 25% (McCue *et al*., 2003). Likewise sludge fermentation can increase the available carbon and improve nutrient removal. Unfortunately, the application of these methods is not a straightforward procedure, since site enlargement is required and usually the fermenters are prepared for permanent use without being flexible to any modifications like flows, retention times, etc. In addition, nutrients are also released from sludge during the fermentation process, increasing the overall amount of nutrients that have to be removed.

When another carbon source in the form of methanol or acetic acid is used, an improvement in BNR performances takes place. However, important disadvantages have to be considered due to the addition of direct organic carbon sources (i.e. methanol) is acutely toxic and present severe handling difficulties. Moreover, price is relatively high and changes with the price of fossil fuels. Thus, finding good alternatives to methanol is a top priority in wastewater treatment facilities that use it as an external electron donor. Substituting another simple organic compound, such as acetate, is technically feasible, but typically is much more costly. Nevertheless, a typical

wastewater treatment plant has a natural internal carbon source in its waste activated sludge, WAS, and therefore reusing the WAS as carbon source for denitrification might replace the addition of external sources. The problem is that WAS, which is generated as consequence of the activated sludge process, is formed by a well-stabilised biomass network (strong cells and bacteria) meaning a low fraction of readily biodegradable COD (COD_{bio}). A pre-treatment is therefore necessary to increase the WAS bio-availability and this is the point where Ultrawaves has developed this application.

It is interesting to remark that in denitrification application does not only take importance soluble COD (COD_s) but colloidal COD as well. In fact, along with the COD_s release after sonication, it is also possible to achieve a very high portion of colloidal COD (which unlike COD_s does not trespassing 0.45 μm membrane filtration). This colloidal COD, which is a much higher portion compared with soluble fraction, is also available as biodegradable carbon source for denitrification. Ultrawaves has estimated that COD_{bio} could be split in around 10 to 20% soluble and 80 to 90% colloidal.

Finally, it should be taken into account that sonication does not only release a COD_{bio} source to denitrify but increases the enzymatic activity as well (Leiyu *et al*., 2010) which indeed is a very important consequence for the denitrification kinetics. By this reason dehydrogenase activity is measured as this enzyme is one of the key in more or less all biodegradation pathways. A higher dehydrogenase activity means that overall enzymatic activity of the activated sludge process is also increased. This means in turns that the biological sludge is of higher activity so that all degradation processes are accelerated inducing a high-rate degradation processes. This effect takes place in all the biological reactor zones where the disintegrated sludge is recycled and has particularly importance in the anoxic tank where denitrification occurs. Figure 3 shows a typical enzymatic activity measurement of non-sonicated (zero value in abscissas axis) and sonicated TWAS at different energy inputs.
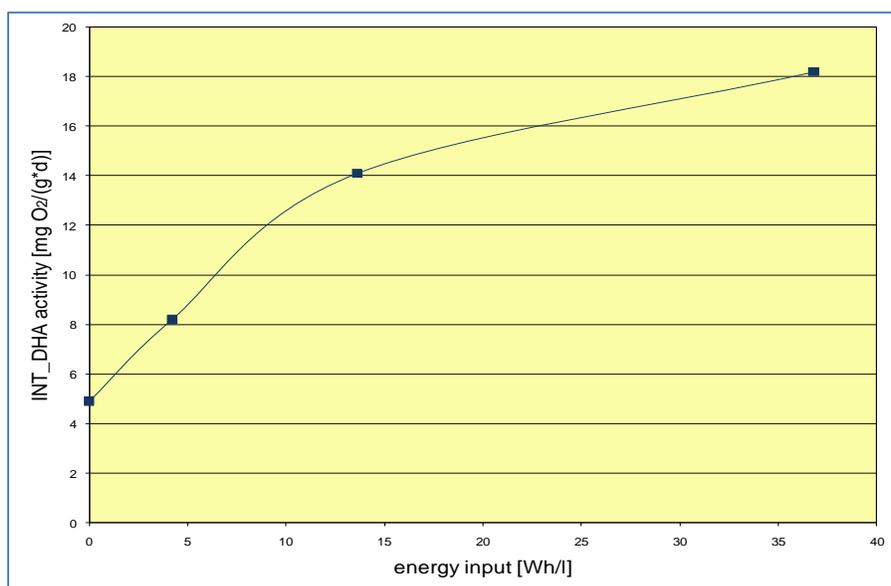

Figure 3: *Dehydrogenase activity on the sludge water phase (source: Crispijana WWTP test, Spain).*

Denitrification as biological process is then stimulated due to the activated denitrifying biomass is stimulated and this causes an additionally acceleration of the microbial processes becoming a high-rate denitrification process (Neis *et al*., 2012).

Estimating the carbon source available in the WAS

In order to be sure with the carbonaceous material availability when using WAS as electron donor source, Ultrawaves has researched up to develop a model where it is possible to estimate the biodegradable carbon source available after its ultrasonic disintegration. Although conceptually is similar, Ultrawaves application does not use WAS but TWAS due to the higher solids content in the flow to sonicate.

TWAS is commonly measured in terms of total solids (TS) and volatile solids (VS) as well. It is very usual to measure TS in % (referred to the kg TS/m^3) and the VS as % of the TS. Ultrawaves model considers the volatile biomass divided in three fractions, the active biomass fraction (X_A), the endogen residue fraction (X_E) and the inert volatile solids (X_I). Active biomass carries out the substrate biodegradation and the remaining volatile masses are inactive and do not serve any function insofar as the biodegradation mechanisms in the process are concerned.

