A review on sludge conditioning by sludge pre-treatment with a focus on advanced oxidation

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Abstract

The production of excess sludge by biological wastewater treatment processes has been a serious issue for the operation of wastewater treatment plants (WWTP) on both economic and environmental sides. To reduce the sludge volume by the separation of water from solid matters, the sludge dewaterability needs to be improved through conditioning processes. Many conditioning methods have been developed and applied for this purpose. Among them, the oxidization techniques have many advantages including lower cost, higher efficiency, and lower environmental impact. This paper reviews the recent progress of sludge conditioning techniques and the basic mechanisms involved. Especially, a detailed review and discussion were dedicated to the oxidization techniques and their applications to sludge dewaterability improvement.

Key words: waste activated sludge; dewatering; dewaterability; advanced oxidation; hydrogen peroxide; Fenton

Nomenclature

AOPs	Advanced oxidation processes
COD	Chemical oxygen demand
CST	Capillary suction time
DNA	Deoxyribonucleic acids
DS	Dry solids
EPS	Extracellular polymeric substances
LB-EPS	Loosely bound EPS
SRF	Specific resistance to filtration
TSS	Total suspended solids
SVI	Sludge volume index
TB-EPS	Tightly bound EPS
WAS	Waste activated sludge
WWTP	Wastewater treatment plant
ZVI	Zero-valent iron

1 Introduction

Many biological wastewater treatment plants (WWTPs) have been employed worldwide to treat domestic wastewater with a high degree of success. However, large amounts of waste activated sludge (WAS) are produced in these sewage treatment facilities. For example, the annual production of dried WAS is estimated to be 10 and 14 million tons in the USA and China, respectively.[1, 2] The sludge treatment and disposal is difficult and expensive due to the large volume to be handled. According to

Canales, et al. [3] up to 60% of the total cost for operating a wastewater treatment plant is for the WAS management.

The management of wastewater treatment processes such as manipulating the food to microorganism (F/M) ratio and controlling the sludge volume index (SVI) could impact sludge dewaterability[4] and hence the volume of sludge produced. However, sludge pre-treatment is most often needed to ensure consistently good dewaterability and stable operation.

A complete sludge treatment train is generally divided into five consecutive steps, namely thickening, stabilization, conditioning, dewatering, and final disposal/reuse. Among them, thickening and dewatering are mainly practiced to reduce the sludge volume by removing water from sludge solids. The sludge thickening processes, including air flotation, biological flotation, centrifugation, flat-sheet membrane filtration and gravity thickening, are primarily developed to separate free/bulk water from sludge solids therefore to reduce the volume of sludge to be treated by the subsequent processes. The solids content in WAS can be increased to 6% through thickening.[5] Stabilization is used to degrade the labile organics and to remove pathogens and odour.[6, 7] This is usually achieved through aerobic/anaerobic digestion, or through adding chemicals such as lime.[8, 9] Conditioning is employed to increase the dewaterability of waste activated sludge through physical disruption or the addition of chemicals including flocculants, acid, ferric chloride and lime. The conditioning process enhances the subsequent dewatering performance through either flocculation or the disruption of the floc structure of sludge particles. Mechanical dewatering is the last step before sludge disposal, which is usually achieved through press filters, centrifuges and dryers. After dewatering process, the water content in the filtered sludge normally decreases to around 80%, i.e. with 20-25% dry solids (DS) in the sludge cake.[5, 10]

Among the five sludge treatment steps, extensive research has been devoted to the sludge digestion, both as a stabilization and as an energy/resource recovery process.

Various pretreatment technologies have been developed to improve the solids destruction and methane production.[11] However, conditioning processes are receiving more and more attention from researchers due to the challenges of ever-increasing amount of sludge with the extensive construction of WWTPs and the emergence of some newly-developed techniques for wastewater purification characterized by high biomass concentrations. Also, more stringent regulations on final sludge disposal/reuse demand higher dewatering performance to minimize the environmental impacts.

Various approaches including both physical (heat treatment, freezing and thawing, and mechanical disintegration) and chemical treatment are widely used to condition sludge for increased dewaterability. Chemical treatment includes the addition of flocculation agents, acid and alkaline. Also, the advanced oxidization conditioning process such as the Fenton oxidization and ozonation processes have been applied recently. In addition to energy-saving advantages compared to physical treatments, the oxidization processes potentially remove recalcitrant compounds in sludge, which might cause environment problems for final sludge disposal. This paper reviews the mechanisms of sludge dewatering and sludge conditioning technologies developed to improve dewatering efficiency. Especially, a particular focus is given to the application of advanced oxidization on improving sludge dewaterability.

