Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Prousek, Josef , Palacková, Eva , Priesolová, Soňa , Marková, Lucia and Alevová, Agnesa(2007) 'Fenton- and Fenton-Like AOPs for Wastewater Treatment: From Laboratory-To-Plant-Scale Application', Separation Science and Technology, 42: 7, 1505 — 1520

To link to this Article: DOI: 10.1080/01496390701290151

URL: http://dx.doi.org/10.1080/01496390701290151

Separation Science and Technology, 42: 1505–1520, 2007
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ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701290151

Fenton- and Fenton-Like AOPs for Wastewater Treatment: From Laboratory-To-Plant-Scale Application

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Abstract: Fenton- and Fenton-like AOPs systems have been utilized for the oxidative degradation of some chlorinated pollutants such as chloral hydrate or 1,1,1-trichloroethane, and for the treatment of real industrial wastewaters. Both ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$) and Mohr's salt $(NH_4)_2Fe(SO_4)_2$. 6 H_2O have been used as Fe^{2+} ion sources. With Mohr's salt (MS) the Fenton- and Fenton-like reaction has been successfully carried out under acidic (pH 3) and neutral (pH 7) reaction conditions. The new Fenton-like system utilizes zero-valent iron (Fe^o) instead of ferrous sulfate has been applied for the 1,1,1-trichloroethane and chloral hydrate degradation. Similarly, the application of catechol- and hydroquinone-driven Fenton reaction for the degradation of chloral hydrate under acidic and neutral pH is a new Fenton-like AOPs approach. The photo-Fenton-like reactions such as $Fe^{3+}/h\nu$, $Fe^{2+}/H_2O_2/h\nu$, and ferrioxalate system have been also studied for the degradation of chloral hydrate. As an irradiation source a daily light or sun light have been used. In comparison with photoreactor experiments the best system was observed to be $Fe^{3+}/h\nu$. In some experiments the influence of standing time prolongation after Fenton reaction on the final degradation efficiency due to hydrolysis of intermediates such as phosgene ($CCl_2{=}O$) has also been studied. The Fenton reaction was successfully utilized for the treatment of real industrial wastewaters, in two cases even in plant-scale applications.

Keywords: Fenton reaction, sludge separation, zero-valent iron, neutral pH use, 1,1,1-trichloethane, chloral hydrate, industrial wastewaters

Received 3 November 2006, Accepted 21 December 2006

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INTRODUCTION

Water quality regulations are becoming stricter in the recent decades due to an increasing social concern about the environment. A very interesting field of concern is what to do with wastewater that contains soluble organic compounds that are either toxic or non-biodegradable. At the present time great efforts are being made to minimize the quantity and toxicity of industrial effluents. Biological treatment of wastewater is often the most economical alternative when compared with other treatment methods. Nevertheless, industrial effluents are known to contain toxic and/or non-biodegradable organic substances and biological processes are not efficient in these cases. Advanced Oxidation Processes (AOPs) have been proposed as an attractive alternative for the treatment of these kinds of wastewaters (1–3). AOPs are methods for the production of highly reactive intermediates, above all hydroxyl radicals, which are able to oxidize almost all organic pollutants.

Fenton- and Fenton-like processes are known as effective and inexpensive AOPs for water and wastewater purification from organic pollutants (4, 5). Single electron transfer in Fenton reaction from ferrous cation to hydrogen peroxide depends on many factors such as the metal chelation agents, dosage, and ratio of Fenton's reagent etc. The important question is whether or not the product of the Fenton reaction is hydroxyl radical. It has been shown that in most systems the Fenton reaction product is hydroxyl radical. A minor point is that $H_2O_2^{\cdot-}$ radical anion is not formed and hence, Fenton reaction is a good example of dissociative electron capture:

$$Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + HO^{\cdot} + H_2O \qquad (1)$$

Further detailed study pointed out to the significance of iron complexation in the reaction course (6). The formation of higher oxidation state intermediate, such as ferryl ($Fe{=}O^{2+}$), was proposed in some cases:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe{=}O^{2+} + H_2O \qquad (2)$$

Thus, the reactive products of Fenton reaction are hydroxyl radical or ferryl. Therefore, the chemistry related to the use of Fenton reagent is above all radical chemistry. The hydroxylation and oxidation of substrates is the result of these reactions (6). It is well known that organic and inorganic compounds presented in the Fenton system greatly affect the rates of the reaction propagation. Many kinds of inorganic and organic compounds can interact with the iron ions and hence greatly influence the mechanism and kinetics of the Fenton reaction.

