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Review

A review of thermal sludge pre-treatment processes to improve dewaterability

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Abstract

As a result of the wide application and utilization of the waste activated sludge process, excess sludge presents a serious disposal problem. Many efforts have been devoted to reduce the excess sludge by treatments such as digestion and dewatering. It has been known for many years that a thermal pre-treatment gives an improvement in the dewaterability of sludges. This paper provides a literature review concerning the optimum treatment conditions to obtain enhanced dewaterability and digestibility of sludge. The main commercial hydrolysis processes (Cambi, Porteous and Zimpro) are discussed. The literature findings concerning the optimum treatment conditions of thermal or thermochemical pre-treatments are reviewed.

The second part of this paper deals with the fundamentals of improving sludge dewatering. The influence of extracellular polymer (ECP) on settling and dewatering characteristics is discussed, together with the importance of cations and ECP-hydrophobicity in the flocculation and dewatering process. Finally, the effect on exocellular polymer, dewaterability, settleability and colloidal stability of activated sludge by treatment with sulfuric acid was studied.

Keywords: Sludge pre-treatment; Hydrolysis; Dewaterability; ECP; Acid treatment

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1. Introduction

Municipal and industrial wastewater treatment plants produce large amounts of waste activated sludge, containing organic and mineral components. WAS from industrial wastewater treatment processes and from municipal treatment facilities that receive substantial industrial water and storm water inputs can be enriched in heavy metals and refractory organic species. Both warrant consideration of sludges as hazardous materials.

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Nomenclature

COD	chemical oxygen demand (mg/l)
CST	capillary suction time (s)
DLVO	Derjaguin, Landau, Verwey and Overbeek
DS	dry solids content (%)
P	pressure (Pa)
PE	polyelectrolyte
T	temperature (°C)
VSS	volatile suspended solids
WAS	waste activated sludge

This sludge is thickened, possibly digested and finally mechanically dewatered to as high a %DS (percentage dry solids content) as possible. Both the reduction of the amount of sludge produced and improving its dewaterability are of paramount importance. Thermal and thermochemical processes have been proposed to meet these, and other, objectives.

The authors have investigated the various possible treatment processes experimentally (thermal hydrolysis, acid or alkaline hydrolysis as well as advanced oxidation techniques). The experimental results will be detailed and discussed in several subsequent papers. The first one "Hot acid hydrolysis as a potential treatment of thickened sewage sludge" is published in this issue and gives a global view of experimental results, i.e. on the degree of DS-reduction, on the fate of the organic and inorganic components of the sludge, and on the improved dewaterability.

Prior to assessing the experimental investigations and results, performed in both laboratory- and pilot-scale equipment, a review of previously published work was considered important, from the point of view of proposed processes and the essential role played by extracellular polymer (ECP). The present paper summarizes these essential literature findings, which will already direct the reader to the potential of these thermal processes and the fundamental phenomena taking place.

2. Review of sludge pre-treatment processes

2.1. Introduction

As a result of the wide application and utilization of the waste activated sludge (WAS) process, excess sludge presents a serious disposal problem: this excess sludge is an inevitable drawback inherent to the activated sludge process, despite sludge minimization in the extended aeration process. Many efforts have been devoted to reduce the excess sludge by treatments such as digestion and dewatering.

It is well known from observations that activated sludge is very difficult to dewater. A lot of work has been done on understanding the nature of water in sludge [1–3]. It is generally assumed that there are different physical states of water. The aqueous phase is generally described as free water and bound water. The bound water needs a higher energy to be removed and some cannot be removed at all. This bound water content is one of the main limiting factors in the water removal efficiency. Reaching higher dry solids can only be done with pre-treatment processes changing sludge structure: the floc structure of the sludge should be changed, bacteria cells opened and the cell content released. The cell water freed under hydrolysis is rich on dissolved organic compounds. The dissolved components can either be used to improve the efficiency of a subsequent biological degradation process or for the recycling of useful components like nitrogen and phosphorus. Other applications are the improvement of sludge dewatering, the reduction of pathogens or the suppression of foaming.

Several disintegration methods have been investigated [4]:

- Heat treatment, in the temperature range from 40 to 180 °C [5,6]. While the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected from the enzymatic hydrolysis by the cell wall. Thermal pre-treatment in the low temperature range from 60 to 180 °C destroys the cell walls and makes the proteins accessible for biological degradation. The input of thermal energy is mostly realized by heat exchangers or by application of steam to the sludge.
- Chemical treatment using ozone, acids or alkali [7,8]. Using acids, alkali, ozone, barely degradable compounds are transferred into more easily degradable ones.
- Mechanical disintegration using ultrasounds, mills, homogenizers and others where the necessary energy is provided as pressure, translational or rotational energy. Mechanical stress of the solids results in tensions and deformations. The cell of the microorganism resists the stress as long as the tension is lower than the strength of the cell wall.
- Freezing and thawing. By freezing and thawing activated sludge the floc structure will be irreversibly changed into a more compact form, the bound water content will be reduced and therefore the sludge dewatering characteristics can be significantly improved.
- Biological hydrolysis with or without enzyme addition [9,10]. The enzymatic lysis cracks the compounds of the cell wall by an enzyme catalyzed reaction. Autolytic processes can be used at ambient temperatures or external enzymes can be added.

