THESIS ON CHEMISTRY AND CHEMICAL ENGINEERING G45

Effects of Organic Reducing Agents on the Fenton-like Degradation of Contaminants in Water with a Ferric Sludge Reuse

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Juri Bolobajev

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KEEMIA JA KEEMIATEHNIKA G45

Orgaaniliste redutseerijate mõju rauasette taaskasutamisega Fenton-tüüpi protsessile reovees sisalduvate saasteainete lagundamisel

JURI BOLOBAJEV

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LIST OF PUBLICATIONS

The present doctoral thesis is based on the following original publications referred to by Roman numerals I-IV in the text:

I. **Bolobajev, J.,** Kattel, E., Viisimaa, M., Goi, A., Trapido, M., Tenno, T., Dulova, N. (2014). Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment. – *Chemical Engineering Journal*, 255, 8-13.

II. **Bolobajev, J.,** Trapido, M., Dulova, N. (2015). Application of different techniques for activation of H_2O_2/Fe^{3+} system: a comparative study. – *Journal of Advanced Oxidation Technologies*, 18, 347-352.

III. **Bolobajev, J.,** Trapido, M., Goi, A. (2015). Improvement in iron activation ability of alachlor Fenton-like oxidation by ascorbic acid. – *Chemical Engineering Journal*, 281, 566-574.

IV. **Bolobajev, J.,** Trapido, M., Goi, A. (2016). Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalytic decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment. – *Applied Catalysis B: Environmental*, 187, 75-82.

Other publications related to the research:

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Bolobajev, J., Trapido, M., Goi, A. (2016). Effect of iron ion on doxycycline photocatalytic and Fenton-based autocatalytic decomposition. – *Chemosphere*, 153, 220-226.

Bolobajev, J., Bilgin Öncü, N., Viisimaa, M., Trapido, M., Balcığlu, I., Goi, A., 2015. Column experiment on activation aids and biosurfactant application to the persulphate treatment of chlorophene-contaminated soil. – *Environmental Technology*, 36, 348-357.

Klauson, D., Kivi, A., Kattel, E., Klein, K., Viisimaa, M., **Bolobajev, J.,** Velling, S., Goi, A., Tenno, T., Trapido, M. (2015). Combined processes for wastewater purification: treatment of a typical landfill leachate with a combination of chemical and biological oxidation processes. – *Journal of Chemical Technology and Biotechnology*, 90, 1927-1936.

Trapido, M., Dulova, N., Epold, I., **Bolobajev, J.** (2014). Emerging micropollutants in water/wastewater: growing demand on removal technologies. – *Environmental Science and Pollution Research*, 21, 12217-12222.

Bolobajev, J., Dulova, N., Trapido, M. (2014). Different activation methods of H_2O_2/Fe(III) for degradation of diuron. – Book of Abstracts of the 15th European Meeting on Environmental Chemistry, (Eds.) J. Čáslavský, R. Komendová, H. Zlámalová Gargošová, Brno Technical University, Brno, Czech Republic, 3-6 December, 2014, 22.

Bolobajev, J., Viisimaa, M., Klauson, D., Goi, A., Trapido, M. (2013). Chemical oxidation for the treatment of oil shale industry effluent: treatment strategies optimization. – Proceedings of the International Conference EA3G2013 "Ozone and Related Oxidants in: Safe Water along its Cycle" in the framework of Wasser Berlin International Trade Fair and Congress. Berlin, Germany, 23-24 April, 2013, 2.8.1-2.8.8.

Viisimaa, M., **Bolobajev, J.,** Goi, A. (2013). Ozonation and ultrasound assisted advanced oxidation processes for degradation of polychlorinated biphenyls in soil. – Proceedings of the International Conference EA3G2013 "Ozone and Related Oxidants in: Safe Water along its Cycle" in the framework of Wasser Berlin International Trade Fair and Congress. Berlin, Germany, 23-24 April, 2013, 3.1.1-3.1.7.

Trapido, M., Dulova, N., Epold, I., **Bolobajev, J.** (2013). Emerging Micropollutants in Water/Wastewater: Growing Demand on Removal Technologies. – e-Proceedings of the 3rd European Conference on Environmental Applications of Advanced Oxidation Technologies, Almeria, Spain, 27-30 October, 2013, P171-1-P171-3.

AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

The contribution of the author to the papers listed below is as follows:

I. The author participated in the experimental work, the interpretation of results and writing of the paper. The author presented the results at the International Conference EA3G2013, in the framework of Wasser Berlin International Trade Fair and Congress, Germany, Berlin, 23-24 April, 2013.

II. The author participated in the writing of the paper, carried out the experimental work and interpreted the results. The author presented the results at the 15th European Meeting on Environmental Chemistry, Brno, Czech Republic, 3-6 December, 2014.

III. The author wrote the paper and is the corresponding author. He supervised the experimental work of M.Sc. student and interpreted the results.

IV. The author wrote the paper and is the corresponding author. He performed the experimental work and interpreted the results.

INTRODUCTION

The substantial growth of production level and demanding regulations related to the environmental protection necessitate using new technologies providing more effective treatment of industrial effluents and wastes. Of particular note is the contamination of water bodies with hazardous substances, which occurs as a result of inappropriate treatment of discharged wastewater effluents. The resulting spread of specific organic compounds, known as micropollutants, in water can negatively influence the fundamental biochemical processes of aquatic biota even at extremely low concentrations. Micropollutants include pharmaceutical ingredients, personal care products, pesticides, steroid hormones and other emerging compounds. Advanced oxidation processes are efficient in wastewater treatment as they demonstrate reaction rates superior to conventional treatment and non-selectivity in degradation of organic contaminants including micropollutants.

The use of the Fenton and related reactions in wastewater treatment is considered as potentially convenient and inexpensive operation method aimed to generate oxidizing species for degradation of organic pollutants. The classical Fenton process encompasses the generation of hydroxyl radical (HO•) from hydrogen peroxide decomposition catalyzed by ferrous iron. HO• is known to be the one of the most powerful oxidants. However, Fenton-based processes have a number of drawbacks that limit the application of this technology on an industrial scale. Among them, the formation of insoluble amorphous ferric oxyhydroxides (ferric sludge) at circumneutral pH requires particular consideration. The oxidation of ferrous iron by H_2O_2 produces the stoichiometric amount of ferric iron, which then undergoes an extensive hydrolysis and precipitates to ferric sludge as the pH is increased from strongly acidic to neutral. The solid fraction in the wastewater interferes the treatment process and needs to be removed before the discharge of treated water.

In the present study, ferric sludge reuse in the Fenton oxidation was proposed as an alternative solution to this problem. The application of the heterogeneous Fenton process catalyzed by ferric sludge in wastewater treatment is considered to minimize the accumulation of undesirable solid wastes in Fenton-based wastewater treatment technology. In order to assess the influence of organic compounds on ferric sludge catalytic behavior the comprehensive study on the interaction of organic constituents with iron either in aqueous phase or on the sludge surface was undertaken. Possible interactions may include the formation of stable complexes between iron ions and organic compounds, or more importantly, the reduction of ferric to ferrous iron. The obtained knowledge represents an important contribution in the field, which allows achieving considerable breakthroughs in Fenton-based processes applications.

ABBREVIATIONS AND SYMBOLS

A	rate of deoxyribose oxidation by HO• in the presence of the target compound
A_0	rate of deoxyribose oxidation by HO• in the absence of the target compound
AA	L-ascorbic acid
Ala	alachlor
AOT	advanced oxidation technology
BOD_7	7-day biochemical oxygen demand
C	concentration
C_0	initial concentration
COD	chemical oxygen demand
DCMU	diuron
DOC	dissolved organic carbon
[DR]	deoxyribose initial concentration
EC	electrical conductivity
GC-MS	gas chromatograph equipped with a mass-spectrometer
[HO•]	HO• concentration
HPLC-MS	high performance liquid chromatograph equipped with a mass-spectrometer
HPLC-PDA	high performance liquid chromatograph equipped with a diode array detector
HPLC-UV	high performance liquid chromatograph with an ultraviolet-visible detector
IC-SCD	ion chromatograph equipped with a suppressed conductivity detector
IUPAC	International Union of Pure and Applied Chemistry
k’	pseudo-first order reaction rate constant
K_a	dissociation constant
K_{OW}	octanol-water partition coefficient
k_{DR}	reaction rate constant of deoxyribose oxidation by HO•
k_S	second-order rate constant of reaction between HO• and target compound
k_d	diffusion-controlled rate constant in water
MDA	malondialdehyde
NIST	National Institute of Standards and Technology
r	rate of the reaction
[S]	concentration of the investigated compound
TBA	2-thiobarbituric acid
TCP	2,4,6-trichlorophenol
TFS	total fixed solids
TN	tannic acid
TS	total solids
TSS	total suspended solids

1. LITERATURE REVIEW

1.1 The general chemistry of the Fenton and Fenton-like processes

The technology based on the Fenton oxidation belongs to the list of advanced oxidation technologies (AOTs) aimed to remove persisted organic pollutants from the water matrix. Hydroxyl radical (HO•) formed in the Fenton process is known to be a powerful oxidant ($E^0 = 2.73$ V) (Latimer, 1952). In spite of the fact that the Fenton process has been extensively studied, since it was discovered by British chemist H.J.H. Fenton in 1894 (Fenton, 1894), its mechanism is not completely understood. Many factors are found to influence the reaction pathway such as pH, temperature, organic substrate to be oxidized, and concentration of hydrogen peroxide and iron.

The most cited mechanism of the Fenton process is based on the hypothesis (Haber and Weiss, 1932) that highly reactive HO• is formed as a result of hydrogen peroxide and ferrous iron (Fe^{2+}) reaction. Hereafter, the iron aquatic forms are abbreviated as Fe^{2+} or Fe^{3+}, i.e. they ligands are dropped from the formulas. Several studies (Barb et al., 1951; Walling, 1975) verified the general Fenton mechanism proposed by Haber and Weiss (1932). The sequence of the reactions (Eqs. 1-7) was found to proceed.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \quad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (2)$$
$$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (3)$$
$$HO\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$
$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (5)$$
$$Fe^{2+} + HO_2\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$
$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (7)$$

In mechanism of the Fenton oxidation, Fe^{2+} is involved in catalytic formation of HO•, influencing the oxidation ability of Fenton's reagent.

Nowadays several improved variations of the classical Fenton reaction known as modified Fenton reactions have been introduced. These modifications are aimed to solve disadvantages in the classical Fenton including costly pre-acidification to maintain appropriate pH and expenses associated with utilization of solid waste in the form of insoluble ferric iron.

Modification can be performed by the use of ferric iron (Fe^{3+}) instead of Fe^{2+} for the activation of H_2O_2 oxidation. This combination of the chemicals is known as Fenton-like reagent. The oxidative mechanism by the Fenton-like reagent is based on the formation of unstable $Fe^{III}(HO_2)^{2+}$ complex (Eq. 8) that further decomposes to Fe^{2+} involved in the production of HO• (Eq. 1) and hydroperoxyl radical ($HO_2\bullet$) (Eq. 9) capable of oxidizing of organic compounds (Pignatello et al., 2006).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{III}(HO_2)^{2+} + H^+ \quad (8)$$
$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2\bullet \quad (9)$$

One should note that the general Fenton-like reaction mechanism is a particular case of the reaction (Eq. 2) in the classical Fenton. Therefore, the classification of the Fenton process by Fe^{2+} or Fe^{3+} mediated H_2O_2 oxidation is meaningless from mechanistic standpoint because Fe^{2+} and Fe^{3+} exist simultaneously in the chain (Eqs. 1-7) (Pignatello et al., 2006). Nevertheless, the significant differences exist in reactivity of the classical Fenton and Fenton-like processes. Fe^{2+} is rapidly oxidized to Fe^{3+} according to reaction (Eq. 1) resulting in immediate consumption of H_2O_2 followed by a burst of HO• in the initial stage of the classical Fenton. Some produced HO• remain unconsumed by organic compound to be oxidized and are scavenged then by H_2O_2 and Fe^{2+} according to the reactions (Eqs. 3, 4) resulting in unproductive consumption of the oxidant. Fenton-like reagent (Fe^{3+}/H_2O_2) is somewhat less reactive and characterized by prolonged action (Ensing et al., 2003). Thus, Fe^{3+} application can reduce H_2O_2 consumption creating more favorable conditions for oxidation.

Other important aspects of the Fenton process are the reactions of hydrolysis and precipitation of iron in aqueous solutions. The reactions have high impact on the overall oxidation reactivity making the understanding of iron chemistry in aqueous media of fundamental significance. The speciation of Fe^{2+} and Fe^{3+} in water as a function of pH is of interest. At pH lower than 3 Fe^{2+} exists mainly as the un-hydrolyzed hexaaquo ion $Fe(H_2O)_6^{2+}$ that interacts with H_2O_2 several orders of magnitude slower than its hydrolyzed forms, $Fe(H_2O)_5(OH)^+$ or $Fe(H_2O)_4(OH)_2$ presented at pH of 3 (Pignatello et al., 2006).

As the pH increases over that value, Fe^{3+} formed in the reactions (Eqs. 1, 4, 6) of the classical Fenton or used in the initial stage of Fenton-like reaction undergoes extensive hydrolysis (Eq. 10) resulting in precipitation of amorphous ferric oxyhydroxides (Sylva, 1972):

$$\begin{aligned} &Fe^{3+} \leftrightarrow Fe(OH)^{2+} \leftrightarrow Fe(OH)_2^{+} \leftrightarrow Fe_2(OH)_2^{4+} \leftrightarrow \\ &\text{other polynuclear species} \leftrightarrow Fe_2O_3{\cdot}nH_2O(s) \end{aligned} \tag{10}$$

Fe^{2+} tends to co-precipitate with ferric oxyhydroxides and oxidation rate of the Fenton reaction decreases as the result of the lack of Fe^{2+} in aqueous phase. In addition, the formation of insoluble iron forms known as ferric sludge at circumneutral pH is considered as the main disadvantage in the Fenton treatment of wastewater. Therefore, optimal pH in the Fenton process is found to be around 3 and the oxidation ability is reduced either at high or low pH.

