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Pilot-scale peroxidation (H$_2$O$_2$) of sewage sludge

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Abstract

Municipal and industrial wastewater treatment plants produce large amounts of sludge. This excess sludge is an inevitable drawback inherent to the waste activated sludge process. Both the reduction of the amount of sludge produced and improving its dewaterability are of paramount importance. Novel pre-treatment processes have been developed in order to improve sludge dewatering, handling and disposal. This paper discusses the oxidation process utilising the catalytic activation of H$_2$O$_2$ by iron salts, referred to as Fenton's reagent. In previous work, the authors described the experimental laboratory results of H$_2$O$_2$-oxidation of thickened sludge. Based upon the optimum conditions obtained in these laboratory tests, pilot-scale experiments are conducted. Peroxidation under its optimum conditions, i.e. (i) through addition of 25 g H$_2$O$_2$ kg^{-1} DS (dry solids content), (ii) in the presence of 1.67 g Fe^{2+}-ions kg^{-1} DS, (iii) at pH 3, and (iv) at ambient temperature and pressure, significantly reduces the amounts of sludge and improves the product quality: the amount DS per equivalent inhabitant per day (DS/IE.d) was reduced from 60 to 33.1 g DS/IE.d and the percentage DS of the sludge cake was 47%, which is high compared with the 20–25% achieved in a traditional sludge dewatering facility. An economic assessment for a wastewater treatment plant of 300 000 IE confirms the benefits. Considering the fixed and variable costs and the savings obtained when the sludge is incinerated after dewatering, a net saving of approx. 950 000 € per year or 140 € per ton DS can be expected.
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1. Introduction

Municipal and industrial wastewater treatment plants produce large amounts of sludge, containing organic and mineral components. This sludge is mechanically dewatered to

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as high a percentage dry solids (DS) as possible. Using centrifuges or belt presses, only 20–25% DS can be obtained. Since the agricultural use of the sludge and landfilling are increasingly restricted, drying and incineration are widely implemented (Baeyens and Van Puyvelde [1]). As a result, the costs related to the treatment of sludge have considerably risen and commonly represent 35–50% of the total operating costs of the wastewater treatment (Baeyens et al. [2]). Reducing the amount of sludge produced and improving the dewaterability are hence of paramount importance. This objective of sludge reduction has stressed the importance of an extended aeration biology, a biological phosphorus removal rather than chemical precipitation, sludge digesters, etc. A further reduction and an improvement of the dewaterability require advanced sludge treatment (AST) methods to alter the sludge structure: bacteria cells should be opened and the cell content released. A fundamental part in understanding the action of these technologies is the essential role played by extracellular polymer (ECP) (Neyens and Baeyens [3]).

Several disintegration methods have been investigated (Müller [4]):

- Heat treatment, in the temperature range from 40 to 180 °C (Kepp et al. [5]; Barjenbruch et al. [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 moderate temperature range from 60 to 180 °C destroys the cell wall and makes the proteins accessible for biological degradation. The input of thermal energy is mostly achieved by heat exchangers or by application of steam to the sludge.
- Thermochemical treatment using acids or alkali (Tanaka et al. [7]; Sakai et al. [8]; Neyens and Baeyens [3]; Neyens et al. [9]): barely degradable compounds are transferred into more easily degradable ones through combined action of temperature and acids or alkali.
- Mechanical disintegration using ultrasound, mills, homogenisers and others where the necessary energy is provided as pressure, translational or rotational energy: mechanical stress of the solids result in tensions and deformations. The cell of the micro-organism resists the stress as long as the tension is lower than the strength of the cell wall (Müller et al. [10]).
- Freezing and thawing (Chu et al. [11]) will irreversibly change the activated sludge floc structure 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 (Guellil et al. [12]; Thomas et al. [13]) relies on enzymatic lysis to crack the compounds of the cell wall by an enzyme catalysed reaction. Autolytic processes can be used at ambient temperatures or external enzymes can be added.

Liu et al. [14] consider chemical oxidation techniques as valuable sludge pre-treatment. In literature, chemical oxidation techniques are especially applicable for (i) the treatment of hazardous organics present at low concentrations such as in contaminated groundwaters, (ii) the use as a pre-treatment step before biological treatment of low-volume, high strength wastewaters, (iii) the treatment of wastewaters with constituents that are resistant to biodegradation methods and (iv) the use as a post-treatment step following biological treatment to reduce aquatic toxicity (Eckenfelder [15]). Although the application of chemical oxidation techniques to treat sludge is less mentioned in literature, the treatment of

sludge with ozone, O_2 (wet oxidation) and hydrogen peroxide/ferrous ions (classic Fenton oxidation) are proposed.

Weemaes et al. [16] and Liu et al. [14] studied the effect of ozonation on characteristics of waste activated sludge. Ozone pre-treatment removes or solubilizes two-thirds of the organic matter in sludge, enhances the subsequent anaerobic digestion but has a negative effect on sludge dewaterability.

Wet or aqueous phase oxidation is a chemo-physical process in which organic material is oxidised in the liquid phase with gaseous oxygen under elevated temperature and pressure. The reduction of the volatile fraction of waste is almost complete while the total sludge solids reduction is 75–80% and the volume of sludge is reduced by 96% (de Bekker and van denBerg [17]). Wet oxidation is comparable in its solids reducing capacity with incineration, without its disadvantages of dewatering needed, of flue gasses and ash residue.