With TS, VS and X_A it is possible to determine how much active biomass exists in the TWAS flow rate. Assuming the rate 1.42 kg COD per kg VSS of biomass (VSS volatile suspended solids) it is possible to calculate the kg of COD (from the active biomass) per unit of volume. It should be remarked that sonication increases COD$_s$ from TWAS but the COD$_{bio}$ (mainly comprised of colloids) increases much more.

$$\frac{\text{kg COD}}{\text{m}^3} = \frac{\text{kg TS}}{\text{m}^3} \times \frac{\text{kg VS}}{\text{kg TS}} \times \frac{1.42 \text{ kg COD}}{\text{kg VS}} \times X_A$$

However, it is necessary to take into account that after the ultrasonic disintegration bacteria and cells are broken down delivering internal material which contents, among others compounds, endogen residue and ammonia-nitrogen (NH$_3$). Available COD to support denitrifcation has to be calculated in order to compensate these deliveries. The effectiveness of sonicated WAS as electron donor in denitrification is then diminished if released NH$_3$ is too great, because NH$_3$ counteracts the goal of TN removal.

According to this, Ultrawaves measures COD and nitrogen delivered after the sonication as well as the rate between both in order to be sure that nitrogen, which comes from cell breakage, is covered with the delivered COD. In the figure 4 it is possible to observe the soluble COD, total soluble nitrogen and the rate between both for non-sonicated (zero value in the abscissas axis) and sonicated sludge at different doses. It is interesting to remark that in this project was used RAS instead of TWAS for carrying out the sonication test, which provides a lower result than using TWAS due to high disintegration degree is better reached when sludge has a higher solids content (around 4.5%) than low solids content (around 0.8%).
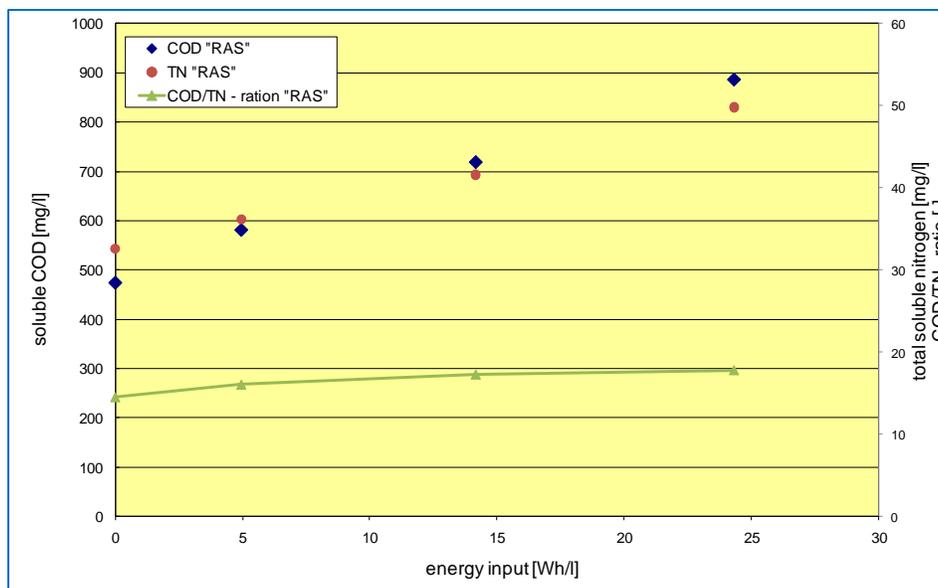
Figure 4: COD, N and COD/N rate measurements (source: Terrassa WWTP project, Spain).

As it is shown in figure 4, the increase of nitrogen in relation to bioavailable COD after the sonication is around 15 times lower (6 times should be enough) for an energy input of 5 Wh/l which is a very common dose in full scale applications.

Nevertheless, COD_s delivered from active biomass fraction is not the only component to be considered due to this COD fraction is not enough to remove all nitrate reached in the application. For this reason it is also considered that sonication modifies also the hydrolysis rate of the particulate endogen COD existing in the sludge.

Tests have proven that the hydrolysis rate for sonicated sludge can reach around 1.7 d^{-1} while conventional sludge remained 0.6 d^{-1} (Trillo *et al*., 2012). Hence, sonication does not only provide COD_s but additionally enhances hydrolysis, which has a very positive effect over the denitrification process because sludge endogen COD is used faster in anoxic zones (it is necessary a lower hydraulic retention time and lower volume in the biological reactor).

Based on these assumptions it has been stated that COD_s is capable to remove around the 10% of the nitrates (1 kg NO_3/6 kg COD) reached through ultrasonic disintegration meaning that remained amount should be removed using COD from particulate fraction. The total average sonication effect in terms of COD_{biod} delivered after the ultrasonic disintegration can be estimated as 0.5 kg COD_{biod}/kg TWAS. This estimation has been demonstrated across fundamental studies (Ditzingen WWTP, Germany) and full scale installations. In the provided references it can be found a detailed study with further details (Terrassa WWTP, Spain).