1.2 The influence of organic substrate to be oxidized on the reactivity of the Fenton process

The presence of organic substrate in the Fenton reaction mixture may play the crucial role in activation of the oxidation process. HO• formed by the Fenton or Fenton-like reactions can initiate the radical mechanism of organic substrate degradation. Depending on the organic molecule structure HO• can attack via an H-atom abstraction from C-H, O-H or N-H bonds, addition to C-C bond, or carbon-carbon double bond (C=C), and conjugation with aromatic ring. Formed organic radicals (R•) can reduce Fe^{3+} to Fe^{2+} (Eq. 11), or oxidize Fe^{2+} regenerating therefore the parent substrate (Eq. 12) (Walling and Johnson, 1975). Regeneration of Fe^{2+} boosts the reactivity of the Fenton activating the formation of HO• according to the reaction (Eq. 1).

$$R\bullet + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \xrightarrow{OH^{-}} ROH \qquad (11)$$

$$R\bullet + Fe^{2+} \rightarrow R^{-} + Fe^{3+} \xrightarrow{H^{+}} RH \qquad (12)$$

Besides of HO• mediated R• interactions with iron ions, there are other important reactions that substantially influence the oxidation ability of the Fenton process. One of the important reactions is that some organic compounds act as ligands (L) forming the complexes with iron ions. As the Fenton process reactivity significantly decreases with increase of pH due to the formation of insoluble iron forms (Section 1.1), organic chelators may solubilize iron at circumneutral pH and support therefore the oxidation process. This phenomenon was studied by Sun and Pignatello (1992), where the presence of organic chelates such as aminopolycarboxylates, polyhydroxy aromatics, porphyrins enhanced hydrogen peroxide oxidation of 2,4-dichlorophenol through the complexes formation.

Possible interactions of iron ions with organic ligands (L) include (1) photolysis of Fe^{3+}-L complexes, (2) stabilization of high valent iron-oxo or iron-peroxo complexes by L, and (3) reduction of Fe^{3+} by neutral organic molecules (Chen and Pignatello, 1997). The efficacy of latter (interaction 3) was shown in the studies (Cheng et al., 2003; Iwanashi et al., 1989; Aruoma et al., 1993) on antioxidant and pro-oxidant action in biological systems. The ability of some organic compounds that possess catecholic, pyrogallolic or quinone structures to activate Fenton-mediated HO• formation by Fe^{3+} reduction to Fe^{2+} was observed.

In the study of Chen and Pignatello (1997) the detailed mechanism of organic compound autocatalytic behavior in the Fenton oxidation was described. Quinone-structure compounds shuttle electron from the HO• adduct of starting aromatic compound to Fe^{3+} facilitating the degradation of the compound. Hydroquinones were able to reduce Fe^{3+} to Fe^{2+} and accelerate therefore HO• production according to the classical Fenton. The autocatalytic oxidation of substituted benzenes by Fe^{3+}/H_2O_2 was characterized by kinetics, where after the initial stage of oxidation supported by slow degradation rate (lag-phase) the reaction cascades into a fast phase, as hydroquinone and quinone intermediates are formed.

The complexity of the Fenton process mechanism together with diverse chemical properties and structural features of organic compounds to be oxidized may lead occasionally to controversial results depending on the reaction conditions. A number of publications referred to ascorbic and tannic acids as compounds with strong anti-oxidant ability that are able to prevent the oxidative damage provoked by peroxidation process in biological systems by means of HO• scavenging (Asada, 1996; Gülçin et al., 2010). On the other hand, the reducing properties of these substances towards transition metals have long been known to induce HO• formation in the Fenton-mediated oxidation processes including DNA-damaging effect (Khan and Hadi, 1998; Nappi and Vass, 2000). The competitive reactions of HO• scavenging and propagation depending on the reaction conditions may result in pro- and antioxidant properties of the compounds, respectively.

There are several studies (Hisanga et al., 1992; Nappi and Vass, 2000) relied on biological systems, where the generation of HO• from H_2O_2 in the presence of mere ascorbic acid without transition metals mediation was observed. The mechanism of HO• formation from H_2O_2 in the presence of ascorbic acid is based on direct electron transfer and proton donation from ascorbate monoanion (AH^-) to H_2O_2 with its subsequent decomposition to HO• and H_2O (Eq. 13). The presence of organic constituents in water with similar to ascorbic acid chemical properties may also influence the overall oxidation efficacy of the treatment process.

$$AH^- + H_2O_2 \rightarrow A\bullet^- + HO\bullet + H_2O \qquad (13)$$

Therefore, the study on the role of organic substances in activation of Fenton's oxidation in wastewater treatment represents an important contribution in the field.

1.3 Ferric sludge in the Fenton-based water treatment

Comprehensive investigations demonstrated high efficacy of the Fenton treatment of several industrial types of wastewater containing aromatic amines (Karthikeyan et al., 2012), organic dyes (Barbusiński, 2005; Soon and Hameed, 2011), pesticides (Huston and Pignatello, 1999; Ikehata and Gamal El-Din, 2005), surfactants (Lin et al., 1999), and explosives (Liou and Lu, 2007; Liou and Lu, 2008). Wastewater treatment based on the Fenton and Fenton-like processes is commonly employed in sequential mode as the preliminary step followed by aerobic or anaerobic bio-oxidation. This strategy relies on the principle that recalcitrant organic pollutants tend to be more degradable chemically than biologically, while the opposite is typical for their degradation by-products.

Usually the Fenton treatment of wastewater consists of four stages such as oxidation, neutralization, coagulation/flocculation, and solid-liquid separation (Figure 1) (Gogate and Pandit, 2004). The pH of water in oxidation stage is usually maintained around 3 that has been found as an optimal for the Fenton oxidation. Then neutralization, usually performed by NaOH addition, is required to remove iron ions from the bulk solution by the Fenton coagulation step. (Neyens and Baeyens, 2003). The Fenton coagulation provided by the precipitation of ferric oxyhydroxides in addition to the Fenton oxidation results in a significant removal of high molecular weight organic pollutants in treated wastewater (Gau and Chang, 1996; Yoo et al., 2001). Precipitated ferric sludge is removed by solid-liquid separation, dewatered and compacted in a sludge thickener and chamber filter press.

In spite of the coagulation results in additional removal of organics, the formation of ferric oxyhydroxides is considered as the main disadvantage of the Fenton treatment due to the continuous accumulation of undesirable solid waste saturated with organic compounds. The high cost of such hazardous waste disposal has limited the application of this technology on an industrial scale.

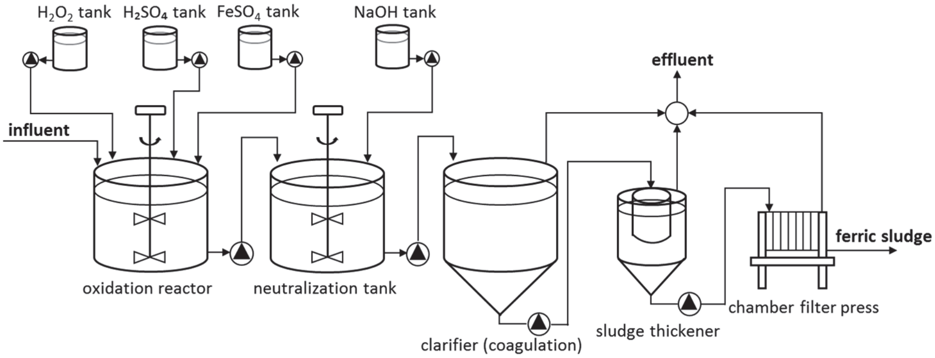


Figure 1. Technological scheme of water treatment based on the Fenton process (modified from Fentox® wastewater treatment set-up (Eisenmann, 2015)).

Several ways of the sludge utilization in the water treatment were proposed as the solution of this problem (Cao et al., 2009; Yoo et al., 2001; Nidheesh and Gandhimathi, 2012). Three main techniques can be distinguished: (1) the thermal treatment of ferric sludge at 300-400 °C with its further dissolution in sulfuric acid and reuse for Fenton-like treatment (Cao et al., 2009), (2) the use of ferric sludge as an additive to improve coagulation (Yoo et al., 2001), (3) the reduction of sludge Fe^{3+} to Fe^{2+} by electrolysis and its reuse for activation of H_2O_2 in the Fenton treatment (Nidheesh and Gandhimathi, 2012). In spite all of the mentioned techniques functioned well the implementation of the additional step would increase the treatment cost on an industrial scale.

Some improvements can be implemented in this field allowing the ferric sludge reduction or productive reuse in the Fenton treatment of wastewater. Nowadays, several modifications of the Fenton such as solar-, ultraviolet-, or electro-Fenton allow minimizing the iron content in the reaction mixture preventing therefore the formation of excessive amounts of ferric sludge. However, more complicated reactors and additional energy used in these methods result in the substantial increase of the overall cost of the Fenton treatment.

Emphasis is needed on the reactions occurring between wastewater organic compounds and Fe^{3+} presented in water either in soluble or solid forms. Depending on the type of the wastewater to be treated by the Fenton process its organic constituents can propagate the autocatalytic oxidation. For example, Fukuchi et al. (2014) investigated the degradation of 2,4,6-tribromophenol by heterogeneous Fenton-like system with iron embedded natural zeolite (Fe-Z). The complete degradation was achieved only in the presence of strong reducing agent hydroxylamine indicating the reduction of Fe^{3+} on the surface of Fe-Z and generation of HO• via the classical Fenton reaction. The application of ascorbic acid in the heterogeneous Fenton process resulted in enhanced degradation of chlorophenols in soil matrix. Ascorbic acid acted either as an iron chelating agent (Romero et al., 2009), or as an iron reductant that bound to the metal oxide (goethite) surface and promoted the iron-reductive dissolution (Lu et al., 2002). These results allow making the presumption that strong organic reductants and chelates may interact directly with ferric sludge supporting the release of iron from solid phase to aqueous media. Therefore, the availability of iron-reducing compounds and chelating agents in wastewater may hypothetically allow the reuse of non-regenerated ferric sludge as a catalyst source of the Fenton-based reaction.

1.4 Micropollutants contaminated water treatment

The existence of micropollutants in natural water is considered as the major concern creating the new challenge to the scientific community. The term “micropollutants” covers the vast spectrum of chemical compounds of anthropogenic or natural origin. The presence of these compounds in environment may cause long-term negative consequences such as bioaccumulation in organisms and carcinogenicity.

Micropollutants include pharmaceuticals, personal care products, steroid hormones, flame retardants, industrial chemicals, pesticides and other emerging compounds that enter the aquatic environment as the result of their large and uncontrolled use. The problem is complicated by the fact that conventional physicochemical and biological treatment methods used in current wastewater treatment plants are not able to remove completely these toxic substances. As the consequence, the fate of micropollutants ends up in natural water bodies as well as in groundwater and soil.

The agricultural use of pesticides is a subset of the larger spectrum of industrial chemicals used nowadays (Ongley, 1996). They are the organic compounds designed for attracting, seducing, and then destroying living organisms undesirable in agriculture. Pesticides deserve the special attention among the list of micropollutants due to their high environmental impact and selective damaging action against specific living organisms. Many pesticides have been reported to induce embryotoxicity and teratogenicity in non-target aquatic biota such as fish, amphibians and invertebrates (Pašková et al., 2011). Moreover, long-term pesticides exposure may lead to their bioconcentration and biomagnification in aquatic organisms making therefore the pollution of water with pesticides of a great concern (Ongley, 1996). Moreover, in the European Union Water Framework Directive 41 priority substances have been set, 14 of which are pesticides (Directive 2008/105/EC).

Alachlor and diuron listed in the Water Framework Directive are widely used herbicides aimed to control most of annual grasses and many broad-leaved weeds. Both compounds reduce photosynthesis of aquatic plants at very low concentrations in water due to their herbicide properties. These substances are related to chemicals that due to their high mobility and moderate persistence in aqueous media can reach groundwater and surface water (EPA, 1998; 2003). Alachlor and diuron have been detected in water bodies at concentrations 2.0 $\mu g\ L^{-1}$ and 1.2 $\mu g\ L^{-1}$, respectively (WHO, 2011; EPA, 2003).

The presence of chlorophenols in water is another matter of a great concern. Chlorophenols are listed as priority pollutants (EPA, 2002) and have been found to be toxic to aquatic biota. Studies on the state of environmental pollution confirm the presence of chlorophenols in surface and groundwater, bottom sediments, atmospheric air and soil (Xie et al., 1986; Paasivirta et al., 1985; Sinkonnen and Paasivirta, 2000). Chlorophenols are formed as by-products in several industrial processes such as disinfection of drinking water with chlorine, bleaching of pulp in paper industry, waste incineration, cooking process and coal pyrolysis (Czaplicka, 2004).

Bioresistant and toxic organic compounds-contaminated water purification usually required the additional treatment step to provide the better quality of discharged water for certain purposes (e.g. water reuse). This can be done either by chemical or physicochemical methods. Physicochemical methods such as coagulation, flocculation, membrane filtration, or adsorption transfer micropollutants from one matrix to another without destroying them. Compounds-concentrated toxic matrixes require therefore supplementary treatment technique such as incineration for their destroying. Biological treatment is able to degrade the compounds only partially. Stasinakis et al. (2009) and Cortés et al. (2002) reported that only 60% of diuron and pentachlorophenol was biodegraded using the activated sludge and a *Rhizopus nigricans* strain, respectively. Alachlor is more persistent, since its biodegradation was lower than 50% after 28 d of incubation (Galassi et al., 1996). AOTs are most suitable for degradation of recalcitrant pollutants as their main advantage is a rapid chemical oxidation of organics. The modification of AOTs for improved and cost-effective elimination of toxic and bioresistant compounds is of a great importance.