Generally, the Fenton oxidation process is composed of four stages: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation and sludge separation. Therefore, the organic substances are removed at two stages of the oxidation and the coagulation. In this AOP, the organic substances (such as dyes, tenzides, and detergents etc.) react by Fenton

AOPs to reduce toxicity and Chemical Oxygen Demand (COD). As a general rule, the initial oxidation of the substrate by the Fenton oxidant generates another radical and thus sets up a sequence of radical reactions. Each step can be potentially influenced by components of the Fenton system. Some economical parameters of Fenton reaction can be principally improved by its modification.

Among the modifications leading to the increase in the yield and decrease of economical requirements one should mention photo-Fenton reaction, utilization of Fenton reaction under neutral pH conditions, and the utilization of zero-valent iron (Fe^o) instead the ferrous sulfate.

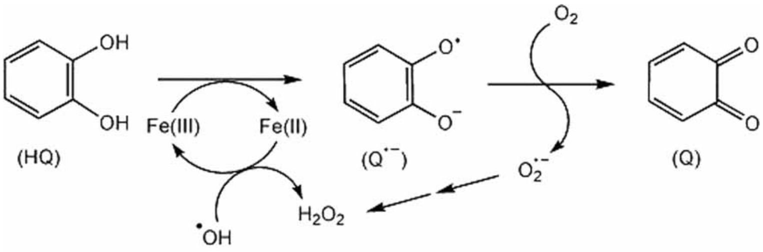
Photochemical AOPs are above all based on the generation of hydroxyl radicals (3). There are several photochemical processes involving iron compounds and hydrogen peroxide that provide alternative ways of generating hydroxyl radicals, such as photo-Fenton reaction. Photo-Fenton reaction and its modifications lead to considerable improvement of destruction of organic pollutants. The photo-Fenton reaction is based on the parallel applying of the Fe(II), Fe(III)/H_2O_2 reagents with near-UV, and visible light. The reasons for the positive effect of irradiation on the degradation rate include the photoreduction of Fe^{3+} to Fe^{2+} - ions, which produce new hydroxyl radicals according to the following mechanism (1):

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + HO^{\cdot} \qquad (3)$$

This is a wavelength dependent reaction and the quantum yield of formation of hydroxyl radical/Fe^{2+} ion decreases with increasing wavelength. For example, the quantum yield of $HO^{\cdot}$ formation is 0.14 at 313 nm and 0.017 at 360 nm. In addition to hydroxyl radicals in this reaction, the photogenerated Fe^{2+} can participate in the Fenton reaction, generating additional hydroxyl radicals.

It is well known that the wood degradation by brown rot fungi, which takes place mainly via non-enzymatic processes, is carried out throughout Fenton-type reactions (7). It was also observed that 4,5-dimethoxycatechol and 2,5-dimethoxyhydroquinone isolated from the brown rot basidiomycete fungus *Gloeophyllum trabeum* may serve as ferric chelators, oxygen-reducing agents, and redox-cycling molecules, acting as electron transport carriers to Fenton's reactions (8, 9). Thus, dihydroxybenzenes, such as catechol and hydroquinone, enhance the formation of hydroxyl radicals in Fenton reaction (Scheme 1).

By this way Fe(III) is reduced by catechol to Fe(II) and catechol is oxidized to semiquinone radical anion ($Q^{\cdot -}$). Oxygen is reduced to superoxide $O_2^{\cdot -}$ and semiquinone $Q^{\cdot -}$ forms quinone (Q). Superoxide is then transformed to hydrogen peroxide which reacts with Fe(II) by Fenton reaction to produce reactive hydroxyl radicals. On the other hand, Pignatello stated (10) that Fe(III) may be solubilized at circumneutral pH by chelation, for example by catechol or hydroquinone. These observations have led to the practical application of catechol-driven Fenton reaction in wastewater treatment AOPs processes for the degradation of recalcitrant water pollutants.



Scheme 1.

The other way of Fe^{3+} reduction to Fe^{2+} is photodecarboxylation of ferric carboxylate complexes. These complexes are photochemically active and generate ferrous ions on irradiation according to equation:

$$Fe(RCOO)^{2+} + h\nu \longrightarrow Fe^{2+} + CO_2 + R^{\cdot} \qquad (4)$$

Again, generated Fe^{2+} can in turn react with H_2O_2 in Fenton reaction.

It is well known, on the other hand that pH plays a very important role in both Fenton and photo-Fenton reaction. In general, it is well accepted that the initial solution pH can significantly influence the efficiency of the homogeneous Fenton reactions, and the optimal solution pH for reactions has been determined to be 2.80 – 3.20 (4). Some ferrous salts, such as Mohr's salt, are stable again at oxidation even at neutral pH. The use of Mohr's salt instead of ferrous sulfate or addition of catechol or hydroquinone as complex agents makes possible to carry out the Fenton reaction at neutral pH (11, 12). Similarly, utilization of zero-valent iron (Fe^{o}) in Fenton reaction under acidic conditions is a new AOPs approach (13).