2 Sludge components and impacts on dewatering

WAS is mainly composed of microbial cells, extracellular polymeric substances (EPS) and water. Microorganisms and EPS are the major parts of the suspended solids (SS) or dry solids (DS) in the sludge cake. Both have impacts on the dewatering performance because water attached to them is hard to be separated.

2.1 Water in sludge

The water in sludge is mainly divided into free water and bound water.[12] The physical properties of free water are similar to bulk water, which is not associated with or affected by the suspended sludge particles. This makes it easy to be separated from sludge through either thickening or dewatering processes. Bound water is a gross term of several forms of water, including interstitial water, surface/vicinal water, and intracellular water.

Interstitial water is held in the sludge floc structure, and can become free water when the floc is destroyed. In contrast, vicinal water is attached on the surfaces of sludge particles by different kinds of forces such as capillary and adsorptive forces.[13] Neyens, et al. [14] claimed that the basic mechanisms for the binding between water molecules and EPS are attributed to the existence of hydrogen bonds and electrostatic interactions, which means both complexation and flocculation processes are involved. Thus, vicinal water is not free to move even the floc structure has been disrupted. A certain amount of water is held inside microorganisms, which are termed intracellular water [15]. There is also a portion water bounded chemically in sludge particles can only be removed by high temperature. [12] It is understandable that high level of vicinal water is undesirable for sludge dewatering because mechanical dewatering cannot remove any more than free water and interstitial water. In general, conditioning process is designed to transform the bound water into free water thus to facilitate the dewatering process.

2.2 Impacts of EPS on dewatering

As major components of activated sludge, extracellular polymeric substances (whose mass content reaches 80%) mainly consist of polysaccharides and proteins excreted by bacteria. EPS can protect cells from external environment through covering outside of the cells and controlling ion exchange. In EPS, polysaccharide and protein represent 70-80% of the total organic carbon,[14] with the rest of organic carbon dominated by deoxyribonucleic acids (DNA) and uronic acids.

The impact of EPS on sludge dewaterability depends on the content of EPS in sludge. The relatively lower dewaterability of the higher loaded sludge was found to be correlated with the higher concentration of EPS in the sludge.[16] Similarly, it was suggested that sludge with lower content of EPS had higher dewaterability due to easy flocculation. The increase of soluble proteins and polysaccharides in solution was found to cause the decrease of sludge dewaterability, [17]

The proteins and carbohydrates in sludge bind with water differently, thus leading to different impacts on sludge dewaterability.[4] Cetin and Erdincler [18] showed that the increase of carbohydrates led to higher sludge dewaterability while the increase of proteins affected it adversely. By comparing the change of proteins and polysaccharides distributions in sludge before and after hydrolysis and acidification, it was found that proteins influenced sludge dewaterability primarily, while carbohydrates and polysaccharides played secondary roles.[19] They found proteins turned into slime form tightly bound EPS (TB-EPS) and pellets after the treatment, thus influencing the sludge dewaterability negatively. It was also reported that the increase of loosely bound EPS (LB-EPS) in sludge had negative effects on sludge dewaterability while TB-EPS had no obvious effects.[20] It was argued that although EPS was an important structure for sludge flocculation, excessive EPS in the form of LB-EPS reduced the floc strength, leading to poor sludge-water separation.

Microbial cells in sludge, which is protected by the TB-EPS could also affect sludge dewaterability. Cells contain intracellular water in the form of hydration,[21] it was found that the disruption of cells led to the release of intracellular water. [22]

2.3 Impacts of sludge properties on dewaterability

Various physical properties of sludge flocs, including surface charge, relative hydrophobicity, flocculating ability and viscosity, were found to affect sludge dewaterability.[4] It was reported that the sludge flocs' physical properties were influenced by the protein content in sludge EPS, and thus its water binding capacity .[23]

Also, it was found that the sludge particle size distribution was changed by the increase of microbial extracellular polymer content in floc, which actually deteriorated the sludge dewaterability .[24]

Different biopolymers existing in waste sludge flocs are linked by different cations. [25]. Although excess monovalent cations (such as sodium) were attributed for low sludge dewaterability, increased concentration of multi-valent ions (such as calcium, magnesium, iron and aluminum) in sludge flocs is beneficial for the sludge dewaterability.[4, 26] The divalent cations, such as calcium and magnesium are capable of linking lectin-like proteins and polysaccharides. Meanwhile, the trivalent cations such as iron and aluminum can bind proteins, polysaccharides and humic acids together. This implies that the efficiency of sludge conditioning would be affected by cations in sludge which are crucial factors maintaining the floc structure.