Several modifications of the Fenton treatment as electro-Fenton with boron-doped diamond anode (Pipi et al., 2014) or Pt anode (Oturan et al., 2010), photo-Fenton with addition of citrate as the complexing agent (Katsumata et al., 2006) and heterogeneous Fenton with magnetic nanoscaled Fe_3O_4/CeO_2 catalyst (Xu and Wang, 2015) were found to be effective for alachlor, diuron and chlorophenols degradation. In these studies more complicated equipment or expensive materials and catalysts were chosen to favor target compound degradation/mineralization rate increase comparing to that of the classical Fenton. There is no doubt that the Fenton treatment requires modification in order to solve its major disadvantage, i.e the ferric sludge accumulation. However, the strategies of the Fenton modification should be based on a simple and cost-effective approach making the practical application widespread.

1.5 The aims of the study

The general aim of the present study was to evaluate the novel strategy in the Fenton-based wastewater treatment targeting to minimize the accumulation of ferric sludge by its reuse as an iron source. The testing of the proposed approach was performed on the original industrial wastewater effluents. The ability of the ferric sludge to activate the Fenton-based oxidation from mechanistic standpoint was of special interest. According to the general hypothesis, specific organic compounds including strong chelating and reducing agents can support the iron-mediated catalysis in the Fenton process. Therefore, emphasis was placed on the interactions between iron of ferric sludge and wastewater organic constituents with chemical properties similar to that of these specific compounds. According to that, the objectives of the research were as follows:

- to perform the reuse of ferric sludge and to evaluate the efficiency of the original industrial wastewater effluents treatment;
- to assess the ability of organic reductants, L-ascorbic (hereinafter referred to as ascorbic) and tannic acids, to activate ferric iron-mediated hydrogen peroxide oxidation of several micropollutants as alachlor, diuron and 2,4,6-trichlorophenol;
- to measure and to compare the formation of HO• in the classical Fenton and Fenton-like reaction mixtures;
- to identify the degradation by-products of alachlor oxidation and to propose the degradation pathway;
- to accomplish the comprehensive kinetic study of the alachlor, diuron and 2,4,6-trichlorophenol degradation by the classical Fenton and Fenton-like oxidation by path integral analyses of target compounds degradation versus time curves and determination of a second-order rate constants for the reaction between HO• and the target compound;
- to assess the ability of tannic acid to activate the ferric sludge hydrogen peroxide oxidation of 2,4,6-trichlorophenol and to propose the catalytic behavior of ferric sludge.

2. MATERIALS AND METHODS

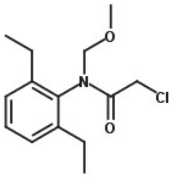
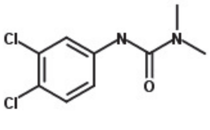
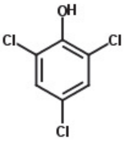
2.1 Reagents and samples

All the reagents and chemicals were of analytical grade. Stock solutions and the micropollutant-spiked water were prepared using ultrapure water obtained from a Millipore ultrapure water ultraviolet-system. The pH was adjusted using sodium hydroxide and sulfuric acid solutions.

The wastewater samples were obtained from a municipal landfill (S1) (operated more than 10 years), a semicoke landfill area of an oil-shale thermal treatment plant (S2), and a plywood manufacturing plant (S3). The collected samples were stored at 4 °C. The main properties and characterization of the wastewaters are given in *Table 1* of *Paper I.*

The experiments on the degradation of micropollutants in water were conducted using the samples spiked with alachlor (purity 99.2%), diuron (≥ 98%), and 2,4,6-trichlorophenol (≥ 97%). These chemicals were obtained from Sigma-Aldrich. Chemical and physicochemical properties of the pollutants are presented in Table 1.

Table 1. The main chemical and physicochemical properties of alachlor, diuron, and 2,4,6-trichlorophenol.

Properties	Alachlor (USDA, 2015)	Diuron (USDA, 2015)	2,4,6-Trichlorophenol (NCBI, 2015)
IUPAC name	2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide	3-(3,4-Dichlorophenyl)-1,1-dimethylurea	2,4,6-Trichlorophenol
Molecular structure			
Chemical structure	$C_{14}H_{20}ClNO_2$	$C_9H_{10}Cl_2N_2$	$Cl_3C_6H_2OH$
Molar mass, g mol^{-1}	269.77	233.10	197.45
Solubility in water at 25 °C, mg L^{-1}	240	42.0	500
log(Kow)	3.52	2.68	3.69

2.2 Experimental procedure

The wastewater samples from different industrial sites and the spiked water samples were treated using Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, ferric sludge/H_2O_2, or mere H_2O_2. All the experiments were conducted in a batch reactor at ambient temperature (21 ± 1 °C). The oxidation of the unbuffered micropollutant-spiked water was carried out at pH 3. The wastewater treatment was conducted without pH adjustment. The oxidation process was initiated by addition of H_2O_2 to the water to be treated with the previously added (if required) Fe^{n+} or ferric sludge. The wastewater treatment was conducted using H_2O_2/Fe^{n+} weight ratio of 5/1 (*Paper I*). In the micropollutant-spiked water oxidation experiments, the H_2O_2/Fe^{n+} molar ratio was kept at 10/1 (*Papers II, III, IV*). The reaction mixture was agitated continuously using a magnetic stirrer. The oxidation was stopped by adjusting the treated samples with a 10-M NaOH solution to pH 10 (*Papers I, II, III*) or by addition of a 0.1-M Na_2SO_3 (*Paper IV*). All the experiments were duplicated. The standard deviation of the duplicated experiments analyses was less than 5%.

In the wastewater Fenton treatment experiments ferric sludge formed as the result of neutralization was separated from supernatant by centrifugation. The thickened ferric sludge was used as the iron source in the wastewater Fenton-like treatment. In the micropollutant-spiked water experiments ferric sludge was synthesized by mixing sodium hydroxide and ferric sulfate with further filtration and washing out of formed sodium sulfate from precipitate.

2.3 Analytical methods

The overview on the analytical methods used for the wastewater and the micropollutant-spiked water characterization and investigation is given in Table 2.

The filtered (0.45 µm) samples from the alachlor- and diuron-spiked water treatment experiments were analyzed (*Papers II, III*) using a Schimadzu liquid chromatograph equipped with a Phenomenex Gemini (150 mm × 2.0 mm inner diameter) NX-C18 (110 Å pore size, 5 µm particle size) column. Alachlor was detected using a gradient elution method and a mass spectrometer (*Paper III*). An isocratic elution and a photodiode array detector were used for the determination of diuron (*Paper II*). The 2,4,6-trichlorophenol concentration in spiked water was measured using an YL-Instrument liquid chromatograph equipped with a Waters Bridge (150 mm × 3.0 mm inner diameter) C18 (3.5 µm particle size) column. Light absorbance was measured by an ultraviolet-visible detector at 295 nm (*Paper IV*).

The HO• concentration in reaction mixture was estimated by the deoxyribose method (Halliwell et al., 1987). This method is based on the oxidative reaction of HO• with deoxyribose to form malondialdehyde (MDA), which then reacts with 2-thiobarbituric acid (TBA). The resultant pink chromophore was detected photometrically at the wavelength $\lambda = 532$ nm. The HO• concentration was equated to formed chromophore using an extinction coefficient of 1.56 × 10^{-5} (M^{-1} cm^{-1}) (Buege and Aust, 1978) (*Papers III, IV*).

Table 2. Analytical methods applied for analysis of water samples.

Parameter/Analysis	Analytical method/Equipment	Paper
COD	Closed reflux colorimetric method (APHA, 2005)	I
BOD_7	Digital oxygen analyzer (APHA, 2005)	I
pH	Digital pH meter	I-IV
EC	Digital EC meter	I
DOC	TOC analyzer	I
TOC	TOC analyzer	I-III
Total nitrogen	TOC analyzer	I
TSS	APHA (2005)	I
TS	APHA (2005)	I
TFS	APHA (2005)	I
Acute toxicity to *Daphnia magna (Cladocera Crustacea)*	24-h toxicity test using DAPHTOXKIT F^{TM} MAGNA (ISO 6341, 1996)	I
Total iron	Spectrophotometric method (Merck, 1994)	I, IV
Ferrous iron	Spectrophotometric method (Merck, 1994)	I, IV
H_2O_2 (stock solution)	Spectrophotometric method, $\lambda = 254$	I-IV
H_2O_2	Spectrophotometric method (Eisenberg, 1943)	I, IV
Anions (F^-, Cl^-, PO_4^{3-}, SO_4^{2-})	IC-SCD	I, IV
Tannins and lignin	Spectrophotometric method (Kloster, 1974)	I
Total phenols	Spectrophotometric method (ISO 6439, 1990)	I
Alachlor	HPLC-MS	III
Diuron	HPLC-PDA	II
2,4,6-Trichlorophenol	HPLC-UV	IV
HO•	Spectrophotometric method (Halliwell et al., 1987; Buege and Aust, 1978)	III, IV
Identification of degradation products	GC-MS	II

The method for determination of a second-order rate constant was proposed by Halliwell et al. (1987) and relies on the competitive reactions of deoxyribose and investigated compound with HO•. 2.8 mM of deoxyribose were oxidized for specific time (30 min) by HO• in the absence and in the presence of the target compound (alachlor or diuron) at various concentrations in each experiment set. After 30 min of oxidation the resultant pink chromophore indicated the amount of HO• consumed by deoxyribose. The addition of the compound resulted in a subsequent consumption of HO• and therefore decreased the amount of HO• consumed by deoxyribose.

The alachlor oxidation intermediates were identified using liquid-liquid extraction with three-step addition of dichloromethane to the water samples. The obtained extracts were dried using Na_2SO_4, filtered through hydrophobic cartridge filter (0.45 μm), concentrated (1/10, v/v) by evaporation, and analyzed by a Shimadzu gas chromatograph mass spectrometer with a ZB-5MS capillary column (30 m × 0.32 mm inner diameter with a film thickness of 0.25 μm).

The dissolved organic carbon (DOC), total organic carbon (TOC), and total nitrogen were determined by an Analytic Jena TOC analyzer. The samples were filtered prior to the DOC and total nitrogen analysis using membrane filters (0.45 μm, cellulose acetate membrane).

3. RESULTS AND DISCUSSION

3.1 Wastewater treatment

An important background for successful application of AOTs is the preliminary removal of suspended solids from water as they tend to increase the dosage of primary oxidants (H_2O_2, O_3, $S_2O_8^{2-}$, etc.), or obstruct the penetration of light in case of photolytic AOTs. In this study *(Paper I)*, the coagulation pre-treatment was used to reduce the reagents dosages in the following Fenton-based treatment due to the partial elimination of suspended solids (turbidity) and high molecular weight organic pollutants such as tannins, lignin, and resin acids. The use of a commercial formulation of a KEMIRA PIX-322 coagulant containing ferric sulfate resulted in a considerable decrease of COD and DOC in samples S1 and S2. In spite of coagulation of S1 was accompanied by a substantial TSS removal ($\geq$ 90 %), more than 90% of COD and DOC remained in S1 indicating the presence of dissolved and rather resistant to coagulation contaminants. In case of S2 a higher treatment efficacy (COD and DOC removal) was achieved due to the considerable decrease in the TSS ($\geq$ 90 %), lignin and tannins ($\geq$ 60%) and phenols ($\geq$ 50%). The coagulation of sample S3 was ineffective as the COD and DOC removals were lower than 10 and 2%, respectively. Thus, the coagulation process applied for the plywood manufacturing plant effluent (S2) treatment was set as the preliminary step in the general treatment sequence. S1 and S3 were treated without pre-coagulation.

Despite the experiment on the Fenton treatment of wastewater without pH pre-adjustment accompanied by the fast decrease of pH in the beginning of the oxidation, the prolonged treatment time was needed to obtain the pH $\approx$ 3. The pH decrease was caused by the hydrolysis of added acidic Fe^{2+}/Fe^{3+} sulfates and by the formation of carboxylic acids during the oxidation of wastewater organic constituents. As a result, the pH values were lower than 3 in S3 after 2 h of the oxidation and in a pre-coagulated S2 (CS2) after 1 h of the oxidation. S1 possessed better pH buffering capacity resulting in a pH decrease to the values of 4 and 3 for a 24-h H_2O_2/Fe^{2+} and H_2O_2/Fe^{3+} treatment, respectively.

The Fenton treatment efficacy of S1, CS2, and S3 evaluated on the basis of COD and DOC removal was independent of initial pH and initially added iron ion form (Fe^{3+} or Fe^{2+}). The latter is consistent with the assumption (Pignatello et al., 2006) that the differentiation of the Fenton catalyzing effect by Fe^{2+} and Fe^{3+} action is “meaningless from mechanistic standpoint” because the initially added Fe^{2+} is rapidly oxidized to Fe^{3+} and thereafter the system is independent of the initial form of iron. This assumption is valid only in those cases where the interactions of Fe^{3+} with the specific organic substances take place (Section 1.2). Otherwise, the Fe^{3+}-mediated H_2O_2 oxidation is a considerably less reactive than the Fe^{2+} one.

The optimization of the oxidant (H_2O_2) dosage is essential for the efficient Fenton-based treatment. The results of the experiment showed the steady correlation between the COD or DOC removal and the oxidant dosage, i.e. the treatment efficacy increase was accompanied by the higher dosages of H_2O_2

(*Paper I, Figures 3 and 4*). The S1 tended to be more recalcitrant to the oxidation than CS2 and S3. The 24-h treatment using COD/H_2O_2 of 1/1.15 (w/w) resulted in 38%, 79% and 64% of COD removal in S1, CS2 and S3, respectively.