Preliminary lab-scale investigations on the use of Fenton oxidation (H_2O_2/Fe^{2+}) on sewage sludge were presented by Mustranta and Viikari [18]; Pere et al. [19]; Lu et al. [20]; Neyens and Baeyens [21] and Neyens et al. [22]. In previous work, the authors described the experimental laboratory results of H_2O_2-oxidation of thickened sludge. Based upon the optimum conditions obtained in these laboratory tests, pilot-scale experiments are conducted. Whereas the purpose of laboratory tests was to select the optimum operating conditions and the best performing flocculation agent, pilot tests are needed to confirm the laboratory results and to define mass and energy balances of a wastewater treatment including this oxidation techniques.
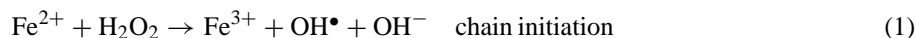
2. H_2O_2-oxidation: theoretical background

H_2O_2 is a strong oxidant (standard potential 1.80 and 0.87 V at pH 0 and 14, respectively) and its application in the treatment of various inorganic and organic pollutants is well established. Numerous applications of H_2O_2 are known in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, organic compounds and chlorine. Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals which are strong oxidants. In general, oxidation processes which are based on the generation of radical intermediates, are termed advanced oxidation techniques (AOT). Hydroxyl radicals (oxidation potential: 2.8 V) are stronger oxidants than ozone and H_2O_2 itself. Hydroxyl radicals non-specifically oxidise target compounds at high reaction rates of the order of $10^9 \, M^{-1} \, s^{-1}$.
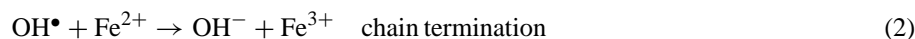
The oxidation processes utilising activation of H_2O_2 by iron salts, referred to as Fenton's reagent, are discussed below.

Fenton's reagent was discovered about 100 years ago, but its application as an oxidising process for destroying toxic organics was not applied until the late 1960s (Huang et al. [23]). Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts.

Fenton's reagent is a mixture of H_2O_2 and ferrous iron. The ferrous iron initiates and catalyses the decomposition of H_2O_2, resulting in the generation of highly reactive hydroxyl radicals (Kitis et al. [24]; Yoon et al. [25]; Lu et al. [20]). The generation of the radicals involves a complex reaction sequence in an aqueous solution (Neyens and Baeyens [21]):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \quad \text{chain initiation} \tag{1}$$

$k_1 \approx 70\,M^{-1}\,s^{-1}$ (Rigg et al. [26])

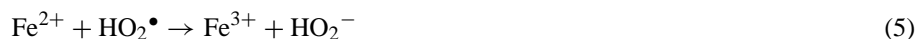$$OH^\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad \text{chain termination} \tag{2}$$

$k_2 = 3.2 \times 10^8\,M^{-1}\,s^{-1}$ (Buxton and Greenstock [27])
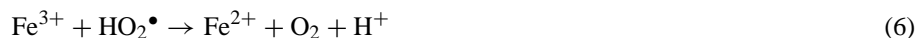
Moreover, the newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen (this reaction is referred to as a Fenton-like reaction). Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in Eqs. (3)–(7).

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}OOH^{2+} + H^+ \tag{3}$$

$k_3 = 0.001\text{–}0.01\,M^{-1}\,s^{-1}$ (Walling and Goosen [28])

$$Fe\text{–}OOH^{2+} \rightarrow HO_2^\bullet + Fe^{2+} \tag{4}$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \tag{5}$$

$k_5 = 1.3 \times 10^6\,M^{-1}\,s^{-1}$ (at pH 3, Bielski et al. [29])

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \tag{6}$$

$k_6 = 1.2 \times 10^6\,M^{-1}\,s^{-1}$ (at pH 3, Bielski et al. [29])

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{7}$$

$k_7 = 3.3 \times 10^7\,M^{-1}\,s^{-1}$ (Buxton and Greenstock [27])

As seen in reaction (7), H_2O_2 can act as an $OH^\bullet$ scavenger as well as an initiator (reaction (1)). Since $k_7 = 3.3 \times 10^7\,M^{-1}\,s^{-1}$ while $k_2 = 3.2 \times 10^8\,M^{-1}\,s^{-1}$, reaction (7) can be made unimportant by maintaining a high ratio of organics (RH) to H_2O_2.

Hydroxyl radicals can add to the aromatic or heterocyclic rings (as well as to the unsaturated bonds of alkenes or alkynes):
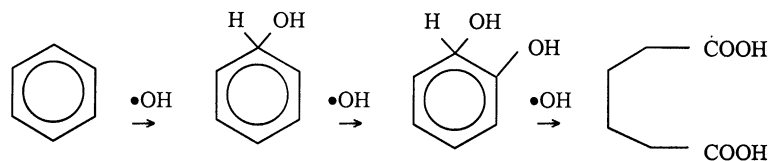
Hydroxyl radicals can also oxidise organics by abstraction of protons producing organic radicals ($R^\bullet$), which are highly reactive and can be further oxidised (Walling and Kato [30]; Venkatadri and Peters [31]; Lin and Lo [32]):

$$RH + OH^\bullet \rightarrow H_2O + R^\bullet \rightarrow \text{further oxidation} \tag{8}$$

If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2, water and for a continued treatment to inorganic salts in the case of substituted organics.