Liu et al. [11] consider advanced oxidation processes (AOPs) as valuable sludge pre-treatment. These processes also enhance dewaterability of sludge [12]. Some investigations have covered a combined chemical and thermal treatment, a combination of alkaline addition and ultrasound or others [13].

2.2. Heat pre-treatment: thermal hydrolysis

2.2.1. Literature review

It has been known for many years that a thermal pre-treatment gives an improvement in the dewaterability of sludges. Brooks [14] observed solubilization of organic matter from samples of WAS and a mixture of primary sludge, and WAS in the order of 40–60 and 20–35%, respectively, when the treatment temperature is 170 °C. Experiments with municipal sewage sludge show that the highest yield of hydrolysis can be achieved at 165–180 °C. The holding time (10–30 min) has little influence on the result. The dissolved components are readily degradable in a digestion process. In addition the dewaterability is increased.

Fisher and Swanwick [15] reported on the effect of high temperature treatment of sewage sludges. They showed that for a wide range of sludges dewaterability was improved at temperatures above 150 °C. Most of the work was above 180 °C where the effect became more pronounced. Unfortunately at these higher temperatures they also reported on the formation of refractory COD compounds (the chemical oxygen demand (COD) is the amount of oxygen required to chemically destroy the organic compounds of wastewater). As part of the study they looked at some selected liquors and concluded that about a third of the liquor COD was not treatable.

Haug and co-workers [16–18] worked on heat treatment at lower temperatures to combine some of the benefits of dewaterability with improved digestibility and at the same time avoid the problems that occurred with higher temperature heat treatments. Haug and co-workers [16–18] showed that it was possible to obtain an improvement in dewaterability of undigested and digested sludges and that the temperature of 175 °C was about the limit for digestibility before digestion was inhibited (presumably because of the formation of inhibitory and/or refractory compounds). The showed that the largest effect on digestibility was for activated sludge but that all sludges tested dewatered better at 175 °C. At that temperature, digestion of the thermally pre-treated sludge resulted in an increase of 60–70% in methane production over not pre-treated sludge. Higher temperatures resulted in decreased gas production. Thermal hydrolysis as pre-treatment has hence given very good results on digester performance. The homogenization of the material goes further than in a mechanical process. The total surface of the particles is significantly increased, enhancing biological degradability.

Other conclusions/observations were:

- Thermal pre-treatment prior to anaerobic digestion may result in net energy production from the system because of increased biodegradability and reduced digester heating requirements. When pre-treating sludge by thermal hydrolysis before digestion, Haug et al. [18] calculated a 25% reduced energy production compared to conventional digestion. This conclusion has been confirmed by 3 years operation of a full-scale plant (80,000 inhabitants equivalent) at Hamar, Norway. The biogas was used to produce both electricity, covering 65% of the plant electrical demand, and heat (100% of the plant requirements). Recycling of liquid sidestreams from thermally pre-treated digested sludge should not significantly increase the oxygen demand on a biological treatment system.
- Odorous compounds normally associated with heat treatment are significantly reduced during digestion of thermally pre-treated sludge.

This optimum temperature of 175 °C is well illustrated. Pinnekamp [19] found optimum conditions for all types of sludge when pre-treated at 135–170 °C and digested under mesophilic conditions.

Hiraoka et al. [20] investigated the thermal pre-treatment at temperatures below 100 °C and revealed an increase of more than 30% in gas production at lower temperatures such as 60 and 80 °C, but the low temperature pre-treatment necessitated a longer contact time than the high temperature treatment.

Li and Noike [21] found the best conditions for pre-treatment of waste activated sludge to be: (i) 170 °C; (ii) between 30 and 60 min holding time; and (iii) a hydraulic retention time of 5–10 days based on both gas production and studies on microbial populations of various species of methanogens. They observed that the hydrolysis effect was greater on carbohydrates and proteins than on lipids. Activated sludge consists of 60% carbohydrate and protein. The biochemical pathway for methanogenic fermentation of proteins and carbohydrates requires that these are hydrolyzed to monomers, de-aminated for amino acids and undergo acetic acid fermentation for sugar monomers. Hydrolysis is the rate limiting step for this pathway, and Li and Noike [21] observed that hydrolysis was probably the rate limiting step for activated sludge. This is not the case with lipids which undergo two carbon decarboxylation to produce acetic acid from long chain fatty acids. They also observed that volatile fatty acids were present in high levels in the digester feed and converged to a common value which was slightly higher than the control. They concluded that this was evidence that there was little or no refractory effects at the temperatures used.

