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Review

Progress and perspectives of sludge ozonation as a powerful pretreatment method for minimization of excess sludge production

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ABSTRACT

The treatment and disposal of excess sludge represents a bottleneck in wastewater treatment plants (WWTP) worldwide, due to environmental, economic, social and legal factors. The ideal solution to the problem of sludge disposal is to combine sludge reduction with the removal of pollution at the source. This paper presents an overview of the potential of ozonation in sludge reduction. The full-scale application of ozonation in excess sludge reduction is presented. Improvements in the biodegradability of the ozonated sludge were confirmed. The introduction of ozonation into activated sludge did not significantly influence effluent quality but improved the settling properties of the sludge. An operation with a suitable sludge wasting ratio seems to be necessary to prevent accumulation of inorganic and inert particles for long-term operation. Sludge ozonation to reduce excess sludge production may be economical in WWTP which have high sludge disposal costs and operational problems such as sludge foaming and bulking. The recommended ozone dose ranges from 0.03 to 0.05 g O_3/g TSS, which is appropriate to achieve a balance between sludge reduction efficiency and cost. An effort to design and optimize an economic sludge reduction process is necessary.

Contents

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1. Introduction

A large amount of sludge is produced by aerobic biological wastewater treatment processes, including the widely used activated sludge process, and has become a serious problem. Excess sludge produced by these processes must be disposed of and disposal may account for up to 65% of the total plant operating costs (Liu, 2003). In China, an increase in both the amount of wastewater and in the treatment rate has resulted in a significant increase in excess sludge production. According to the State Environmental Protection Administration of China (SEPA, 2005), the amount of wastewater discharged is estimated to reach 64 billion tons per year by 2010, producing about 11.2 million tons of dry solids per year. In the EU countries, following the implementation of the Urban Waste Water Treatment Directive 91/271/EEC which requires further extensive wastewater treatment and an end to sea disposal of sewage sludge, an increase in wastewater treatment plants (WWTP) of nearly 40% was expected between 1998 and 2005, producing about 9.4 million tons (dry weight) every year, while in 2010 it is expected to exceed 10 million tons (Pérez-Elvira et al., 2006). It is estimated that about 10 million dry tons of sewage sludge are produced in the United States (Bandosz and Block, 2006). New stringent regulations regarding sludge treatment and disposal as well as social and environmental concerns have resulted in a considerable impetus to develop strategies to reduce excess sludge production (Wei et al., 2003).

In order to reduce excess sludge production, new sludge disintegration processes, which involve mechanical, chemical, thermal and biological methods, have been developed and are now increasingly available on a commercial basis (Boehler and Siegrist, 2006; Bougrier et al., 2006; Chu et al., 2008; Ginestet, 2006; Liu and Tay, 2001; Low and Chase, 1999; Müller et al., 1998; Winter, 2002; Yan et al., 2009). Generally, these strategies to reduce sludge production are based on lysis-cryptic growth. The biomass growth on the lysates is termed cryptic growth, to distinguish from growth on the original organic substances (Mason et al., 1986). When disintegration methods are applied, microbial cells undergo lysis or death during which cell contents (substrate and nutrients) are released. The organic autochthonous substrate is reused in microbial metabolism and a portion of the carbon is liberated as respiration products. This results in a reduction in the overall biomass production (Low and Chase, 1999). As shown in Fig. 1, there are two stages in cryptic growth: lysis and biodegradation. The rate-limiting step is the lysis stage.

Of these techniques to disintegrate sludge, ozonation of sludge is one of the effective ways and yields the highest degree of disintegration (Müller, 2000). It is well documented that excess sludge production can be greatly reduced by partial ozonation of the returned sludge in an activated sludge process (Ramakrishna and Viraraghavan, 2005; Sakai et al., 1997; Yasui and Shibata, 1994). Ozonation also improves the settling properties of the sludge and reduces bulking and scumming (Caravelli et al., 2006; Deleris et al., 2002; Kamiya and Hirotsuji, 1998; Weemaes et al., 2000). In Japan and some EU countries, sludge ozonation has been successfully applied in practice and is the promising process to reduce sludge production (Caffaz et al., 2005; Sievers et al., 2004; Vergine et al., 2007; Yasui et al., 1996).

This paper presents an overview of the application of sludge ozonation technologies in pilot-scale and full-scale plants as well as cost and energy evaluations not only in China but worldwide. Changes in the characteristics of activated sludge after ozonation, the impact of ozonation on sludge reduction and the biological wastewater treatment including nitrification and denitrification, settling properties and dewatering conditions are also evaluated.

2. Effects of ozonation on the characteristics of activated sludge

2.1. *Fate of sludge after ozonation*

Ozone is a powerful oxidant and can oxidize a wide range of organic and inorganic compounds. Ozone has strong cell lytic activity, and can kill the microorganisms found in activated sludge and further oxidize the organic substances released from the cells (Cui and Jahng, 2004; Saktaywin et al., 2005). The process of sludge ozonation is generally described by the sequential decomposition reactions of floc disintegration, solubilization,

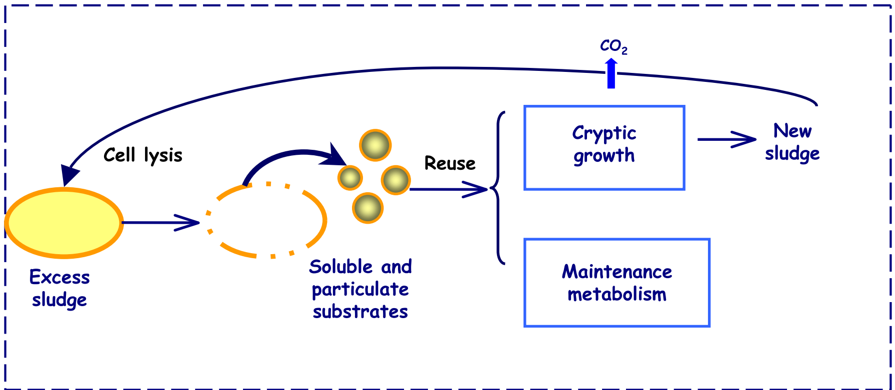

Fig. 1 – Schematic diagram of cryptic growth.