Other positive side effects when disintegrated WAS is used as carbon source

Independently of the electron donor capacity, disintegrated WAS should be also considered as a method (widely known) to reduce excess sludge production as well as an efficient, simple and

innovative solution to combat associated problems with filamentous microorganisms and even a way to improve sludge dewatering. These three effects, excess sludge production reduction, bulking and foaming complete elimination and dewaterability enhancement, have a very positive impact when the ultrasound technology is applied to support denitrification since three new profits has to be added to the economic balance. Below, a brief description of each mentioned effect.

Excess sludge reduction
One of the mechanisms for excess sludge reduction to be integrated in the biological reactor is known as cell lysis and cryptic growth. The term cryptic growth was introduced to indicate the reutilisation of intracellular compounds (both carbonaceous compounds and nutrients) released from cell lysis for the growth of viable cells of the same population. The organic autochthonous substrate cannot be distinguished from the growth on the original organic substrate in influent wastewater, and by this is named cryptic growth. This form of repeated metabolism of the same organic carbon reduces the overall biomass production significantly. This reduction occurs because during each metabolic process a portion of the carbon is mineralized as product of respiration (Wei *et al.*, 2003).

It has been tested that sonication is a good cell lysing technique and it has been assessed the solubilisation rate of biomass after sonication (Gaudy *et al.*, 1971). Ultrasound causes cell lysis with the consequent solubilisation of cellular constituents, which become substrate available for further biodegradation. Cryptic growth process is thus induced which results in an overall reduction of sludge production. The maximum growth yield for heterotrophic bacteria under aerobic conditions (Y_H) is typically 0.67 mg $COD_{synthetized}$/mg $COD_{removed}$. In the presence of cell lysis and cryptic growth Y_H can reach up to the value of 0.43 mg $COD_{synthetized}$/mg $COD_{removed}$ for pure cultures (Canales *et al.*, 1994) meaning an important reduction.

In order to control the process and avoiding undesirable results, it is necessary to monitor the right percentage of WAS to be treated (Ultrawaves always treats TWAS instead of WAS due to the flow rate is much more reduced). If too much WAS is disintegrated and recycled back to the biological reactor, there would be then insufficient microorganisms in the aeration zone to remove the organic contamination in the wastewater influent as well as the new substrate included in the disintegrated WAS. In this sense, Stress Factor (SF) provides a good approach. SF is termed as follows.

$$SF\ (d^{-1}) = \frac{\text{Amount of sludge treated per day (kg×d}^{-1})}{\text{Amount of sludge in the biological reactor (kg)}}$$

Furthermore, although theoretically it is possible to achieve a zero excess sludge production, it should not be done because up to 30% of inorganic compounds and persistent hazards (high effluent COD values and SVI as well) might accumulate in the wastewater treatment system and deteriorate the process efficiency. Best excess sludge reduction rates are obtained for SF not higher than 0.2 d^{-1} (Camacho *et al.*, 2002).

Combatting bulking and foaming
The destruction of the filamentous sludge is mainly caused by hydro-mechanical effects in the advent of the collapse of cavitation bubbles generated by ultrasonic waves. Low ultrasound doses are able to destroy the filamentous network of bulking or floating sludge. The thin filaments are much more exposed to the ultrasonic shearing forces than the flocs and are cut into small pieces.

Since the remaining flocs are not interconnected by filamentous organisms any longer, the activated sludge flocs become smaller and much more compact after ultrasonic treatment (Nickel, 1999). A smaller floc size improves the activated sludge settling properties in the secondary clarifier. In this regard ultrasonic treatment of the return sludge from the secondary clarifier is an interesting approach to overcome problems with floating suspended matter discharged from secondary settlers, which could be eliminated without using chemicals. This led Ultrawaves to sonicate a partial flow RAS and recycling back to the aeration tank.

Sludge volumetric index (SVI) is very helpful to monitor settling characteristics of activated sludge because high values mean poor settling properties while low values mean a tend to settle well. According to the German normative ATV-DVWK-A131E at SVI over 150 ml/g the sludge will bulk and the clarifier will stop operating properly. One of the most interesting applications of the Ultrawaves technology is precisely combating bulking & foaming associated problems where reductions over 65% in the SVI are reached with low energy doses (around 1 kWh/m^3) applied to treat only around 1% of the RAS flow.

Dewaterability improvement
After TWAS disintegration new floc aggregates are formed due to the mix with the non-sonicated biomass. Cell internal compounds are released into the medium and displace the water from the floc interstices which leads to a re-arrangement of sludge aggregates forming more suitable structures (in terms of less water content) to be dewatered.

Sludge dewaterability depends crucially on the size of the suspended particles (Friedrich and Potthof, 1988). The broadening of the size distribution leads to a considerably enhanced dewatering behaviour. Therefore, it is reasonable to destroy partially WAS aggregates prior to sludge stabilisation and polymer addition. Better results have been found with no more than 50% of WAS treated. In addition, partial WAS flow to be treated has to be destroyed up to reach cell lysis in order to release intracellular bounded water into the medium which can be easier to remove from the sludge with the mechanical dewatering units.