In the present study, therefore, our main research aims in practical application of Fenton- and Fenton-like AOPs were the utilization of neutral pH conditions in Fenton reaction similarly as the utilization of zero-valent iron instead of ferrous sulfate. Above mentioned AOPs systems have been utilized for the degradation of chlorinated pollutants such as chloral hydrate and 1,1,1-trichloroethane. The new approach, namely catechol-driven Fenton reaction has also been tested for the degradation of chloral hydrate under acidic and neutral pH conditions. Similarly, Fenton reaction was also used for the treatment of real industrial wastewaters, even in plant-scale applications.

METHODS

Reagents

All reagents used in this work were analytical reagent grade and were used as received. Ferrous sulfate, ferric sulfate, Mohr's salt, potasium chromate, silver nitrate, sodium chloride, sodium hydroxide, sulfuric acid, hydrogen peroxide

(30%, w/w) were purchased from Lachema (Brno, Czech Republic). Oxalic acid, hydroquinone, and catechol were purchased from Aldrich. Polyaluminium chloride (PAC-10, Novaflok, Slovakia) was used as a coagulant and 0.1% water solution of Zetag 57 (Allied Colloids, The Netherlands) was used as a flocculant. All the stock solutions were prepared in deionized water.

Degradation Procedures

Each experiment was carried out in a 500 ml Erlenmayer flask and the reaction mixture was continuously stirred with a magnetic stirrer (MM 2A, at 300 r.p.m.), ensuring the uniform mixing of the solution. The reaction temperature was in the range 22–24°C. All experiments were performed at pH 3 or 7, some of these in the dark.

Fenton- and Fenton-like AOPs experiments were generally carried out at pH 3 or 7 with 300 ml of water solution which was placed in the Erlenmayer flask. Needed amounts of ferrous sulfate or Mohr's salt and then 30% hydrogen peroxide were added to the well-stirred reaction mixture. After 1 or 2 h of reaction, the resulting solution was allowed to stand 0.5 h and then it was neutralized by sodium hydroxide solution. After sludge filtration released, chloride ions were argentometrically determined. The final efficiency was calculated from the ratio of the observed amount of released chloride ions after the treatment process versus theoretical amounts of chloride ions before the treatment process × 100 (%).

In the experiments with the prolongation of standing time after Fenton reaction the efficiency of released chloride ions increases during standing time due to hydrolysis of phosgene ($Cl_2C{=}O$), which is formed by chloral hydrate degradation as a relative stable intermediate. In water phosgene is hydrolyzed in the time scale of days (see Figs. 1 and 2).

The experiments with the $Fe^o/H_2O_2/H_2SO_4$ AOP system were generally carried out as follows: to the 300 ml of treated water solution 0.05 ml of concentrated sulfuric acid was added and then approximately 3 g of iron shavings activated before their utilization (Note 1) were also added and after 10 min of induction time a needed amount of hydrogen peroxide (30%) was added (Note 2). After 1 h of reaction the resulting solution was allowed to stand 0.5 h and then it was neutralized by sodium hydroxide. The formed ferric hydroxide sludge was filtered off and released chloride ions were determined in pure water solution.

Note 1. Technical shavings must be cleared by soap and activated by 20% sulfuric acid and washed by distilled water immediately before the use.

Note 2. Hydrogen peroxide was added by the small portions during all reaction time (e.g., 0.8 ml of H_2O_2 can be added by small 0.2 ml portions every 15 min during 1 h reaction time).

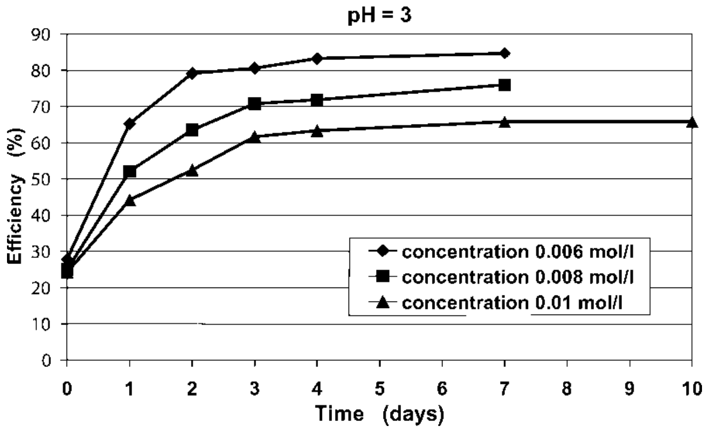


Figure 1. Degradation of chloral hydrate by Fenton reaction at pH 3. Influence of standing prolongation on total degradation efficiency by phosgene intermediate hydrolysis during ten days. Reaction conditions: reaction time was 1 h, Fenton's reagent ratio was H_2O_2:MS = 875 : 1290 mg · l^{-1}. Time 0 represents yields after Fenton reaction.