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

Following ozonation, the characteristics of the sludge are greatly changed. The flocs are broken down into fine, dispersed particles. Floc disintegration and solubilization generates a large number of micro-particles dispersed in the supernatant in addition to soluble organic substances. The fate of sludge after ozonation is examined by four types of COD, total COD, soluble COD (SCOD), suspended micro-particle COD and residual COD. Yeom et al. (2002) studied the effects of ozone dose on the fate of the ozonated sludge. The raw sludge consists mainly of residuals (99.2%) with a negligible soluble fraction (0.8%). At an ozone dose of 0.05 g O_3/g TSS, the fractions of residuals, SCOD, micro-particles and mineralization were 63.9%, 19.6%, 13.8% and 2.7%, respectively. As ozonation continued, the fraction of SCOD and micro-particles greatly increased and became dominant. The fractions of the four types of COD were 45.3%, 25.7%, 23.9% and 5.1%, respectively with an ozone dose of 0.1 g O_3/g TSS. With further increase in ozone dose, the mineralization became greater. 20.1% of mineralization was obtained at a higher ozone dose of 0.5 g O_3/g TSS. Chu et al. (2008) also showed similar results. At an ozone dose of 0.06–0.16 g O_3/g TSS, the fractions of residuals, SCOD, micro-solids and mineralization were 43–15%, 15–31%, 25–34%, and 16–21%, respectively.

During ozonation, soluble nitrogen, phosphorus and COD concentrations increase. Organic nitrogenous and phosphorus compounds are the major contributors to the increase in soluble nitrogen and phosphorus concentrations (Chu et al., 2008; Dogruel et al., 2007).

2.2. *Changes in sludge properties after ozonation*

The ozonation of sludge leads to a decrease in the ratio of volatile suspended solid (VSS)/TSS and pH value. The ratio of VSS/TSS decreased from 78% in raw sludge to 73% in ozonated sludge with a dose of 0.16 g O_3/g total solid (TS) (Bougrier et al., 2006), and pH decreased from 6.2 to 3.0 at an ozone dose of 0.5 g O_3/g TS (Deleris et al., 2002). In addition, the water content of sludge decreased with increased ozone dose (Zhao et al., 2007). Sludge disruption changes the water distribution in the biomass by releasing a considerable amount of water trapped within the floc structure. The bound water content decreased rapidly and then leveled off at an ozone dose of higher than 0.5 g O_3/g TS (Bougrier et al., 2006). Zeta-potential increased according to ozone dose and was enhanced at doses above 0.5 g O_3/g TS (Bougrier et al., 2006).

Particle size was also modified after ozonation. Ozonation did not appear to greatly affect particle size at lower ozone doses (Zhang et al., 2009). In the study by Bougrier et al. (2006), the medium diameter of particles before and after ozonation (0.16 g O_3/g TS) was 36.3 μm and 32.6 μm, respectively. Zhao et al. (2007) reported that the media diameter of sludge particles reduced from 6 μm to 4 μm at an ozone dose of 0.04 g O_3/g TSS. Higher ozone doses resulted in an increase in small particles due to sludge destruction by ozonation which occurred due to disruption of the biomass during sludge treatment. Park et al. (2004) reported that the mean particle size decreased from 70 μm to 40 μm with an ozone dose of 0.5 g O_3/g TSS. With a further ozone dose of 5 g O_3/g TSS, the highest peak of particle size distribution was identified around 5 μm (Park et al., 2003).

2.3. *Impact of ozone dose on biomass activity*

Saktaywin et al. (2005) reported that phosphorus accumulating organisms (PAOs) and general heterotrophic bacteria lost their viability after exposure to zone. This viability decreased exponentially with the degree of sludge solubilization. Around 70% of sludge was inactivated at an ozone consumption of 0.03–0.04 g O_3/g TSS. Researchers have reported that at an ozone dose of 0.05 g O_3/g TSS, 97% of heterotrophic organisms (Lee et al., 2005) and 80% of nitrifying bacteria (Kobayashi et al., 2001) were inactivated. Colony forming units (CFUs) decreased to around 10% at an ozone consumption below 0.05 g O_3/g TSS (Yasui and Shibata, 1994).

Dziurla et al. (2005) reported that lowest ozone dose leading to a decrease in the maximum oxygen uptake rate was estimated to range between 0.9 and 13.6 mg O_3/g COD_{sludge}, depending on the sludge tested. Zhao et al. (2007) found that both the TTC-ETS (2,3,5- triphenyltetrazolium chloride-Electron Transport System) and INT (2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetrazolium chloride)-ETS activity increased slightly at an ozone dose less than 0.04 g O_3/g TSS and then reduced quickly. Ozonation may affect dehydrogenase activity in sludge when the ozone dose is higher than 0.04 g O_3/g TSS (Nishimura et al., 1999).

Yan et al. (2009) have used the PCR-DGGE approach to analyze alterations in the microbial population during the sludge-ozonation process. It was found that no obvious alteration in bacterial DNA was detected by DGGE analysis at an ozone dose less than 0.02 g O_3/g TSS. When the ozone consumption was increased, several bands in the DGGE fingerprint disappeared, indicating that bacteria began to breakdown and release their DNA due to ozonation. At ozone levels above 0.06 g O_3/g TSS, only two bands remained. The sequence results determined that these two surviving strains belonged to the *Rhodocyclaceae* family: genus *Azonexus* and genus *Ferribacterium*. Finally, when the ozone dose was more than 0.08 g O_3/g TSS, DNA samples extracted from the ozone-treated sludge failed to be amplified by PCR. The sludge completely lost its protease enzyme activity when the ozone dose was more than 0.10 g O_3/g TSS.