Recent investigations have shown that mixed sludge where a partial WAS flow has been previously sonicated is the most appropriate sludge to be dewatered as compared with mixed sludge where 100% of WAS is sonicated and conventional mixed sludge as well (Friedrich and Potthof, 1988). Dried matter content after dewatering when WAS is 100% is disintegrated increases around 11% with respect to the conventional case. However, when WAS is partially disintegrated the dried matter content increases around 19%. It should be understood that in

this context mixed sludge means a mixture of primary and secondary sludge both of them thickened and mixed just as this mix is received by the appropriate sludge handling unit.

Assessing the application

It has been referred that Ultrawaves technology allows the use of disintegrated WAS as suitable carbon source for denitrification stage which also implies other positive side effects to be considered. Under this circumstance it is interesting to estimate a comparison between Ultrawaves application and other alternatives carbon sources commonly used in denitrification, such as methanol and acetic acid. It has been considered that the total cost for nitrogen removal is mainly divided in three different blocks which are chemical, due to the external carbon source added (for the ultrasonic technology is internal carbon source), disposal, due to the excess sludge production and electrical, due to needed aeration for the excess sludge production.

Calculations which will follow have been estimated using basic and standard principles, so relativized because the process multi-diversity. Thus, chemical, disposal and energy costs have been considered as standard ones inside the UK and by this circumstance the currency used in all the calculations is the sterling pound (£). In the same way, for all the ultrasonic applications, it has been considered a standard thickened activated sludge (TWAS) featured with 4% of total solids content (TS) and 75% of volatile solids (VS) where VS is referred to TS.

Chemical costs
This is the mainly block as represents the essence of this paper which is targeted to the ultrasonic technology as supplementary electron donor to support denitrification. It takes sense then to make a comparison among selected carbon sources in terms as described below.

Parameter	Methanol	Acetic acid	Ultrawaves
Density	790 kg/m^3	1,060 kg/m^3	4 kWh/m^3 ([1])
COD	1,185 kg COD/m^3 CH$_3$OH	1,630 kg COD/m^3 CH$_3$COOH	20 kg COD$_{bio}$/m^3 TWAS$_{US}$ ([2])
COD	1.50 kg COD/kg CH$_3$OH	1.07 kg COD/kg CH$_3$COOH	0.50 kg COD$_{bio}$/kg TWAS$_{US}$ ([3])
Cost	0.40 £/kg CH$_3$OH	0.90 £/kg CH$_3$COOH	0.10 £/kWh
£/COD	0.27 £/kg COD	0.84 £/kg COD	0.02 £/kg COD
£/d	0.27 £/d ([4])	0.84 £/d ([4])	0.02 £/d ([5])

Figure 5: Different carbon sources comparisons in terms of price and rates.

([1]) Referred to the ultrasonic energy applied per volume of TWAS treated.
([2]) TWAS$_{US}$ means sonicated TWAS (assuming 4% in TS content) and COD$_{bio}$ means biodegradable COD. It is also assumed that all the effects of the Ultrawaves disintegration in terms of soluble and colloidal COD, and enzymatic activity as well is equivalent to 20 kg of COD$_{bio}$ per 5 kW of ultrasonic power applied.
([3]) Assuming WAS thickened (TWAS) at 4% in total solids (TS) content.
([4]) Per kg/d of COD coming from external carbon sources added.
([5]) Per kg/d of COD coming from disintegrated sludge added.

Rates expressed in figure 5 in terms of £/d should be understood as explained in ([4]) and ([5]), that is, as daily cost per kg/d of COD added coming from external carbon sources and TWAS treated.

Disposal costs associated with the excess sludge production
Ultrasonic disintegration represents an autochthonous carbon source (due to the facility by itself is the carbon source provider) as compared with methanol and acetic acid which have to be considered as external carbon sources. When an external carbon source is added to support denitrification biodegradable COD at the inlet increases just in the added quantity, which has side impact in the sludge production.

Parameter	Methanol	Acetic acid	Ultrawaves
Source/NO_3	3.20 kg CH_3OH/kg NO_3	3.74 kg CH_3COOH/kg NO_3	12 kg $TWAS_{US}$/kg NO_3 ([6])
COD/N	4.8 kg COD/kg NO_3	4 kg COD/kg NO_3	6 kg COD_{bio}/kg NO_3
Yield ([7])	+ 0.28 gr VSS/gr COD	+ 0.20 gr VSS/gr COD	- 0.16 gr VSS/gr COD ([8])
VSS generated	+ 0.28 kg VSS/d ([9])	+ 0.20 kg VSS/d ([9])	- 0.16 kg VSS/d ([10])
Disposal cost ([11])	150 £/dry ton VS	150 £/dry ton VS	150 £/dry ton VS
£/d	+ 0.042 £/d ([12])	+ 0.030 £/d ([12])	- 0.024 £/d ([13])

Figure 6: *Sludge disposal costs when different carbon sources are used in denitrification.*

([6]) Assuming that 6 kg COD_{bio}/kg NO_3 is required.
([7]) With COD/N it is possible to calculate the anoxic yield (Y) for the external carbon sources using the following equation (marked as +). Other authors have corroborated calculations derived from here (Christensson *et al.*, 1994).

$$Y = \frac{\left[1 - \left(\frac{2.86}{COD/N} \right) \right]}{1.42}$$

([8]) As explained in the excess sludge reduction issue, ultrasonic disintegration induces a cell lysis and cryptic growth process which means a significant reduction in the excess sludge production. Thus, assuming 0.24 (= 0.67 - 0.43) mg $COD_{synthetized}$/mg $COD_{removed}$ and 1.48 mg COD/mg VSS, it is possible to estimate an ultrasonic yield reduction around 0.16 mg VSS/mg COD (marked as -).
([9]) Same as ([4]).
([10]) Same as ([5]).
([11]) Assuming a proportional disposal cost for the dry solids in terms of VS (≈75% of TS).
([12]) Same as ([9]).
([13]) Same as ([10]).