3 Sludge conditioning to improve dewaterability

3.1 Measuring the sludge dewaterability

In the processes of sludge conditioning and dewatering, Both CST and SRF tests are widely used as quantitative indexes for the evaluation of the dewatering performance. CST stands for the time needed for completing the filtration of sludge, which is an empirical index. It was applied widely for measuring sludge dewaterability due to its easy operation. On the other hand, SRF is also applied as the index of the sludge dewaterability by measuring the extent of water yielded during filtration process. It is based on the proportional relationship between viscosity of sludge and the decrease of pressure over a certain distance.

The relationship between SRF and CST is:

$$CST = C_1 * SRF * \mu * w + C_2 * \mu$$

In the equation, C_1 and C_2 stands for the coefficients related to CST, μ stands for the viscosity of the filtrate (Ns/m^2), and *w* is the solid content of the filtrate (Kg/m^3). [27]

Other methods are also applied for measuring sludge dewaterability:

- The bound water measurement methods, such as the centrifugation method, dilatometric measurement as well as differential scanning calorimetry, could measure the bound water concentration in sludge. [4, 28, 29]
- It was also found that the sludge rheological properties were related to sludge dewaterability. Ormeci applied torque rheology techniques on the optimaztion of polymor dosing for full scacle WAS.[30] More recently, Ormeci and Ahmad developed a method to measure the shear during the sludge conditioning process,[31] which could also contribute to the operation of automatic conditioning and dewatering system.
- Dry solids (DS) contents in sludge cake were sometimes also applied as an index for sludge dewaterability,[32, 33] which stood for the residuals after evaporation under 105 ^{o}C.
- Other physical sludge properties such as surface charge, relative hydrophobicity or viscosity were found having relationships with sludge dewaterability,[4] thus the measurement of these parameters might also be helpful to understand the sludge dewaterability indirectly.

3.2 Chemical conditioning

The chemical treatment methods include the addition of flocculation agents, acid-alkaline treatment, enzyme addition, ozonation, and advanced oxidation processes (AOPs). Among them, the oxidation processes will be elaborated in a separate section.

Addition of flocculation agent

Inorganic flocculation agents, such as ferric chloride or lime are the traditional chemicals for sludge conditioning for decades. It was found that crystalloids were formed outside the flocs which could easily transmit the stresses into the flocs thus facilitating the separation of water during dewatering processes.[34] Organic flocculation agents were also investigated extensively for their effects on sludge dewatering. By applying both single and dual polymers on the improvement of sludge dewaterability, it was found that skeletal structure was formed and the filterability was improved after the treatment. [35] Ma and Zhu developed a new kind of copolymers by grafting cationic poly onto nonionic polyacrylamide, and demonstrated that such kind of copolymers could improve sludge dewaterability better than homopolymers and dualpolymer systems.[36]

However, as the polymer flocculation agent is difficult to degrade, its persistent impacts on environment after final disposal is still a technological hurdle .[37]

Acid/alkaline treatment

Many studies have illustrated the effect of pH on flocculation characteristics of sludge. The stabilization of flocs in sludge was deteriorated due to electrostatic repulsion between inter-surfaces of sludge when pH value fell below 2.[38] The best flocculation could be attained when pH fell into the range of 2.6-3.6 theoretically, which is also the isoelectric point of the sludge. Similarly, Liu et al. reported the reduction rate of CST was around 80% while the pH was reduced to 2.4.[39] Nowadays, acids are often applied with other kinds of reagents. Chen et al. investigated the effect of acids on sludge dewaterability as well as its combination with surfactant, and got the optimum results at pH=2.5 while adding the acids and surfactant simultaneously.[10]

The sludge dewaterability could also be improved by high pH due to the decomposition of sludge structure, which results in the release of bound water and EPS from sludge.[40] [41]Thermochemical processes, which incorporate the thermal and acid/alkaline treatment, had also been applied to sludge conditioning successfully. Neyens, et al. [42] found the dry solids (DS) of filtered sludge cake increased from 28% to 46% under pH=10 and 100 °C.

