Review

A review of classic Fenton's peroxidation as an advanced oxidation technique

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Abstract

Hydrogen peroxide (H_2O_2) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. Still H_2O_2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H_2O_2 concentrations. Improvements can be achieved by using transition metal salts (e.g. iron salts) or ozone and UV-light can activate H_2O_2 to form hydroxyl radicals, which are strong oxidants. Oxidation processes utilising activation of H_2O_2 by iron salts, classically referred to as Fenton's reagent is known to be very effective in the destruction of many hazardous organic pollutants in water.

The first part of our paper presents a literature review of the various Fenton reagent reactions which constitute the overall kinetic scheme with all possible side reactions. It also summarises previous publications on the relationships between the dominant parameters (e.g. [H_2O_2], [Fe^{2+}], ...). The second part of our review discusses the possibility of improving sludge dewaterability using Fenton's reagent.
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1. Introduction: the use of hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a strong oxidant (standard potential 1.80 and 0.87 V at pH 0 and 14, respectively) (Degussa Corporation [1]) and its application in the treatment of various inorganic and organic pollutants is well established. Numerous applications of H_2O_2 in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, and chlorine, are known (Venkatadri and Peeters [2]).

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Nomenclature

AOT	advanced oxidation technique
ECP	extracellular polymer
BOD	biochemical oxygen demand (mg/l)
COD	chemical oxygen demand (mg/l)
SCOD	soluble chemical oxygen demand (mg/l)
DS	dry solids content (%)
ODS	organic part of the DS (%)
k	rate constant ($M^{-1} s^{-1}$)
PE	polyelectrolyte
RH	organic substrate
$R^\bullet$	organic radical
$[Fe^{2+}]_0/[H_2O_2]_0$	initial concentration of Fe^{2+} versus initial concentration of H_2O_2
$\Delta[Fe^{2+}]/\Delta[H_2O_2]$	consumption ratio of ferrous ion to hydrogen peroxide
SRF	specific resistance to filtration
TOC	total organic carbon (mg/l)
CST	capillary suction time (s)
Blanco	initial untreated sludge sample

H_2O_2 is also useful in the treatment of the gaseous sulphur oxides and nitrogen oxides being converted to the corresponding acids. Other related uses include the bleaching of pulp and paper and organic synthesis. H_2O_2 has applications in the surface treatment industry involving cleaning, decorating, protecting and etching of metals (L'air Liquide [3]).

By dissociation into oxygen and water H_2O_2 can also supply oxygen to micro organisms in biological treatment facilities and in the bioremediation of contaminated sites. It can be used as a disinfecting agent in the control of undesirable biofilm growth. Since the oxygen concentration is generally rate limiting during the in situ biodegradation of organic contaminants, several applications using injection of H_2O_2 into the subsurface have been successfully attempted to enhance the biodegradation activity (Calabrese and Kostecki [4]). H_2O_2 can be decomposed into water and oxygen by enzymatic and nonenzymatic routes.

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:

- ozone and hydrogen peroxide

$$O_3 + H_2O_2 \rightarrow OH^\bullet + O_2 + HO_2^\bullet$$

- iron salts and hydrogen peroxide

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$$

- UV-light and hydrogen peroxide

$$H_2O_2[+UV] \rightarrow 2OH^\bullet$$

The oxidation processes utilising activation of H_2O_2 by iron salts, referred to as Fenton's reagent, are discussed below.

In general, oxidation processes which are based on the generation of radical intermediates, are termed advanced oxidation techniques (AOT; Venkatadri and Peeters [2]). Hydroxyl radicals (oxidation potential: 2.8 V) are stronger oxidants than ozone and H_2O_2. Hydroxyl radicals non-specifically oxidise target compounds at high reaction rates (of the order of $10^9\,M^{-1}\,s^{-1}$ as described later).

2. Fenton's reagent

2.1. Introduction

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. [5]).
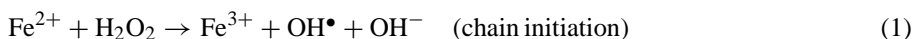
Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants.
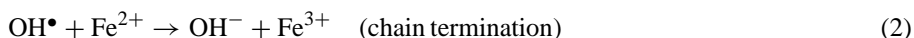
2.2. Kinetic scheme

Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the reaction (Kitis et al. [6]; Yoon et al. [7]; Lu et al. [8])

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

The ferrous iron (Fe^{2+}) initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution

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

$k_1 \approx 70\,M^{-1}\,s^{-1}$ (Rigg et al. [9])

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

$k_2 = 3.2 \times 10^8\,M^{-1}\,s^{-1}$ (Buxton and Greenstock [10]).

Moreover, the newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in Eqs. (3)–(7).

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

$k_3 = 0.001–0.01\,\mathrm{M^{-1}\,s^{-1}}$ (Walling and Goosen [11]).

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

The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction [reactions (3) and (4)] (Walling and Goosen [11]; De Laat and Gallard [12]).

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

$k_5 = 1.3 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$ (at pH = 3, Bielski et al. [13]).

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

$k_6 = 1.2 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$ (at pH = 3, Bielski et al. [13]).

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

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

As seen in reaction (7), H_2O_2 can act as an $OH^\bullet$ scavenger as well as an initiator [reaction (1)].

Hydroxyl radicals can oxidise organics (RH) by abstraction of protons producing organic radicals ($R^\bullet$), which are highly reactive and can be further oxidised (Walling and Kato [14]; Venkatadri and Peters [2]; Lin and Lo [15])

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

Since $k_7 = 10^7\,\mathrm{M^{-1}\,s^{-1}}$ while $k_2 > 10^8$ (7) can be made unimportant by maintaining a high $[RH]/[H_2O_2]$ ratio.