Recently Elbing and Dünnebil [22] investigated the effects of thermal hydrolysis on mesophilic digestion of waste activated sludge. After pre-treatment at 135 °C, the volatile solids destruction in the digester increased to 135 and 235% above the reference level at an increasing 12 and 15 days retention time, respectively.

2.2.2. *Full-scale installations*

The major growth of heat treatment occurred during the 1960s at temperatures typically about 200–250 °C for the two main hydrolysis processes: Porteous and Zimpro.

The first Porteous process plants in the UK were at Halifax and Horsham in 1939. It was a method of heating sludge at a minimum of 185 °C for 30 min. Raw sludge was forced by ram pump through a heat/heat exchanger and steam/heat exchanger into the reaction vessel and held for at least 30 min at about 200 °C. The sludge was returned from the reaction vessel to the settlement tanks where the liquor was removed. This process was developed into a continuous flow process and there were up to 30 installations in the late 1960s. Most of these were operated to give optimum dewatering before incineration. Lumb [23] reported values of 52% DS in the sludge cake at Halifax. An increase from 20% DS from raw sludge cake to 40% DS in hydrolyzed sludge cake was achieved at Colorado Springs [24] and at Pudsey 50% DS in the sludge cake was observed [25]. Escalating energy costs coupled with operating problems led to the early closure of all of these plants throughout the 1970s.

Zimpro was originally designed as a wet oxidation method in the US in 1954. The first Zimpro project in the UK was at Hockford. In this case destruction of organisms was seen as an advantage. The Zimpro method originally worked by high pressure wet oxidation of sludge solids at about 250 °C and aimed to destroy up to 65% of COD. At this temperature the process became exothermic. All UK Zimpro plants were shut down due to problems with odor, corrosion and high strength COD liquor. This process is still industrially used but Zimpro has modified the hydrolysis process for municipal sludge (low pressure oxidation (LPO)) at reduced temperatures ($<$200 °C) with very little oxidation occurring.

The Cambi process has successfully combined the optimum thermal hydrolysis pretreatment with anaerobic digestion to give a safe, stackable and stable product that meets customer needs. Tests of dewaterability carried out by Cambi showed an increase of the dewaterability between 60 and 80% [26].

2.3. Combined thermochemical pre-treatment

2.3.1. Literature review

The influence of thermochemical pre-treatment on several sludge characteristics (e.g. dewaterability, COD solubilization, %DS in filter cake, etc.) has been studied experimentally by numerous investigations and is reviewed in Table 1. This table does not include advanced oxidation techniques, proceeding at ambient or moderate temperatures. These techniques (H_2O_2, O_3, etc.) have been previously reviewed and studied by Neyens et al. [40].

Tanaka et al. [7] compared three different methods of pre-treatment in terms of volatile part of the suspended solids (VSS) solubilization and methane production of combined WAS. The effect of these three pre-treatments were evaluated under each optimum condition obtained by Tanaka et al. [7], i.e. the chemical condition at the dose 0.6 g NaOH/g VSS, the thermal one at 180 °C and the thermochemical process at 130 °C for 5 min with 0.3 g NaOH/g VSS. As shown in Table 2, the thermochemical pre-treatment gave the best result in the solubilization and the methane production, though the cost of pre-treatments had not been considered. After thermochemical pre-treatment, the methane production was 2.2 times higher rate than for the control sludge without any pre-treatment.

Biodegradability of the three main organic components of WAS was given by Pinnekamp [19] as 65, 52 and 39% for lipid, carbohydrate and protein, respectively. Since protein, the largest constituent of WAS, is the least biodegradable, the 63% solubilization of particulate protein by the pre-treatment will substantially enhance the subsequent digestion of the WAS.

Table 1
Literature data on the results of several thermochemical pre-treatment processes

Reference	Main conclusions			
	Reagent	Temperature (°C)	Time	Results
[27,28]	H_2SO_4	121	5 h	75–80% TSS solubilized
[29]	H_2SO_4	120	5 h	60–70% TSS solubilized
[30]	H_2SO_4	150–200	15–40 min	Enhanced conditioning
	KOH	150–200	15–40 min	Hampered conditioning
[31,32]	HCl	175–200	1 h	52–54% COD solubilized
	NaOH	175–200	1 h	54–55% COD solubilized
	$Ca(OH)_2$	175	1 h	40% COD solubilized
[33]	Base/H_2SO_4	60–90	1–20 min	Significantly improved dewaterability
[34,35]	NaOH	20–40	0.5–24 h	45% of COD solubilized Gas production increased by 112% over control levels
[36]	H_2SO_4/base	165	75 min	Filter cakes >65% DS
[37]	H_2SO_4	150–160	1 h	Significantly improved dewaterability
[38]	H_2SO_4	90	1 h	50–60% TSS solubilized Filter cakes >50% DS
[39]	NaOH	95	1 h	55–65% dry organic matter solubilized Filter cakes >43% DS