Reductive dehalogenation was carried out with zero-valent iron (Fe^o) with 300 ml of 1,1,1-trichloroethane water solution which was placed in the Erlenmayer flask at neutral pH with activated iron shavings (3 g per run) under daily light access. Every day the chloride ions concentration was analyzed in small 10 ml sample.

Daily light and sun irradiation photochemical experiments were performed in 250 ml Simax round bottom flasks with 100 ml of reaction solution volume at pH of 3.0. The methods such as direct photolysis, $Fe^{3+}/h\nu$ and $Fe^{3+}/C_2H_2O_4/h\nu$ photochemical systems were used for chloral hydrate initial concentration of 1×10^{-3} mol · l^{-1}.

Catechol-driven Fenton reaction was carried out in the dark as follows: To the 300 ml of chloral hydrate solution with the initial concentration of $c = 5 \times 10^{-3}$ or 1×10^{-2} mol · l^{-1} at pH 3 or pH 7 in Erlenmayer flask (coated with alumina foil) the 0.387 g of Mohr's salt was added under stirring. Then 10 mg of catechol or hydroquinone was added and after approximately 2 min 0.8 ml of 30% hydrogen peroxide was added. After 2 h of reaction time the mixture was allowed to stand without the stirring. In small 10 ml samples after their neutralization by 20% NaOH solution and after their filtration the concentration of released chloride ions was analyzed immediately after catechol-driven Fenton reaction (2 h) (Note 1). Similarly during standing period the chloride ions concentration was measured after 2 h or 72 h of standing time (see Table 1).

Note 1. The same experimental procedure was used for the Fenton reaction without catechol or hydroquinone addition.

Industrial wastewater treatment was carried out as follows:

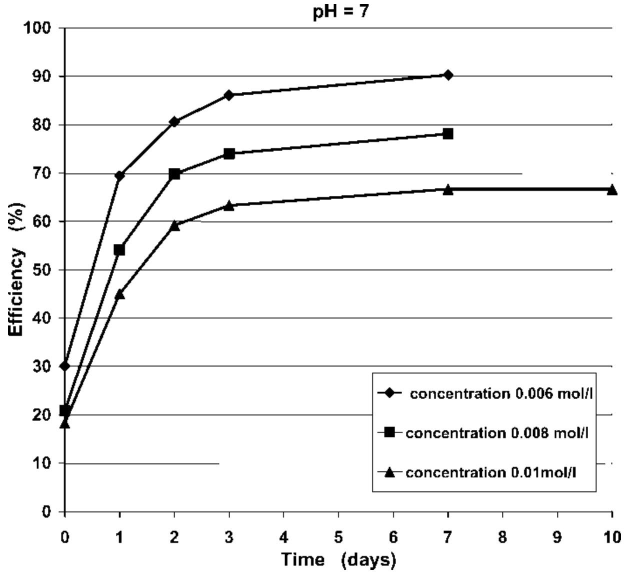


Figure 2. Degradation of chloral hydrate by Fenton reaction at pH 7 and influence on total degradation efficiency by phosgene intermediate hydrolysis during a ten days. Reaction conditions are the same as in Fig. 1.

Wastewater from chemical joint-stock company Duslo (Sala, Slovakia) was a strong colored and odorous water with initial COD value of 1 495 mg $\cdot$ l^{-1} and with high mineralization of 6 g $\cdot$ l^{-1}. For the treatment process the classical Fenton reaction was used at pH 3 with the Fenton's reagent concentration ratio of H_2O_2:$FeSO_4$ = 875:500 mg $\cdot$ l^{-1} or with its two-, three- and four-multiples. After 1 h of reaction time, the resulting solution was allowed

Table 1. Efficiency (%) of chloral hydrate degradation by catechol- and hydroquinone-driven Fenton reaction at pH 3 or 7 for initial chloral hydrate concentration of c = 5.10^{-3} mol $\cdot$ l^{-1}[a]

	Efficiency (%)			
	Catechol addition		Hydroquinone addition	
Time (h)	pH 3	pH 7	pH 3	pH 7
0	56.7	61.7	53.3	61.7
2	70.0	75.0	63.3	71.1
72	88.3	86.7	88.3	86.7

[a] The degradation efficiency of Fenton reaction without catechol or hydroquinone addition was for both pH values 33.3%.