2.4. *Effects of ozone treatment on biodegradability of activated sludge*

Improvements in the biodegradability of the ozonated sludge have been confirmed by several researchers (Weemaes et al., 2000; Yeom et al., 2002). It was found that around 60% of the soluble COD generated due to ozonation was in a biodegradable form at the early stage of ozonation, while the remaining soluble organic matter was refractory (Saktaywin et al., 2005). According to Nagare et al. (2008), around 80–90% of solubilized organics were biodegradable at a solubilization degree of 0.3.

For raw sludge, it was reported to take 24 days to produce 300 mL of biogas per gram of COD added, and around 15–18 days for ozonated sludge to produce the same amount of biogas at an ozone dose of 0.10–16 g O_3/g TS (Bougrier et al., 2006). According to Yeom et al. (2002), the ozonated sludge at 0.1 g O_3/g TSS showed about 2–3 times greater biodegradation compared with the raw sludge in both aerobic and anaerobic conditions for 5 days. In aerobic conditions, the biodegradation of the ozonated sludge after 15 days was 45.4%, 63.0% and 77.1% at an ozone dose of 0.02, 0.05 and 0.1 g O_3/g TSS, respectively, compared with 36% degradation for raw sludge. With anaerobic digestion, biodegradation increased with ozone dose up to 0.2 g O_3/g TSS. However, further increases in ozone dose did not improve biodegradation. This was because ozone was also utilized to oxidize the biodegradable products produced initially and consequently ozone was not consumed to transform the remaining refractory organic matter.

It is interesting to note that ozone dose is a very important parameter when discussing the sludge-ozonation process. The used definition of ozone dose varies from g O_3/g TSS, g O_3/g TS to g O_3/g COD_{sludge}, depending on the research authors. It is difficult to make a comparison of different sludge-ozonation processes without a definition of ozone dose. There, some standard ozone dose, such as g O_3/g TSS, should be suggested to allow a comparison of sludge ozonation performance for practical applications.

3. Application of sludge ozonation technologies

3.1. *Efficiency of sludge ozonation stage*

Producing ozone for sludge treatment is costly and is the major limitation to its use in full-scale plants. Optimization of the sludge ozonation stage must be one of the main research objectives in the near future. The efficiency of sludge solubilization is the most important parameter in evaluating the performance of sludge ozonation. It should be mentioned that there is also a variety of definitions for sludge solubilization efficiency, such as COD solubilization, TSS or VSS elimination and TOC solubilization, in which COD solubilization and TSS elimination are used most often in the relevant literature. Table 1 shows data from published studies on the efficiency of sludge solubilization based on COD solubilization except where otherwise indicated. Efficiency values depended on the properties of the sludge and the operating conditions. Generally, the reported efficiency of sludge solubilization was 30–60% using ozone oxidation. At a higher rate of ozone consumption, the rate of sludge solubilization was found to decrease. This might be due to the fact that ozonation of sludge is a very complex process. In a mixed liquor like activated sludge, the action of ozone is targeted on either the soluble or solid recalcitrant compounds. It has been reported that ozone may first react with the soluble fraction of the activated sludge and then attack the particulate fraction (Cesbron et al., 2003). With an increase in ozone dose, more intracellular substances are released. The soluble fraction has a screening effect on the particulate matter attacked by ozone, which results in little improvement in sludge solubilization at higher ozone doses (Cesbron et al., 2003). Furthermore, it was reported that following ozonation, some radical scavengers, such as lactic acid and SO_4^{2-} released from the microbial cell into the soluble part, which might have inhibited the future indirect reaction of ozone (Yan et al., 2009). In order to achieve a more cost-effective technology, mineralization of biodegradable organic compounds should be avoided in this type of process.

Manterola et al. (2008) affirmed that gas flow rate was an important factor affecting ozone mass transfer and not ozone gas concentration. An increase in COD solubilization was observed for those higher gas flow rates that corresponded to lower ozone gas concentrations with the same applied ozone dose due to the fact that higher flow rates increased the ozone mass transfer from gas to liquid. The low input ozone concentration and high flow rate could enhance the sludge lysing effects at the same ozone dose (Wang et al., 2008).

Initial TSS concentration is another parameter which should be considered in sludge-ozonation processes. Deleris et al. (2000) concluded that the degree of solubilization increased when the sludge concentration to be treated was increased. Saktaywin et al. (2005) noted a non-significant dependence between these parameters, and Egemen et al.

Table 1 – Literature data on the efficiency of sludge solubilization.

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

a Recalculated assuming the conversion biomass to COD as 1.2 g COD/g SS.
b TSS elimination.

(2001) found that the degree of solubilization remained almost constant at sludge concentrations higher than 3000 mg/L. Manterola et al. (2008) reported that the initial TSS concentration affected sludge solubilization during the ozonation process at ozone doses of 10–20 mg O_3/g TSS.

With respect to the mode of ozone introduction, most ozonation processes are operated in batch mode. Research has shown that intermittent ozonation was preferred over continuous ozonation (Egemen et al., 1999). The study by Kamiya and Hirotsuji (1998) demonstrated that an ozone dose of more than 30 mg O_3/g MLSS d was needed for continuous ozonation to reduce sludge generation to 50%, while only 11 mg O_3/g MLSS d was required for intermittent ozonation.