Table 2
Solubilization and methane production of combined WAS under optimum conditions of various pre-treatments [7]

Process	Solubilization rate (%)	Relative CH_4 production (8-day digestion)
Chemical (0.6 g NaOH/g VSS)	15.5	1.4
Thermal (180 °C)	30	1.8
Thermochemical (0.3 g NaOH/g VSS, 130 °C)	46	2.2

2.3.2. Full-scale installations

In the mid 1980s and in response to the pending US 503 regulations and other national regulation in Europe, a growing number of technologies emerged based on hydrolysis using acid, alkaline, heat and combinations. The idea was to have a one hit physicochemical approach to producing a pasteurized product. None of the developed processes has been successfully commercialized because of costs involved and poor-quality product: Synox, Protox and Krepro are commercial illustrations of this.

The Protox process used low temperature acid hydrolysis to improve activated sludge dewatering. The aim was to make a dried product from WAS sludge. It was trailed by Wessex Water in the mid 1990s. It was not a true hydrolysis operation, some of the dewaterability improvement was probably due to changing the isoelectric point of the sludge.

The Synox process was piloted at Jacksonville (Florida). During the 1980s various methods were attempted to improve hydrolysis by reducing hydrolysis temperatures and using sequential acid and alkaline hydrolysis. Early work by Union Carbide suggested that this could give Class A product and that metals could also be recovered. The process suffered from high chemical costs. The US 503 regulations differentiate between Classes A and B disinfection of sewage sludge, with Class A being far superior (2000 times more stringent) to Class B in its pathogen destruction. Class A technologies have shown that they reduce pathogens below detectable levels.

The Krepro process is similar to Synox. Sponsored by Kemira and situated at Helsinborg in Sweden this process also uses sequential acid treatment, hydrolysis and in this case also uses ferric salts and alkali. The aim is to separate sludge into three fractions: an organic dewatered fraction (to be used as a fuel), a liquid fraction to be used as carbon source for denitrification and ferric phosphate to be used as fertilizer. The process suffers from lack of markets for its product thus reducing its proposed revenues.

3. Fundamentals of improving the sludge dewaterability

3.1. Sludge dewatering and settling from the point of extracellular polymers

3.1.1. Extracellular polymer

Extracellular polymers are thought to be of considerable importance in bioflocculation, settling, and dewatering of activated sludge [41–44]. One reason for the difficulty in activated

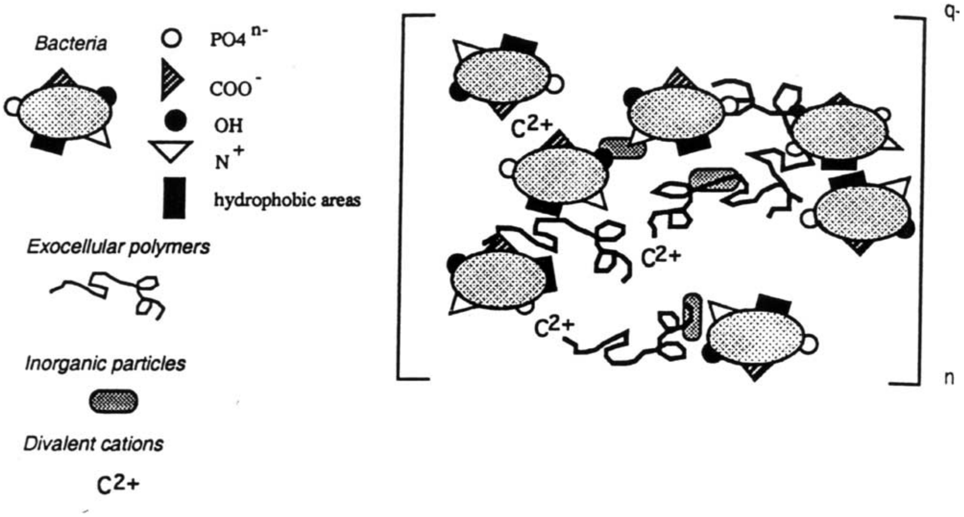

Fig. 1. Schematic representation of the activated sludge floc on an arbitrary scale of size [41].

sludge dewatering is the presence of extracellular polymer (ECP). ECP is present in varying quantities in sewage sludge, occurring as a highly hydrated capsule surrounding the bacterial cell wall and loose in solution as slime polymers. ECP is thought to aid the survival of the bacterial cell by preventing desiccation and acting as an ion-exchange resin, controlling the ionic movement from solution into the cell [45]. Polysaccharide, protein and DNA, which entraps the water and causes a high viscosity, are the main components of ECP but also humic-like substances, lipids and heteropolymers such as glycoproteins [41,46] are present. Extracellular DNA is formed from lysis of dead cells, proteins and polysaccharides from cell metabolism.