Enzyme treatment

Enzyme addition could also initiate the hydrolysis of EPS and cells in sludge, thus lead to the removal of bound water from sludge. A series of hydrolase was applied for the sludge conditioning and achieved noticeable improvement on sludge dewaterability, i.e. DS in the filtered cake increased from 28.1% to 32.4%.[43] One kind of commercial enzyme mixture was used for improving the dewatering capacity of digestion sludge, and 50% increase of DS was attained. However, pilot scale reactors located in US only achieved limited efficiency.[44] In general, the application of enzymes on the sludge conditioning is still limited due to its difficulties in operation and the high operational cost.

3.3 Physical treatment

Physical treatments, including heat treatment, freezing/thawing and mechanical disintegration, are used widely as a sludge conditioning process to improve its dewatering performance.

Heat treatment

The temperature for heat treatment normally falls in the range of 40-180 °C. During heat treatment, proteins in EPS were found to be denatured. Also, cell walls of bacteria were broken.[45] In the meantime, the thermal hydrolysis of extracellular and intracellular materials leads to decomposition of sludge structure therefore to improve the removal rate of the bound water. Neyens et al. operated a semi-pilot-scale reactor at 120 °C under neutral condition for 60 min, and attained the increase of DS by 43% for the filter cake. [45] The first full-scale heat treatment process located in Norway was reported to increase DS from 15-20% to 30-40%, while 60% of the COD in sludge was converted to biogas.[46]

Freezing/thawing treatment

Freezing/thawing treatment is able to break the microbial cells and the floc structure, and thus releases the bound water from sludge. The flocculent structure characteristics such as density and morphology was found to change greatly with low freezing speed.[47] The dewaterability was increased by 82% compared to untreated sludge. Similarly, it was reported that the slow-frozen process achieved better sludge dewaterability than fast-frozen process.[48] The data showed that after the slow-frozen treatment at 10 ℃, the average dewatering rates increased by 7 times.

Mechanical disintegration treatment

Mechanical approaches are mainly based on the mechanisms of cavitation or activation of free radicals. The effect of ultrasound on sludge dewaterability was found to be limited, although the decrease of EPS in the sludge is observed.[49] However, positive effect on sludge dewaterability by ultrasonic treatment was also reported.[40] The contradictions imply that the effect might only available in a certain range of ultrasonic density or certain sludge.

3.4 Sludge dewatering processes

Many techniques are applied on the sludge dewatering processes. The main devices for sludge dewatering include vacuum filter, centrifuge, belt press and dryer.

For sludge dewatering, rotary vacuum filters are mostly used, which could separate the solids and water by the suction effect. Vacuum filters have been applied to sludge dewatering for several decades. Recent research has focused on the optimization of operational parameters for the filters. It was found that the operational parameters of vacuum filters were affected by the morphological and physical characteristics of the sludge, such as particle distribution and distribution [50, 51].

Centrifuge and belt press are also common devices for the separation of solids and water in sludge by centrifugal force and pressure, respectively. It was found that the simultaneous addition of acid and surfactant could lead to the improvement of dewatering efficiency by centrifuge[10]. On the other hand, a novel electro-osmotic belt filter was also developed for sludge dewatering, which was demonstrated to be a cost-saving device compared to the traditional belt presses[52].

Dryers are also widely used for the removal of water in sludge thermally. According to Chen et al.,[53] the dryers could be mainly categorized as direct, indirect and combined sludge dryers. More recently, some researchers focused on the application of drying reed beds. Uggetti et al.,[54] applied drying reed beds on sludge dewatering and found the TS increased up to 20-30%. Similarly, Stefanakis et al.,[55] also reported its promising dewatering effects on surplus activated sludge.