3.2. *Processes of sludge reduction by ozonation*

Because of the well-known potential and performance of sludge ozonation in reducing the amount of sludge for disposal, full-scale plants using sludge ozonation are increasing. Table 2 shows the various full-scale applications of sludge ozonation for sludge reduction, where 40–100% of sludge reduction was achieved as a result of these applications.

Sludge ozonation can be added at different locations in the WWTP as shown in Fig. 2. Ozonation can be introduced to the returned activated sludge line (Route I) or to the sludge digestion line (Route II).

For Route I, a combined system of an activated sludge process and ozonation has been successfully developed to reduce excess sludge production by promoting cryptic growth. A fraction of the recycled sludge passes through the process of ozonation and the treated sludge is then decomposed during biological treatment.

For Route II, ozonation is adopted as pretreatment before anaerobic/aerobic digestion, or as post-treatment of the digested sludge. Ozonation is used to enhance the solubility of sludge solids and increase the degree of degradation. Both the final amount of sludge for disposal and the digestion time can thus be reduced. For anaerobic digestion, biogas production can be increased.

3.3. *Application of sludge ozonation in biological wastewater treatment processes*

According to the configuration of the biological reactors, different combined systems with sludge ozonation to reduce excess sludge production have been reported.

3.3.1. *Conventional activated sludge process-ozonation*

Yasui and Shibata (1994) proposed and developed an activated sludge process coupled with ozonation for sludge reduction. Research by Kamiya and Hirotsuji (1998) showed that excess sludge production was reduced by 50% per day at an ozone dose of 0.01 g O_3/g TSS in the aerobic tank. When the ozone dose was kept as high as 0.02 g O_3/g TSS, no excess sludge was produced.

3.3.2. *A/O process-ozonation*

A lab-scale A/O process with ozonation of excess sludge was developed to establish a sludge-less process with a nitrogen-controlled effluent (Cui and Jahng, 2004). Results showed that the solubilized sludge acted as a reducing power for denitrification as well as a nitrogen source. 24–41% of COD contained in the ozonated sludge was found to be consumed for denitrification. However, the remaining COD was not assimilated further even in the presence of nitrate.

3.3.3. *A^2/O process-ozonation*

Suzuki et al. developed an anaerobic-oxic-anoxic (A/O/A) system equipped with ozonation and a phosphorus absorption column to achieve excess sludge reduction and phosphorus recovery. During 92 days of operation, total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) removal efficiencies were 85%, 70% and 85%, respectively, which were slightly lower than the control system. A reduction in sludge of 34–127% was obtained at an ozone dose of 0.29–0.32 g O_3/g TSS. Both PO_4-P and organic phosphorus were dissolved following sludge ozonation and around 80% of phosphorus was recovered.

3.3.4. *Sequenced Batch Reactor (SBR)-ozonation*

Intermittent ozonation of two-thirds of the recycled sludge was performed twice a week in a lab-scale SBR with an ozone dose ranging from 0.01 to 0.03 g O_3/g TSS and an ozone concentration of 33 mg/L in the gas phase. A decrease in

Table 2 – Full-scale application of ozonation for sludge treatment.

Capacity	Wastewater type	Ozonation	Period	Sludge reduction (%)	Source
Activated sludge process with partial ozonation of returned sludge					
450 m^3/d	Municipal	V = 4.5 m^3, 0.034 g O_3/g TSS	9 months	100	Sakai et al., 1997
550 kg BOD/d	Pharmaceutical	Higher than 0.015 g O_3/g TSS	10 months	100	Yasui et al., 1996
12700 m^3/d	Industrial	3–4 kg O_3/h, 0.05–0.1 g O_3/g TS	2 months	40	Vergine et al., 2007
22000 m^3 BOD/d	Chemical	5 kg O_3/h, 0.056 g O_3/g TS	5 years	45	
850 m^3 BOD/d	Slaughter-house	0.45 kg O_3/h, 0.026 g O_3/g TS	2 years	60–80	Wolff and Hurren, 2006
400,000 p.e.	Chemical	10 kg O_3/h	6 months	40–80	
Anaerobic digestion with ozonation					
Digestion tank: 1125 m^3	Sewage	24 kg O_3/d Ozonated sludge: 22–44 m^3/d	2 years	70	Yasui et al., 2005
Feed sludge: 25 m^3/d 17,000 p.e.	Municipal	V = 6 m^3, 1 kg O_3/h, 0.03–0.06 g O_3/g TSS		55.5	Winter, 2002; Sievers et al., 2004
Aerobic digestion with ozonation					
12000 p.e. Digestion tank: 400 m^3	Municipal	V = 3.7 m^3, 0.01–0.014 g O_3/g TS	9 months	78	Caffaz et al., 2005

sludge growth of about 50% was obtained and only a slight decrease in effluent quality was noticed during a period of 33 days (Huysmans et al., 2001). Jin and NgWun (2004) found that almost zero sludge yields were observed at an ozone dose of 0.05 g O_3/g TSS and a sludge recirculation rate of 0.4 L/Ld during 2 months of operation.

3.3.5. *Membrane Bioreactor (MBR)-ozonation*

Research has shown that the combination of an ozonation unit with MBR obtained an excellent permeate quality and a small sludge yield (He et al., 2003; Jiang et al., 2007). The amount of ozonated sludge was 0%, 2% and 4% of the reactor volume, and the average sludge yields were 0.130, 0.082 and 0.039 kg mixed liquor suspended solid (MLSS)/kg COD after 120 days of operation (He et al., 2006). Increasing the amount of the ozonated sludge resulted in a significant decrease in sludge production. According to Wang et al. (2008), an almost constant MLSS concentration of 8000 mg/L with a zero sludge yield coefficient and good effluent quality with the exception of TP could be achieved in an MBR coupled with a sludge-ozonation process.