Table 2. Efficiency (%) of chloral hydrate degradation by catechol- and hydroquinone-driven Fenton reaction at pH 3 or 7 for initial chloral hydrate concentration of $c = 1.10^{-2}$ mol · l^{-1}[a]

	Efficiency (%)			
	Catechol addition		Hydroquinone addition	
Time (h)	pH 3	pH 7	pH 3	pH 7
0	32.5	35.8	32.5	34.2
2	38.3	43.3	37.5	40.0
72	55.8	64.2	62.5	62.5

[a] The degradation efficiency of Fenton reaction without catechol or hydroquinone addition was for both pH values 19.2%.

to stand 0.5 h and then it was neutralized by sodium hydroxide solution. The utilization of flocculant (0.05% water solution of Zetag 57) in the final coagulation and sedimentation process has led to the higher COD removal and to the increase of the sedimentation rate. After 1 h of sedimentation the COD removal in clear water layer was measured.

Wastewaters from cosmetic joint-stock company De Miclen (Levice, Slovakia) (14, 15) are foam wastewaters containing as the main nonbiodegradable compounds some tensides and detergets. In the laboratory treatment scale the Fenton's reagent concentration of 1X (H_2O_2:$FeSO_4$ = 875:500 mg · l^{-1}) was used similarly as in the wastewater treatment plant (WWTP) scale in the chemical pretreatment step. After 1 h of Fenton reaction the resulting solution was allowed to stand 0.5 h and then the solution was neutralized by sodium carbonate solution and coagulated with polyaluminium chloride (PAC) and flocculated with 0.1% water solution of Zetag 57. After sludge separation the pretreated wastewater was treated in the biological treatment step. Some inlet and outlet parameters and results before and after treatment processes are given in Tables 3 and 4. It is interesting to note that in laboratory-scale experiments the results with Fenton pretreatment and with activated sludge treatment processes were in all cases worse then in plant-scale treatment in WWTP.

Wastewater from chemical joint-stock company Istrochem (Bratislava, Slovakia) originated from the production of 2-mercaptobenzothiazole (2-MBT) with the initial parameters of COD 22 472 mg · l^{-1}. The treatment process was composed of three steps. In the first step the coagulation treatment process with PAC was carried out followed by Fenton reaction treatment in the second step. Finally, the lime coagulation was applied as the third step of treatment process. It appeared that the optimal amount of PAC used in the first step is 5 ml of PAC for one liter of treated technological wastewater. The Fenton's reagent concentration

Table 3. Wastewater parameters in inlet of WWTP De Miclén (Levice)

Indicators 2000	Projection values in 1997 ($mg \cdot l^{-1}$)	Real values in 1999 ($mg \cdot l^{-1}$)	Real values in ($mg \cdot l^{-1}$)
BOD_5	1286	420	1910
COD_{Cr}	2143	760	3436

used in the second step of the treatment process was 1X (i.e., H_2O_2:$FeSO_4$ = 875:500 $mg \cdot l^{-1}$) and reaction time was 1 h. In the third step different doses of powdered lime were used in the final coagulation step. As it appeared from the obtained results in these test sufficient dose was 0.5 $g \cdot l^{-1}$. The obtained results from all three steps of treatment processes are summarized in Table 5.

Analyses

The progress in the degradation of studied pollutants was evaluated by measurement of COD or BOD values and by Cl^- ion concentration (16). Chemical Oxygen Demand (COD) was conducted by the semi-micro method (16) in a thermoreactor (MERK TR 200) at 150°C, and the pH was measured by pH-meter (Ion-Activity Meter MS 20).

RESULTS AND DISCUSSION

Chlorinated Compounds Degradation

1,1,1-Trichloroethane and Chloral Hydrate

The degradation of 1,1,1-trichloroethane in the atmosphere occurs mainly by reaction with hydroxyl radicals to give chloral (CCl_3CHO) in almost quantitative yields. Chloral is readily photolyzed by sunlight with a quantum

Table 4. Treated water parameters in outlet from WWTP with the utilization of continuos (1999) discontinuous (2000) treatment process

Indicators	Permitted values ($mg \cdot l^{-1}$)	Attained values ($mg \cdot l^{-1}$)	Efficiency (%)
BOD_5	200	26/47	93.8/98
COD_{Cr}	400	48/87	93.7/98

Table 5. COD removal from Istrochem wastewater after three steps of treatment processes

	COD $(mg \cdot l^{-1})$	Efficiency (%)
Row wastewater	22 472	—
Coagulation pretreatment with PAC (First step)	11 678	48
Fenton treatment (1X) (Second step)	5 337	76.3
Final coagulation with powdered lime (Third step)	3 998	82.2

efficiency close to unity. Chloral photolysis produces phosgene ($CCl_2{=}O$), CO, and Cl^- radicals.