4. Sludge conditioning by advanced oxidization processes

4.1 Mechanisms of Fenton reaction

Although Fenton reaction has been found more than one century ago, its basic mechanisms involving the production of free radicals was not clear until the early half of the 20th century.[56] Still in controversy, but researchers usually considered the traditional Fenton reaction process as a sequence of reactions as below (Eq. 1-9):

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^- \qquad \text{Eq. 1}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet}/O_2^{\bullet -} + H^+ \qquad \text{Eq. 2}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet}/O_2^{\bullet -} + H_2O \qquad \text{Eq. 3}$$

$$Fe(III) + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow Fe(II) + O_2 + H^+ \qquad \text{Eq. 4}$$

$$Fe(II) + {}^{\bullet}OH \rightarrow Fe(III) + OH^- \qquad \text{Eq. 5}$$

$$Fe(II) + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow Fe(III) + H_2O_2 \qquad \text{Eq. 6}$$

$$HO_2^{\bullet}/O_2^{\bullet -} + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow H_2O_2 + O_2 \qquad \text{Eq. 7}$$

$${}^{\bullet}OH + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow H_2O + O_2 \qquad \text{Eq. 8}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad \text{Eq. 9}$$

Reactions 1-6 stand for the process of hydroxyl radicals generation from peroxide with the catalysis of Fe(II) and Fe(III). According to the stoichiometric equations, cycles of iron between Fe(II) and Fe(III) initiate the overall reactions. Fenton reactions are normally operated at low pH around 3 to avoid possible precipitation of ferric ions. Eq. 8 describes the consumption of peroxide which leads to the chain termination. Fenton reactions could also begin from the reactions between ferric salt and peroxide as shown in reaction 2, which is termed as "Fenton-like" reaction.

Some modified Fenton methods, including photo-Fenton and electro-Fenton reactions, were also applied to improve the oxidization efficiency of classical Fenton reaction. [57, 58] The photo-Fenton method mainly applies the photolysis of iron complex and peroxide in solution which produces free radicals as well as iron ions. The electro-Fenton applies the electrochemical mechanism and dissolves solid iron electrodes.

As an effective oxidization technique, Fenton peroxidation process has been considered as the most commonly used method on industrial wastewater treatment, such as the removal of nitrobenzene and phenol from liquid [59] and the reduction of toxicity in phenolic wastewater. [60] Fenton peroxidation process could also be applied on wastewater discoloration[61] as well as landfill leachates treatment. [62]

4.2 Application in sludge conditioning

Researchers have already applied Fenton reagent on conditioning of sludge for several decades (Table 1). After the oxidization treatment of pulp sludge, the sludge filterability was found improved.[16] It might be contributed by the improvement of sludge hydrophobicity due to the hydroxyl group was converted to carboxyl group, as well as the decreased surface charge density. Mustranta and Viikari [63] also demonstrated that the Fenton reagent at low concentration could improve the filtration capacity of activated sludge from different source effectively after the treatment for 1-2 hours.

Table 1. Summary of literature finding on Fenton reagents treatment (Fe^{2+} +H_2O_2) on sludge conditioning.

Sludge	**pH**	**Solids concentration (mg/*L*)**	**Dosage (mg Fe/g solids)** [a]	**Dosage (mg H_2O_2/g solids)** [a]	**Ratio of Fe^{2+}/H_2O_2** [b]	**Treatment time (min)** [c]	**SRF** [d] **reduction (%)**	**DS** [d] **increase (%)**	**CST** [d] **reduction (%)**	**Reference**
Settling tank	<3.5	20010 (TS)	300[50-300]	300[100-300]	1[0.17-1]	50	92.13	N/A	48.6	[64]
WAS	3	8300 (SS)	1084[181-1084]	361	3 [0.5-3]	2 [2-120]	95	N/A	N/A	[65]
Alum sludge (water treatment)	6	2850	21[3.5-2100]	105[3.5-3510]	0.2[0.001-600]	1	N/A	N/A	48 ± 3	[37]
Sedimentation tank	6	2850	20	125	0.16	1	N/A	N/A	47	[66]
2 kinds of WAS	3	N/A	1.67	25	0.07	60	N/A	79.1and 90.3	N/A	[33]
Activated sludge from 4 different	3	20000-30000	0.93-1.4	33-50	0.03	30	33-100	N/A	10-96	[16]

pulp and paper plants	

[a] The dosage is shown as the optimal dosage [investigated range].

[b] The Fe2+/H2O2 ratio is shown as the optimal ratio [investigated range].

[c] The treatment time is shown as the optimal treatment time [investigated range].

[d] SRF: Specific resistance to filtration; CST: Capillary suction time; DS: Dry solid.