The overall floc structure is negatively charged and is the result of physicochemical interactions between microorganisms (mainly bacteria), inorganic particles (silicates, calcium phosphate and iron oxides), exocellular polymers and multivalent cations (see Fig. 1) [47]. Exocellular polymers (ECP) have two different origins: (1) from cell structures either because of metabolic excretion or cell lysis of microorganisms (proteins, DNA, polysaccharides and lipids); and (2) from the wastewater itself, i.e. from the adsorption of organic matter (e.g. cellulose, humic acids, etc.).

Activated sludge flocs are known to show a much greater cohesive force than traditional mineral flocs. Several types of forces and mechanisms are thought to be involved in this cohesion: bridging by negatively charged ECP and/or by polyvalent cations such as Ca^{2+} or Fe^{3+}, hydrophobic interactions and DLVO type of interactions. Sludges in many aspects resemble colloidal suspensions: the solute species are charged Brownian objects with sizes between a few nanometers and a few tens of nanometers. Hence, the theoretical approaches developed for colloids have been applied to sludges, including the definition of the isoelectric point. Typically, interactions and stability of colloids are treated in terms of the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory. This

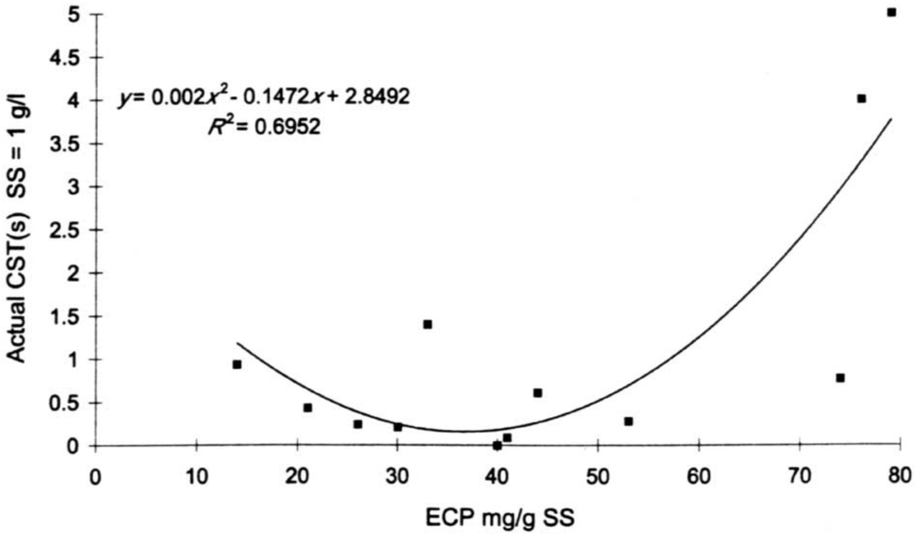

Fig. 2. The relationship between the quantity of ECP present and sludge dewaterability [45].

model is based on the balance between van der Waals attraction and electrostatic repulsion [48,49].

3.1.2. *Influence of ECP on sludge dewaterability*

One of the main influences on sludge dewaterability is the particle size distribution [50]. Flocculation changes the particle size distribution of a sludge, binding small particles together, thereby influencing the sludge dewatering characteristics. ECP can therefore be expected to have an influence on sludge dewaterability through the high level of hydration of the polymer surrounding the bacterial cell and its role in flocculation. Houghton et al. [45] tried to establish the relationship that exists between the quantity of ECP present and the dewaterability of different types of sludges. The relationship between sludge dewaterability, as measured using the CST test, and the level of microbial ECP present for activated sludge is shown in Fig. 2. There appears to be a level of ECP at which the sludge should be easiest to dewater.

Increasing levels of ECP are initially thought to aid sludge dewaterability by improving the level of sludge flocculation. This decreases the number of small particles present in the sludge, a factor that has been shown previously to make a sludge easier to dewater [50]. Once a certain level of sludge flocculation has been attained, further increases in ECP become detrimental to sludge dewaterability. It is envisaged that this is due to the highly hydrated nature of the ECP retaining water within the sludge matrix, which counteracts the benefit of flocculation.

The establishment of a relationship between sludge dewaterability and the quantity of ECP present in different sludge types will enable decisions to be made at plant level that ensure maximum dewaterability of the waste sludge. By altering process parameters, e.g. sludge age, retention time, operation temperature, it may be possible to manipulate the level of ECP produced.