The organic free radicals produced in reaction (8) may then be oxidised by Fe^{3+} according to the following reaction (Tang and Tassos [33]):

$$R^\bullet + Fe^{3+}\text{–oxidation} \rightarrow R^+ + Fe^{2+} \tag{9}$$

The sequence of reactions (1), (2), (8) and (9) constitute the present accepted scheme for the Fenton's reagent chain.

Although this basic mechanism of the Fenton's peroxidation is well known, the responsible mechanisms for enhanced properties of the treated sludge are not fully understood: the oxidative conditioning might be based on partial oxidation and rearrangement of the surface components of the sludge flocs (Pere et al. [19]; Neyens and Baeyens [21]).

3. Materials and methods

3.1. Experimental set-up

The reactor is constructed as a multitank of $1\,m^3$ equipped with a mixer of variable rotational speed (25–250 rpm). The reactor is coupled to a pilot-scale filter press. Fig. 1 illustrates the experimental set-up.
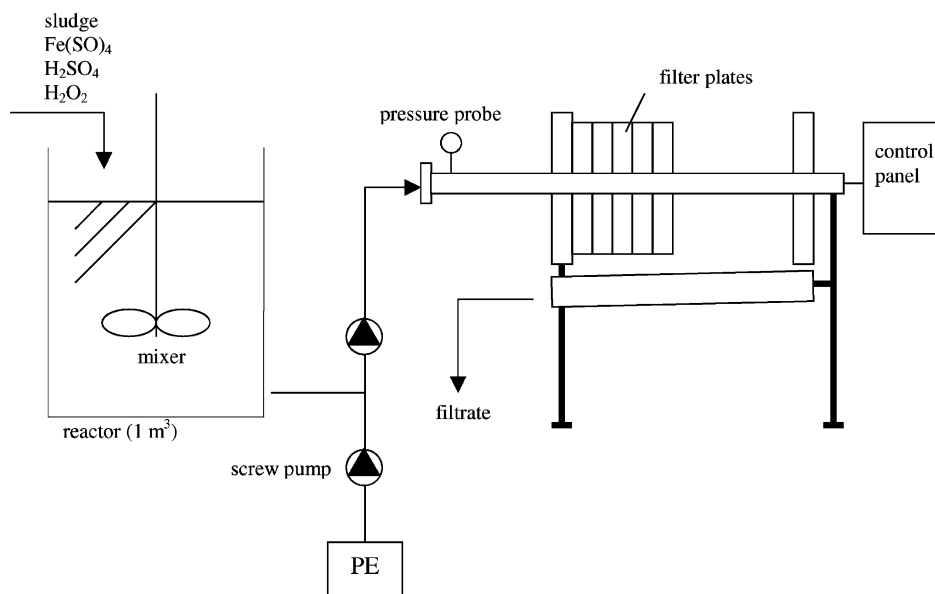

Fig. 1. Experimental set-up.

3.2. Procedure

Samples of 1 m^3 sludge were batch-treated at different but fixed operating conditions. The treatment consisted in firstly adding H_2SO_4 (from a solution containing 1750 g H_2SO_4 l^{-1} solution) to adjust the pH to 3, then adding Fe^{2+} ($FeSO_4$) at the given concentration and adding the required amount of H_2O_2 (from a solution containing 390 g H_2O_2 l^{-1} solution). The oxidation reaction takes place at ambient temperature and pressure. The mixture was stirred at 100 rpm. The oxidation releases reaction gases (mostly CO_2 and small organic molecules) and the time of reaction was considered as the time when the gas production is stopped. This time varies between 60 and 90 min for the conditions studied in this paper. The emitted gases should preferably be sent to a biofiltration bed to avoid odour nuisance. After reaction, the sludge mixture is neutralised with $Ca(OH)_2$ and polyelectrolyte (PE) is added. Finally, the sludge is dewatered in the pilot-scale filter press.

Samples prior to any treatment will be referred to in the text, tables and figures as 'blank'-samples. All results are related to the equivalent property for the 'blank'-untreated sludge sample. Tests were repeated three times under identical conditions and average values were determined. Results were within ±10% of the average value, and therefore experimental results discussed hereafter should be considered within a range of the indicated average value ±10% (e.g. percentage DS in the cake is 47 ± 4.7%).

3.3. Materials

3.3.1. Sewage sludge

Sludge samples were obtained from the underflow of the thickener (approx. 6% DS) at a municipal sewage treatment plant in Harelbeke (Belgium). The organic dry solids content (ODS) was approx. 55%. The density of the untreated (6% DS) sludge was 1.048 kg l^{-1}.

3.3.2. Polyelectrolytes (PE)

A wide range of polyelectrolytes (cationic, anionic, non-ionic) were tested to enhance flocculation of the sludge treated with hydrogen peroxide. The products which performed best on lab-scale were selected. These products are commercial cationic polyelectrolytes: Nalco$^{®}$ MU 085 and Degussa Stockhausen$^{®}$ K 111 L. The performance of these polyelectrolytes is tested on pilot-scale. All results are compared with the equivalent property when using the Ciba$^{®}$ ZETAG 7878 FS40, the latter is used in most wastewater treatment plants with filter presses. Product specifications of all polyelectrolytes used are given in Table 1.