If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2, water and in the case of substituted organics, inorganic salts if the treatment is continued.
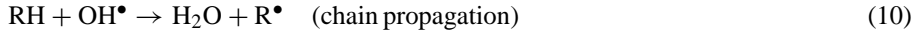
Walling [16] simplified the overall Fenton chemistry [reaction (1)] by accounting for the dissociation water

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{9}$$
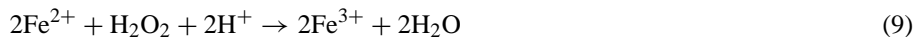
This equation suggests that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidations (Hickey et al. [17]). In the presence of organic substrates (RH), excess ferrous ion, and at low pH, hydroxyl radicals can add to the aromatic or heterocyclic rings (as well as to the unsaturated bonds of alkenes or alkynes)
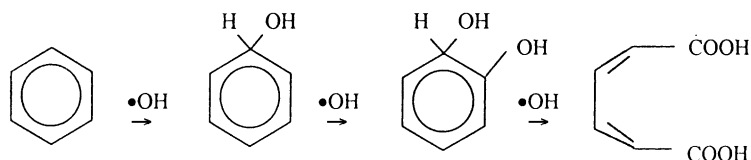
They can also abstract a hydrogen atom, initiating a radical chain oxidation (Walling [16]; Lipczynska-Kochany et al. [18])
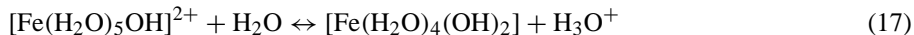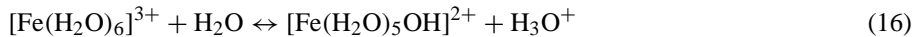
$$RH + OH^\bullet \rightarrow H_2O + R^\bullet \quad \text{(chain propagation)} \tag{10}$$

$$R^\bullet + H_2O_2 \rightarrow ROH + OH^\bullet \tag{11}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{12}$$

The organic free radicals produced in reaction (10) may then be oxidised by Fe^{3+}, reduced by Fe^{2+}, or dimerised according to the following reactions (Tang and Tassos [19])
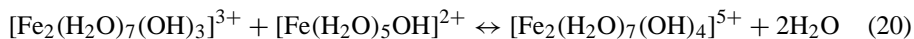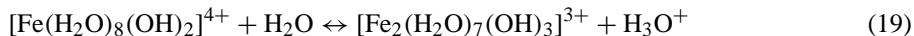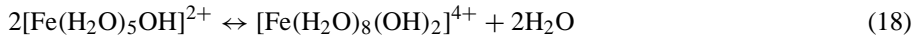
$$R^\bullet + Fe^{3+}\text{-oxidation} \rightarrow R^+ + Fe^{2+} \tag{13}$$

$$R^\bullet + Fe^{2+}\text{-reduction} \rightarrow R^- + Fe^{3+} \tag{14}$$

$$2R^\bullet\text{-dimerization} \rightarrow R\text{--}R \tag{15}$$

The sequence of reactions (1), (2), (10) and (13) constitute the present accepted scheme for the Fenton's reagent chain.

The ferrous ions generated in the above redox reactions (8) and (9) react with hydroxide ions to form ferric hydroxo complexes according to (Walling and Kato [14], Lin and Lo [15])

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+ \tag{16}$$

$$[Fe(H_2O)_5OH]^{2+} + H_2O \leftrightarrow [Fe(H_2O)_4(OH)_2] + H_3O^+ \tag{17}$$

Within pH 3 and 7, the above complexes become

$$2[Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe(H_2O)_8(OH)_2]^{4+} + 2H_2O \tag{18}$$

$$[Fe(H_2O)_8(OH)_2]^{4+} + H_2O \leftrightarrow [Fe_2(H_2O)_7(OH)_3]^{3+} + H_3O^+ \tag{19}$$

$$[Fe_2(H_2O)_7(OH)_3]^{3+} + [Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe_2(H_2O)_7(OH)_4]^{5+} + 2H_2O \tag{20}$$

which accounts for the coagulation capability of Fenton's reagent. Dissolved suspended solids are captured and precipitated. It should be noted that large amounts of small flocs are consistently observed in the Fenton oxidation step. Those flocs take a very long time, sometimes overnight, to settle out. Chemical coagulation using polymer is therefore necessary. Fenton's reagent is known to have different treatment functions, as mentioned earlier, depending on the $H_2O_2/FeSO_4$ ratio. When the amount of Fe^{2+} employed exceeds that of H_2O_2, the treatment tends to have the effect of chemical coagulation. When the two amounts are reversed, the treatment tends to have the effect of chemical oxidation.

Reaction (13) competes with both the chain termination reaction [reaction (2)] and with the propagation reaction (10) of Fenton chemistry. This competition for hydroxyl radical between Fe^{2+}, RH and Fe^{3+} leads to the non-productive decomposition of hydrogen peroxide and limits the yield of hydroxylated (oxidised) organic compounds. Therefore, the stoichiometric relationship between Fe^{2+}, RH and Fe^{3+} has to be established to maximise the efficiency of the degradation process.

2.3. Stoichiometric relationship

The key features of the Fenton system are believed to be its reagent conditions, i.e. $[Fe^{2+}]$, $[Fe^{3+}]$, $[H_2O_2]$ and the reaction characteristics (pH, temperature and the quantity of organic and inorganic constituents). Because these parameters determine the overall reaction efficiency, it is important to understand the mutual relationships between these parameters in terms of hydroxyl radical production and consumption.

Yoon et al. [7] studied these relationships and classified them in three categories according to the quantity of the $[Fe^{2+}]_0/[H_2O_2]_0$ ratio (initial concentration of Fe^{2+} versus initial concentration of H_2O_2). Their results are now summarised.