Table 3
Literature data on the influence of cations on the floc structure

Reference	Main conclusions
[51]	Divalent cations (e.g. Ca^{2+} and Mg^{2+}): Are involved in the chemical structure of bacterial aggregates and biofilms, because of their ability to bind to negatively charged chemical groups Act as bridging agents inside the organic exocellular matrix of the flocs Ca^{2+} is measured in higher amounts than Mg^{2+} which is related to its affinity for ECP
[52]	Ca^{2+} has a higher binding capacity than Mg^{2+} on ECP in activated sludge
[53]	Cations are an integral part of the floc structure and an excess of monovalent cations relative to divalent cations in the influent to an activated sludge treatment plant leads to poorly dewatering sludges and poor effluent quality
[54]	The protein component of the biopolymer is most important in determining floc properties
[55,56]	Iron plays an important role in determining floc structure and dewatering properties, specifically, the interaction between iron and the protein component in the biopolymer

3.1.3. *Influence of cations on floc structure*

Since bacterial surfaces, ECP and eventually inorganic particles provide negative adsorption sites, the role of divalent cations in the floc stability must be emphasized. Reported results are summarized in Table 3.

In spite of the importance of divalent cations in flocculation processes, there is a lack of information about either their accumulation in the exocellular structures of the sludge flocs or their affinity with specific constituents of the ECP. Novak et al. [55] investigated the role of iron in determining floc structure and dewatering properties, specifically, the interaction between iron and the protein in the biopolymer. The polymer conditioning appeared to depend directly on the solution protein content. The protein released into solution, e.g. by acid treatment, causes deterioration in the dewatering behavior of sludges. The major role of conditioning chemicals appears to be to coagulate the solution biopolymer, especially protein. Conditioners have been thought to interact with flocs. It appears that the more important role is to coagulate solution colloids. It is believed that the release of protein into solution is due primarily to the reduction and solubilization of iron and this leads to a weaker binding to protein in the biofloc. Novak et al. [55] showed that when iron is added for conditioning of WAS protein is preferentially removed from solution and this removal is accompanied by a decrease in the CST (capillary suction time), again suggesting that it is the protein component that contributes to dewatering problems. The CST test is a type of static filtration test for sludges that measures the filtration rate (time for free water to pass between two electrodes) using filter paper as the medium. It is used primarily to indicate filter cake permeability.

Murthy and Novak [56] stated that ferric chloride was capable of removing most of the solution protein and some of the solution polysaccharide. The removal of biopolymers was associated with a removal of soluble COD and supernatant turbidity. The effluent quality at municipal plants is typically better than at industrial plants for similar concentrations of monovalent and divalent cations. Municipal plants may have greater levels of divalent and trivalent cations such as iron. The presence of these iron ions may promote additional retention of biopolymers within the sludge flocs.

Table 4
Literature data on the influence of ECP on sludge surface and settling

Reference	Main conclusions
[41]	The exocellular matrix plays an important role in the surface characteristics, both the nitrogenous content of the sludge, exocellular DNA and Mg^{2+} ions are able to reduce the negative charge of the sludge surface
[57]	A low surface charge is related to good settling (low SVI value)
[58]	A high surface charge is not inconsistent with good settling conditions: the reason for this is that surface charge reduction is not the prime mechanism in bioflocculation because polymers are also able to bridge the cells physically

3.1.4. Influence of ECP on sludge surface and settling

Settling characteristics of sludge are defined by the surface charge and physical bridging as illustrated by results of Table 4. It is reported that ECP reduces the charge of the sludge surface, thus facilitating coagulation and settling. Moreover, bioflocculation might occur, again improving the settling properties.

3.1.5. ECP and hydrophobicity

Hydrophobic interactions result from the behavior of entities (particles or molecules) incapable of interacting electrostatically or establishing hydrogen bonds with water and therefore drawn together when plunged in an aqueous phase.

3.1.5.1. Influence of ECP-hydrophobicity on flocculation. Biological sludges are highly hydrated structures and little attention has been paid to the role of hydrophobicity in flocculation. Microorganisms with different hydrophobicities have been shown to occur in activated sludge. The influence of ECP-hydrophobicity and other properties have been studied experimentally and are reviewed in Table 5.

ECP enhances floc adhesion. The internal hydrophobicity is high at low concentrations of ECP, leading to an improved settling. At higher concentrations, steric effects and gel-formation might prevent cell coagulation.

3.1.5.2. Influence of ECP composition on surface properties and hydrophobicity of flocs. It appears that the proportions of ECP components (proteins/carbohydrates and/or proteins/(carbohydrates + DNA)) are more important than the quantities of individual ECP components in controlling hydrophobicity and surface charge. The effect of the ECP composition on the sludge hydrophobicity has been studied by numerous investigations (Table 6).