Table 1
Specifications of used polyelectrolytes

	ZETAG 7878 FS 40	MU 085	K 111 L
Kind of product	Emulsion	Emulsion	Emulsion
Chemical type	BC/DIMADA	Acrylamide/adame-quat	Acrylamide/adame-quat
Cationic (%)	80	50	30
Branching (%)	40	100	100

The polyelectrolytes are added to the peroxidized and neutralised sludge as 0.1% solutions in water. Mixing occurred at a rotational speed of 250 rpm during 2 min.

3.4. Relevant properties and their definition

The 'blank' reference sludge sample contains suspended and dissolved matter of organic and mineral nature. After evaporation of H_2O (105 °C), the total dry solids are measured. Further calcination at 605 °C drives off the organic matter and the mineral dry solids content (MDS) is weighed as residual ash. The same procedure is applied to determine the DS/ODS/MDS-content of mechanically dewatered sludge (filter cake).

The rate of filtration was determined by the measurement of the capillary suction time (CST), using the apparatus and procedure described in Vesilind and Davis [34]. A CST-value of approx. 20 s is recognised as corresponding to a sludge of good dewatering characteristics.

Preliminary tests using CST-measurements on peroxidized sludge revealed that the required optimal PE-dosage is 10 kg PE-product (50% active material) per ton DS when the ZETAG 7878 FS 40 is used and 6.7 kg PE-product when using the MU 085 or the K 111 L. Peroxidation reduces the DS-content with respect to the blank by approx. 20%, the DS-content is hence taken at 80% from the untreated sludge sample.

Biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrogen-components, phosphates and sulphates are common wastewater characteristics and are defined according to the standard analytical methods (Baeyens et al. [2]).

Heavy metals were measured by AAS and ICP–MS.

4. Results

4.1. Laboratory tests

Neyens et al. [22] described the experimental results of peroxidation of thickened sludge (6% DS content). The process implied the use of hydrogen peroxide and was achieved in the presence of Fe^{2+}-ions as a catalyst (both 0.167 and 1.67 g Fe^{2+} kg^{-1} DS were used in the study). The influence of the pH on the Fenton reaction (H_2O_2/Fe^{2+}) was considerable and the oxidation should be carried out at pH 3. Sulphuric acid (H_2SO_4) was used to adjust the pH to 3, where the formation of radicals by the Fe^{2+}-catalyst is optimum. Fe^{2+}-ions are not stable at a pH above 4 where Fe^{3+}-ions are formed which precipitate as iron hydroxide and therefore can not be recycled back to Fe^{2+}-ions.

To fully determine the most appropriate operating conditions when using chemical oxidation by H_2O_2, major governing parameters were combined in experiments to assess the influence of the amount of H_2O_2 and associated variables (temperature, pH, Fe^{2+}, reaction time). Properties that were measured are: dry solids and organic matter of both filtrate and dewatered sludge (filter cake obtained by vacuum filtration of treated sludge); filtration characteristics such as CST and the volume of the resulting filter cake which gives an indication concerning dewaterability; properties of the water phase (BOD, COD, nitrogen, phosphates and heavy metals).

As a result of the experimental findings, it could be concluded that adding an amount of approx. 5 g H_2O_2 kg^{-1} DS in the presence of 1.67 g Fe^{2+}-ions kg^{-1} DS at pH 3 (reaction time of 60 min) can be considered as a useful sludge treatment, yielding:

- a considerable reduction of DS and ODS in the filter cake of approx. 20%;
- an improved dewaterability with a 30% reduction of the sludge volume, and a 30% increase of the cake DS-content when compared with the 'blank' sludge sample;
- a reduced CST-value by approx. 40 s when compared with the 'blank' sample;
- a preferentially release of ODS into the water phase, converting this into a more biodegradable and accessible carbon-source for nitrification/denitrification.

4.2. Pilot-scale tests

Based on the proposed optimum conditions obtained in the laboratory tests, pilot-scale experiments are conducted. All experiments are performed at pH 3 (adding 145 g H_2SO_4 kg^{-1} DS) and in the presence of 1.67 g Fe^{2+}-ions kg^{-1} DS. The amount of H_2O_2 added varies between 5 and 50 g H_2O_2 kg^{-1} DS. The peroxidation process occurs at T_a and P_a. The oxidation releases reaction gases (CO_2, H_2O) and the time of reaction is considered as the time when the gas production is stopped. This time varies between 60 and 90 min depending on the amount of hydrogen peroxide added. After reaction, the sludge is neutralised by adding 55.6 g $Ca(OH)_2$ kg^{-1} DS.

The normalised space velocity used in the pilot reactor is between 0.67 and 1 m^3 m^{-3} h^{-1}. For an average molecular weight of the biomass of 113 g mole^{-1}, the space time yield varies between 350 and 530 moles m^{-3} h^{-1}.

In order to investigate the optimum amount of H_2O_2 and the best performing polyelectrolyte, laboratory tests are repeated on pilot-scale using the polyelectrolytes described above.

(i) The total amounts of DS and ODS as determined by drying and calcining the sludge are reduced during peroxidation due to the release of reaction products (water, CO_2 and small organic molecules) (Fig. 2). Adding 50 g H_2O_2 kg^{-1} DS results in a 30% reduction of DS and ODS, adding 25 g kg^{-1} DS reduces the amounts of DS and ODS by more than 20%.