3.3.6. *Anaerobic digestion with ozonation*

Based on the results of both lab-scale and pilot-scale experiments, Goel et al. (2003a) concluded that combining anaerobic digestion with ozonation achieved a higher VSS removal efficiency of 81%. The non-decomposed fraction of VSS compounds in the municipal sludge was only 12% in the ozonation system and 37% in the control system. The biogas production in the test reactor was 1.3 times higher than that in the control reactor. 0.54–0.47 N m^3 of methane gas was produced by the degradation of 1 kg of total volatile solid compounds. The biogas was composed of 59–61% methane, 38–40% CO_2 and 1–2% miscellaneous gas, which did not show a significant variation between the two systems (Yasui et al., 2006). The water content of the dewatered sludge cake from the train with ozonation was about 10% lower than

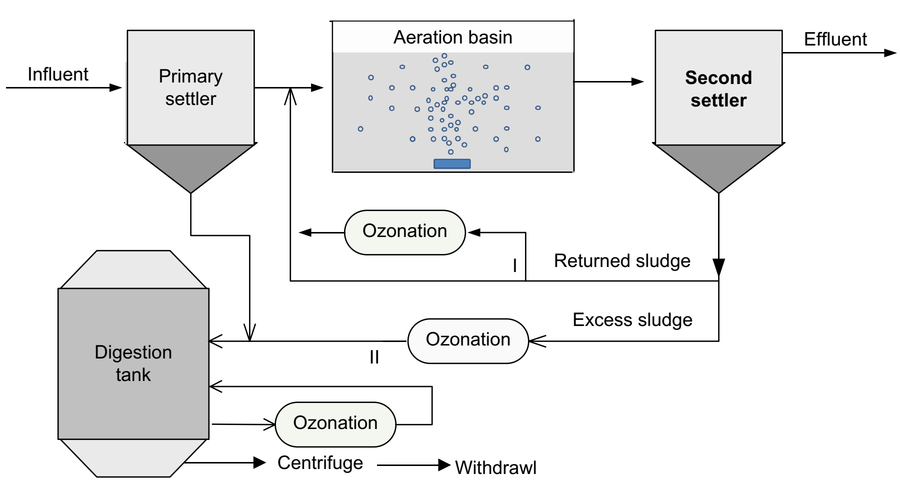

Fig. 2 – Application of ozonation for sludge reduction.

that of the control sludge under similar dewatering conditions (Goel et al., 2004). The configuration with post-ozonation of digested sludge was found to be superior with respect to degradation efficiencies and lower accumulation of total volatile solids, this configuration also required a lower ozone dose (Goel et al., 2003b). For a full-scale anaerobic digestion process combined with ozonation for 2 years of operation, it has been reported that dewatered sludge cake production was reduced by more than 70% and the water content of the dewatered sludge cake was reduced by about 12%. Furthermore, the remarkable reduction in dewatered sludge cake volume makes it possible to reduce N_2O discharge and the consumption of fossil fuel in the subsequent sludge incineration processes (Yasui et al., 2006). Bernal-Martinez et al. (2007) found that pretreatment of sludge with ozonation allowed an increase in polycyclic aromatic hydrocarbons (PAHs) biodegradability or bioaccessibility leading to the enhancement of PAHs removal during sludge anaerobic digestion. Carballa et al. (2007) studied the effect of ozone pretreatment on the removal of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge. Results showed that with the exception of carbamazepine, which was only removed with pre-ozonated sludge (up to 60% under thermophilic conditions), ozonation did not affect the removal efficiency of PPCPs during sludge anaerobic digestion.

3.3.7. *Aerobic digestion with ozonation*

Caffaz et al. (2005) described using aerobic digestion to stabilize the excess sludge in a full-scale municipal WWTP. A fraction of the digested sludge was fed to an ozonation contactor and then returned to the aerobic digester. During 9 months of operation, aerobic digestion efficiency increased up to 89% with a specific dose of 9.7 mg O_3/g TSS, compared with conventional treatment with only air, whose efficiency was 30% on average. Ozone treatment improved settling characteristics and it was possible to maintain a very high solid concentration in the aerobic digester (15–20 g/L) without problems. Reductions in nitrate and total inorganic nitrogen concentrations were observed but the soluble phosphorous concentration increased, compared with the control. The results of acute toxicity tests using *Vibrio fisheri* showed that supernatant samples of digester sludge before and after ozonation can be classified as "weakly toxic" because the inhibition index (I%) was less than 30%.

4. Impact of ozonation on performance of biological wastewater treatment

4.1. *Effluent quality*

Significant attention has been paid to the influence of sludge ozonation on effluent quality in the biological treatment process. During ozonation, inert dissolved and colloidal COD is released into the bulk solution, which leads to an increase in inert SCOD in the effluent during long-term operation. A slight increase in effluent COD was observed during long-term operation (Huysmans et al., 2001; Kamiya and Hirotsuji, 1998; Lee et al., 2005; Sakai et al., 1997; Yasui et al., 1996). SS and SCOD in the effluent were always satisfactory at a level of 10 and 15 mg/L, respectively, in a pilot-scale activated sludge system coupled with sludge ozonation for 112 days of operation without excess sludge wasting (Kamiya and Hirotsuji, 1998). Deleris et al. (2002) showed that the efficiency of the combined system was preserved although there was a 5% decrease in total COD elimination. The 20 mg/L COD increase observed in the effluent was related to the production of a non-biodegradable COD fraction during the ozonation stage. The recirculation of ozonated sludge to the reactor increased the nitrogen loading, and the effluent TN concentrations were slightly higher compared to the control run without sludge ozonation (Chiavola et al., 2007; Sakai et al., 1997). According to Sakai et al. (1997), the slight increase in effluent SS resulted in a slightly higher effluent BOD concentration. Phosphorus removal in the ozone train was comparatively low. Most of the phosphorus released by sludge ozonation was discharged as part of the soluble component in the effluent due to the reduced sludge discharge. Results of the metal analysis in sludge showed that in the ozone train the content of acid-insoluble materials, Fe, and Al were more than double or triple, while the difference in heavy metals, Mg, and Ca was comparatively small (Sakai et al., 1997).