Chlorinated ethanes are prone to reductive dehalogenation. In the case of 1,1,1-trichloroethane reduction leads to acetic acid CH_3COOH.

The corresponding oxidative degradation initiated by hydroxyl radicals (e.g., Fenton reaction) leads to monochloroacetic acid $ClCH_2COOH$ (17, 18).

In our study some Fenton- and Fenton-like AOPs systems for the degradation of 1,1,1-trichloroethane and chloral hydrate have been utilized. Namely the reductive dehalogenation with zero-valent iron, Fenton reaction at pH 3 or 7, photo-Fenton-like reactions, $H_2O_2/Fe^o/H_2SO_4$ Fenton-like system, and catechol-driven Fenton reaction.

Figures 1 and 2 illustrate the influence of standing time prolongation on the total degradation efficiency of chloral hydrate at pH 3 and 7. As it appeared from Figs. 1 and 2 the standing time prolongation after Fenton reaction led to the higher degradation efficiency at both pH values used. Phosgene ($Cl_2C{=}O$) as an intermediate of chloral hydrate degradation (18, 19) slowly hydrolyzed during a few days to HCl, water and CO_2 (19). By this way the substantially higher degradation efficiencies were achieved then immediately after Fenton reaction (see Figs. 1 and 2 at time 0). After 7 days total phosgene hydrolysis was carried out and for initial chloral hydrate concentration of $0.006\ mol \cdot l^{-1}$, for example, the 90% yield of degradation was achieved.

Fenton reaction was also applied for the degradation of 1,1,1-trichloroethane with the use of Mohr's salt at pH 3 and 7. For the purpose to test different Fenton's reagent, the 1X, 2X and 1Y (see Figs. 3 and 4) concentrations have been used. Similarly the 1,1,1-trichloroethane concentrations that commonly occur in natural or waste waters, have been studied. From the obtained results it is clear that high degradation efficiencies have been achived for all Fenton's reagent concetrations in the case of lower 1,1,1-trichloroethane concentrations such as 3.10^{-4} or $1 \cdot 10^{-4}\ mol \cdot l^{-1}$. The utilization of higher doses of hydrogen peroxide (1.6 ml) or reaction time prolongation (2 or 4 h) for the initial concentration of 1,1,1-trichloroethane $c = 5.10^{-3}\ mol \cdot l^{-1}$ led in all experiments to decrease of the final degradation efficiency.

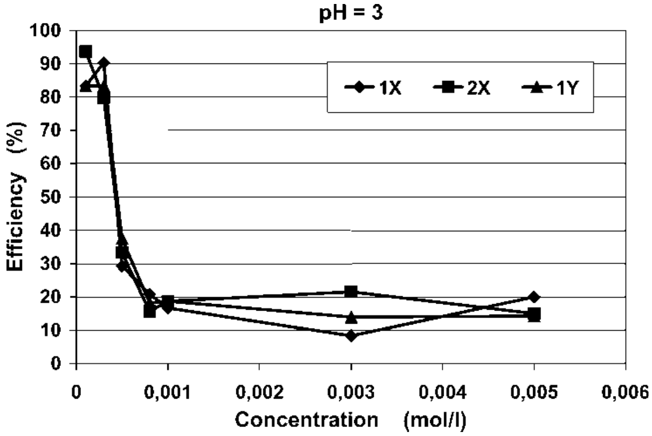


Figure 3. Degradation of 1,1,1-trichloroethane by Fenton reaction at pH 3. Reaction time was 1 h. 1X, 2X and 1Y mean the Fenton's reagent concentration ratio with the utilization of Mohr's salt (MS). 1X (H_2O_2:MS = 875:1290 mg · l^{-1}), 2X (H_2O_2: MS = 1750:2580 mg · l^{-1}), 1Y (H_2O_2:MS = 875:2580 mg · l^{-1}).