(ii) The filtration rate, as determined from CST-measurements, increases with increasing dosage of H_2O_2, as illustrated in Fig. 3. The lower CST-values correspond to a higher filtration rate. Using the MU 085 or the K 111 L, the results are significant with a reduction of over 50% when adding 25 g H_2O_2 kg^{-1} DS. The tests show that the ZETAG 7878 FS40 performs best for the blank, untreated sludge (this product is hence used in common wastewater treatment plants (WWTP) with filter presses) but fails when used for the oxidised sludge.

(iii) The residual volume of the cake phase, as measured from the pilot-scale filtration, decreases with increasing dosage of H_2O_2, as illustrated in Fig. 4. The volume of the filter cake is significantly reduced, indicating a better dewaterability when increasing amounts of H_2O_2 are used. The reduction is very important for a H_2O_2-dosage up to 25 g kg^{-1} DS. Higher additions do not significantly improve the results. The fraction of filter cake obtained using MU 085 and K 111 L is significantly smaller than the fraction
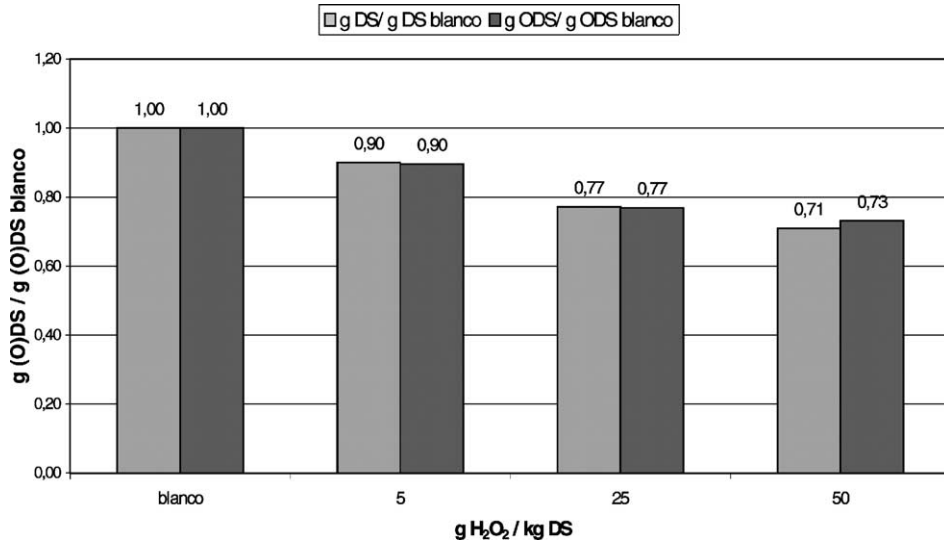
Fig. 2. Evolution of DS and ODS during peroxidation for increasing amounts of H_2O_2.

obtained using ZETAG 7878 FS40. This fraction is determined by two factors: (i) the release of DS in the water phase which is approx. equal for the three polyelectrolytes, and (ii) the percentage DS in the filter cake, which is lower for ZETAG 7878 FS40 as illustrated in Fig. 5 below.
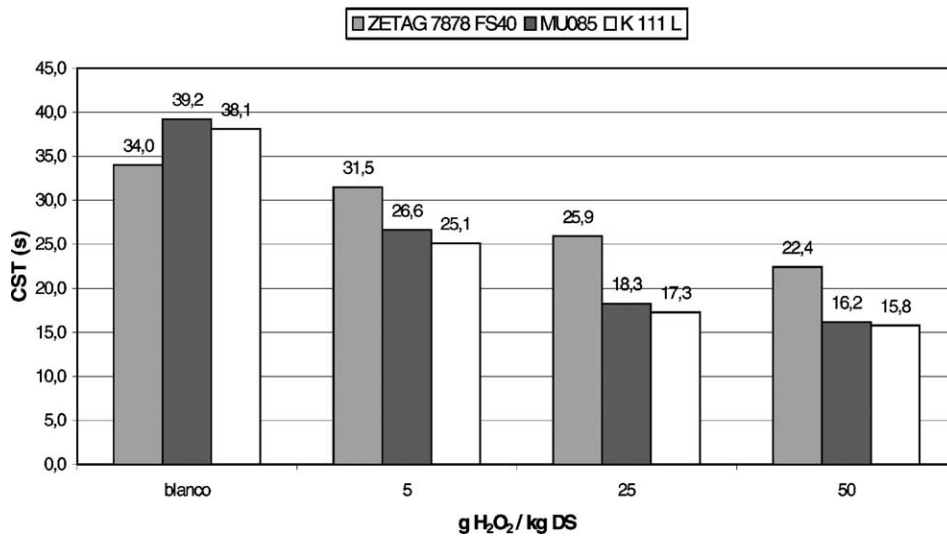