2.3.1. High ratio of $[Fe^{2+}]_0/[H_2O_2]_0$ (≥ 2)

The Fenton reaction begins by producing $OH^{\bullet}$ from the reaction between ferrous ion and hydrogen peroxide [reaction (1)]. When the Fenton reaction in the absence of organics is initiated under $[Fe^{2+}]_0/[H_2O_2]_0$ (≥ 2), the consumption ratio of ferrous ion to hydrogen peroxide ($\Delta[Fe^{2+}]/\Delta[H_2O_2]$) becomes about 2, and radical chain reactions are quickly terminated. This is because the $OH^{\bullet}$ produced as a result of reaction (1) mainly reacts with the ferrous ion [reaction (2)] and not hydrogen peroxide [reaction (7)]. This explanation is supported by the fact that the reaction between $OH^{\bullet}$ and the ferrous ion is ten times faster than that between $OH^{\bullet}$ and hydrogen peroxide [$k_2 = 3.2 \times 10^8 \, M^{-1} \, s^{-1}$ (Buxton and Greenstock [10]) and $k_7 = 3.3 \times 10^7 \, M^{-1} \, s^{-1}$ (Buxton and Greenstock [10])]. Results of Fig. 1 confirm this explanation: in the absence of organics (RH), while satisfying approximately the consumption ratio ($\Delta[Fe^{2+}]/\Delta[H_2O_2]$) of two, considering that the most of the ferrous ion and hydrogen peroxide are consumed within minutes under these reagent conditions due to the rate constant of reaction 1 ($70 \, M^{-1} \, s^{-1}$) ($[Fe^{2+}]_0 = 10 \, mM$ and $[H_2O_2] = 5 \, mM$).
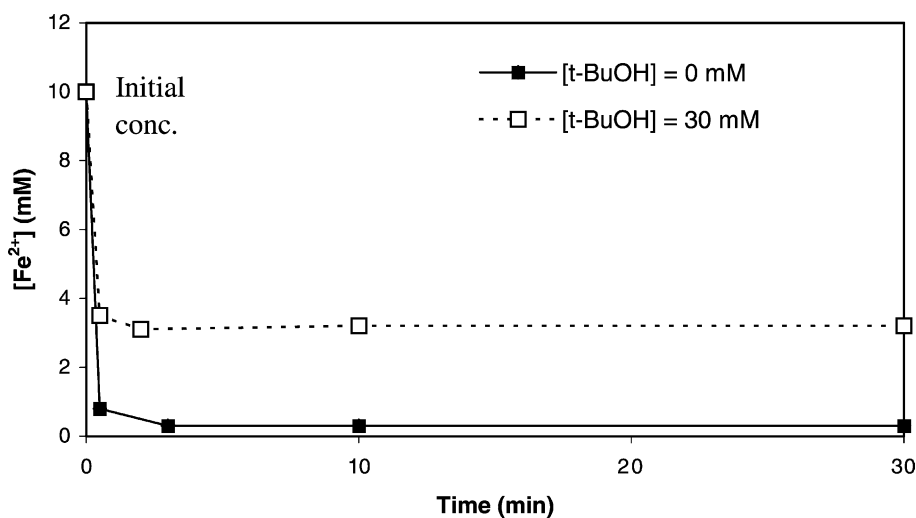

Fig. 1. Concentration vs. time profiles for Fe^{2+} in the absence or presence of *t*-butanol (experimental conditions: $[Fe^{2+}]_0 = 10 \, mM$, $[H_2O_2]_0 = 5 \, mM$) (© IWA Publishing, reprinted with permission from Yoon et al. [7]).

On the other hand, the presence of RH affects only the behaviour of the ferrous ion, not the hydrogen peroxide (Fig. 1). This is because the organics compete with ferrous ion for OH$^\bullet$ [reactions (2) and (8)]. The presence of organics reduces the $\Delta[Fe^{2+}]/\Delta[H_2O_2]$ ratio to less than two ($\Delta[Fe^{2+}]/\Delta[H_2O_2] \approx 1.3$ in Fig. 1), which means that the ferrous ion is utilised as a major reactant, not as a catalyst in the Fenton reaction.

Yoon et al. [7] studied the effect of the Fenton reaction in the removal of landfill leachate organics. They used a $[Fe^{2+}]_0/[H_2O_2]_0$ ratio of 1.25. In that case, the Fenton reaction can be divided into two processes. The first process is an initial oxidation at a low pH of about 3. The second process, which follows the oxidation process, is coagulation at a high pH of 7–8. It is interpreted that the coagulation step in the Fenton reaction had a primary role in the selective removal of organics, though the Fenton reaction is not a coagulation one. However, since the efficiency of organic removal in the Fenton reaction was higher than coagulation, the Fenton reaction in landfill leachate treatment process may be called a type of "enhanced coagulation".

2.3.2. Medium ratio of $[Fe^{2+}]_0/[H_2O_2]_0$ (=1)

Fig. 2 presents results of hydrogen peroxide concentrations at an average $\Delta[Fe^{2+}]_0/\Delta[H_2O_2]_0$ ratio (=1). Regardless of the presence of organics, hydrogen peroxide rapidly converts all ferrous to ferric ion via reaction (1). In the absence of RH, hydrogen peroxide decomposes slowly through ferric ion induced radical chain reactions [reaction (3)] just after the rapid consumption of hydrogen peroxide. The reduction of the ferric ion [reactions (3) and (4)] is significantly lower than reaction (1) and is the rate-determining step. To have a continued decrease of hydrogen peroxide, ferrous ion must be formed by the reduction of ferric ion. Then, the Fenton reaction can be characterised by two specific systems, i.e.
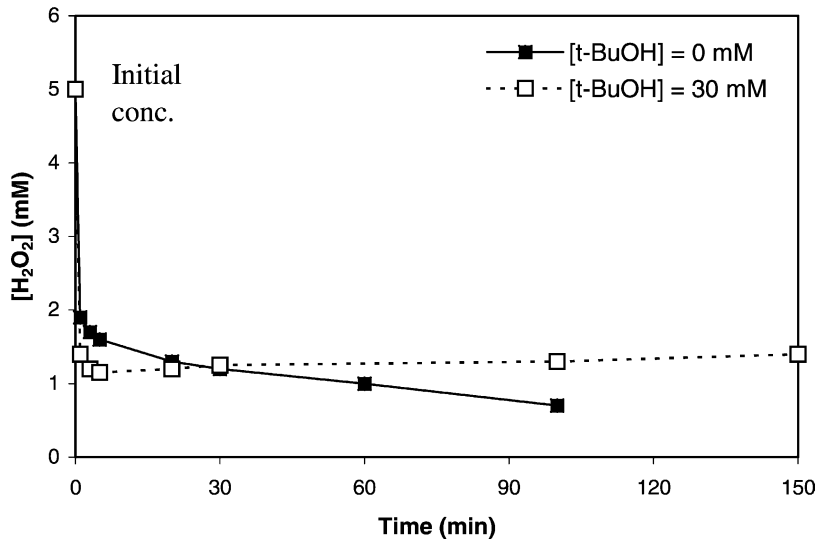