As can be observed, methanol and acetic acid mean an extra cost in sludge for disposal in terms of £/d (0.042 and 0.030 respectively) per kg/d of COD from each external carbon source added to support denitrification. On the contrary, ultrasound means a saving (0.024) per kg/d of COD coming from disintegrated sludge due to the excess sludge production reduction reached as consequence of the induced cell lysis and cryptic growth process in the biological reactor.

Electrical costs associated with the excess sludge production
More VSS in the biological reactor produced by the external carbon source addition also means a higher carbonaceous oxygen demand, which is required by the microorganism in the aeration tank. This circumstance has to be considered as other part of the operational costs.

Parameter	Methanol	Acetic acid	Ultrawaves
Yield	+ 0.28 gr VSS/gr COD	+ 0.20 gr VSS/gr COD	- 0.16 gr VSS/gr COD
VSS generated	+ 0.28 kg VSS/d	+ 0.20 kg VSS/d	- 0.16 kg VSS/d
Oxygen ([14])	0.75 kg O_2/kg COD	0.75 kg O_2/kg COD	0.75 kg O_2/kg COD
Oxygen transfer	2 kg O_2/kWh	2 kg O_2/kWh	2 kg O_2/kWh
Energy cost	0.1 £/kWh	0.1 £/kWh	0.1 £/kWh
£/d	+ 0.038 £/d ([15])	+ 0.038 £/d ([15])	- 0.038 £/d ([16])

Figure 7: Electricity costs when different carbon sources are used in denitrification.

([14]) Assuming that is necessary a demand of 0.75 kg of carbonaceous oxygen (O_2) of per kg of COD applied to the biological process (Ekama and Marais 1984).
([15]) Same as ([4]).
([16]) Same as ([5]).

Electrical costs have been only assessed in terms of kg of oxygen per kg of COD added to the biological reactor as an approach to the equivalent costs in blowers and mixers. As standard ratio per kg/d of COD added, methanol and acetic involve an extra cost in electricity required in the aeration in terms of £/d (0.038) while the ultrasonic alternative involves a saving (0.038) due to the excess sludge production reduction.

Dewatering costs associated with the excess sludge production
Although this parameter is interesting to assess, it is very difficult to evaluate in a paper like this due to the dewatering effect of the ultrasonic disintegration provides an effect which has to be measured in a global sludge balance. That would mean other sludge handling units, as primary sludge which is out of this scope, should be considered as well.

Nevertheless, due to the excess sludge reduction previously calculated, an extra saving in polymer can also be reached.

Parameter	Methanol	Acetic acid	Ultrawaves
VSS generated	+ 0.28 kg VSS/d	+ 0.20 kg VSS/d	- 0.16 kg VSS/d
Polymer dosage ([17])	3 kg polymer/ton VS	3 kg polymer/ton VS	3 kg polymer/ton VS
Polymer cost	2 £/kg polymer	2 £/kg polymer	2 £/kg polymer
£/d	+ 0.002 £/d ([18])	+ 0.001 £/d ([18])	- 0.001 £/d ([19])

Figure 8: Polymer costs when different carbon sources are used in denitrification.

([17]) Assuming a polymer dosage in terms of VS (≈75% of TS).
([18]) Same as ([4]).
([19]) Same as ([5]).

Similarly to the disposal cost analysis, methanol and acetic mean an extra cost in the polymer addition required in terms of £/d (0.002 and 0.001) per kg of each external carbon source added. However, the ultrasonic alternative brings a new saving (0.001) per kg/d of COD coming from disintegrated sludge due to less excess sludge produced means less amount of polymer to be used in the dewatering unit.

Finally, it is interesting to remark that dewatering is improved around 2 points after the ultrasonic disintegration for the reasons explained formerly. If conventional sludge dewatering reaches 20% in the final cake dryness, which is a very common value, with ultrasonic treatment the value should be not lower than 22% (reaching sometimes even 24%).

The total balance

Summarising all the items in which the application has been divided it is possible to assess a systemic approach. Obviously, the increase in dewaterability has not been considered and will not appear in this study. Figure 9 shows all the rates in £/d per each kg/d of COD added.

Parameter	Methanol	Acetic acid	Ultrawaves
Chemical (£/d)	+ 0.270	+ 0.840	+ 0.020
Disposal (£/d)	+ 0.042	+ 0.030	- 0.024
Electrical (£/d)	+ 0.038	+ 0.038	- 0.038
Dewatering (£/d)	+ 0.002	+ 0.001	- 0.001
Consumables Ultrawaves (£/d)	+ 0.000	+ 0.000	+ 0.044
Total (£/d)	**+ 0.352**	**+ 0.909**	**- 0.043**

Figure 9: Total costs when different carbon sources are used in denitrification.