Considerably higher dosage of H_2O_2 in the non-catalyzed H_2O_2 oxidation (COD/H_2O_2 = 1/3.45, w/w) comparing to that of the Fenton (COD/H_2O_2 = 1/1, w/w) resulted in only 11% of COD removal in both S1 and S3 indicating the unproductive decomposition of H_2O_2. More than 50% of COD and DOC were removed at COD/H_2O_2 of 1/1 (w/w) in CS2 due to the catalytic action of dissolved iron (90 mgFe_{total} L^{-1}) remained in the bulk solution after coagulation. Higher improvement in the efficiency of CS2 treatment was obtained by the addition of iron salts to maintain the H_2O_2/Fe^{n+} ratio of 5/1 (w/w).

Providing the better treatment efficacy of investigated wastewaters the high dosages of iron catalysts were used. This resulted in the formation of large amounts of undesirable ferric sludge as pH of treated wastewater was increased to the values close to 9. To overcome this problem ferric sludge was reused as the oxidation catalyst in the Fenton-based treatment of wastewater samples pre-acidified to pH 3. The pre-acidification was applied for the following reasons: (1) to obtain highest oxidation efficacy as the pH optimum for the Fenton-based processes is near 3, and (2) to support iron leaching from ferric sludge to the aqueous phase at acidic conditions. The assumption of iron leaching process was confirmed with the further analysis of the treated wastewater samples indicating the concentrations of total dissolved iron of 340-400 mg L^{-1}. The oxidation mechanism can be initiated by Fe^{3+} or Fe^{2+} in aqueous phase (Eqs. 1-9), or by the decomposition of H_2O_2 to the oxidative species directly on the surface of ferric oxyhydroxides known as heterogeneous catalysis (*Eqs. 5-9 of Paper I*) (Lin and Gurol, 1998). Employing the reused iron-containing sludge during four treatment cycles (*Paper I, Figure 1*) showed nearly identical to the classical Fenton treatment COD removal (*Paper I, Figure 5*).

The application of AOTs for the treatment of highly organics loaded wastewater is considered as the preliminary step prior to the biological treatment as the recalcitrant pollutants tend to be more degradable chemically than biologically, while the opposite is usually distinctive for their degradation products. As the preliminary coagulation of S2 showed the effective removal of polyphenols such as tannins known to be toxic to the aquatic microorganisms (Sierra-Alvarez et al., 1994), the biodegradability of S2 increased therefore of up to 65% (*Paper I, Figure 6*) after the pre-treatment by coagulation. The following Fenton treatment showed biodegradability (BOD_7/COD) increase of up to additional 20%. BOD_7/COD as well as COD and DOC removal in the Fenton-based experiments utilizing ferric sludge within four treatment cycles was close to that of the H_2O_2/Fe^{2+} and H_2O_2/Fe^{3+} treatment systems.

The high efficacy of the Fenton-based treatment with a non-regenerated sludge reuse for the different wastewater types indicated the possibility to employ this method as a novel technological approach.

3.2 Improvement in iron activation ability of alachlor and diuron Fenton-like oxidation by reductant L-ascorbic acid

Although the ferric sludge reuse resulted in a substantial reduction of COD and DOC as well as improved the biodegradability of wastewater, the study of Fe^{3+} mediated H_2O_2 activation mechanism relied only on theoretical basis, and therefore, continued to engage the attention. The special emphasis was placed on the reactions of wastewater organic constituents and Fe^{3+}. For this reason, the alachlor- and diuron-spiked waters were treated using Fe^{3+}/H_2O_2 in the presence of ascorbic acid (AA). It was assumed that the wastewater samples organic constituents and their degradation by-products possess similar to ascorbic acid properties in organic radical formation and in the reduction of Fe^{3+} to Fe^{2+}. Deprotonated ascorbic acid, ascorbate monoanion ($pK_a = 4.25$; Kortum et al., 1961), undergoes a two-step oxidation to generate dehydroascorbic acid through the intermediates as semidehydroascorbate and ascorbyl (A^{-}•) radicals, which are involved in the transformation of Fe^{3+} to Fe^{2+} supporting therefore HO• induced oxidation of alachlor and diuron (Figure 2).

To evaluate the ability of Fe^{2+} and Fe^{3+} to catalyze the H_2O_2 oxidation and the influence of ascorbic acid on propagation of the HO• formation an indirect measurement of HO• by the deoxyribose method was used (*Paper III, Figure 1*). The Fe^{2+}/H_2O_2 combination known as the classical Fenton's reagent demonstrated the immediate burst of HO• characterized by a substantial increase of HO• content with the maximum concentration achieved after 10 s. In contrast, the Fe^{3+}/H_2O_2 showed a weak ability of Fe^{3+} to activate the HO• production. The rate limiting step in Fe^{3+}-catalyzed H_2O_2 oxidation is the reductive decomposition of $Fe^{III}(HO_2)^{2+}$ complex to HO_2• and Fe^{2+} (Eq. 9) with the reaction rate constant of $2.7 \cdot 10^{-3}$ s^{-1} (De Laat and Gallard, 1999) that is several orders of magnitude lower than that of the classical Fenton reaction (Eq. 1) ($k = 53$ $M^{-1}s^{-1}$; Barb et al., 1951). The addition of ascorbic acid to the Fe^{3+}/H_2O_2 allowed overcoming the rate limiting step by donation of electron to Fe^{3+} supporting therefore the propagation of HO• according to the classical Fenton (*Paper III, Figure 1*). The effect of $Fe^{3+} \leftrightarrow Fe^{2+}$ cycling initiated by immediate Fe^{3+} reduction and Fe^{2+} oxidation provided by ascorbic acid and H_2O_2, respectively, resulted in higher amount of HO• formed comparing to that of the classical Fenton.

A notable HO• production was observed in H_2O_2/AA system in the absence of any iron ion (*Paper III, Figure 1*). According to the study of Nappi and Vass (2000) H_2O_2 reacts with ascorbate monoanion to produce A^{-}• and HO• (Eq. 13). In spite of HO• production was considerably lower than that in Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2/AA, this combination proved the occurrence of analogous to the Fenton processes HO• generation, which may take place in wastewater treatment.

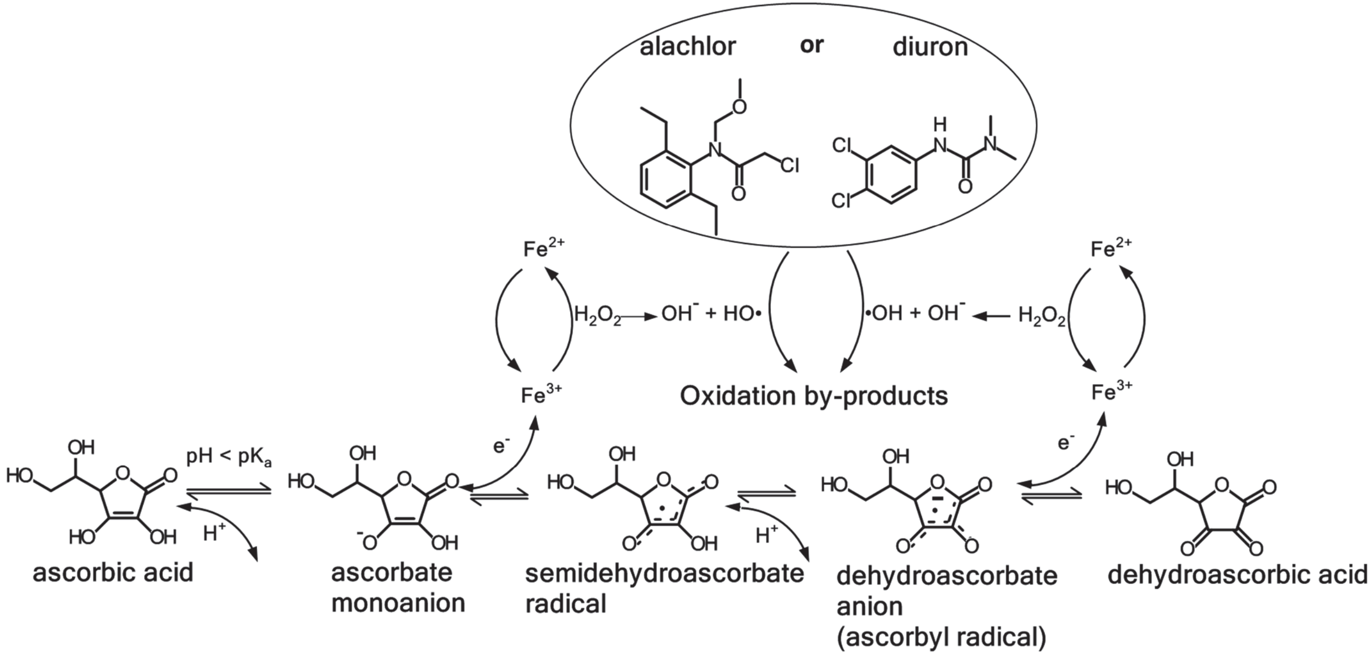


Figure 2. Proposed mechanism of Fe^{3+} reduction by ascorbic acid with the propagation of hydroxyl radical production from H_2O_2 and ensuing alachlor and diuron oxidation.

3.3 Kinetics of alachlor and diuron degradation

To estimate the role of HO• in the oxidation of the target compounds a second-order rate constant of reaction between HO• and target compound was calculated. The method for determination of a second-order reaction rate constant was proposed by Halliwell et al. (1987) and relies on the competitive reactions of deoxyribose and the target compound with HO•. The competitive reactions can be expressed using concentration of formed pink chromophore. To simplify the calculations the light absorbance of resultant pink chromophore after 30 min of oxidation was taken as the measure of the deoxyribose and HO• reaction rate (Eq. 13).

$$r = A = \frac{d[HO\cdot]}{dt} \tag{13}$$

Then this rate can be mathematically expressed by Eqs. (14) and (15)

$$A = k_{DR}[DR][HO\bullet] \tag{14}$$

$$A_0 = k_{DR}[HO\bullet][DR] + k_S[HO\bullet][S] \tag{15}$$

where A and A_0 are the rates of deoxyribose oxidation by HO• with and without addition of the target compound (substrate, S), respectively; (k_{DR}) is a reaction rate constant of deoxyribose oxidation by HO•; [DR] is the initial concentration of deoxyribose; [HO•] is the HO• concentration; [S] is the target compound initial concentration; k_S is the second-order reaction rate constant of target compound oxidation by HO•.

A linear dependence between 1/A and the concentration of target compound can be established (Figure 3) by dividing of A_0 by A (Eqs. 16, 17). A plot of 1/A versus concentration of the compound [S] gives a straight line which allows the calculation of the second-order reaction rate constant (k_S) from its slope as shown in Eq. (18).

$$\frac{A_0}{A} = 1 + \frac{k_S[S]}{k_{DR}[DR]} \tag{16}$$

$$\frac{1}{A} = \frac{1}{A_0}\left(1 + \frac{k_S[S]}{k_{DR}[DR]}\right) \tag{17}$$

$$k_S = \text{slope}\cdot k_{DR}\cdot[DR]\cdot A_0 \tag{18}$$

Deoxyribose reacts with HO• with reaction rate constant of $k_{DR} = 3.1\cdot10^9$ $M^{-1}s^{-1}$ (Halliwell et al., 1987). Thus, the calculated second-order reaction rate constants of HO• with alachlor and diuron were $6.9\cdot10^9$ and $3.3\cdot10^9$ $M^{-1}s^{-1}$, respectively. The second-order reaction rate constant of HO• with alachlor was close to that of a diffusion-controlled rate constant in water $k_d = 7 \times 10^9$ $M^{-1}s^{-1}$ calculated using Fick's first law of diffusion and the Stokes-Einstein equation. Therefore, the oxidation of alachlor by HO• can be characterized as a diffusion-controlled reaction in water. That demonstrated the predominant role of HO• among other oxidative species in oxidation of alachlor. Thus, the alachlor degradation rate may be limited by the rate of HO• generation and the competitive reactions of HO• with other components in the reaction mixture.

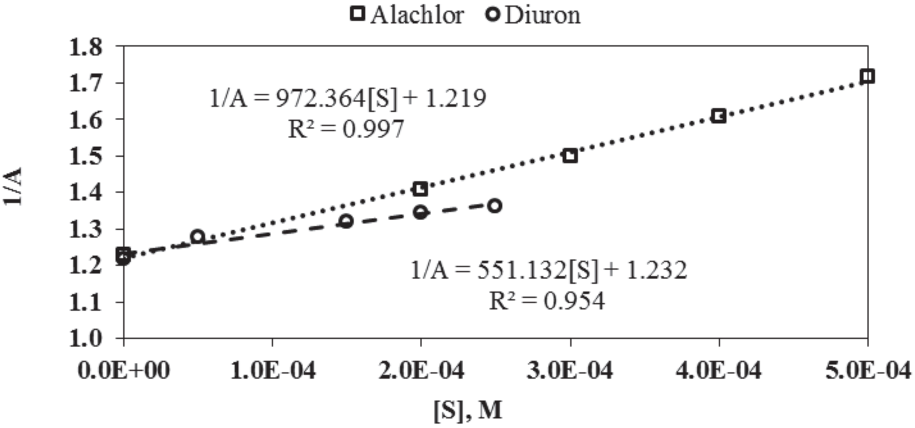


Figure 3. Consumption of HO• expressed as 1/A (A is light absorption of pink chromophore at 532 nm) depending on the initial concentrations of alachlor and diuron ([S], M). [S] varied from 2 × 10^{-4} to 5 × 10^{-4} M and from 5 × 10^{-5} to 2.5 × 10^{-4} M for alachlor and diuron, respectively.