Optimizing the Fenton treatment conditions for sludge conditioning has been the research focus over the last ten years. Neyens and Baeyens [5] compared various reaction pathways of Fenton reactions with different ratios of ferrous/peroxide (≥2, =1, and <1). They concluded that the proportion of ferrous and peroxide in the reagent was an important parameter in sludge conditioning by affecting the chemical kinetics of Fenton reactions.[5] The most effective conditioning parameter for Fenton peroxidation treatment is determined to be 1 mg/37 mg ferrous/peroxide per 6.3g DS of sludge at pH=3, which led to the increase of DS by 30% and reduction of CST by 44%. Buyukkamaci [64] also applied different concentrations of ferrous salt and peroxide on biological sludge. The highest reduction of CST and SRF was attained at the concentration of 0.30 mg Fe^{2+} /mg TS and 0.30 mg H_2O_2 /mg TS. Another study attained the lowest SRF in sludge cake at 1.08 mg Fe^{2+} /mg SS and 0.36 mg H_2O_2/mg SS, respectively. [65]

Fenton processes for sludge conditioning can also change the sludge physical properties. Thermal conductivity increased significantly after Fenton peroxidation treatment, along with the increase of DS, compared to the untreated sludge from different sources [33]. The authors also compared the effect of different conditioning process including thermal hydrolysis, acid/ alkaline hydrolysis and concluded that Fenton peroxidation was one of the most effective methods for sludge conditioning.

The Fenton-like reaction was also examined for improving sludge dewatering ability. Lu et al. applied Fenton-like reagent (Fe^{3+}/H_2O_2) on WAS and attained promising effect (Reduction rate of SRT by around 85%).[37] The treatment efficiency of Fenton-like reactions with different metal ions (such as Cu^{2+}, Zn^{2+} etc.) besides Fe^{2+} was limited. Beyond classical Fenton process, lab-scale photo-Fenton process was also applied in sludge treatment. Tokumura, et al. [57] incorporated a photo reactor with a UV lamp as the photo source. They found the release of COD from sludge and the decomposition of the dissolved COD as well. They also reported that when the mass ratio of Fe and peroxide was 1/100, the treatment efficiency reached the maximum.

The solar energy was later introduced as a photo source for using the photo-Fenton method. [67] However, the sludge dewaterability characteristics were not involved in these works.

Furthermore, other techniques were also introduced with the combination of Fenton process. A magnetic zone was used in the Fenton reaction reactor for the conditioning of anaerobically digested sludge.[68] It was found that the existence of magnetic zone could reduce the surface tension therefore to facilitate the oxidation of sludge by Fenton reagent.

The economic analysis on the operation of sludge peroxidation can save 52 € for every ton of DS compared to thermal and thermochemical hydrolysis methods.[14] Similarly, Tony, et al. [37] also compared the cost for sludge conditioning by Fenton reagent with polymer flocculent, which is the most widely used method currently, and came to the conclusion that the cost of these methods fell into the same range, other than the extra advantages of Fenton process on environment. A pilot-scale Fenton peroxidation treatment of sludge with promising treatment efficiency by the addition of 25g H_2O_2/1.67g Fe^{2+} per kg DS attained net saving of 950000 € per year.[45] All these results collectively showed that Fenton reagent is an economical sludge conditioning for improving dewaterability.

Fenton reagent was also found helpful for the destruction of pathogens in sludge, [69] as well as the removal of micropollutants, such as PAHs and steroid estrogens.[70, 71] Fenton reagent was also effective in the heavy metal leaching in sludge.[72]

4.3 Effect of advanced oxidation processes on dewatering processes

Although a few researchers tried to examine the relationship between the advanced oxidation pretreatment and dewatering processes, there are still significant research gaps at present. Lu et al.,[65] found moisture of the sludge decreased after Fenton pretreatment, which could facilitate the following dewatering step. Dewil et al.,[33] also found the Fenton processes could improve the sludge's thermal conductivity, thus for a multiple hearth dryer, much less plates are needed compared to the conventional sludge without Fenton pretreatment. Neyens et al.,[14] reported the enhancement of Fenton processes on the floc strength, which is considered as an important effect on facilitating the operation of vacuum filtration for sludge dewatering process[73]. Obviously, further research should be done on the effect of pretreatment with advanced oxidation processes on improving the dewatering efficiency, such as the effect of advanced oxidation on different kinds of dewatering devices and the optimization of the operational parameters for the dewatering devices.