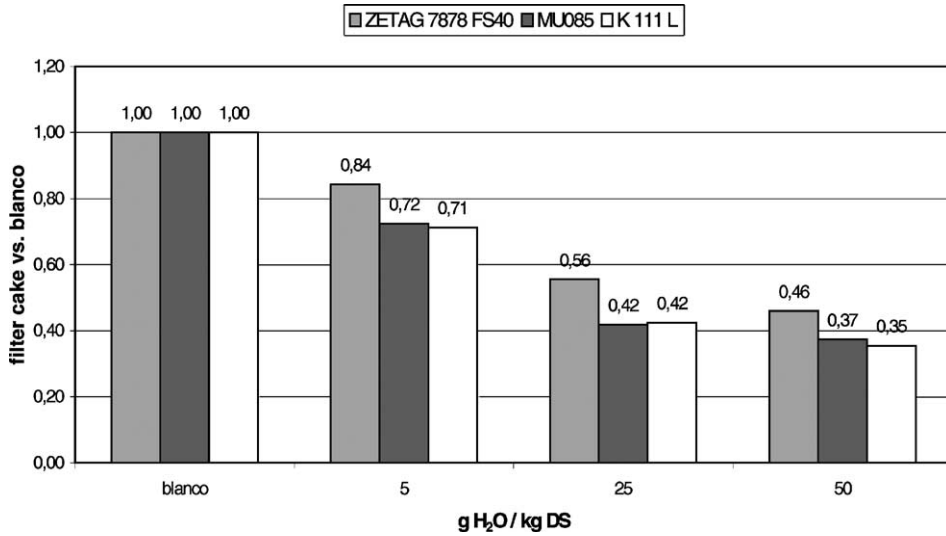Fig. 3. CST-values of peroxidized sludge for increasing amounts of H_2O_2.

☐ ZETAG 7878 FS40 ■ MU085 ☐ K 111 L

Fig. 4. Residual volume of the filter cake for increasing amounts of H_2O_2.

(iv) The analysis of the filter cake reveals that the percentage of DS increases significantly when more H_2O_2 is added to the blank sludge (Fig. 5). The addition of 25 g H_2O_2 kg^{-1} DS increases the DS-content of the cake by approx. 20% compared to the blank untreated sludge when MU 085 or K 111 L are used.

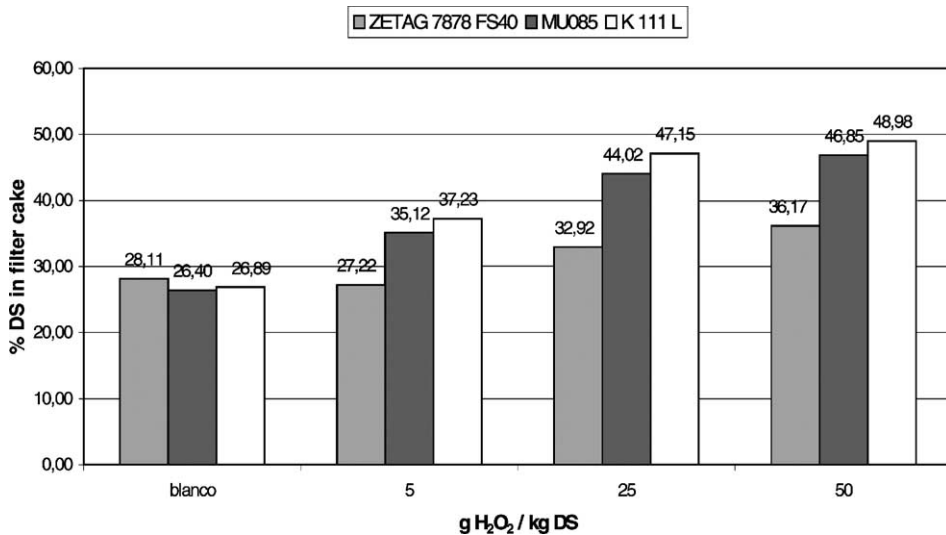(v) The effect of peroxidation on the properties of the water phase is reflected in various findings:

☐ ZETAG 7878 FS40 ■ MU085 ☐ K 111 L

Fig. 5. Percentage of DS in the filter cake for increasing amounts of H_2O_2.
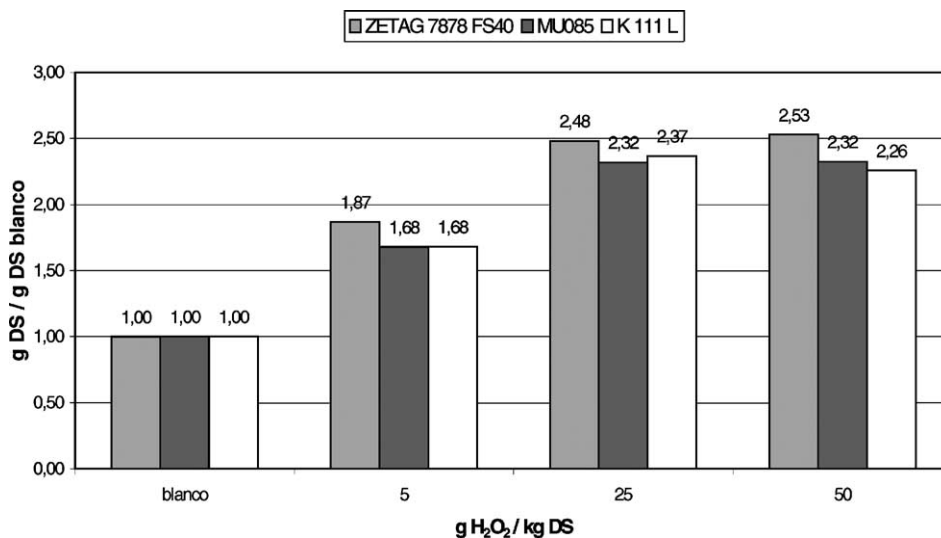
Fig. 6. DS in the water phase for increasing amounts of H_2O_2.