A kinetic study accomplished by path integral analyses of the target compounds concentration profiles versus time showed that degradation by the Fenton-based processes followed a pseudo-first order reaction kinetic law. The pseudo-first order reaction rate constant (k') was calculated by plotting ln(C_0/C) as a function of time by linear regression (Eq. 19). The obtained slope of the straight line indicated the constant value (Table 3).

$$ln\left(\frac{C_0}{C}\right) = k' \cdot t \qquad (19)$$

In spite of HO• amount formed in Fe^{3+}/H_2O_2/AA was higher than that in Fe^{2+}/H_2O_2 (*Paper III, Figure 1*), the delay in HO• formation was observed. This resulted in a slightly slower oxidation rate of alachlor and diuron by Fe^{3+}/H_2O_2/AA (Table 3; inset of Figure 4 shows the alachlor degradation delay within the first minute of the oxidation).

More than a ten-fold increase of a pseudo-first order reaction rate constant was observed in alachlor and diuron degradation by Fe^{3+}/H_2O_2/AA comparing to that by Fe^{3+}/H_2O_2. The degradation of alachlor by Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2/AA was characterized by the multiple-step oxidation supported by a fast phase (0-1 min) that is explained by a rapid HO• formation in the first minutes of the reaction (*Paper III, Figure 1*) and by the following slower decay (1-120 min) where almost all Fe^{2+} is oxidized to Fe^{3+}. As to the Fe^{3+}/H_2O_2 system, the oxidation of alachlor in the slow phase can be explained by the retarded reduction of Fe^{3+} to Fe^{2+} or by the reactions (Eqs. 8, 9).

The alachlor degradation (Figure 4) and HO• formation (*Paper III, Figure 1*) by H_2O_2/AA in the absence of iron mediation indicated that AA in the Fe^{3+}/H_2O_2

system may be involved not only in the Fe^{3+} reduction, but also in the HO• formation resulting in improved contaminant degradation.

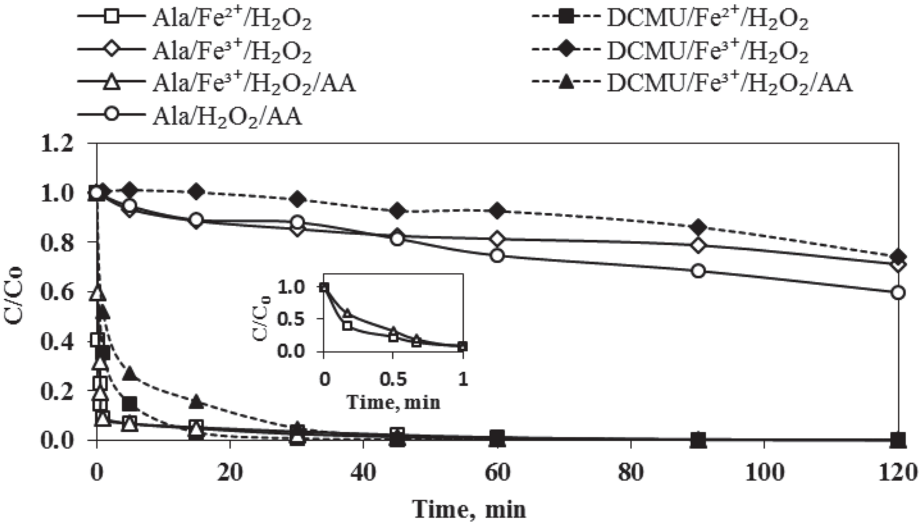


Figure 4. Degradation of alachlor (Ala) and diuron (DCMU) by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$ (AA - ascorbic acid) and H_2O_2/AA (for alachlor) within 120 min of the treatment. The initial concentrations of the target compounds were [Ala] = [DCMU] = 100 µM. The molar ratios of $Ala/Fe^{n+}/H_2O_2/AA = 1/2/20/2$ and $DCMU/Fe^{n+}/H_2O_2/AA = 1/1/10/1$were used. Inset is the enlargement of Ala degradation by Fe^{2+}/H_2O_2 and $Fe^{3+}/H_2O_2/AA$ within the first minute of the reaction.

Table 3. Pseudo-first order reaction rate constants (k', min^{-1}) of alachlor (Ala) and diuron (DCMU) degradation by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$ (AA-ascorbic acid) and H_2O_2/AA (R^2–regression coefficient).

Process	k'·10^{-2} (min^{-1}), (treatment time)	R^2
$Ala/Fe^{2+}/H_2O_2$	270 (0-1 min) 3.6 (1-120 min)	0.906 0.988
$Ala/Fe^{3+}/H_2O_2/AA$	240 (0-1 min) 3.0 (1-120 min)	0.995 0.978
$Ala/Fe^{3+}/H_2O_2$	0.22 (0-120 min)	0.979
$Ala/H_2O_2/AA$	0.40 (0-120 min)	0.942
$DCMU/Fe^{2+}/H_2O_2$	12 (0-120 min)	0.976
$DCMU/Fe^{3+}/H_2O_2/AA$	7.6 (0-120 min)	0.996
$DCMU/Fe^{3+}/H_2O_2$	0.23 (0-120 min)	0.925

Therefore, the hypothesis of ascorbic acid ability to reduce ferric iron improving activation of the Fenton oxidation (Fe^{3+}/H_2O_2) was confirmed. The presence of organic pollutants in wastewater with similar to ascorbic acid properties of interaction with Fe^{3+} through organic radical formation by the following reduction of Fe^{3+} to Fe^{2+} may support the recycling of non-regenerated ferric sludge for the Fenton oxidation activation.

3.4 Alachlor and diuron mineralization by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$ and alachlor degradation by-products

Assuming that H_2O_2 is the general oxidizing agent the mineralization of alachlor and diuron may proceed according to the reactions (Eqs. 20, 21), respectively.

$$C_{14}H_{20}ClNO_2 + 38H_2O_2 \rightarrow NO_3^- + 14CO_2 + 47H_2O + Cl^- + 2H^+ \quad (20)$$

$$C_9H_{10}Cl_2N_2 + 27H_2O_2 \rightarrow 2NO_3^- + 9CO_2 + 30H_2O + 2Cl^- + 4H^+ \quad (21)$$

Less than 5% of TOC removal was achieved during alachlor and diuron degradation by Fe^{3+}/H_2O_2 indicating unsubstantial mineralization degree by the Fe^{3+}-mediated H_2O_2 oxidation (Figure 5). Although diuron underwent slower degradation comparing to that of alachlor (Table 3, Figure 4), the higher TOC removal during diuron degradation was observed using Fe^{2+}/H_2O_2 and $Fe^{3+}/H_2O_2/AA$ systems. Thus, less than 20% of alachlor was mineralized by Fe^{2+}/H_2O_2 (Ala/Fe^{2+}/H_2O_2 = 1/2/20), while diuron oxidation contrarily resulted in more than 40% of TOC removal using two times lower Fe^{2+} and H_2O_2 dosages (DCMU/Fe^{2+}/H_2O_2 = 1/1/10). TOC removal by H_2O_2/AA was not observed.

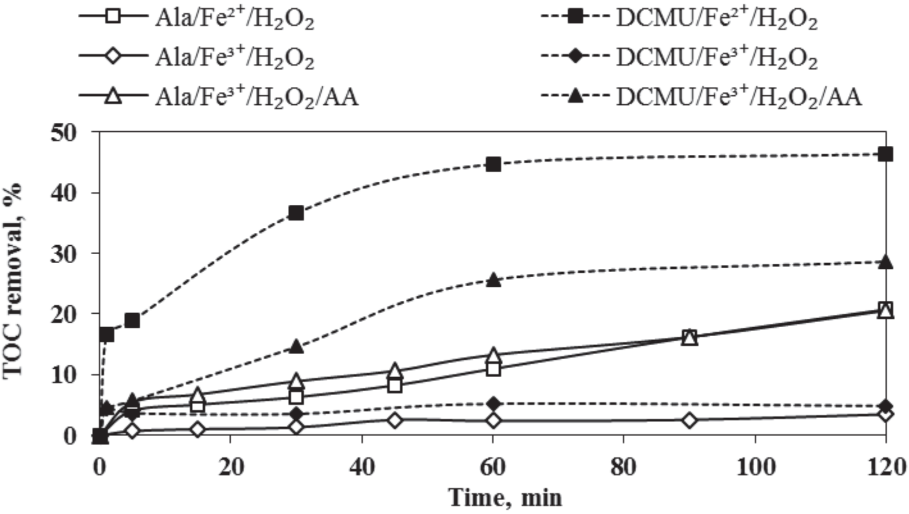


Figure 5. Removal of TOC (% of initial) during alachlor (Ala) and diuron (DCMU) degradation by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$. [Ala] = [DCMU] = 100 μM. The molar ratios were Ala/Fe^{n+}/H_2O_2/AA = 1/2/20/2; DCMU/Fe^{n+}/H_2O_2/AA = 1/1/10/1.

An analysis of m/z spectra obtained by GC-MS and their comparison to NIST database allowed identification of primary oxidation intermediates of alachlor oxidation (*Paper III, Table 2, Figure 6*). HO• can attack alachlor by abstracting H from C-H and N-H or O-H bonds, by addition to C-C bond or to conjugate aromatic ring. Consequently, the oxidation pathway of alachlor oxidation can be divided into six main categories: (1) hydroxylation, (2) cleavage of hydrogen atoms, (3) scission of the C-N bond, (4) attack of the ether bond, (5) addition reaction to the aromatic ring, and (6) cyclization reaction.

In the reaction of alachlor hydroxylation the substitution of –Cl to –OH group initiated by HO• resulted in formation of 3-(2,6-diethylphenyl)-1-hydroxyhexan-2-one (A) (Figure 6).

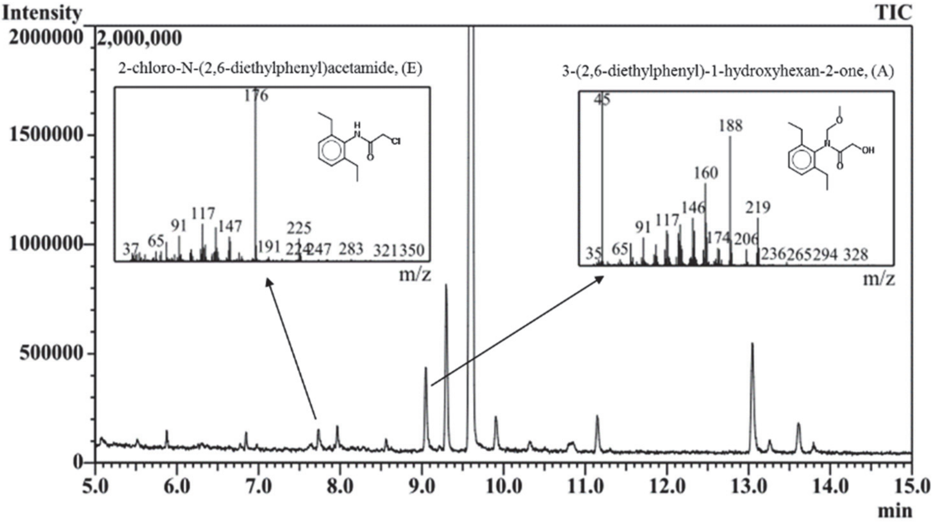


Figure 6. The GC-MS chromatogram and m/z spectra of some alachlor oxidation intermediates (E and A) after 10 s of the treatment with $Fe^{3+}/H_2O_2/AA$.

A and B compounds had similar spectra, but their m/z values differed by 2 units (m/z of 251 and 249, respectively). According to that the cleavage of hydrogen atoms and the presence of double bond between carbon atoms were proposed indicating the formation of N-(2-ethenyl-6-ethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide (B). N-(2,6-diacetylphenyl)-2-hydroxy-N-methylacetamide (C) had identical to (B) m/z value of 249. The mass spectrum of another intermediate N-(2-acetyl-6-ethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide (D) was obtained at a retention time of 10.2 min and it is the probable precursor of (C). The presence of by-products C and D has not been reported earlier. Chloro-N-(2,6-diethylphenyl)acetamide (E) (Figure 6) was formed by the scission of C-N bond. The attack of ether bond led to the formation of 2-chloro-N-(2,6-diethylphenyl)-N-(hydroxymethyl)acetamide (F).

HO• is prone to aromatic ring, or to C-C bond addition. Two isomers (G, H) where –OH group is located on the aromatic ring, or ethyl groups were identified. The isomers are degraded then to compound (K) by elimination of hydroxymethyl group. As the result of the cyclization reactions, which are typical for oxidation of alachlor by AOTs (Katsumata et al., 2006; Haag and Yao, 1992) the intermediates (L, M) were formed. However, the precursors of compound (L) were not detected on the GC-MS chromatograms.

The identification of alachlor degradation by-products may allow for the prediction of a secondary pollution caused by toxic intermediates formation. The progressive degradation of alachlor by Fe^{2+}/H_2O_2 and $Fe^{3+}/H_2O_2/AA$ resulted in the complete degradation of eleven found intermediates in 120 min indicating the high efficacy of the treatment methods applied. Moreover, the oxidation by-products of alachlor can result in similar to ascorbic acid organic radical formation, or in the competitive to ascorbic acid reaction of reduction of Fe^{3+} to Fe^{2+} by electron transfer (Section 1.2); however, because of their relatively low concentration, this effect was negligible if any.

3.5 Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalytic decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment

The plywood manufacturing plant wastewater effluent consists of tannins (*Paper I, Table 1*) known to be a strong transition metal-chelating (Sungur and Uzar, 2008) and reducing agents (Gülçin et al., 2010). Therefore, the presence of tannins in wastewater may express similar to ascorbic acid property to improve Fe^{3+} activation ability of organic contaminants in the Fenton-like oxidation by the formation of stable complexes with ferric iron and by the reduction of Fe^{3+} to Fe^{2+}. Additionally to tannins mono- and polychlorinated phenols are present in wood processing water effluents formed during the bleaching process with chlorine containing agents. Tannins (Kalyanaraman et al., 2015) and chlorophenols (Olaniran and Igbinosa, 2011) are biorecalcitrant compounds. Therefore, the appropriate technology for their elimination from water effluents is of a great importance.