It is well known that different photochemical AOPs systems are also used for wastewater treatment. High cost in some cases is the reason for their limitation in practical treatment processes. Some simple photochemical degradation processes generally occur under environmental conditions. Such systems are mainly direct photolysis and photocatalytic degradation by sunlight irradiation. This is a reason why our interest has been focused on these types of photochemical degradation processes. The four different

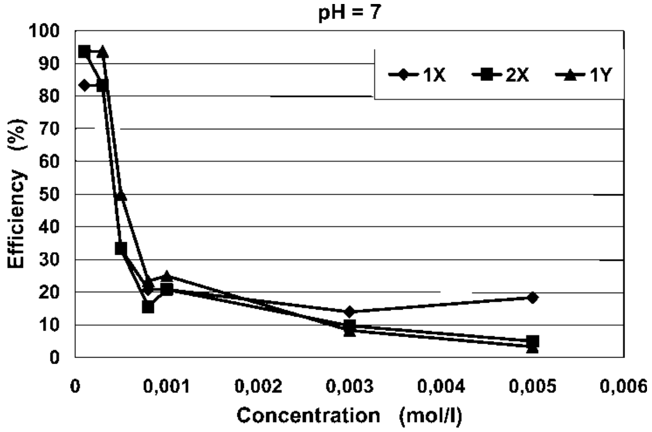


Figure 4. Degradation of 1,1,1-trichloroethane by Fenton reaction at pH 7. Reaction time was 1 h. 1X, 2X and 1Y have the same meaning as in Fig. 3.

degradation systems such as reductive dehalogenation under daily light with zero-valent iron, direct photolysis and $Fe^{3+}/h\nu$ or ferrioxalate photochemical processes $Fe^{3+}/C_2H_2O_4/h\nu$ were studied.

Reductive dehalogenation of 1,1,1-trichloroethane, for example, for initial concentration of 5.10^{-4} and 8.10^{-4} led after 7 days to the 83.3% and 52.1% of degradation efficiencies. It is a very cheap degradation system and again for lower concentrations the efficiencies are sufficiently high. For direct photolysis, $Fe^{3+}/h\nu$ and $Fe^{3+}/C_2H_2O_4/h\nu$ systems and chloral hydrate initial concentration of 1.10^{-3} $mol \cdot l^{-1}$ after 8 days of reaction time under sun irradiation the resulting degradation efficiencies were 16.6%, 87.5% and 66.6%, respectively. It is clear that in comparison with photodegradation experiments carried out in the photoreactor where the ferrioxalate system was the most effective, here the most effective is the simple $Fe^{3+}/h\nu$ system. On the other hand, in the case of dyes degradation, photoreactor experiments with photoferrioxalate AOP system were more effective than other ones (results are not shown).

It is also of great importance for the practical application of Fenton-like system the utilization of zero-valent iron (Fe^o) in Fenton reaction instead of ferrous sulfate, the system $Fe^o/H_2O_2/H_2SO_4$. By this way different halogenated compounds were successfully degraded, for example, 1,1,1,-trichloroethane for initial concentration of 1.10^{-3} $mol \cdot l^{-1}$ was degraded with 56.5% of degradation efficiency after 1 h reaction time and 0.8 ml dose of hydrogen peroxide partly added during all reaction time. In the case of a similar compound such as 1,1,2,2-tetrachloroethane it appeared that the achieved degradation efficiency depended on the hydrogen peroxide addition way and on the reaction time. Degradation of this compound leads after 0.5 h, 1.5 h and 3 h of reaction time to 37%, 65%, and even 90% of degradation efficiency, respectively, while classical Fenton reaction has led to the more lower efficiencies (from 12 to 27%). It is interesting to note that this AOP system has a great advantage in two points: dissolving of zero-valent iron by sulfuric acid provides needed ferrous ions during all reaction time and partial addition of hydrogen peroxide provides the prolongation of Fenton reaction.

From our preliminary experiments it appeared that ortho-dihydroxy compounds, mainly dihydroxybenzenes (20) greatly affect the rates of the reaction propagation in the Fenton reaction. Dihydroxybenzenes, such as catechol or hydroquinone, have been found to greatly catalyze the Fenton degradation of organic compounds, which was attributed to the fact that they can quickly reduce ferric ions to ferrous ions, and hence accelerate the slow step of the Fenton reaction (see Scheme 1). In order to compare the efficiencies of the classical $Fe(II)/H_2O_2$ Fenton system and catechol- and hydroquinone-driven Fenton reaction a parallel study with and without the addition of catechol or hydroquinone has been carried out under neutral (pH 7) and acidic (pH 3) reaction conditions. In our study, chloral hydrate was used as a simple halogenated model compound. For initial concentration of 5.10^{-3} mol · l^{-1} and pH 3 the degradation efficiency was 57% for the catechol-driven Fenton reaction after 2 h of reaction time, while without the catechol addition was only 33%. Similar results have been obtained at pH 7 for both catechol and hydroquinone (see Tables 1 and 2). Mohr's salt was used in all experiments. It is interesting to note that similar results for both catechol- and hydroquinone-driven Fenton reaction have been achieved with the utilization of ferrous and ferric sulfate under neutral conditions. Thus, for the initial chloral hydrate concentration of 5.10^{-3} mol · l^{-1} after 2 h reaction time the degradation efficiency was 70.0% for both catechol or hydroquinone use in the case of ferrous sulfate and pH 7. Similarly for the same initial concentration and ferric sulfate at pH 7 the degradation efficiency was 73% for catechol and 70% for hydroquinone.