Fig. 2. Concentration vs. time profiles for H_2O_2 in the absence or presence of *t*-butanol (experimental conditions: $[Fe^{2+}]_0 = 5\,mM$, $[H_2O_2]_0 = 5\,mM$) (© IWA Publishing, reprinted with permission from Yoon et al. [7]).

the ferrous system and the ferric system, which depend on the oxidation stage of the iron initially added or the major oxidation state of the iron present. The ferrous system refers to the case where the primary reaction, which produces $OH^\bullet$, is the reaction between the ferrous ion and hydrogen peroxide [reaction (1)]. The ferric system refers to the case in which the ferric ion induced reactions (3) and (4) must be preceded in order to produce $OH^\bullet$ via reaction (1). Results of Fig. 2 fall under the ferric system just after the consumption of hydrogen peroxide and the slow consumption of hydrogen peroxide occurs since the ferric ion can be mainly reduced by hydrogen peroxide.

However, the presence of RH has an impact on the behaviour of the hydrogen peroxide in two ways: (i) no further hydrogen peroxide decomposition occurs just after the initial decrease of hydrogen peroxide, since the reaction of RH with $OH^\bullet$ [reaction (8)], overwhelms the reaction of hydrogen peroxide with $OH^\bullet$ [reaction (7)]; (ii) the presence of excess RH can hinder the reaction between $OH^\bullet$ and the ferrous ion, which may have been the major route of $OH^\bullet$ consumption in the absence of RH. Therefore, the remaining ferrous ion can react with the hydrogen peroxide and show a slightly higher consumption of hydrogen peroxide at the initial stage of the reaction as compared with that observed in the absence of RH (Fig. 2).

2.3.3. Low ratio of $[Fe^{2+}]_0/[H_2O_2]_0$ ($\ll 1$)

In the absence of RH, a slow decomposition of hydrogen peroxide occurs caused by ferric ion, which induces radical chain reactions (ferric system) immediately after the initial rapid depletion of hydrogen peroxide. However, the presence of RH almost stops the decomposition of hydrogen peroxide by ferric ion (ferric system), as shown in Fig. 3. These results can be explained in the manner shown in Fig. 2. One difference between this case and that shown in Fig. 2 is that the amount of hydrogen peroxide decomposition, induced by the initial ferrous ion (ferrous system) in the presence of RH, is smaller than in the
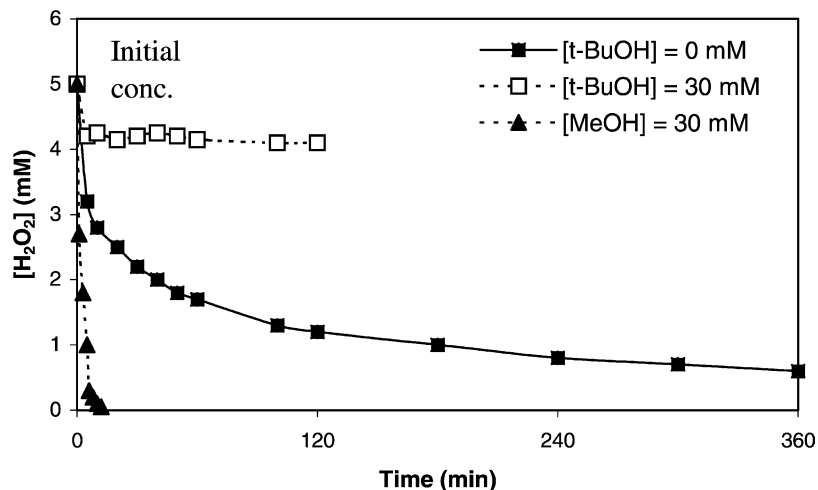

Fig. 3. Concentration vs. time profiles for H_2O_2 in the absence or presence of *t*-butanol (experimental conditions: $[Fe^{2+}]_0 = 1\,mM$, $[H_2O_2]_0 = 5\,mM$) (© IWA Publishing, reprinted with permission from Yoon et al. [7]).

absence of RH: at a low ratio of $\Delta[Fe^{2+}]_0/\Delta[H_2O_2]_0$ ($\ll$1), $OH^\bullet$ reacts to a greater extent with H_2O_2, producing $HO_2^\bullet$ via reaction (7). Therefore, additional $HO_2^\bullet$ can participate in propagating radical chain reactions by reducing ferric to ferrous ion [reactions (6) and (7)], and can result in larger consumption of hydrogen peroxide than occurs in the absence of RH.

2.4. Influence of the structure of hazardous components

Kinetic degradation of aromatic pollutants with the system Fe^{2+}/H_2O_2 was reported earlier (Yoon et al. [20]; Wei et al. [21]; Lipczynska-Kochany [22]) but less attention was given to the mineralisation of these substances. The degradation of alicyclic compounds was given little attention since most of the water pollutants with a low biodegradability have an aromatic structure.

Ruppert and Bauer [23] studied the influence of the structure of several organic pollutants on the way they are mineralised by OH-radicals. As shown in Figs. 4 and 5, all of the aromatic substances studied were strongly degraded after several hours, while the organic carbon of cyclohexanol and cyclohexanone was hardly attacked. In alicyclic compounds the attack of the electrophilic OH-radicals cannot occur at conjugated C=C double bonds in contrast to aromatic compounds where ring opening and further degradation takes place.