A study by Dignac et al. (2000) showed that although sludge ozonation caused a slight increase in TOC in the effluent, the organic matter in the effluent following sludge ozonation was mainly composed of protein and sugar moieties, which are harmless to the environment.

4.2. *Stability of nitrification*

Research has showed that nitrification capacity is not affected by ozonation (Huysmans et al., 2001). In an activated sludge-ozonation process for treating real domestic wastewater, the ammonium removal efficiency of the ozonation run and the control run were similar during 50 days of operation. Furthermore, active biomass measurements revealed that autotrophic biomass seemed to be less affected than heterotrophic biomass. At the same organic loading rate, heterotrophic biomass concentration during ozonation was more than 10% lower than that for the control. In contrast, the autotrophic biomass concentration during the ozonation run was 40% higher (Deleris et al., 2002). The nitrifiers are normally overgrown by faster-growing heterotrophs and may therefore be partly protected in the sludge floc and not exposed to ozone as much as the heterotrophs (Böhler and Siegrist, 2004). The study by Dytczak et al. (2007) showed that although additional ammonia released from recycled sludge after ozonation was approximately 5.9% more in an SBR, the ammonium in the effluent was always below the detection limit of 0.3 mg/L and nitrite was not detected, indicating complete nitrification. Nitrification aims to form bacterial clusters to protect against environmental stressors (Wolff and Hurren, 2006).

Vergine et al. (2007) assessed autotrophic biomass activity using a set-point titration technique in an activated sludge process treating textile wastewater coupled with partial ozonation of the returned sludge. After 7 weeks of ozonation treatment, the specific ammonium oxidation rate was approximately halved, while the specific nitrite oxidation rate was almost the same. However, the reduction in ammonium oxidation activity did not translate to a reduction in the nitrification capacity of the plant, since no ammonium nitrogen removal was affected.

4.3. *Improvement of denitrification*

Denitrification is often limited by the carbon source in the plant inlet. The solubilized compounds and the unsettled micro-particles of the ozonated sludge have been proved to be an effective carbon source for denitrification (Ahn et al., 2002; Böhler and Siegrist, 2004; Cui and Jahng, 2004; Dytczak et al., 2007), leading to substantial cost savings in reactors which are carbon-limited. Ahn et al. (2002) conducted batch denitrification tests using solubilized and unsettled organics from the ozonated sludge at 0.1 g O_3/g TSS as a carbon source. The denitrification rate ranged from 0.011 to 0.081 g NO_3-N/g VSS d, which was comparable with other carbon sources commonly used for denitrification (Table 3) (Metcalf and Eddy, 1991). In a pilot-system which consisted of the A^2/O process and sludge ozonation, the solubilized and unsettled fraction of the ozonated sludge was recirculated to the anoxic phase. During 60 days of operation the TN removal efficiency increased by around 10% although there was variable nitrogen removal efficiency (Ahn et al., 2002). Dytczak et al. (2007) reported that denitrification during the initial anoxic phase in an anoxic/aerobic SBR was enhanced by ozonation to 20% in the recycled sludge. This decrease in nitrate in the final effluent was around 5% at a dose of 0.01 g O_3/g TSS and increased to around 20% at a dose of 0.08 g O_3/g TSS, indicating improved total denitrification.

4.4. *Sludge settling properties and dewatering conditions*

An improvement in the settling properties of the sludge and a reduction in bulking and foaming are well documented following sludge ozonation (Caravelli et al., 2006; Deleris et al., 2002; Kamiya and Hirotsuji, 1998; Paul and Debellefontaine, 2007; Vergine et al., 2007; Weemaes et al., 2000). Sludge disintegration produces smaller flocs and a turbid supernatant. Recirculation of the ozonated sludge leads to an equalization in particle size distribution, which improves sludge settling (Böhler and Siegrist, 2004). In addition, the increased apparent food-to-microorganism (F/M) ratio favors the production of extracellular polymer substances (EPS) in ozonated reactors, enhancing flocculation, which has the potential to improve settling (Dytczak et al., 2006). According to Wolff and Hurren (2006), following the use of sludge ozonation, the floc becomes rounder and more compact which also improves the settling properties. The sludge index (SVI) also decreases.

In an aerobic SBR, partial ozonation of the returned sludge with doses of 0.016–0.080 g O_3/g TSS, reduced the SVI from about 59 mL/g TSS to 43 mL/g TSS and decreased this value even more in the alternating A/O SBR to around 30 mL/g TSS. Microscopic observation showed a significant reduction in filamentous bacteria in the ozonated lane (Deleris et al., 2002).

Research has shown that ozonated sludge allows low dewatering and filterability, compared with raw activated sludge. Proteins released by cell lysis have a negative effect on sludge dewatering due to their surface charge and cations are needed for the destabilization of sludge flocs. Moreover, the unsettled micro-particles may have an adverse influence on sludge filtration leading to a more compact filtration layer with reduced permeation of liquids. A strong increase in the capillary suction time (CST) value from 151 s to 382 s after ozonation with a dose of 0.1 g O_3/g TSS has been reported (Bougrier et al., 2006). The filtration of sludge is related to the ozone dose. The specific resistance to filtration (SRF) value rapidly increased at an ozone dose up to 0.2 g O_3/g TS and then decreased dramatically at a dose of 0.5 g O_3/g TS (Deleris et al., 2002).