Similar to that of alachlor and diuron degradation, Fe^{3+}/H_2O_2 was less reactive than the classical Fenton process (Fe^{2+}/H_2O_2) for 2,4,6-trichlorophenol oxidation. The degradation by the Fenton-like treatment was followed by a lag-phase resulting in a complete oxidation at a four-fold higher concentrations of reagents than that by Fe^{2+}/H_2O_2 (Figure 7). The organic substrate to be oxidized plays an important role in Fenton-based process. The lag-phase caused by a rate-limiting step of the reductive decomposition of the $Fe^{III}(HO_2)^{2+}$ complex (Eq. 9) cascaded then into a fast phase as the specific oxidation by-products are formed. The oxidation of phenol and its derivatives is followed by the formation of catechol-, hydroquinone- and quinone-structure compounds (Xu and Wang, 2015; Gaya et al., 2010; Chaliha and Bhattacharyya, 2008). Quinones are able to shuttle electron from the HO• adduct to Fe^{3+} accelerating therefore the degradation of the initial compound. Hydroquinones and catechols are known to reduce Fe^{3+} to Fe^{2+} under acidic condition and promote the formation of HO• via reaction (Eq. 1). Fe^{2+} concentration profile in Fe^{2+}/H_2O_2 system demonstrated Fe^{3+} reduction caused by 2,4,6-trichlorophenol oxidation by-products (*Paper IV, Figure 2*). Using a rate constant value of 53 $M^{-1}s^{-1}$ (Barb et al., 1951) for the reaction (Eq. 1) an estimation of initial Fe^{2+} oxidation rate in the reported conditions yields a half-life of about 2 min, which is not consistent with prolonged Fe^{2+} concentration depletion in reaction mixture. In addition, slow but remarkable increase of Fe^{2+} was observed after 30 min. Both findings led to the assumption of Fe^{3+} reducing process by 2,4,6-trichlorophenol degradation intermediates reflecting therefore on Fe^{2+} concentration profile in the reaction mixture.

In the presence of tannic acid at concentration of 10 mg L^{-1} the degradation of 2,4,6-trichlorophenol by Fe^{3+}/H_2O_2 increased and proceeded without any lag-phase (Figure 7). In addition, the expected HO• formation was observed (*Paper IV, Figure 7*) confirming the assumption of Fe^{3+}/H_2O_2 activation due to Fe^{3+} reduction by tannic acid. 2,4,6-Trichlorophenol oxidation was only slightly slower than that by the classical Fenton (Fe^{2+}/H_2O_2) using similar dosages of Fe^{n+} and H_2O_2. The reductive role of tannic acid in activation of the H_2O_2 oxidation by Fe^{3+} can be explained by its molecular structure (*Paper IV, Figure 3*), which consists of several monomers of gallic acids attached to each other by depside bonds, or to a central polyol (such as glucose) by ester bonds (Mueller-Harvey, 2001). Gallic acid forms unstable complex with Fe^{3+} followed by its further reductive decomposition to Fe^{2+} and quinone group (Hynes and Coinceanainn, 2001). In aqueous solutions ferric salts undergo an extensive hydrolysis and at pH 3 Fe^{3+} is presented mainly in the form of $Fe(OH)^{2+}$ (Eq. 10). Tannic acid exhibited Fe^{3+}-reductive properties according to the mechanism described in *Paper IV, Figure 3* and therefore boosted the reactivity of the Fenton-based process towards 2,4,6-trichlorophenol degradation by improving iron redox cycling and as a result enhanced activation of the H_2O_2 oxidation.

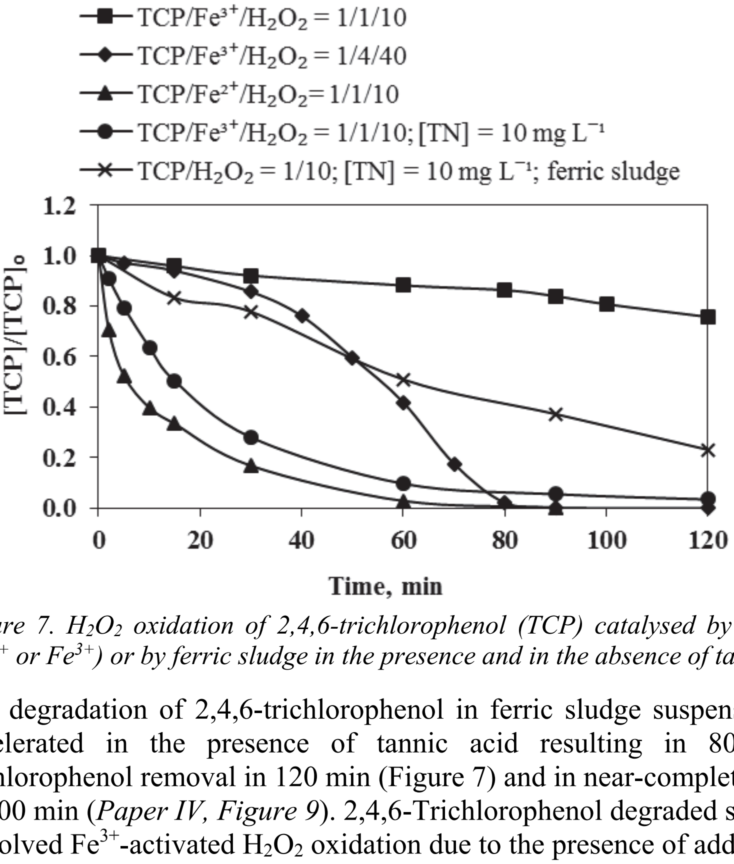


Figure 7. H_2O_2 oxidation of 2,4,6-trichlorophenol (TCP) catalysed by dissolved iron (Fe^{2+} or Fe^{3+}) or by ferric sludge in the presence and in the absence of tannic acid (TN).

The degradation of 2,4,6-trichlorophenol in ferric sludge suspension was also accelerated in the presence of tannic acid resulting in 80% of 2,4,6-trichlorophenol removal in 120 min (Figure 7) and in near-complete degradation in 300 min (*Paper IV, Figure 9*). 2,4,6-Trichlorophenol degraded slower than by dissolved Fe^{3+}-activated H_2O_2 oxidation due to the presence of additional step of iron leaching, which limited the overall degradation rate. The total iron content in aqueous phase after 300 min was 14 µM. Considering acidic reaction media (pH 3) and the presence of tannic acid possessing chelating and reducing properties three main iron dissolution mechanisms were proposed: protonation, complexation, and reduction.

The mechanism of iron dissolution by protonation relies on protons (H^+) binding with an OH-group on the hydrated substrate surface (*Paper IV, Figure 10, step 1, a*). This reaction then weakens the Fe-O bond in ferric oxyhydroxide with slow detachment of surface Fe^{III} species into solution (*Paper IV, Figure 10, step 2, a*). Dissolution by complexation involves the attachment of a chelating compound (tannic acid) onto the ferric oxyhydroxide crystal surface (*Paper IV, Figure 10, step 1, b*). Prior to adsorption, strongly complexing ligands (tannic acid) in the solution exchange for a protonated OH-group bound to the substrate (ferric oxyhydroxide). The surface ion-ligand complex ultimately detaches into the aqueous phase (*Paper IV, Figure 10, step 2, b*). The high polarity of the surface complex in ferric oxyhydroxide weakens the bond strength between iron on the surface and its neighboring atoms facilitating iron dissolution. Dissolution by reduction implies that the Fe^{III} sites on the substrate (ferric oxyhydroxide) surface gain an electron from the adsorbed solute (electron donor) and are reduced to Fe^{II} (*Paper IV, Figure 10, step 2, c*). The newly formed Fe^{II} at the substrate surface has a less stable bond with oxygen than its predecessor Fe^{III}, thus the Fe^{II} is more easily detached from the surface than Fe^{III} (*Paper IV, Figure 10, step 3, c*).

Since protons in the phenolic OH-groups of gallic acid (tannic acid monomer) have pKa of 8.7, 11.4, and above 13 (Eslami et al., 2010), the extent of tannic acid dissociation at pH 3.0 is small and tannic acid was mostly present in solution in undissociated form. As tannic acid deprotonation is required prior to complexation (*Paper IV, Figure 10, b*) and reduction (*Paper IV, Figure 10, c*), the probability of iron dissolution from ferric sludge by these mechanisms is low. Thus, the most evident mechanism of iron dissolution at pH 3.0 is ferric oxyhydroxide protonation with Fe^{III} release to aqueous solution (*Paper IV, Figure 10, a*) followed by Fe^{III} reduction to Fe^{II} by tannic acid in aqueous phase.

The study on 2,4,6-trichlorophenol degradation by Fenton-based processes in the presence of tannic acid highlighted the important role of wastewater organic constituents, which are able to reduce Fe^{3+} and as a result to activate the oxidation supporting the reuse of ferric sludge as a catalyst source.

4. CONCLUSIONS

The effects of reducing agents on the degradation of organic compounds in Fenton-like system with a ferric sludge reuse was studied. The following conclusions can be drawn:

1. The application of the Fenton-based process utilizing ferric sludge as an iron source demonstrated efficacy similar to the classical Fenton treatment and resulted in substantial COD and BOD_7 removal in a municipal landfill, a semicoke landfill area of an oil-shale thermal treatment plant and a plywood manufacturing plant wastewaters. The proposed technological scheme minimizes the production of hazardous solid waste (ferric sludge).
2. Contrary to the promising results obtained in the industrial wastewater treatment experiments, the degradation of the micropollutants (alachlor, diuron and 2,4,6-trichlorophenol) in spiked water by Fe^{3+}/H_2O_2 system exhibited substantially lower degradation rates than that by Fe^{2+}/H_2O_2. The latter served as the basis for the hypothesis on the presence of specific organic constituents in investigated wastewater samples, which facilitated the Fe^{3+} catalytic behavior.
3. Activators, tannic and ascorbic acids, enhanced the catalytic activity of iron in Fe^{3+}/H_2O_2 oxidation of alachlor, diuron and 2,4,6-trichlorophenol confirming the influence of organic substrate on the reactivity of iron, and hence on the degradation rate of organics. The expected increase of HO• formation in Fe^{3+}/H_2O_2 system with addition of either tannic or ascorbic acids was observed. Both activators exhibited Fe^{3+}-reductive properties and boosted the reactivity of the Fenton-like process by improving of iron redox cycling.
4. The kinetic study accomplished by path integral analyses of target compounds concentration versus time indicated that some degradation profiles did not accurately fit into pseudo-first or pseudo-second kinetics resulting in relatively low correlation coefficient values. Therefore, the multiple-step oxidation based on pseudo-first reaction kinetics was assumed to reflect the probable degradation pathway. The estimation of a second-order rate constant for the reaction of HO• with alachlor ($k = 6.9 \times 10^9$ $M^{-1}s^{-1}$) by the deoxyribose method indicated that the reaction rate is close to that of diffusion-controlled reactions in water and hydroxyl radical play the dominant role in oxidation.
5. Phenylacetamide structure intermediates of alachlor oxidation were identified. Two of them have not been reported previously. The oxidation pathway was proposed including hydroxylation reaction, cleavage of hydrogen atoms, scission of the C-N bond, attack of the ether bond, addition reaction to the aromatic ring and cyclization reaction.
6. The acidic conditions (pH = 3) facilitated the release of Fe^{3+} from solid phase of ferric sludge. The subsequent reduction of Fe^{3+} to Fe^{2+} in aqueous phase by tannic acid, constituent of wastewater, promoted the Fenton-like degradation of 2,4,6-trichlorophenol.

This study highlighted the ability of organic reducing agents, constituents of wastewater, to improve iron redox cycle making the application of the ferric sludge reuse as innovative strategy of the Fenton wastewater treatment.

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ABSTRACT

Effects of Organic Reducing Agents on the Fenton-like Degradation of Contaminants in Water with a Ferric Sludge Reuse

The stringent discharge limits of various wastewaters containing xenobiotics, biorecalcitrant and persistent pollutants necessitate the use of the novel methods aiming to improve the quality of discharged effluents. Advanced oxidation processes are widely used in wastewater treatment technology as they demonstrate reaction rates superior to conventional treatment methods and non-selectivity in degradation of refractory substances. Advanced oxidation processes are near ambient temperature and pressure processes aimed to generate hydroxyl radicals in sufficient quantity to oxidize organic pollutants. Among the list of advanced oxidation processes, the Fenton process deserves special attention as its main benefit is potentially convenient and economical way to generate hydroxyl radicals. The traditionally accepted Fenton reaction encompasses the interaction of H_2O_2 with iron ions to form hydroxyl radical. However, several features of this process such as the formation of insoluble ferric oxyhydroxides (ferric sludge) at circumneutral pH and the maximum treatment efficacy in narrow pH range (pH 2-3) are considered as the main disadvantages of the Fenton wastewater treatment and therefore have limited the application of this technology on an industrial scale.

In this study, the reuse of ferric sludge without any regeneration as an iron source in the Fenton-based process was exhibited to overcome the general drawbacks related to this technology. This feasible solution allowed minimizing the production of hazardous ferric waste. To test the proposed technological improvement a municipal landfill leachate, a wood soaking basin effluent from a plywood manufacturing plant and a leachate collected from a semicoke landfill area of an oil-shale thermal treatment plant were subjected for the subsequent Fenton-based treatment. Employing the reused iron-containing sludge during the four treatment cycles showed nearly identical to the classical Fenton improvement in biodegradability as well as substantial chemical oxygen demand and dissolved organic carbon values decrease.