4.4 Alternative advanced oxidation processes for sludge conditioning

Similar to the catalysis of hydrogen peroxide, Fe(II) could also activate persulfate and form sulfate radicals with high redox potential and strong oxidizing capability. Different from the Fenton reactions usually occurring under acid condition, the Fe(II)-persulfate reactions are mainly operated under neutral condition. The Fe(II)-persulfate oxidization process was widely applied on the decomposition of refractory organics. [39, 74, 75]

For sludge conditioning, Zhen et al. [21, 22, 76, 77] demonstrated that the Fe(II)-persulfate treatment improved the dewaterability of sludge. CST reduction rate by 88.8% was achieved in a very short treatment time, i.e. less than 1 min.[77] Zhen et al. also discovered that the sulfate radicals formed during the reaction could destruct EPS and the microbial cells in sludge effectively. The treatment decomposed and solubilized EPS and flocs, thus transforming bound water into free water. Meanwhile, the dewaterability was not affected significantly by the bound EPS after treatment.[77]

When the Fe(II)-persulfate oxidization process was combined with the electrolysis process, it was found that the TB-EPS around the cells will be decomposed and transformed into LB-EPS and slime EPS, with the bound water being released. This facilitated the destruction of cells in sludge and further improved the dewaterability of sludge.[22] On the other hand, the combination of thermal treatment and

Fe(II)-persulfate process could also improve the dewaterability by decomposing the protein-like substances in EPS as well as destructing the polymeric backbone. [21, 76] Compared to the traditional Fenton reagent which has no residual anions in sludge, the sulfate ions produced by the Fe(II)-persulfate reactions might need post-treatment. However, its high treatment efficiency may offset the drawback.

5. Sludge conditioning by other strong oxidants

5.1 Ozone treatment

For decades, ozonation, as a pretreatment method, has been employed to enhance the sludge degradability for the following sludge digestion stage.[78, 79] It was demonstrated that the ozone treatment oxidized the organics in sludge thus facilitating the anaerobic/aerobic digestion. However, only a few of these works focused on improving the sludge dewaterability by ozonation treatment. Some results reported that the sludge dewaterability was actually deteriorated due to the effect of ozonation. The possible reason for the deterioration of sludge dewaterability was suggested to be the formation of smaller particles due to the destruction of sludge floc, which then blocked the filter during the measurement.[78, 80, 81] It was also reported that the aerobic digestion process following ozonation further improved the sludge dewaterability by degrading the fine particles produced by ozonation process.[82]
There are also some results showed that the ozonation treatment enhanced the sludge dewaterability. The improvement of sludge dewaterability was attained at a low dose rate of 0.005 gO_3/gTSS while higher dose rates deteriorated the dewaterability.[83] Another report found the optimal dose rate to be 0.05 gO_3/gTSS for the sludge dewaterability. [84] The release of protein into solution due to cell lysis caused by higher

dose rate of ozone might contribute to the decreased dewaterability. In contrast, Park, et al. [85] found a different trend using ozonation process for sludge conditioning. The specific resistance to filtration (SRF) value increased with the increasing addition of ozone up to the dose rate of 0.2 gO_3/g DS. The SRF value then decreased for higher dose rates of ozone. At the same time, the concentration of micro particles and turbidity also showed the similar trend. It's evident that the optimal dose rate of ozone might vary significantly for different kinds of sludge.

5.2 Ferrate treatment

Compared to ozone, Fe(VI) has much higher redox potential under acidic conditions (2.2V). Ferrate (FeO_4^{2-}), as a strong oxidant reagent and precursor of coagulating agent, was reported on its use for the improvement of sludge dewaterability.
The addition of potassium ferrate was found to improve the sludge dewaterability (measured by SRF) at pH=3, while decrease the dewaterability at pH⩾4. [86] Both the increase of DS and CST were attained after treatment by potassium ferrate.[87] The transformation of TB-EPS into LB-EPS due to the oxidization of ferrate might lead to the higher CST observed. Also, it was reported that ferrate treatment liquidized the sludge solids into gel-like matters, making it impossible to dewater by vacuum filter and belt press, but achieves better solid-water separation performance by centrifugal dewatering. [88]

6. Conclusions

For the improvement of sludge dewaterability, Fenton oxidization processes were applied, either alone or in combination with other treatments. Other strong oxidants like ozone and ferrate were also employed to achieve the same purpose. Sludge dewaterability was improved due to the separation/release of bound water from solids and cells in sludge, and/or the flocculation of fine sludge particles. It was shown advanced oxidation is a cost-effective and environment-friendly process for sludge conditioning.