3.2. Sludge dewatering and settling from the point of acid treatment

3.2.1. Acid-induced ECP release from the activated sludge surface

It is interesting to improve activated sludge dewatering from the point of reducing ECP. Chen et al. [62] observed that the acid condition can change the microorganism surface properties. Activated sludge is an aggregation of many microorganisms and many cell materials, e.g. polysaccharide, protein, DNA, humic-like substances, lipids and heteropolymers such

Table 5
Literature data on the influence of hydrophobicity of ECP on flocculation

Reference	Main conclusions
[46]	ECP possess both hydrophobic and hydrophilic properties ECP may be involved in floc cohesion in two ways: (i) Through the hydrophilic chains, represented by polysaccharides creating a matrix in which bacteria are embedded (ii) Through a glue, creating bridges or reticular points between polysaccharides represented by hydrophobic heteropolymers 50% of the precipitable ECP at pH 2 contains protein and carbohydrate (77 and 66%, respectively), which supports the idea that the large quantities of ECP are glycoproteins. This supports the hypothesis of hydrophobic ECP participating in the organization of flocs
[59]	A strong correlation exists between the hydrophobicity of cells and their degree of attachment to activated sludge flocs
[41]	Settleability is improved at low concentration of ECP and when the internal hydrophobicity is high
[60]	The flocculating ability of sludge is controlled by the physicochemical properties, including hydrophobicity and surface charge, rather than the quantity of ECP The compressibility of sludge is controlled by the quantity of ECP. This can be partially explained by steric forces arising from the ECP. The ECP molecules extend out from cell surfaces and therefore physically prevent the cells from forming close contact. The ECP may also form a dense gel that resists the expression of water from gel pores

as glycoproteins compose the ECP and adhere to the sludge surface. They investigated the influences of acid pre-treatment on activated sludge ECP, dewatering and settling.

Chen et al. [62] note that there is a drastic decline in the sludge volume when pH was less than 3, which suggests that the lower the pH, the more efficient the centrifugal dewatering. Buchner-funnel filtration was also used in this study to evaluate effects of pH on dewatering.

Table 6
Literature data on the influence of composition of ECP on hydrophobicity and surface charge

Reference	Main conclusions
[46]	The hydrophobic fraction of ECP was made up only of proteins and not of carbohydrates The presence of a large amount of hydrophilic and mainly neutral carbohydrates may be contributing to the more hydrophilic nature of sludge The importance of the ratio of proteins to carbohydrates in determining the surface charge could be related to the unique charge properties of proteins. The amino groups in proteins carry positive charges and can neutralize some of the negative charge from carboxyl and phosphate groups and therefore decrease the net negative surface charge of sludge flocs
[61]	The proportion of ECP components (proteins/total carbohydrates) was more important than the quantities of individual ECP components in determining the surface charge of both anaerobic and aerobic sludge flocs
[60]	A strong inverse correlation exists between the surface charge and hydrophobicity of sludge. This is explained since the surface charge is related to the ionizable groups present on sludge surfaces; it increases the polar interactions of ECP with water molecules. Therefore, the more charged the sludge surfaces, the lower the hydrophobicity
[42]	An inverse correlation exists between zeta potential and water contact angle for sludge treating pulp and paper mill effluents

The water content of dewatered sludge changes with a variant pH value. Chen et al. [62] illustrate that the optimum pH value for filtration dewatering is 2.5. Further decrease of the pH does not improve the dewatering capacity.

One of the reasons for acid treatment improving dewatering is that it can cause ECP to leave the activated sludge surface, which makes it easy to pack the sludge aggregates and to reduce the water content of dewatered sludge.

Chen et al. [62] also express the effects of pH value on ECP concentration in the filtrate and indicate that with the decrease of pH, the amount of ECP in the filtrate was increased, and more ECP is released from the activated sludge surface, which resulted in more compact sludge aggregates and the improvement of mechanical dewatering. However, in the case of pH less than 2.5 as stated before, as more ECP is released to the water and blocked the filter paper, the dewatering efficiency was not increased with further increase of acidity, which was opposite to the centrifugal dewatering.

Chen et al. [62] studied the effects of treating activated sludge with sulfuric acid at pH 2.5 on its settling character. It is reasonable to say that by treating activated sludge at pH 2.5; its settleability can also be improved by the reduction of surface ECP.

3.2.2. Acid-induced reduction of shear sensitivity

Solid/liquid separation processes are of importance in the operation of activated sludge systems in order to achieve effluents of high quality and excess sludge containing a high solids fraction. The effluent quality is determined by the effectiveness of secondary clarifiers in separating solids from the liquid phase through settling of suspended solids, whereas the solids content in the excess sludge is determined by the ability of the sludge to yield water within a limited time scale by mechanical means such as filtration or centrifugation. Activated sludge normally contains a fraction of non-settleable solids, which can be considered as the primary source of solids in the effluent from well-designed clarifiers. The concentration of non-settleable solids can be described by the residual turbidity of sludge water after settling. It has further been shown that the amount of supracolloidal particles in the size range 1–100 μm seems to be an important factor for the filterability of activated sludge [50,63]. The reason for this is generally believed to be blinding of the sludge cake or filter medium due to clogging with fine particles. Given this background, it can be assumed that the amount of fine particles in a sludge will be of importance for both clarification and filterability.