For the system combining a biological wastewater process and ozonation, the negative impact of ozonation on dewaterability is minimal. According to Dytczak et al. (2006), after ozonation the average CST of sludge from a combined SBR and ozonation system increased slightly from 5.9 s to 6.2 s. For ozonation of the digested sludge, a decrease in water content of the dewatered sludge cake was reported.

Table 3 – Comparison between ozonated sludge and other carbon sources commonly used for denitrification.

Carbon source	Denitrification rate (NO_3-N/g VSS d)	Typical value (NO_3-N/g VSS d)
Methanol	0.12–0.90	0.43
Wastewater	0.03–0.11	0.07
Endogenous	0.017–0.048	0.035
Solubilized organics by ozonation	0.011–0.081	0.05

5. Cost and energy evaluation

Sludge ozonation is a potential technique for reducing sludge. The decision to apply this system mainly depends on the magnitude of capital investments, energy costs and sludge disposal costs. Both operational and capital costs in the ozonation-activated sludge process are high due to the energy required for ozone production. Taking into account the increased costs of sludge disposal, the operational cost and the investment needed for sludge ozonation may be offset by the decreased operational costs for sludge treatment and disposal. Economical estimates have suggested that the operational cost of the whole process of combining activated sludge and sludge ozonation was lower than that of the conventional activated sludge process when the costs of sludge dewatering and disposal were considered (Yasui et al., 1996). Ahn et al. (2002) using a simple economic analysis, reported that the ozonation process may be more economical than incineration for sludge treatment and disposal at small and medium-sized WWTP.

In order to improve the overall economics of energy recovery from anaerobic digestion of municipal sludge, Komatsu et al. (2007) proposed a new mesophilic–thermophilic hybrid anaerobic digestion process with ozonation of digested sludge, in which slowly biodegradable ozonated sludge was digested rapidly in the thermophilic condition, and soluble organic components remaining in the thermophilic

Table 4 – Comparison of the total cost before and after ozone treatment.

Items	Total operation cost (€)	
	2003 without ozonation	2004 with ozonation
Sludge treatment and disposal	24237	4485
Ozone pilot plant		4749
Total	24237	11234

condition were converted to biogas efficiently in the mesophilic condition. The reduced ozone consumption and improved solid-biogas conversion reached 78.6%. When applied to the municipal WWTP of 150,000 p.e., this process yielded electricity at only 3.0 cent/kW h lower than the market price (5.4 cent/kW h).

Caffaz et al. (2005) reported a saving equal to 54% of the total sludge treatment cost in the Torre WWTP, using the combined treatment of ozone-aerobic digestion. As shown in Table 4, due to a significant decrease in the cost of disposal, the total cost of sludge treatment in 2004 using ozonation decreased by €13000, compared with that in 2003 without ozonation. The operational costs of the ozone pilot plant consisted of oxygen, energy for the pump, ozone generator and destroyer and maintenance costs.

When the cost of investment for the ozone equipment is considered, the sludge-ozonation process may not be economical. Boehler and Siegrist (2006) carried out an economic-efficiency and energy-balance calculation for an existing Swiss WWTP (35000 p.e.) with sludge ozonation. The economic-efficiency calculation consisted of investment, operational and maintenance costs as well as additional costs due to biogas reduction and the cost reduction for sludge disposal. As shown in Table 5, the costs for investment and the operation of sludge ozonation were not offset by the lower sludge treatment costs for transport, conditioning, dewatering, drying, incineration and ash disposal. It should be mentioned that the small size and the specific design of the WWTP (12 lanes) generated high investment costs. In addition, the costs for liquid oxygen were high. The energy consumption was estimated based on ozone production from liquid oxygen. Ozonation requires energy for ozone production (12.5 kW h/kg O_3), transfer to the sludge (2.5 kW h/kg O_3) and energy consumption to produce liquid oxygen (0.5 kW h N m^{-3} O_2). A reduction in sludge of 30% increased the total electric energy consumption of a municipal WWTP by approximately 20% (Boehler and Siegrist, 2006).

In summary, sludge ozonation may be economical for larger plants with high sludge disposal costs or may be of interest to plants where operational problems such as foaming and bulking sludge can be reduced.

6. Discussion

Although ozonation-assisted sludge reduction processes have been successfully applied in practice, the problems associated with these processes should also be considered. For a combined system of an activated sludge process coupled with partial ozonation of the returned sludge, accumulation of inert particles should be considered because such particles are not discharged from the reactor to the same extent as those in the conventional process. Although research in pilot-scale and full-scale operations has shown that inert organic substances do not accumulate significantly (Dytczak et al., 2007; Yasui et al., 1996), an operation with a suitable sludge wasting ratio seems to be necessary to prevent accumulation of inorganic and inert particles for long-term operation, and a longer SRT is required to biologically decompose the inert materials. In addition, phosphorus would not be removed if there was no excess sludge production. It should be stressed that after the introduction of ozonation into activated sludge processes, nutrients released by cell lysis may increase downstream and require removal. An increase in oxygen supply may be needed to guarantee effluent quality. Furthermore, the study by Dytczak and Oleszkiewicz (2008) showed that after prolonged daily ozone treatment, sludge floc becomes stronger, denser, and more ozone-resistant. These findings suggested that, for prolonged operation of partial sludge ozonation, an increase in ozone dose may be required to continuously maintain the expected solids destruction level. This in turn will increase the operational costs of the treatment.