Although sludge conditioning by advanced oxidation process has been successful in the lab and a few pilot tests, the main hurdles of full application might include occupational health and safety concerns and possible production of harmful secondary compounds during the oxidization processes. Many of the chemicals used for the oxidization pretreatment are unstable, corrosive or harmful. Also, the processes have to be operated under low pH. Harsh operation conditions due to the oxidization reactions require it to be operated by skilled staff using special devices. Future research should address some of these hurdles. For example, better design of the reactors or processes and the selection of chemicals need to be addressed by future research.

Furthermore, most of the research focused on the use of classic Fenton peroxidation till now. Only a few pilot-scale tests had been operated so far. Thus, data is still lack for large-scale operation, especially for the treatment of different types of waste sludge. In addition, there is limited research on alternative oxidization processes such as Fe(II)-persulfate oxidization process and ozonation process. More optimization and pilot-scale tests should be carried out for the wider application of classical Fenton reagent in sludge conditioning. Also, more fundamental research is still needed to understand the basic mechanisms of alternative advanced oxidation processes due to their promising effectiveness.

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Supplementary information

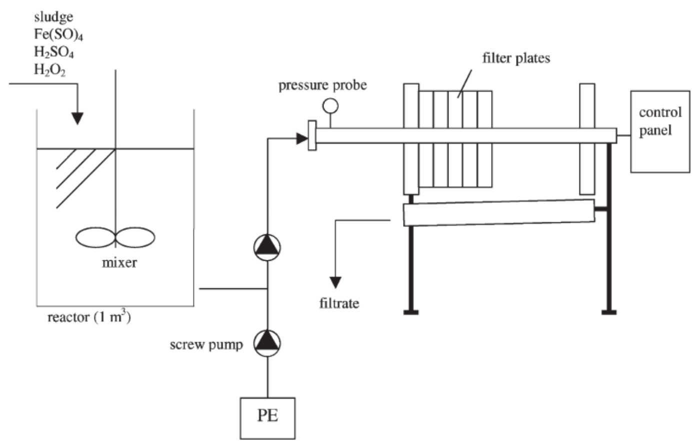

Fig. 1 An experimental AOPs process for sludge conditioning and dewatering. Reprinted with permission from Ref. 45. Copyright (2003) Elsevier.

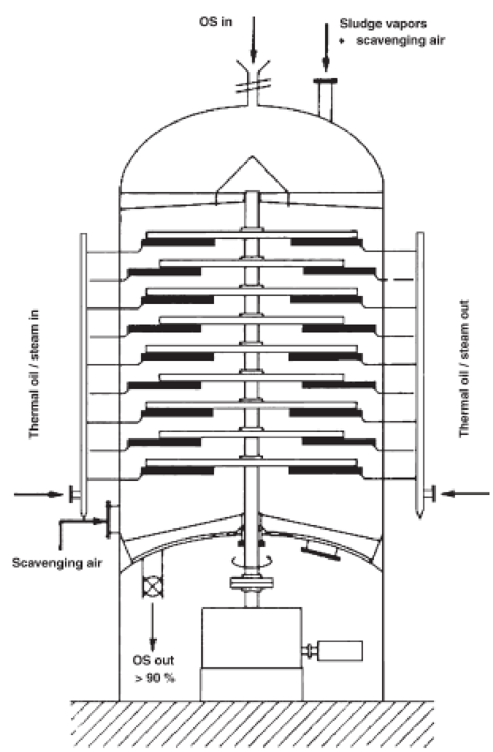

Fig. 2 Multiple hearth dryer for sludge drying. Reprinted with permission from Ref. 33. Copyright (2005) Elsevier.

Table 1, Economic analyses of the AOPs conditioning processes in an assumed WWTP with a population equivalent of 300,000[a]

Parameters	Without AOPs conditioning	With AOPs conditioning (Fe(II)+Hydrogen peroxide)
Amount of WAS subject to conditioning (dry tone/y）	6,570	6,570
Fixed equipment costs (EUR/year)	Not applicable	40,000
Maintenance costs (EUR/ year)	Not applicable	10,000
Chemical costs and electricity (EUR/ year)	Not applicable	400,000
Transport and incineration (EUR/year)	1,900,000	500,000
Total Cost (EUR/year)	1,900,000	950,000
Total Saving with ZVI+HP conditioning (EUR/year)	1,900,000-950,000=950,000	

[a] The table is based on the economic analyses from Ref 45.