Although the novel Fenton-based wastewater treatment strategy demonstrated the distinctive advantage, the study on Fe^{3+}-mediated H_2O_2 activation mechanism relied only on theoretical basis and therefore continued to engage the attention. The special emphasis was placed on the reactions of wastewater organic constituents and Fe^{3+}. For this reason, the comprehensive study on the degradation of organic contaminants alachlor, diuron and 2,4,6-trichlorophenol by Fenton-like processes in the presence of either ascorbic or tannic acids was conducted to test the ability of water constituents in activation of Fe^{3+}-catalyzed H_2O_2 oxidation using ferric sludge as an iron source. Ascorbic and tannic acids are known to be strong organic chelating agents and reductants. It was assumed that both compounds participate in the iron redox cycling and complexing, and

as a consequence, improve Fenton-based oxidation of contaminants in water supporting therefore ferric sludge reuse.

As a result, investigated activators, ascorbic and tannic acids, enhanced the catalytic activity of iron in Fe^{3+}/H_2O_2 oxidation of alachlor, diuron and 2,4,6-trichlorophenol confirming therefore the influence of organic substrate on the reactivity of iron, hence on the degradation rate of organics. The expected increase of hydroxyl radicals formation in Fe^{3+}/H_2O_2 system with addition of either tannic or ascorbic acids was observed. Both activators exhibited Fe^{3+} reductive properties and boosted the reactivity of the Fenton-like process by improving of iron redox cycling, and as a result enhanced the H_2O_2 oxidation. The identification of the primary alachlor degradation by-products by GC-MS technique indicated the presence of phenylacetamide compounds and allowed the prediction of alachlor probable degradation pathway including the hydroxylation, cyclization reactions, cleavage of hydrogen atoms, scission of C-N bond, attack of the ether bond and HO- addition to the aromatic ring.

This study raised the subject of general Fenton-like chemistry, i.e. the interaction of iron with organic compounds that was observed in Fenton-based wastewater treatment using ferric sludge as an iron source. The proposed technique of ferric sludge reuse may result in an increased treatment efficacy and facilitate the minimization of negative effects concerning the utilization of solid ferric wastes.

KOKKUVÕTE

Orgaaniliste redutseerijate mõju rauasette taaskasutamisega Fenton-tüüpi protsessile reovees sisalduvate saasteainete lagundamisel

Üha karmistuvad keskkonnanõuded ksenobiootilisi ja raskelt lagundatavaid ühendeid sisaldavate reovete puhastamise osas nõuavad uute reoveepuhastustehnoloogiate väljatöötamist ning juurutamist.

Reovee puhastamistehnoloogias kasutatakse järjest enam süvaoksüdatsiooniprotsesse (ingl k advanced oxidation processes ehk AOPs), mille eeliseks võrreldes klassikaliste protsessidega on saasteainete, sealhulgas raskesti lagundatavate ühendite mitteselektiivne ja kiire keemiline oksüdeerimine veekeskkonnas. AOP-d määratletakse kui oksüdatsiooniprotsessi, mis toimub keskkonnatemperatuuril ja rõhul ning mille käigus tekivad kõrge reaktsioonivõimega hüdroksüülradikaalid (HO•), mis oksüdeerivad orgaanilisi saasteaineid. Süvaoksüdatsiooniprotsesside hulka kuuluv Fentoni-protsess väärib erilist tähelepanu, sest selle peamisteks eelisteks on lihtsus ja ökonoomne HO• genereerimine. Klassikalises Fentoni reaktsioonis toimub HO• genereerimine vesinikperoksiidist (H_2O_2) Fe^{2+}-ioonide katalüüsival toimel. Selle reaktsiooni puudusteks on efektiivse oksüdatsiooni toimumine kitsas pH piirkonnas (pH 2-3) ja mittelahustuva raudhüdroksiidi teke neutraalses veekeskkonnas. Need puudused takistavad Fenton-protsessi rakendamist reoveepuhastustehnoloogias tööstuslikus mastaabis.

Käesoleva doktoritöö eesmärgiks oli uurida rauasette taaskasutamise võimalikkust Fenton-tüüpi protsessis rauaallikana (katalüsaatorina) ilma eelneva regenereerimiseta. Pakutud innovaatiline protsess võimaldaks vähendada keemilise sette teket ning sellega lahendada Fentoni protsessi rakendamisega kaasnevat rauasette käitlemise probleemi. Doktoritöö käigus uuriti eksperimentaalselt selle protsessi efektiivsust prügilanõrgvee, puidutööstuse reovee ja põlevkivituhamägede nõrgvee puhastamisel. Eksperimentidest selgus, et protsessi efektiivsus keemilise hapnikutarbe ja lahustunud orgaanilise süsinikusisalduse vähenemise järgi oli samaväärne klassikalise Fentoni protsessi efektiivsusega isegi tekkinud rauasette neljakordsel taaskasutamisel, samuti paranes töödeldava reovee biolagundatavus.

Kuna rauasette taaskasutamisega Fenton-tüüpi protsess osutus efektiivseks, kerkis esile vajadus uurida selle käigus toimuva reaktsiooni mehhanismi, eriti rauasettes sisalduvate Fe^{3+}-ühendite katalüüsivat toimet. Selleks uuriti orgaaniliste saasteainete (alakloori, diurooni ja 2,4,6-triklorofenooli) lagundamist nimetatud Fenton-tüüpi protsessis askorbiin- või tanniinhappe kui aktivaatorite (tugevate kompleksimoodustajate ja redutseerijate) juuresolekul. Eksperimendid näitasid, et uuritavad aktivaatorid suurendasid märgatavalt Fe^{3+}-ühendite katalüütilist mõju alakloori, diurooni ja 2,4,6-triklorofenooli oksüdatsioonile H_2O_2-ga. Samuti leidis kinnitust eeldatav HO• tekke suurenemine askorbiin- ja taniinhapete lisamisel Fe^{3+}/H_2O_2 reaktsioonisüsteemile. Mõlemad aktivaatorid on efektiivsed Fe^{3+} redutseerijad, mille tõttu on nendel oluline roll $Fe^{3+}\leftrightarrow Fe^{2+}$ tsüklis ning H_2O_2 oksüdeerimisvõime suurendamisel rauasette taaskasutamisega Fenton-tüüpi protsessis.

Peamiste alakloori lagunemisproduktide identifitseerimisel integreeritud gaaskromatograafia ja mass-spektromeetria abil tehti kindlaks fenüülatsetamiidi derivaatide olemasolu reaktsioonisegus. Nimetatud analüüsimeetod võimaldas välja selgitada ka alakloori lagunemisreaktsiooni võimalikku mehhanismi, mis sisaldab hüdroksüleerimis- ja tsükliseerimisreaktsioone, C-H ja C-N sidemete lõhustumist ning eetri sideme atakeerimist.

Seega käesolevas doktoritöös tehti eksperimentaalselt kindlaks rauasette taaskasutamise võimalikkus Fentoni-tüüpi protsessis ning põhjendati seda reaktsioonimehhanismi uuringutega. Töö tulemuste juurutamine reovee tehnoloogias võib oluliselt parandada ksenobiootilisi ja raskelt lagundatavaid ühendeid (ka mikrosaasteainete) sisaldava reovee puhastamise efektiivsust ning lahendada Fentoni-reaktsiooni puudutavaid probleeme.

APPENDIX A. PUBLICATIONS

PAPER I

Bolobajev, J., Kattel, E., Viisimaa, M., Goi, A., Trapido, M., Tenno, T., Dulova, N. (2014). Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment. – *Chemical Engineering Journal*, 255, 8-13.

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Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment

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HIGHLIGHTS

- Reused ferric sludge as an effective catalyst for the Fenton-based process.
- Observed a similar Fenton-based treatment efficacy for up to 4 ferric sludge reuses.
- Revealed the effective catalytic properties of ferric-sludge without any prior regeneration.
- Displayed a similar treatment efficiency using dissolved iron or ferric sludge in the catalysed Fenton process.

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ABSTRACT

A mature municipal landfill leachate (S1), a wood soaking basin effluent from a plywood manufacturing plant (S2), and a leachate collected from a semicoke landfill area of an oil-shale thermal treatment plant (S3) were subjected to the Fenton/Fenton-based treatment (H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+} and H_2O_2/sludge systems). The results of ferric coagulation trials indicated a high efficacy in S2; thus, only pre-coagulated samples (cS2) were further treated by the H_2O_2/iron systems. Irrespective of reaction duration, S1 was more recalcitrant to oxidation than cS2 and S3. The optimal COD/H_2O_2 weight ratio for cS2 and S3 was 1:1 with respective 21(35) and 36(45)% residual COD(DOC). In the case of S1, the COD/H_2O_2 w/w of 1:3.45 proved the most efficient with 30 and 35% residual COD and DOC, respectively. The results also indicated an increase in BOD_7/COD ratio and a reduction in the acute toxicity to *Daphnia magna* of the studied wastewater samples after the Fenton/Fenton-based treatment. The application of the Fenton-based process catalysed with iron-containing sludge exhibited efficacies similar to classical Fenton treatment over four reuse cycles. The reuse of ferric sludge without any regeneration as an iron source in the Fenton-based process was displayed as a feasible solution to minimise the production of hazardous ferric waste and reduce the overall cost of the treatment process.

1. Introduction

The Fenton process has been extensively studied and successfully used for the treatment of a wide range of different wastewaters. For example, the Fenton process can be used to treat highly loaded, refractory, toxic and coloured wastewaters which cannot be biologically treated [1–3]. However, the practical application of the Fenton process is limited mainly because of the large amount of ferric sludge produced during neutralisation after oxidation. The solid waste sludge, which is potentially hazardous because of residual organics adsorbed from treated wastewater, requires proper treatment and disposal to specific sites. This resultant sludge is therefore the main obstacle preventing the application of the full-scale Fenton process in industrial wastewater treatment [1].

The iron-containing sludge could be reused as a coagulant for water/wastewater pre-treatment prior the Fenton process, resulting in up to 50% reduction in the required coagulant [4]. However, the ferric sludge could be effectively utilised only once in this type of reuse system. To minimise the above-mentioned sludge formation, two approaches have been investigated: the use of heterogeneous catalysts and the reuse of the iron-containing sludge. The application of a heterogeneous catalyst, such as naturally occurring minerals [5], iron-containing clays [6,7], iron immobilised on a solid support [8,9], and zero-valent iron [10–12], in the Fenton

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process reduces the amount of ferric sludge formed, results in extended periods of catalyst use without regeneration or replacement and efficiently removes the catalyst form the treated wastewater by sedimentation or filtration. The majority of heterogeneous catalysts studied to initiate the Fenton/Fenton-based reaction resulted in additional homogeneous hydrogen peroxide catalysis because of the leaching of ferrous ions into the surrounding solution, notably in acidic condition [5,10].

During the Fenton treatment of wastewater, the oxidation and coagulation of ferric-hydroxy complexes both contribute to the removal of the organic compounds; therefore, the complete elimination of the coagulation step may be undesirable when a high overall process efficacy is desired. Accordingly, the sludge recycling/reusing methods resulting in a lower sludge production than traditional treatment processes could be more preferable than those eliminating the coagulation step. The use of iron-containing sludge as a catalyst for the Fenton process has been performed mainly after thermal regeneration and subsequent re-dissolution of iron-containing solids by acid [13,14], chemical regeneration with reducing agent [15] and electrochemical reduction [16,17]. All mentioned techniques functioned well, but increased the overall cost of wastewater treatment because of the additional sludge regeneration step.

The main objective of this study was to minimise the production of iron-containing sludge by completely reusing it as an iron source in the oxidation part of the Fenton-based treatment. The alternative without any regeneration is proposed to reduce the overall cost of the process without eliminating the coagulation step in the Fenton treatment, which contributes to the overall treatment efficacy of the process.

2. Experimental

2.1. Chemicals and materials

Hydrogen peroxide (PERDROGEN™, ⩾30%) and ferrous sulphate heptahydrate ($FeSO_4·7H_2O$, ⩾99%) were purchased from Sigma–Aldrich, ferric sulphate hydrate ($Fe_2(SO_4)_3·xH_2O$, Fe 21–23%) was obtained from Riedel-de Häen. All other chemicals were of analytical grade and used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System). Sodium hydroxide and sulphuric acid aqueous solutions were used to adjust the pH.

The studied wastewater samples were comprised of: (i) Sample 1 (S1) – a mature municipal landfill leachate (the landfill has operated for more than 10 years) (October, 2013), (ii) Sample 2 (S2) – a wood soaking basin effluent from a plywood manufacturing plant (the wastewater is rich in lignin, water-soluble wood, mechanical particles, and extractives such as terpenes, resin acids, triglycerides, fatty acids, and phenolic compounds) (April, 2013), and (iii) Sample 3 (S3) – a leachate collected from a semicoke (hazardous waste rich in phenols such as phenol, p-cresol, dimethylphenols, resorcinol, 5-methylresorcinol and 2,5-dimethylresorcinol) landfill area of an oil-shale thermal treatment plant (March, 2013). The collected wastewater samples were stored at 4 °C. The main properties of wastewater samples are presented in Table 1.

2.2. Experimental procedure

The coagulation with ferric sulphate (KEMIRA PIX-322, Fe_{total} 12.5 ± 0.3%) was performed in a jar test apparatus (Kemira, Finland). The wastewater volume in each jar was 0.6 L. The coagulant doses (Fe_{total}) varied in the range of 100–1000 mg L^{-1}. The operating conditions were as follows: 1 min of fast mixing at 400 rpm ($G = 956\ s^{-1}$), 30 min of slow mixing at 40 rpm ($G = 30\ s^{-1}$), and 24 h of sedimentation. Afterward, the supernatant was collected for further analysis.

Table 1
General chemical properties of the wastewater samples.