The amount of fine particles present at a given shear in a turbulent flow system is expected to be dependent upon the sludge floc strength, as these particles presumably are produced by erosion of existing flocs [64,65]. Furthermore, the amount of fine particles is affected by the ability of these to flocculate upon collision with existing flocs, which is described as the fraction of collisions that result in flocculation [66]. It can therefore be expected that the colloidal stability of the sludge system has an impact on the simultaneously occurring processes of particle erosion and flocculation.

Mikkelsen et al. [57] produced evidence for the effect of changed colloidal stability upon clarification and filterability through controlled chemical manipulations of sludge, one of these manipulations is adjustment of pH trough addition of concentrated HCl or 1 M NaOH. These chemical manipulations were expected to cause changes in sludge surface charge density, leading to changes in the electrostatic repulsion between sludge particles

Table 7
Surface charge density and shear sensitivity for sludge samples after chemical manipulations [57]

pH	Surface charge density (meq./g SS)	Shear sensitivity (s^2)
3.2	0.25	0.025
5.9	−0.07	0.045
7.3	−0.27	0.062
9.1	−0.29	0.170

and hence altering the colloidal stability characterized by the shear sensitivity. The shear sensitivity is a descriptor of the ease with which fine particles are eroded from the sludge surface relative to the ability of such fine particles to be flocculated upon collision with sludge flocs. Increased electrostatic repulsion through increased surface charge density is expected to cause increased shear sensitivity, since according to the principles of DLVO theory, increasing deflocculation and decreasing flocculation is the result of increased electrostatic repulsion, provided that only negligible change of attractive van der Waals forces is concomitantly induced. Results for the measured surface charge density and shear sensitivity for the sludge samples are shown in Table 7. It shows that decreasing pH results in decreased negative surface charge density. As expected this causes a decreased shear sensitivity by decreased electrostatic repulsion. Adjustment of sludge pH was expected to cause changes of the surface charge density through changes of the dissociation of H^+ from functional surface groups.

Mikkelsen et al. [57] showed that the residual turbidity (characterized by modified CST) was found to increase with increasing sludge shear sensitivity. This was expected as a consequence of an increasing number of fine particles at any applied shear intensity. There was a similar dependence between shear sensitivity and specific resistance to filtration (SRF). The possible reasons for the increasing SRF are a generally increased resistance from the cake solids or increased blinding. They revealed a close to linear dependence between the shear sensitivity and the cake filtration coefficient, which can be interpreted as a result of less irregularly shaped sludge flocs, caused by erosion of the floc surface, leading to a less porous sludge cake. Finally, Mikkelsen et al. [57] showed that the greater impact of the shear sensitivity was found on the blinding coefficient, indicating increasing importance of the blinding phenomenon with increasing shear sensitivity.

Similar observations for SRF have been reported by Karr and Keinath [50] for altering pH values and by Keiding and Nielsen [67] for removal of Ca^{2+} through ion exchange. Karr and Keinath [50] explained the changed filterability as an effect of changed particle size distribution, since the amount of supracolloidal particles was increased with increasing pH.

4. Conclusions

Many efforts have been devoted to reduce the excess sludge of WAS processes by treatments such as digestion and dewatering. A higher dewaterability can only be achieved by using pre-treatment processes changing sludge structure:

- Thermal pre-treatment methods are able to obtain an improvement in dewaterability of undigested and digested sludges and a temperature of 175 °C is optimal to do so. Porteous, Zimpro and Cambi are commercial illustrations of this thermal pre-treatment process.
- Combined thermochemical pre-treatment methods using acids or alkali to treat the heated sludge are reviewed, results are given in Table 1. Different optimum conditions are suggested by numerous investigations. Synox, Protox and Krepro are commercial illustrations.
- Extracellular polymers are of considerable importance in bioflocculation, settling, and dewatering of activated sludge:
    - ECP has a dual effect on dewaterability: improved flocculation at low concentrations and reduced flocculation at high concentrations through water retention in the sludge matrix.
    - Divalent cations (e.g. Ca^{2+} and Mg^{2+}) act as bridging agents inside the organic exocellular matrix of the flocs, an excess of monovalent cations relative to divalent cations in the influent to an activated sludge treatment plant leads to poorly dewatering sludges and poor effluent quality.
    - ECP reduces the charge of the sludge surface, thus facilitating coagulation and settling.
    - ECP enhances floc adhesion, the internal hydrophobicity is high at low concentrations of ECP, leading to an improved settling; at higher concentrations, steric effects and gel-formation might prevent cell coagulation.
- Pre-treating activated sludge with sulfuric acid has significant effects on its exocellular polymer, dewaterability and settleability. Controlling the pH of the sludge at 2.5 was suggested as a possibility to improve mechanical dewaterability.

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