- The amounts of DS and ODS released in the water phase increase with increasing amounts of H_2O_2 added as illustrated in Fig. 6. Adding 25 g H_2O_2 kg^{-1} DS yields a considerable release of DS, concentrations are over a two-fold of the concentrations in the blank water phase. The release of DS and ODS into the water phase at a given dosage of H_2O_2 is independent of the polyelectrolyte used.
    The water phase of the sludge treated with K 111 L (25 g H_2O_2 kg^{-1} DS) is studied.
- The release of heavy metals into the water phase is limited (Table 2) when compared with the laboratory tests (Neyens et al. [22]) due to the neutralisation with $Ca(OH)_2$ causing a partial precipitation of metal hydroxides.
- The BOD/COD ratio stays nearly the same for the peroxidized sludge (Table 3).
- Nitrogen is released according to the data of Table 4. Tables 3 and 4 enable the calculations of the BOD/N and COD/N ratios of the liquor phase.
- The concentration of phosphorus in the water phase increases from 3 to 4.3 mg P l^{-1}. The concentration of sulphate in the liquor also nearly stays the same, i.e. 1035 mg l^{-1}

Table 2
Evolution of heavy metals as a result of peroxidation

	Water phase of untreated sludge (mg l^{-1})	Water phase of peroxidized sludge (mg l^{-1})
Cd	<0.001	0.011
Cr	0.015	0.048
Cu	0.019	1.33
Hg	<0.0005	<0.0005
Ni	0.172	0.319
Pb	0.023	0.063
Zn	0.350	9.14

Table 3
Evolution of COD and BOD as a result of peroxidation

	Water phase of untreated sludge (mg $O_2 \, l^{-1}$)	Water phase of peroxidized sludge (mg $O_2 \, l^{-1}$)
COD	2230	696
BOD	1030	313
BOD/COD	0.46	0.45

Table 4
Evolution of N-components as result of peroxidation

	Water phase of untreated sludge (mg $N \, l^{-1}$)	Water phase of peroxidized sludge (mg $N \, l^{-1}$)
Kj.–N	104.2	149.6
$NO_2^- $–N NO_3^-–N	<0.1	1.5

in the water phase of the untreated sludge and $1030 \, \text{mg} \, l^{-1}$ in the water phase of the peroxidized sludge.

5. Economy of using H_2O_2-oxidation

5.1. Mass and energy balances

Based upon these findings, treating sewage sludge with $25 \, \text{g} \, H_2O_2 \, \text{kg}^{-1}$ DS and using K 111 L as flocculating agent seems to be a promising AST. Mass and energy balances of a wastewater treatment using this oxidation technique for the case of a daily sludge production of 60 g DS per equivalent inhabitant (IE) are studied. Concluding results are illustrated in Fig. 7 and Table 5 for the proposed optimum conditions. The data clearly illustrate the benefits of implementing the advanced oxidation technique.

Unlike other AST methods [e.g. thermal and thermochemical hydrolysis (Neyens et al. [35])], peroxidation is a simple process that occurs at ambient temperature and pressure. No extra energy is hence needed for the treatment. The amount DS/IE.d is reduced from 60 to 33.1 g DS/IE.d. This reduction of DS and ODS is due to both the release of reaction products (water, CO_2 and small organic molecules) and to the release of DS and ODS in the water phase. The percentage DS of the sludge cake is 47%, which means a 20% increase compared to the traditional sludge treatment facility, resulting in a reduced energy for subsequent drying as compared with the traditional treatment (88.4 kJ/IE.d compared to 457 kJ/IE.d).

5.2. Costs

A WWTP of 300 000 IE with sludge dewatering and incineration is used for the economic assessment. For the case of a daily sludge production of 60 g DS/IE.d, a total annual amount of 6 570 ton has to be dealt with.
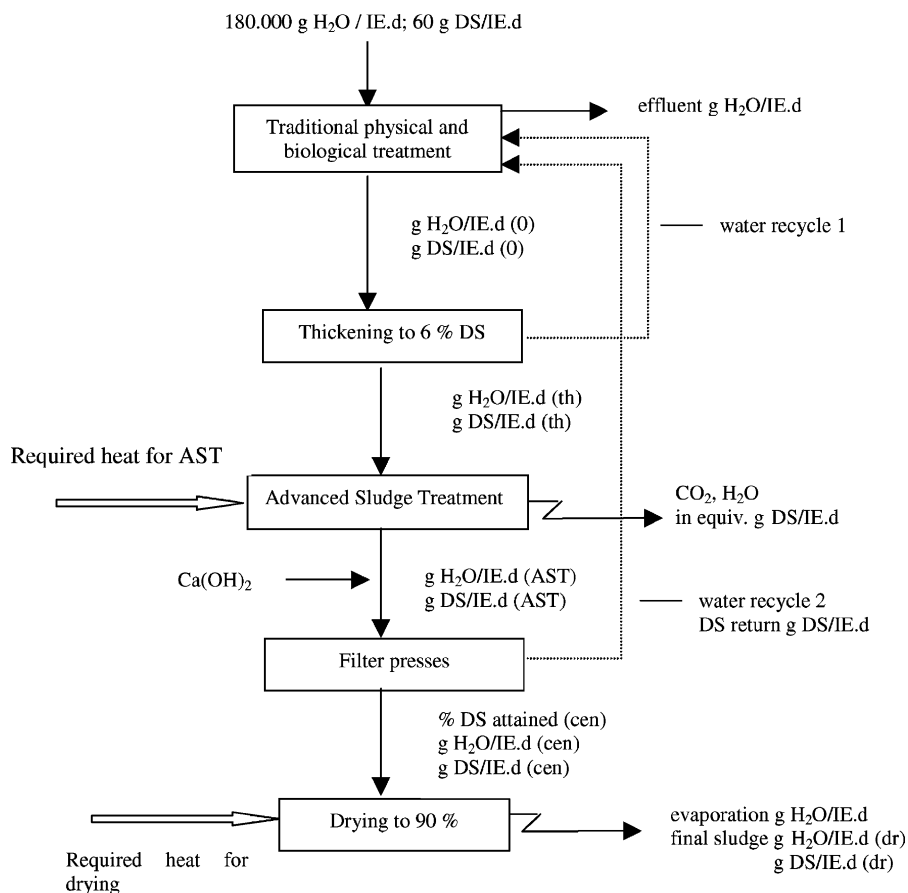
Fig. 7. Mass and energy balances of a wastewater treatment implementing H_2O_2-oxidation (data are given in Table 5).