Industrial Wastewater Treatment

Wastewater from Chemical Joint-Stock Company Duslo (Šal̆a, Slovakia)

This wastewater was strong colored and odorous with initial COD of 1 495 mg · l^{-1} and with high mineralization of 6 g · l^{-1}. For the treatment process the classical Fenton reaction was used at pH 3 with Fenton's reagent ratio of H_2O_2:$FeSO_4$ = 875:500 mg · l^{-1} or with its two-, three-and four-multiples. The utilization of flocculant in final coagulation and sedimentation process has led to the higher COD removal and to the increase of sedimentation rate. For example, after 1 h reaction time for basic Fenton's reagent ratio concentration the final COD removal was 90%.

Wastewater from Cosmetic Joint-Stock Company De Miclén (Levice, Slovakia)

In 1999 the new mechanical-chemical-biological wastewater treatment plant (WWTP) has started its continuous operation in the cosmetic company De Miclén (Levice, Slovakia). In this WWTP the Fenton reaction has been used as a chemical pretreatment step, which was followed by biological treatment step with activation. The main role of Fenton reaction was to decrease organic pollutant concentration and to degrade different tensides and detergents or other biological persistent compounds. The inlet parameters of row wastewater are given in Table 3.

In 1999 the WWTP has worked in continuous treatment process. In this case the wastewater is pumped to the storage tank in which own Fenton reaction was performed during approx. 2 h. After Fenton's pretreatment the sedimentation followed and then the water is pumped to the activation tank for biological treatment. Result parameters obtained after continuous (in the year 1999) and discontinuous (in the year 2000) treatment processes are summarized in Table 4. The cost for 1 m^3 of row wastewater treatment has been calculated to be 20 to 25 Sk.

A similar treatment process was used for the wastewater from the chemical joint-stock company Istrochem (Bratislava, Slovakia). This wastewater originated from the 2-mercaptobenzothiazole manufacture. Initial parameters were COD 22 472 $mg \cdot l^{-1}$, pH 7.05, chloride concentration of $30,000\, mg \cdot l^{-1}$ and the concentration of soluble compounds was 73, $800\, mg \cdot l^{-1}$. After PAC coagulation in the first step of treatment process followed by Fenton reaction treatment in the second step with the lime coagulation in the third step the final result COD removal was 76.3%. Because in the first step of the treatment process formed sludge is composed mainly from insoluble Al(III) complexes of 2-MBT, it is possible to recycle it and use it again as a row material. The most important step in this treatment process is the removal of strong antioxidant 2-MBT because of its inhibition of Fenton reaction in the second step of the treatment. Without the coagulation treatment in the first step the efficiency of Fenton reaction was very low. Results obtained in all three steps of treatment processes are summarized in Table 5.

Some general conclusions may be drawn from the above mentioned examples of industrial wastewater treatment by Fenton AOPs processes:

(i) the suitability of Fenton AOPs for the industrial wastewater treatment must be verified in lab-scale tests in detail,
(ii) the amount of chemical reagent must be determined for any wastewater, which favorably influenced the resulting cost of treating process,
(iii) final coagulation and flocculation treatment is a very important part of all Fenton AOPs processes,
(iv) from the practical point of view the fully automatic system is the best application of Fenton reaction in the industrial wastewater treatment processes,
(v) in the great technological companies it is of great advantage to use the direct application of Fenton reaction on the high concentrated technological streams; by this way of application the economical claims will be significantly reduced,
(vi) Fenton reaction degrades many recalcitrant water pollutants, which is impossible for some other AOPs methods used at this time.

CONCLUSION

All of the Fenton- and Fenton-like AOPs systems examined were able to degrade each of the studied compounds. It has been documented that Fenton reaction is possible to carry out also at neutral pH conditions and that zero-valent iron (Fe^o) can be used not only in reductive dehalogenation but also in Fenton reaction instead of ferrous sulfate. High efficiencies achieved in catechol-driven Fenton reaction well documented this new Fenton-like AOPs process. Wastewater treatment processes show some features of the new possibilities in the purification of industrial wastewaters.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education of the Slovak Republic by VEGA Grant No. 1/2462/05 and by APVT Grant No. 20-029804.

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