In a continuous system associating ozone and biological treatment, both the applied ozone dose and the quantity of sludge ozonated have a considerable influence on the system performance. It was reported that ozonation of 4–9% (activated sludge system) and 20% (SBR) in the returned activated sludge had no significant negative impact on the final effluent quality (Dytczak et al., 2007; Sakai et al., 1997). For the applied ozone dose to reduce sludge production, the necessary ozone dose for sludge reduction has been reported to range from 0.02 to 0.5 g O_3/g TSS (Boehler and Siegrist, 2006; Caffaz et al., 2005; Deleris et al., 2002; Lee et al., 2005; Sakai et al., 1997; Sievers et al., 2004; Vergine et al., 2007; Wolff and Hurren, 2006; Yasui et al., 1996). The most commonly used dose was lower than 0.05 g O_3/g TSS. Higher ozone doses produced less excess sludge. However, ozone overdosing increased operational costs and residual ozone may inhibit biomass production which plays a role in organic degradation. In addition, at higher levels of ozone consumption, increasing rates of sludge solubilization were found to decrease. Longer ozonation also resulted in the oxidation of released materials. A study by

Table 5 – Specific cost for the observed WWTP based on sludge reduction of 2.82 kg SS p.e.$^{-1}$ y^{-1} and ozone consumption of 0.5 kg O_3 p.e.$^{-1}$ y^{-1} (0.05 g O_3/g SS).

Items	Costs	Units (€)
Investment (annual), maintenance	2.84	p.e.$^{-1}$ year^{-1}
Oxygen consumption and hire bearing and conditioning of oxygen, energy consumption for ozonation production and entry	1.01	kg $SS^{-1}_{reduced}$
Cost benefit due to sludge reduction	−1.57	p.e.$^{-1}$ year^{-1}
Minus cost due to loss of biogas	−0.56	kg $SS^{-1}_{reduced}$
Net costs for sludge ozonation	1.25	p.e.$^{-1}$ year^{-1}
	0.45	kg $SS^{-1}_{reduced}$
	0.009	m^{-3} water treated

Yasui et al. (1996) indicated that sludge reduction is dependent on ozone dose and the amount of sludge to be ozonated in the activated sludge process coupled with ozonation. The ozone dose must be at least 0.015 g O_3/g TSS. Complete elimination of excess sludge has been achieved by Sakai et al. (1997) at an ozone dose of 0.034 g O_3/g TSS and by Yasui and Shibata (1994) at a dose of 0.05 g O_3/g TSS per day in the aerobic tank. According to the literature and the full-scale application of ozonation, the recommended ozone dose ranges from 0.03 to 0.05 g O_3/g TSS, which is appropriate to achieve a balance between sludge reduction efficiency and cost.

Several studies have compared ozonation with other disintegration methods, and the performance of these methods can be compared on the basis of the specific energy applied per mass of solids treated. All investigations using ozone treatment resulted in high COD release, whereas considerably less COD was released using mechanical disintegration (Boehler and Siegrist, 2006; Camacho et al., 2002; Müller et al., 1998; Müller, 2000). Thermal and mechanical treatments result in the breakdown of microorganisms, while the oxidative treatment destroys the flocs and disrupts the microorganisms. 35% of COD is released after 24 h of contact time at 95 °C, 60% of COD is released at 500–700 bars after 10 passes and 60–65% of TOC is released by ozonation. Sievers et al. (2004) found that compared with mechanical and thermal treatment of sludge, the mass reduction potential of ozonation was higher as were the costs.

In summary, the main advantages of sludge ozonation are as follows (Boehler and Siegrist, 2006; Liu, 2003; Pérez-Elvira et al., 2006; Wei et al., 2003; Yasui et al., 2006):

(1) Ozonation is a well proven technology for sludge reduction and is successful in full-scale plants.
(2) The sludge settleability was highly improved and bulking and foaming could be reduced.
(3) No significant accumulation of inert solids occurred in the aeration tank at the optimal ozone dose and sludge wasting ratio.
(4) Higher solids degradation efficiency and methane production during anaerobic digestion with ozonation.

Typical drawbacks of sludge ozonation are as follows:

(1) High capital costs related to equipment and high operational costs for ozone production.
(2) Sludge ozonation causes a slight increase in TOC and phosphorus concentration in the effluent.
(3) Consumption of ozone for the degradation of other possible organic materials which may be present.
(4) Metals present in the initial sludge are transferred to the liquid phase and should be purified.

In recent studies, the ozonation of sludge was analyzed more deeply. For example, the effects of sludge ozonation on the removal of persistent pollutants, such as PAH, PPCPs (Bernal-Martinez et al., 2007; Carballa et al., 2007), and on EPS content and composition (Dytczak and Oleszkiewicz, 2008) were evaluated. In future studies, more attention should be paid to the impact of sludge ozonation on the microbial community and microfauna populations in the bioreactor. The application of biological and chemical techniques, including PCR-DGGE, FISH, and analysis of bio-macromolecule enzymatic activities, leads to a better understanding of the reaction mechanism of the combined processes. In addition, an effort to design and optimize an economic sludge reduction process is necessary.

7. Conclusions

Sludge ozonation to reduce excess sludge has been successfully applied in full-scale industrial and municipal wastewater treatment. The sludge-ozonation process is generally described by the sequential decomposition reactions of floc disintegration, solubilization, and the subsequent oxidation of released organics to carbon dioxide (mineralization). The introduction of ozonation into activated sludge does not significantly influence the effluent quality and the settling properties of the sludge are improved. Enhancement of the anaerobic/aerobic stabilization processes using sludge ozonation was observed. An operation with a suitable sludge wasting ratio seems to be necessary to prevent accumulation of inorganic and inert particles for long-term operation. Sludge ozonation may be economical for WWTP which have high sludge disposal costs and operational problems such as sludge foaming and bulking. The recommended ozone dose ranges from 0.03 to 0.05 g O_3/g TSS, which is appropriate to achieve a balance between sludge reduction efficiency and cost. In future studies, more attention should be paid to the impact of sludge ozonation on microbial community and microfauna populations in the bioreactor for a better understanding of the reaction mechanism of the combined processes.

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