As shown in Figs. 6 and 7, H_2O_2 decrease during reaction was in good correlation with the TOC (total organic carbon)-degradation. For all aromatic substances studied degradation curves became linear after the first 30 min, until H_2O_2 was completely exhausted. During degradation of cyclohexanol and cyclohexanone only a slight decrease of the oxidant could be observed. The continued destruction of nitroaniline after exhaustion of H_2O_2, as shown in Fig. 5, was attributed to photo-Fenton reactions (Ruppert and Bauer, [23]).
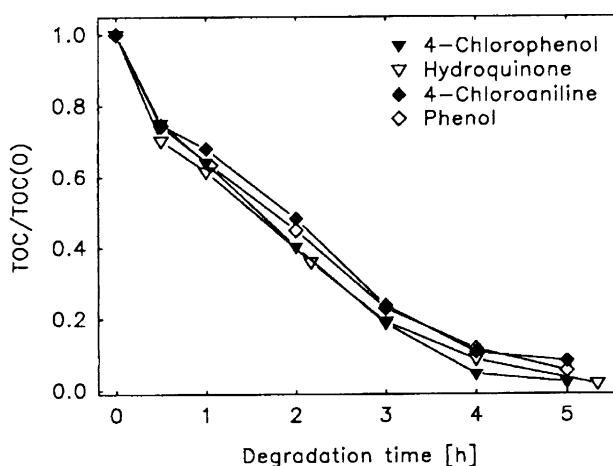

Fig. 4. Effect of degradation time on degradation of TOC for 4-chlorophenol, hydroquinone, 4-chloroaniline and phenol (experimental conditions: [substrate]$_0$ = 1 × 10^{-3} mol l^{-1}, [H$_2$O$_2$]$_0$ = 1 × 10^{-2} mol l^{-1}, [Fe^{2+}]$_0$ = 2.5 × 10^{-4} mol l^{-1}) (Ruppert and Bauer [23]).
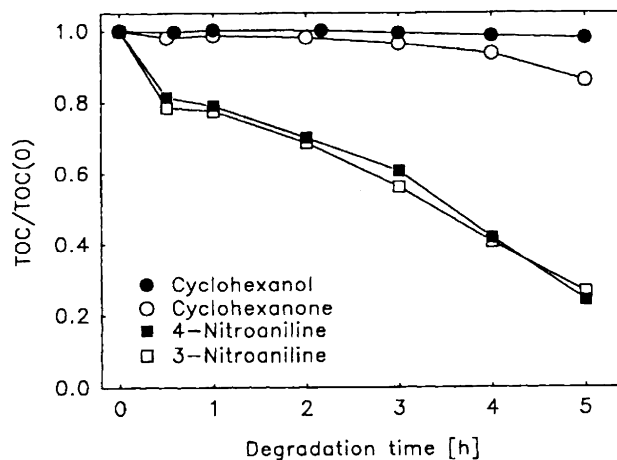
Fig. 5. Effect of degradation time on degradation of TOC for cyclohexanol, cyclohexanone, 4-nitroaniline and 3-nitroaniline (experimental conditions: [substrate]$_0$ = 1×10^{-3} mol l^{-1}, [H$_2$O$_2$]$_0$ = 1×10^{-2} mol l^{-1}, [Fe^{2+}]$_0$ = 2.5×10^{-4} mol l^{-1}) (Ruppert and Bauer [23]).
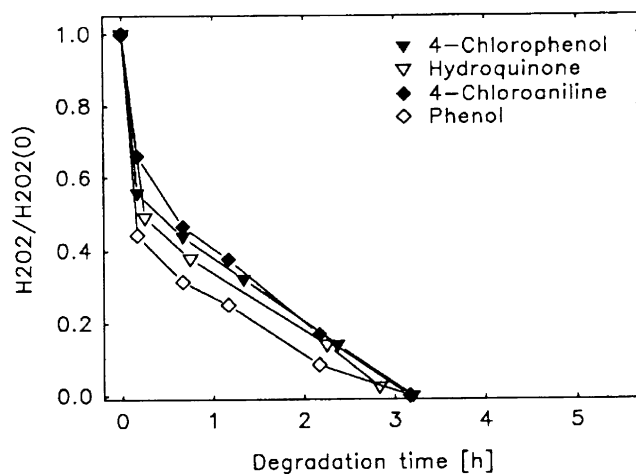

Fig. 6. Effect of degradation time on degradation of H$_2$O$_2$ for 4-chlorophenol, hydroquinone, 4-chloroaniline and phenol (experimental conditions: [substrate]$_0$ = 1×10^{-3} mol l^{-1}, c_0(H$_2$O$_2$) = 1×10^{-2} mol l^{-1}, c_0(Fe^{2+}) = 2.5×10^{-4} mol l^{-1}) (Ruppert and Bauer [23]).

2.5. Electrochemically generated peroxide

There is at present a considerable interest in the development of electrochemical technology for the treatment of effluents, particularly the destruction of organic waste (Harrington and Pletcher [24]).
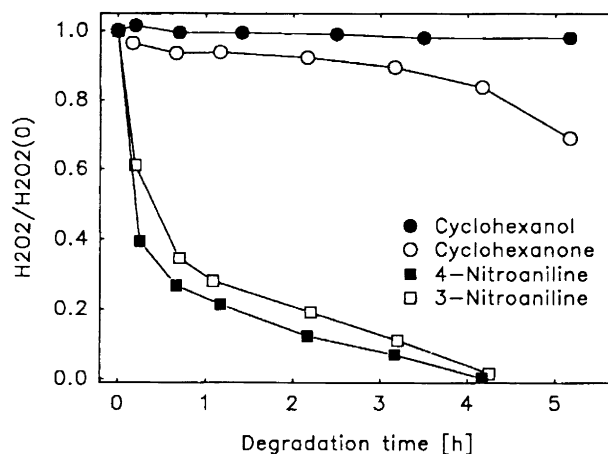
Fig. 7. Effect of degradation time on degradation of H_2O_2 for cyclohexanol, cyclohexanone, 4-nitroaniline and 3-nitroaniline (experimental conditions: [substrate]$_0$ = 1×10^{-3} mol l^{-1}, [H_2O_2]$_0$ = 1×10^{-2} mol l^{-1}, [Fe^{2+}]$_0$ = 2.5×10^{-4} mol l^{-1}) (Ruppert and Bauer [23]).

Hydrogen peroxide as a redox mediator in indirect electrolysis has several unique characteristics (Pletcher [25]). Firstly, it is a strong oxidising agent produced at the cathode under rather mild conditions by the reduction of oxygen. The source of the oxygen may be air or oxygen enriched air. The on site electrogeneration of the H_2O_2 and its use as a dilute solution in or close to the electrolysis cell greatly reduces the hazards associated with the H_2O_2-chemistry. In general, these reactions lead to water and hence leave no stoichiometric residuals in the reaction environment or effluent stream.