As can be noted, all the costs involved in the ultrasonic technology working have been considered including consumable costs (sonotrodes reposition). To understand these numbers is precise to develop a comparison between a pair of carbon sources due to the fact that using ultrasound means no external carbon sources to be used and then numbers have to be cancelled accordingly. Figure 10 explains this circumstance (as dragging from the beginning, negative values means savings).

Parameter	Ultrawaves vs methanol	Ultrawaves vs acetic acid
Chemical (£/d)	- 0.250	- 0.820
Disposal (£/d)	- 0.066	- 0.054
Electrical (£/d)	- 0.076	- 0.076
Dewatering (£/d)	- 0.003	- 0.002
Consumables Ultrawaves (£/d)	+ 0.044	+ 0.044
Total (£/d)	**- 0.351**	**- 0.908**

Figure 10: Relative savings when ultrasound is used instead of external carbon sources.

To exemplify these and other numbers some case studies are provided below.

Some references

Denitrification application is each time being more demanded due to all the improvements involved in the same installation. On the contrary, there is no much detailed information available for the existing installations as it should be required for this paper.

Bünde WWTP, Germany

This facility decided to utilise the Ultrawaves ultrasound technology in order to disintegrate TWAS and use it as internal carbon source to support denitrification. The installation was carried out in 2006 as an alternative to the original plan for improvements in the process quality which consisted of the purchase and addition of expensive carbon sources to denitrify. Some plant data are the following.

- Plant size: 40,000 PE (actual load 54,000 PE).
- Flow rate: 12,000 m^3/d (dry weather).
- Sludge feed: Primary and TWAS separately thickened.
- COD of the raw wastewater: 380 mg/l (70 mg/l in the final effluent allowed).
- BOD_5 of the raw wastewater: 200 mg/l (10 mg/l in the final effluent allowed).
- TN in the raw wastewater: 50 mg/l (15 mg/l in the final effluent allowed).
- Biological process: alternating nitrification denitrification at a total sludge age of 22 days.
- Sludge stabilisation: 2 parallel anaerobic digester tanks.
- Stabilisation problems: high VS content in sewage sludge, poor dewaterability and floating sludge during the winter.

The installation consisted of one 5 kW Ultrawaves ultrasound reactor (USR) in order to treat around 30% of the TWAS, meaning 1 m^3/h (TWAS at 4 to 5% in TS content) to be treated with an ultrasonic dose of 5 Wh/l. As a result of the USR utilisation, an autochthonous carbon source was provided (avoiding a purchase of 500 kg CH_3OH/d) and associated problems with sludge stabilisation were solved as well. Figure 11 shows a diagram of the installation.
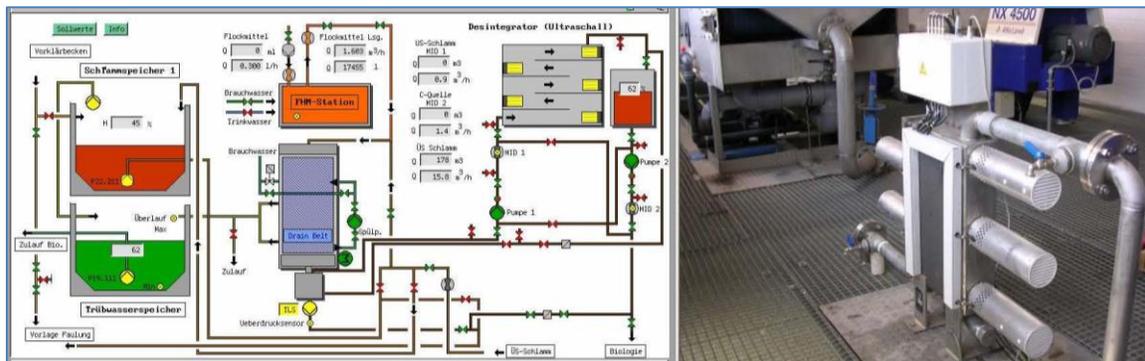

Figure 11: Scheme of sludge treatment in Bünde WWTP and picture of the ultrasonic reactor installed.

To assess the solution numerous and measurement studies were made in the wastewater treatment plant. Nitrogen removal as well as sludge reduction are shown below in the figure 12.

Parameter	Conventional	Ultrawaves	Difference	Variation (%)
Period	March-July	March-July	4 months	N/A
Year	2005	2006	1 year later	N/A
Q (m³/d)	12,834	16,101	3,267	25.46
COD$_{influent}$ (kg/d)	3,838	4,682	844	21.99
N$_{influent}$ (kg/d)	494	669	175	35.43
N$_{inorg\ effluent}$ (kg/d)	93.6	65.4	- 28.2	- 30.13
N removed (kg/d)	400.4	606.6	203.2	50.75

Figure 12: *Nitrogen removal efficiency after the USR application.*

Differences and variations are referred to the conventional column as starting data and then negative values mean conventional values higher than Ultrawaves values (as should be expected for nitrogen levels in the final effluent). As can be observed, even in worst conditions (more flow and load) the ultrasonic application was able to remove more than 200 kg/d of nitrogen than conventional operation, meaning a variation of more than 50%. As a result, a significant reduction of the nitrogen concentration in the effluent (< 5 mg/l) was reached.

However, as referred above, Ultrawaves application does not only affect denitrification step but sludge production reduction as well. Figure 13 provides the numbers.