The fixed costs are estimated at approx. 50 000 € per year. The process requires sulphuric acid to adjust the pH to 3. This acid treatment requires the use of corrosion-resistant construction materials and the equipment costs are therefore considered 40 000 € per year when debited in 10 years. The maintenance costs are approx. 10 000 € per year.

Variable costs consist of chemical costs and electricity. Chemical costs involved are rather high: except from H_2O_2, peroxidation necessitates H_2SO_4, $FeSO_4$ and $Ca(OH)_2$ for neutralisation. This cost is compensated by the fact that the reaction proceeds at ambient conditions, thus without the need of energy supply, electricity is only necessary for the pumps. In total, the sum of the variable costs is 400 000 € per year.

Considering that the mechanically dewatered sludge is incinerated, there is a saving of almost 1 400 000 € per year because of the fact that the dewatered sludge will have a DS-content of 45% compared to 25% in the traditional sludge treatment facility.

Table 5
Data of mass and energy balances of Fig. 3, for the case of a daily sludge production of 60 g DS/IE, considering a WWTP including sludge thickening and dewatering

	Traditional	Peroxidation
Effluent (g H_2O/IE.d)	179,820	179,820
g H_2O/IE.d (0)	3.940	3.940
g DS/IE.d (0)	60	60
Water recycle 1 (g H_2O/IE.d)	3,000	3,000
g H_2O/IE.d (th)	940	940
g DS/IE.d (th)	60	60
g H_2O/IE.d (AST)	–	940
g DS/IE.d (AST)	–	46.2
Required heat for AST (kJ/IE.d)	–	–
CO_2, H_2O (equiv. g DS/IE.d)	–	13.8
$Ca(OH)_2$ (g/IE.d)	–	0.3
Water recycle 2 (g H_2O/IE.d)	760	902.7
DS return (g DS/IE.d)	–	13.1
Percentage DS attained in filter press	25	47
g H_2O/IE.d (cen)	180	37.3
g DS/IE.d (cen)	60	33.1
Required heat for drying (kJ/IE.d)	457	88.4
Evaporation (g H_2O/IE.d)	173.3	33.6
Final sludge (g H_2O/IE.d)	6.7	3.7
Final sludge (g DS/IE.d)	60	33.1

Considering the costs and the savings, there is a net saving of 950 000 € per year or 140 € per ton DS for a WWTP of 300 000 IE.

6. Conclusion

The costs related to sludge treatment have risen considerably. The reduction of the amount of sludge produced and the dryness of the sludge cake are hence of paramount importance. This paper discusses the oxidation processes utilising activation of H_2O_2 by iron salts, referred to as Fenton's reagent.

Based on the proposed optimum conditions obtained in laboratory tests, pilot-scale experiments were conducted. All experiments were performed at pH 3 and in the presence of 1.67 g Fe^{2+}-ions kg^{-1} DS. The amount of H_2O_2 added varied between 5 and 50 g H_2O_2 kg^{-1} DS. The peroxidation process occurred at T_a and P_a during 60–90 min. After reaction, the sludge was neutralised by adding 55.6 g $Ca(OH)_2$ kg^{-1} DS. Three flocculation agents were compared with respect to their ability to enhance the dewaterability of the sewage sludge. As a result of these experimental findings, it can be concluded that adding an amount of approx. 25 g H_2O_2 kg^{-1} DS under the proposed conditions of pH, T, P, time and Fe^{2+} in combination with K 111 L polyelectrolyte can be considered as a promising sludge treatment, yielding:

- a considerable reduction of DS and ODS in the filter cake of over 30%;

- an improved dewaterability with a 60% reduction of the sludge volume, and a 20% increase of the cake DS-content when compared with the 'blank' sludge sample;
- a reduced CST-value by approx. 20 s when compared with the 'blank' sample.

Mass and energy balances of a wastewater treatment implementing this oxidation technique for the case of a daily sludge production of 60 g DS per equivalent inhabitant (IE) were studied. The data clearly illustrated the benefits of implementing the AST. An economic assessment was made for a WWTP of 300 000 IE. Considering the fixed and variable costs as well as the energy savings for incinerating the sludge after dewatering, a net saving of approx. 950 000 € per year or 140 € per ton DS can be expected.

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