Interest centres on the electrogeneration of the H_2O_2 in neutral or slightly acidic media, often with a low electrolyte concentration. The slightly acidic solutions allow the addition of Fe^{2+} which enhances the rate and efficiency of the reactions of hydrogen peroxide with organic molecules. An aqueous acidic solution containing both Fe^{3+} and O_2 is reduced at a cathode to give the active H_2O_2/Fe^{2+} composition (Fenton's reagent). Introduction of the Fenton's reagent into effluents containing relatively low amounts of organics so that the ratio of [H_2O_2]:[organic] is high, should be an effective method of effluent treatment because of the wide variety of organic molecules that can be converted to CO_2. This treatment is limited to solutions containing <1000 ppm chemical oxygen demand (COD; Pletcher [25]). The reason is associated with energy consumption. The energy consumption for an effluent treatment process is proportional to the concentration of organics in solution and the number of electrons involved in the conversion of the organics into CO_2. Due to the low COD-concentrations, the chemistry possible in dilute solutions should be differentiated from that employing very concentrated solutions, e.g. peracid chemistry.

It has been confirmed that in this way the COD in aqueous solutions resulting from a wide variety of organics (including aromatic, aliphatic and azo dyes) can be decreased to <10 ppm (Harrington and Pletcher, [24]). These successful results should be capable of pushing this chemistry into industrial technology.

3. Improving sludge dewaterability by Fenton's reagent

Municipal and industrial wastewater treatment plants produce large amounts of sludge, containing organic and mineral components. Due to the high organic loadings and/or to an unfavourable carbon/nitrogen-ratio of wastewater together with an inappropriate design of treatment plants, problems may arise, mostly noticed as bulking or viscous sludge with poor dewaterability. This sludge is mechanically dewatered to as high percentages dry solids content (DS) (dry solids) as possible. Using common 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 [26]). 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. [27]). 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 using an extended aeration biology, using a biological phosphorus-removal (instead of chemical precipitation), using sludge digesters, etc. A further reduction and an improvement of the dewaterability require advanced technologies, such as Fenton reaction.

The difficulty in activated sludge dewatering is mainly attributed to the presence of extracellular polymer (ECP). ECP is present in varying quantities in sewage sludge, occurring as either a highly hydrated capsule surrounding the bacterial cell wall or loose in solution as slime polymers. ECP is thought to aid the survival of the bacterial cell by preventing dessication and acting as an ion-exchange resin, controlling the ionic movement from solution into the cell (Houghton et al. [28]). 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 are present (Urbain et al. [29]; Jorand et al. [30]).

Pere et al. [31] noted that surface properties, like the concentration of ECP, were related to zeta-potential measurements with particle electrophoresis as well as to water contact angle measurements on filter cakes prior to and after the oxidative conditioning: the sludges with high zeta-potentials and low contact angles were sludges with high amounts of ECP. Precisely these sludges with a high surface charge density as well as a high hydrophilicity (low contact angle) prevent efficient flocculation.

The experimental results of Pere et al. [31] indicate that peroxidation of sludge enhances the flocculation and dewaterability. The responsible mechanism is not fully understood, but the oxidative conditioning might be based on partial oxidation and rearrangement of the surface components (extracellular polymers) of the sludge flocs.

The effects of temperature, hydrogen peroxide concentration, pH and reaction time on the dewaterability of the sludges were tested by Neyens et al. [34] (Fig. 8). The specific resistance to filtration (SRF), also known as the Buchner funnel test, is one means of comparing filtration/dewaterability characteristics of treated and untreated sludges in dewatering applications. Although the Buchner-funnel-laboratory-method involves the application of vacuum filtration, the specific resistance characteristic that it provides is independent of which dewatering method will be adopted.
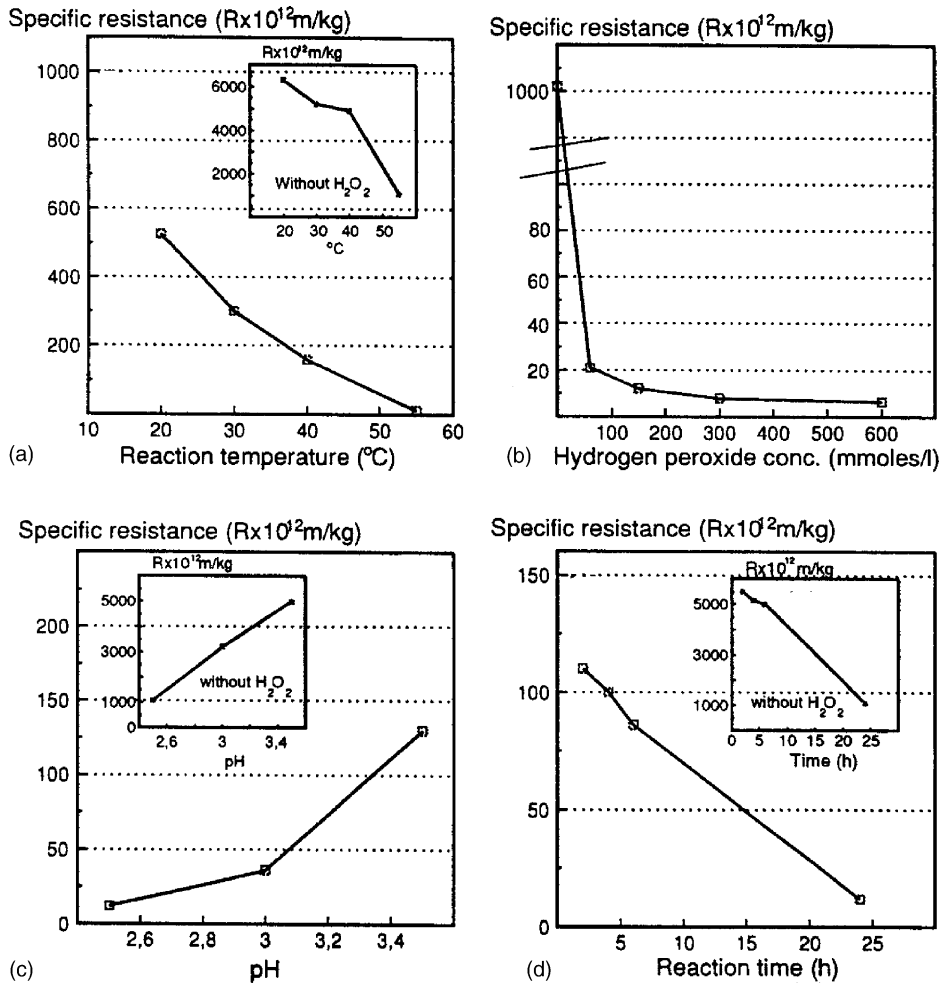
Fig. 8. Effects of operating conditions on the SRF in the oxidation treatment of activated sludge (© IWA Publishing, reprinted with permission from Mustranta and Viikari, [32]): (a) temperature (600 mM H_2O_2; 0.5 mM $FeSO_4 \cdot H_2O$; pH 2.5; 24 h); (b) H_2O_2-concentration (55 °C; 0.5 mM $FeSO_4 \cdot 7H_2O$; pH 2.5; 24 h); (c) pH (55 °C; 150 mM H_2O_2; 0.5 mM $FeSO_4 \cdot 7H_2O$; 24 h); (d) reaction time (55 °C; 150 mM H_2O_2; 0.5 mM $FeSO_4 \cdot 7H_2O$; pH 2.5).