Parameter	Conventional	Ultrawaves	Difference	Variation (%)
Period	March-July	March-July	4 months	N/A
Year	2005	2006	1 year later	N/A
Q (m³/d)	12,834	16,101	3,267	25.46
COD$_{influent}$ (kg/d)	3,838	4,682	844	21.99
COD$_{period}$ (ton)	480	585	105	21.88
WAS$_{period}$ (ton)	267	232	-35	13.11
(WAS/COD)$_{period}$	0.56	0.40	-0.16	-28.70

Figure 13: *Sludge reduction efficiency after the USR application.*

As observed, WAS/COD (which is the specific sludge production) was reduced more than 28%, meaning a significant saving in sludge disposal costs. Considering COD$_{period}$ and (WAS/COD)$_{period}$, it is possible to calculate 280 kg WAS/d reduced (35×1,000/125) with only 5 kW of ultrasonic power. Period was considered as 125 days.

Other positive results as the reduction of the organic fractions, a complete elimination of the associated problems with bulking and foaming, and an improvement in the sludge cake dewaterability of more than 2 points were also reached. Thus, taking into account only the chemical cost (125 €/d regarding methanol purchase), profits associated with ultrasonic disintegration provided a ROI around 2 years.

Terrassa WWTP, Spain
This project was carried out to demonstrate to the Spanish government the goodness of the estimations made regarding ultrasound forecast. In 2007 was redacted the project to upgrade

the facility up to 75,000 m^3/d including BNR. Both requirements implied the biological reactor expansion which was difficult to carry out due to the lack of space. A deep study was developed in order to optimise spaces and a fix biomass system type IFAS (Integrated Fixed Activated Sludge) was installed. Some parameters of the influent wastewater details are given below.

-   Design flow rate: 75,000 m^3/d (actual flow rate 45,000 m^3/d).
-   COD: 454 mg/l.
-   DBO$_5$: 240 mg/l.
-   TN: 60 mg/l (actual TKN 70 mg/l).

With these data, COD/TKN rate in the biological reactor influent is around 7.5 which is insufficient to remove nitrogen through a conventional nitrification-denitrification process. This implies the need to add an external carbon source in order to achieve desired nitrogen levels (TN < 10 mg/l) in the final effluent. Figure 14 shows pictures of the biological reactor where it is possible to note bulking and foaming presence (caused mainly for the required sludge ages to nitrify).

Figure 14: Terrassa WWTP biological reactor pictures.

To evaluate ultrasonic predictions, a pilot plant was built inside the same facility to assess the application in the same conditions as the full scale facility works. This provided the study with the highest dose of realism due to most of the studies released for same applications are carried out inside laboratories, which means a very different environment and surround conditions.

Figure 15: Terrassa WWTP pilot plant pictures.

A proportional ultrasonic system was provided in accordance to the pilot plant dimensions as it is shown in the figure 16.

Technical features	Conventional	Terrassa
Flow rate to be sonicated	30 m^3/d	450 l/d
Ultrasonic frequency	20 kHz	20 kHz
Ultrasonic power	5 kW	1 kW
HRT inside the USR	0.87 to 1.74 min	0.87 to 1.74 min

Figure 16: Conventional USR vs USR system provided in Terrassa pilot plant.

Performances were studied under three working conditions for assessing the best configuration to reach a reduction of no less than 5 mg/l in the TN. Figure 17 shows all details obtained.

Parameter	Conditions 1	Conditions 2	Conditions 3
WAS	1,350 l/d	1,350 l/d	900 l/d
Sonicated WAS flow	450 l/d	450 l/d	450 l/d
Sonicated WAS/WAS	33%	33%	50%
MLSS	2 g/l	2 g/l	1 to 2 g/l
Sonicated WAS load	0.9 kg/d	0.9 kg/d	0.45 to 0.9 kg/d
Ultrasonic dose	4.6 kWh/m^3	9.2 kWh/m^3	4.6 kWh/m^3
NO$_3$ removed concentration	6 to 8 mg/l	8 to 12 mg/l	6 to 8 mg/l
NO$_3$ removed load	72 to 96 g/d	96 to 144 g/d	72 to 96 g/d
Rate kg N-NO$_3$/kg WAS	0.08 to 0.11	0.11 to 0.16	0.08 to 0.11

Figure 17: Comparisons of the obtained results (pilot plant flow rate: 12 m^3/d).

First conclusion to be considered is that treating around 30% of WAS flow (the pilot plant had not obviously TWAS) is completely enough to provide with the required COD$_{bio}$ to remove more than 5 mg NO$_3$/l. In addition, different rates N-NO$_3$/WAS obtained show that estimations developed when COD$_{bio}$ from WAS was assessed are correct. Assuming an average (in the three conditions) of 0.10 kg N-NO$_3$/kg WAS and considering the rate 6 kg COD/kg N-NO$_3$, it is possible to obtain around 0.5 kg COD$_{bio}$/kg WAS as predicted.

It can be seen how in the three performances it is possible to reach the minimum of 5 mg/l in nitrate removed concentration. According to condition 2, more energy applied means more nitrates to be removed which could be interesting in some cases. Conditions 1 and 3 remove similar nitrate load due they worked under identical disintegration conditions. It is possible then to assess a new rate between nitrates removed (or equivalently COD delivered) and sonication dose applied.

COD$_s$ measurements were in the range of 100 to 150 mg COD$_s$/l (meaning 45 to 68 g COD$_s$/d) for the three working conditions. These quantities are not enough to denitrify the 6 to 8 mg NO$_3$/l (meaning 72 to 96 g NO$_3$/d) reached. Then, as also previously estimated, sonication should substantially modify the hydrolysis rate of the particulate endogen COD. In order to

demonstrate this asseveration hydrolysis constants were measured for different sludges as it is shown in the figure 18.

Sludge type	Hydrolysis rate
Normal WAS	0.6 d^{-1}
Terrassa WAS	0.7 d^{-1}
Terrassa sonicated WAS	1.7 d^{-1}

Figure 18: Measured hydrolysis rates.

It was demonstrated that sonicated WAS has a much higher hydrolysis constant (nearly 185%) than conventional sludge, and then it has been demonstrated that sonication does not only provide a COD_s source but improves sludge hydrolysis rate as well. This means a quicker use of the endogen COD in the anoxic zones (meaning less hydraulic retention time and less tank volume).

Costs analysis was developed under two important aspects. First one is that sludge reduction and dewatering (which are an important part of the savings) were not considered in the calculations, and the second one is that for particular reasons methanol prices were lower. All the remaining prices were referred to Spanish standards and rates. Figure 19 shows comparative costs with external carbon sources as acetate and methanol for the full scale application where ultrasound alternative includes energy consumption and sonotrode replacement costs, as well as prices (amortisation per year) for all the USR units necessary.

Parameter	Acetate (25%)	Methanol	Ultrasound
Electron donor source cost	0.35 €/l	0.17 €/kg	0.10 €/kWh
Requisite	6.155 m^3/y	1.533 ton/y	263 MWh/y
Price	2.16 M€/y	0.27 M€/y	0.12 M€/y

Figure 19: Prices per year of the different carbon source alternatives.

Under these conditions ultrasound represents only 6.7% of the cost when acetate is used as carbon source and 44% when methanol. To finish, it would be remarkable the fact that during sonication periods (from October 2009 to August 2010) bulking and foaming associated problems were completely stopped. Information provided here is being used actually by the Spanish administration in the official tender.

Wujiang WWTP, China
The wastewater treatment plant operator decided to use the Ultrawaves reactor for sewage sludge cell disintegration in order to develop a carbon source to replace methanol. Excess sludge reduction was also pursued. A brief snapshot of the plant is given below.

- Plant design capacity: 85,000 m^3/d.
- Biological process: A^2/O (Anaerobic-anoxic-oxic).
- Effluent standard: the first class, criteria B (TN ≤ 15 mg/l).
- Methanol cost: 0.75 yuan/m^3 (electricity cost not included).

Ultrasonic installation treated around 20 to 40% of TWAS flow, meaning a reduction in the effluent TN-concentration of 3 mg/l (20% more). TN and total phosphorous (TP) in the final effluent were decreased up to 10 and 0.3 mg/l respectively. At the same time sludge production reached a reduction of 20 to 25%. These results avoided the purchase of a huge amount of methanol and saved money due to less sludge for disposal was generated. The full scale installation meant a payback of 3 years.

Datansha WWTP, China
The facility decided to use Ultrawaves technology for exactly the same reasons as above. A brief data of the plant are the following.

- Design capacity: 150,000 m^3/d.
- Biological process: A^2/O.
- Sludge production for disposal: 61 ton dry sludge/d.
- Final destination: Dewatered sludge is disposed in sanitary landfill with garbage.

TN in the final effluent was reduced more than 3 mg/l (25% of improvement) and sludge for disposal was reduced around 20%. Full scale installation brought a ROI within 3 years.
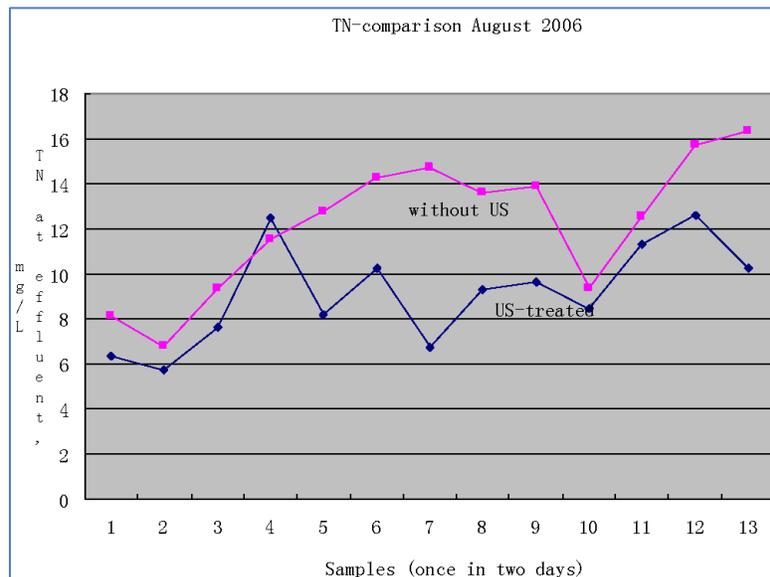

Figure 20: *TN concentration in the final effluent evolution across the time.*

Other references and potential references
Ultrawaves application in this innovative but well proven field is evolving and references like Ellmendingen in Germany, Gaobeidian and Wuxi in China and some other under confidential development are ongoing.

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