By gathering bench data on Buchner filtration time and filtrate volume, and combining these with actual filter pressure, filter area, sludge solids concentration and filtrate viscosity, the specific resistance to filtration of the sludge can be calculated in accordance with the following equation:

$$r = \frac{2bPA^2}{\mu c}$$

where b is the slope of filtration rate (s/cm^3) versus filtrate volume (s/cm^6); P the filtration pressure (g/cm^2); A the area (cm^2); μ the viscosity (g/(cm s)); c the weight of solids/unit volume of sludge prior to filtration (g/cm^3); r the specific resistance (s^2/g).

They illustrated that the filterability of the sludge was strongly dependent both on the reaction temperature and on the concentration of hydrogen peroxide in the oxidative treatment. At low temperatures ($<40\,^\circ$C) a high hydrogen peroxide concentration and a long reaction time were necessary in order to obtain satisfactory dewaterability of the sludge. An increasing temperature shortened the incubation time required. Similarly, at higher temperatures the amount of hydrogen peroxide needed could be reduced. It was also obvious that the lower the pH, the faster the filtration rate became. The optimal pH of the treatment was 2.5–3. On the other hand, when very low hydrogen peroxide concentrations were used at pH 3, a reaction temperature of 80–90 $^\circ$C was necessary for satisfactory dewaterability of sludge (Fig. 9).

The pH is the key parameter of the treatment efficiency for Fenton's reagent. As stated earlier, the Fenton process has the highest efficiency when the pH is around 3. At higher pH, the oxidation efficiency of Fenton's reagent may decrease because ferric ions could form Fe(OH)$_3$ (Snoeyink and Jenkins [33]). Fe(OH)$_3$ has a low activity and will not react with hydrogen peroxide (Lu et al. [8]). The ferric ions in the solution that can react with hydrogen peroxide are so reduced [reaction (3)]. In the mechanism in which ferric ions react with hydrogen peroxide, reaction (3) is the rate-limiting step. When the pH is too low and the concentration of hydrogen ions is too high, it will slow down the formation of FeOOH^{2+}, which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well. The earlier reactions may retard the Fenton reaction.

Lu et al. [8] illustrated that there is a considerable effect of pH on the reduction of SRF in the *Fenton system*. If the pH is decreased, the SRF is reduced. A pH of 2.6 is optimal, at this pH there is a 96% reduction of SRF compared to the SRF obtained at pH 7. Concerning the pH for the *Fenton-like system*, only little variation was found. There is no optimal pH-value but an optimal pH-range from 2.5 to 4.5. In this range, the SRF is reduced by 85% compared to the SRF at pH 7.

Neyens et al. [34] describe the experimental results of peroxidation of thickened sludge (6% DS content). To fully determine the most appropriate operating conditions when using chemical oxidation by H$_2$O$_2$, major governing parameters are combined in experiments to assess the influence of the amount of H$_2$O$_2$ and associated variables (temperature, pH, Fe^{2+}). All results are related to the equivalent property for the 'blanco'-untreated sludge sample. Properties that are measured are: DS and organic part of the DS (ODS) of both filtrate and dewatered sludge (filter cake obtained by vacuum filtration of treated sludge); filtration characteristics such as CST (capillary suction time) and the volume of the resulting filter cake which indicates dewaterability; properties of the water phase biochemical oxygen demand (BOD; COD; nitrogen; phosphates and heavy metals). As a result of the experimental findings, it can be concluded that adding an amount of approximately 0.037 g H$_2$O$_2$/100 ml sludge at pH $= 3$ and in the presence of Fe^{2+}-ions (1 mg Fe^{2+}/100 ml thickened sludge [approximately 6% DS]) can be considered as a useful sludge treatment, yielding:

- a considerable reduction of DS and ODS in the filter cake of approximately 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 'blanco' sludge sample;
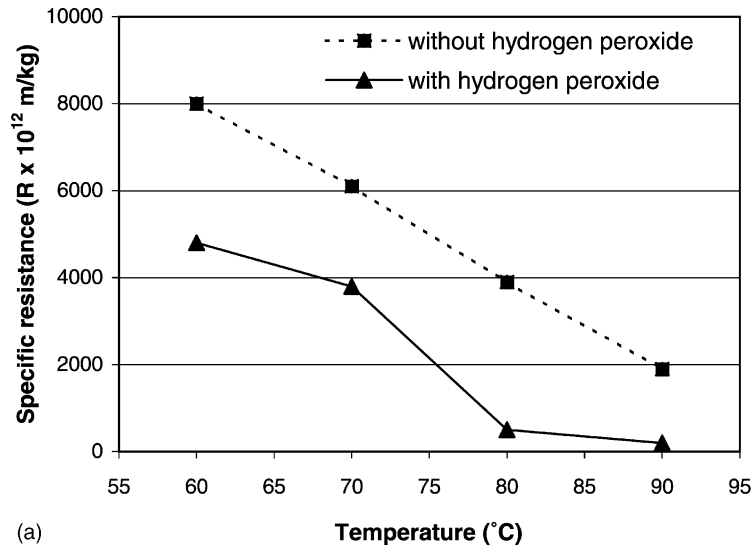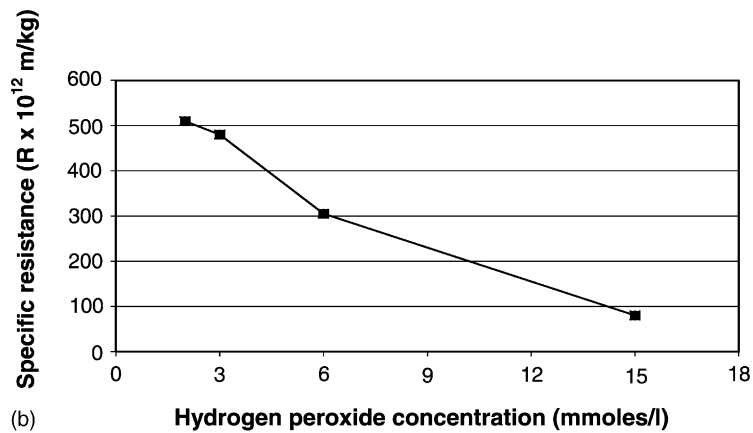
Fig. 9. Effect of operating conditions on the SRF in the oxidation treatment of activated sludge (© IWA Publishing, reprinted with permission from Mustranta and Viikari, [30]): (a) temperature (6 mM H_2O_2; 0.02 mM $FeSO_4 \cdot 7H_2O$; pH 3; 4 h); (b) H_2O_2-concentration (90 °C; pH 3; 4 h).

- a reduced CST-value by approximately 40 s when compared with the 'blanco' sample.

Mustranta and Viikari, [32] studied the influence of Fenton oxidation on several characteristics of the effluent (filtrate), such as COD. They illustrated that the Fenton oxidation treatment was successful in increasing both the extent and rate of biodegradation. The greater biodegradability of the oxidation by-products may be due to production of smaller, more oxidised and more biodegradable by-products such as carboxylic acids, formic acid or formaldehyde.

Table 1
Effects of metal compounds on the specific resistance values of activated sludge in the oxidation treatment (experimental conditions: $[H_2O_2]_0 = 60$ mM, $T = 25\,°C$, pH 3) (Mustranta and Viikari [32])

Metal compound	SRF ($\times 10^{12}$ m/kg)
–	55
$FeSO_4 \cdot 7H_2O$	32
$MnSO_4 \cdot H_2O$	34
$CuSO_4 \cdot 5H_2O$	31
$CoCl_2 \cdot 6H_2O$	30
$ZnSO_4 \cdot 7H_2O$	25

The amount of soluble chemical oxygen demand (SCOD) in the filtrate increases after centrifugation and filtration while the COD in the sludge phase decreases. The decrease of COD in the sludge phase is caused by the continuous oxidation of organic material which results in the formation of alcohols, aldehydes, organic acids and CO_2. The increase of SCOD in the filtrate is caused by the formation of small molecular weight compounds.

The COD-values increased with increasing temperature. The more efficient the treatment is with respect to filterability, the more small molecular weight compounds are formed, thereby increasing the COD-value. The rather high COD-values of the sludge filtrates could be avoided to some extent by using a lower reaction temperature and a higher hydrogen peroxide concentration.

Neyens et al. [34] noted that peroxidation preferentially releases organic part of the dry solids (ODS) into the water phase. The slightly increased BOD/COD-ratio of the filtrate makes this phase more biodegradable and converts it into an accessible carbon source for nitrification/denitrification.

Mustranta and Viikari [32] illustrated that the amounts of soluble Fe, Zn and Cu in the water phase increase with increasing reaction time as a result of two actions. Firstly, metal oxides are formed by the oxidative treatment with hydroxyl radicals. These oxides are soluble and end up in the water phase. Secondly, some metals appear as complexes with organic material: the complexes are destroyed by hydroxyl radicals and the metal ions are released. Neyens et al. [34] also stated that heavy metals are released in the water phase, and can be subsequently precipitated, thus reducing the residual heavy metal concentration in the remaining DS.

Several transition metal compounds were tested as substitutes for ferrous sulphate in the oxidative treatment (Mustranta and Viikari, [32]) and proved able to react with oxygen in a variety of ways due to their ability to share the unpaired electrons of oxygen.

The specific resistance values obtained were rather similar for all the metal salts (Table 1). Treatment without any added metal compound was also efficient due to the fact that sufficient iron is available in the sludge to initiate the catalytic production of hydroxyl radicals from hydrogen peroxide.

4. Conclusions

Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. In the first part of our paper

we review briefly the various reactions which constitute the overall kinetic scheme with all possible side reactions; we also summarise previous findings about the relationships between the dominant parameters (e.g. $[H_2O_2]$, $[Fe^{2+}]$, ...).

In the second part of our paper, we study the effect of Fenton treatment on the dewaterability of sewage sludge. As a result of the wide application of the waste activated sludge process, excess sludge is an inevitable drawback inherent to the process. This sludge is mechanically dewatered to as high percentages of DS as possible. Reducing the amount of sludge produced and improving the dewaterability are hence of paramount importance. A further reduction and an improvement of the dewaterability require advanced technologies, like the classic Fenton peroxidation. The paper described the experimental findings.

- One reason for the difficulty in activated sludge dewatering is the presence of ECP. Peroxidation of sludge enhances the flocculation and dewaterability. The oxidative conditioning might be based on partial oxidation and rearrangement of the surface components (extracellular polymers) of the sludge flocs.
- The dewaterability of the sludge is strongly dependent on the concentration of hydrogen peroxide, the reaction temperature, the pH and the Fe^{2+}-concentration in the oxidative treatment.
- Fenton oxidation was successful in increasing both the extent and rate of biodegradation. The amount of SCOD in the filtrate increases after dewatering while the COD in the sludge phase decreases. Heavy metals are released in the water phase.

Drawbacks associated with the use of Fenton oxidation are the safety hazards associated with using H_2O_2 and the need to firstly reduce the pH, followed by a subsequent neutralisation.

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