Parameter	S1	S2	S3
COD, mg L^{-1}	5928 ± 280	5145 ± 213	2100 ± 190
BOD_7, mg L^{-1}	3160 ± 190	1607 ± 126	375 ± 11
BOD_7/COD	0.53	0.31	0.18
DOC, mg L^{-1}	2002 ± 12	1260 ± 11	493 ± 1
TN, mg L^{-1}	480 ± 2.3	11.5 ± 0.3	15.5 ± 1.5
Conductivity, μS cm^{-1}	7.2	973	9000
pH	7.32	4.75	7.9
TS (105 °C), mg L^{-1}	6770 ± 70	2549 ± 34	8650 ± 10
TFS (600 °C), mg L^{-1}	3010 ± 230	516 ± 6	7639 ± 17
TSS (105 °C), mg L^{-1}	1900 ± 180	912 ± 140	21 ± 7
F^-, mg L^{-1}	23.5 ± 1.7	62	1
Cl^-, mg L^{-1}	2280 ± 10	557	6146
PO_4^{-3}, mg L^{-1}	–	66	42
SO_4^{2-}, mg L^{-1}	114 ± 3	161	1510
Total phenols, mg L^{-1}	–	51	6
Daphnia magna EC_{50}, %	7.9 ± 1.7	15.3 ± 2.2	19.5 ± 2.9
Lignin and tannins, mg L^{-1}	–	560 ± 10	–

The $H_2O_2/Fe^{2+}(Fe^{3+})$ and H_2O_2/sludge systems with neutralisation/sedimentation step are hereinafter referred to as the Fenton and Fenton-based treatment, respectively. All the Fenton/Fenton-based process trials were performed in batch mode and in non-buffered solutions. Half-litre wastewater samples were treated in 1 L cylindrical glass reactor with a permanent agitation speed (400 rpm) for a period of 1–24 h. The catalyst ($FeSO_4·7H_2O$ or $Fe_2(SO_4)_3·xH_2O$) was added, and after complete dissolution of the catalyst, the Fenton reaction was initiated by adding H_2O_2. The pH of the wastewater samples was not adjusted in the subsequent treatment, if not specified otherwise. The weight ratio of $H_2O_2/Fe^{2+}(Fe^{3+})$ was maintained at 5:1, which is optimal [18]. The oxidation was halted by neutralising the treated samples with NaOH (10 M) to a pH approximately 9 under mechanical stirring. Neutralisation led to the iron precipitating as ferric-hydroxy complexes. This process was followed by an iron sludge settling period of 24 h (for effective thickening of the sludge). Finally, the supernatant was collected for further analysis. During the sludge reuse trials, the additional solid–liquid separation of ferric-hydroxy complexes from the solution was performed by centrifugation (10 min, 4000 rpm). The concentrated sludge was used as an iron source for the Fenton-based oxidation (pH 3) without any chemical or thermal pre-regeneration. The scheme for the ferric sludge reuse in the Fenton-based treatment of wastewater samples is presented in Fig. 1.

The experiments on wastewater oxidation with non-catalysed hydrogen peroxide were conducted in identical reactors and treatment conditions for the respective Fenton treatment trials.

All experiments were duplicated and the data on the initial parameters of wastewater samples were verified with at least three replicates. The results of the analysis are presented as the mean with a standard deviation below 4% in all cases. The experiments were performed at ambient room temperature (22 ± 1 °C).

2.3. Analytical methods

The chemical oxygen demand (COD) was determined with a closed reflux colorimetric method [19]. The correction for the hydrogen peroxide interference on COD test was performed by the correlation equation reported by Kang et al. [20]. The total suspended solids (TSS), total solids (TS), total fixed solids (TFS), and a 7-day biochemical oxygen demand (BOD_7) were determined according to APHA [19]. The acute toxicity of the initial and treated samples to *Daphnia magna* (*Cladocera, Crustacea*) was measured

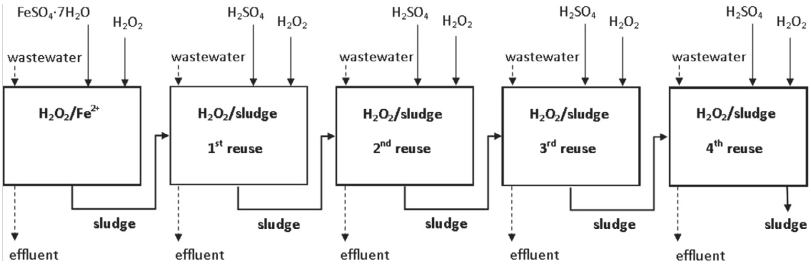

Fig. 1. Wastewater treatment scheme with the iron-containing sludge reuse in the Fenton-based process (all the H_2O_2/sludge systems operated at pH 3).

with DAPHTOXKIT F™ MAGNA (MicroBioTest Inc, Belgium) by a 24-h toxicity test according to ISO 6341 [21]. A computer program PROBIT was used to estimate the half-maximal effective concentration (EC_{50}, immobilisation as the endpoint) and the 95% confidence limits. The pH was measured using a digital pH meter (Schott CG-840, Germany) and the electrical conductivity was measured using a digital EC meter (HANNA Instruments HI9032, USA). The total and ferrous-iron concentration in the solution was measured by the phenanthroline method [19]. The initial hydrogen peroxide concentration in the stock solutions was measured spectrophotometrically at $\lambda = 254$ nm; the residual hydrogen peroxide concentration in the treated samples was measured by a spectrophotometric method with Ti^{4+} [22] by a Heλios-β UV/VIS spectrophotometer (Thermo Electron Corporation, USA). The concentration of F^-, Cl^-, PO_4^{3-} and SO_4^{2-} ions was measured by ion chromatography with chemical suppression of the eluent conductivity (761 Compact IC, Metrohm Ltd., Switzerland). The total concentration of tannin and lignin was measured by a spectrophotometric method using tyrosine adapted from Kloster [23]. The total phenols were measured spectrophotometrically with aminoantipyrine according to ISO 6439 [24]. The dissolved organic carbon (DOC) and total nitrogen (TN) was measured in filtered (Puradisc Aqua, 0.45 μm, CA membrane) wastewater samples by a TOC analyser multi N/C® 3100 (Analytik Jena, Germany). The total organic carbon (TOC) was measured in 10% HCl pre-acidified and 105 °C pre-dried sludge samples by the high temperature combustion system HT 1300 connected to a multi N/C® 3100 (Analytik Jena, Germany).

3. Results and discussion

3.1. Coagulation

An important requirement of effective sludge reuse is the primary removal of the suspended solids from the wastewater by any separation technique such as flocculation, sedimentation, and filtration. Otherwise, the solids could accumulate in the iron reuse cycles because they would be continuously retained within the Fenton sludge.

In the present study, the coagulation process was utilised to remove suspended organic and inorganic compounds from wastewater samples and provide a pre-treatment step before subsequent chemical oxidation for potential reduction in the amount of oxidant required. A commercial formulation containing ferric sulphate was applied as a common coagulant in the treatment of wastewater samples. Based on the TSS of the wastewater samples (Table 1), employing a coagulation process was expected to effectively reduce COD in S1 and S2 and result in low treatment efficacy for S3. Up to 40% and 33% removal of COD and DOC, respectively, was achieved in the S2 pre-coagulated sample, mainly because of a considerable decrease in the TSS ($\geqslant$90%), lignin and tannins ($\geqslant$60%), total phenols ($\geqslant$50%) content. The results of the S1 coagulation showed an effective TSS removal ($\geqslant$90%) with high residual COD and DOC values ($\geqslant$90 and 92%, respectively). The high COD and DOC values indicated that mainly dissolved contaminants were present in the wastewater. For S3, the coagulation process efficacy was expected to be low, and the observed COD and DOC reduction was not higher than 10 and 2%, respectively.

From the results, coagulation proved an effective pre-treatment technique for the plywood manufacturing plant effluent (S2); therefore, only pre-coagulated with Fe_{total} at a dose of 200 mg L^{-1} samples (cS2) were subjected to the Fenton/Fenton-based treatment. S1 and S3 were treated by the Fenton/Fenton-based process without any pre-treatment step.

3.2. The Fenton treatment – optimisation of the process

The results of the coagulation trials indicated that the efficacy of the Fenton-based treatment in S1 and S3 will be mainly because of the oxidation step and subsequent coagulation of the oxidised by-products. The results of cS2 treatment indicate an overall purification efficacy of coagulation and the subsequent Fenton process.

The Fenton oxidation catalysed by Fe^{2+}/Fe^{3+} was applied to the studied samples to demonstrate the difference, if any, in catalysing hydrogen peroxide. Additionally, wastewater samples were treated both with and without adjusting the pH to acidic ~3 values, as required in classical Fenton reactions [25,26]. During the beginning of the oxidation without pH adjustment, a fast decrease in the reaction mixture's pH (initial pH values for S1, cS2, and S3 were 7.32, 4.5, and 7.9, respectively) was observed in all samples/systems. This decrease was because of the acidity of added iron catalyst and hydrogen peroxide and the acidic by-products formation. In the H_2O_2/Fe^{3+} systems, the pH after the treatment was considerably lower than in the H_2O_2/Fe^{2+} system for identical treatment conditions mainly because of the higher Fe^{3+} catalyst acidity (reduction of pH after Fe^{2+} and Fe^{3+} addition 1–1.5 and 4.5–5 units, respectively, for S1 and S3). As a result, the pH values were lower than 2.6 in the oxidation systems of cS2 and S3 after 1 h of oxidation; pre-oxidised S1 pH values were 4.3 and 2.9 for H_2O_2/Fe^{2+} and H_2O_2/Fe^{3+} systems, respectively, indicating a good buffering capacity in the landfill leachate sample. The rates of the Fe^{3+} catalysed Fenton reactions usually reach a maximum at a pH slightly below 3 [25]. Moreover, our previous results of a synthetic dye solution treatment by Fenton-based process (hydrogen peroxide catalysed with Fe^{3+} and pH regulated to 3) indicated a similar efficacy to the classical Fenton process [27]. Thus, according to the results of the reduction in COD and DOC, the efficacy of the Fenton-based treatment was independent of pH and catalyst type for S1, cS2, and S3 after 24, 1 and 2 h of oxidation, respectively. The observed results indicated substantial dependence of the treatment efficacy on the initial chemical characteristics of treated wastewater samples.

In general, considerable improvement in treatment efficacy in the cS2 and S3 samples was observed during the first 1 and 2 h of the Fenton oxidation, respectively (Fig. 2). Further increases in oxidation time, up to 24 h, resulted in 1–3% and 6–8% additional COD and DOC removal, respectively. For S1, Fe^{2+}/Fe^{3+} catalysed hydrogen peroxide systems at pH 3 resulted in an effective treatment both in terms of COD and DOC removal after 4-h of oxidation; in the trials without pH regulation, prolonged oxidation of up to 24 h was needed.

In the treated cS2 and S3 samples, only traces of residual hydrogen peroxide was detected after 1 and 2 h of the Fenton oxidation, respectively. These measurements were performed after neutralisation and 24-h sedimentation steps (usually referred to as the coagulation step in the Fenton process), during which the hydrogen peroxide could auto-decompose. Accordingly, the subsequent treatment efficacy improvement in the prolonged oxidation trials could be explained by the sorption effect of the large amounts of small ferric flocs, which are consistently observed in the Fenton oxidation stage. Similarly, only traces of hydrogen peroxide were observed in the S1 samples treated by Fenton treatment with a 4-h (pH 3) and 24-h (initial pH) oxidation step, respectively.

To compare the Fenton treatment efficacy at similar conditions, the effect of H_2O_2 dosage was investigated after a 24-h oxidation. Determining the optimal oxidant to contaminant ratio is essential to optimise the Fenton-based oxidation. Figs. 3 and 4 present the results of the treatment of the wastewater samples with different hydrogen peroxide to COD weight ratios. All investigated wastewater samples demonstrated a similar connection between COD and DOC removal and oxidant dosage; an increase in the COD/H_2O_2 ratio led to an improvement in wastewater treatment efficacy. Irrespective of reaction duration, S1 was more recalcitrant to oxidation than cS2 and S3. Thus, the 24-h treatment of S1 at a COD/H_2O_2 w/w of 1:1.15 resulted in 62% residual COD. For S2 and S3, at similar treatment conditions (COD/H_2O_2 w/w of 1:1), the residual COD comprised 21 and 36%, respectively. The optimal COD/H_2O_2 weight ratio for cS2 and S3 was 1:1 with respective 35 and 45% residual DOC and with more than 98% of the phenols and 99% of the lignin and tannins removed from S2. For S1, a COD/H_2O_2 w/w of 1:3.45 proved the most reasonable with 30 and 35% residual COD and DOC, respectively.

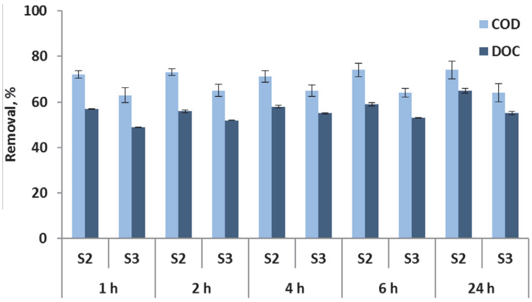

Fig. 2. COD and DOC removal versus the oxidation time during the Fenton treatment of cS2 and S3 at a COD/H_2O_2 weight ratio of 1:1 without pH adjustment.

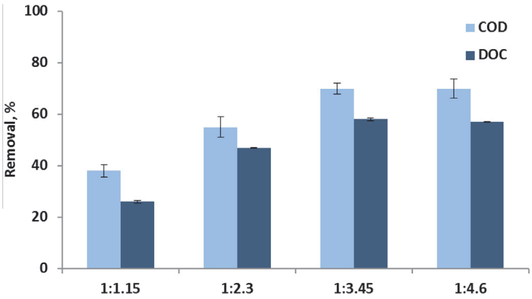

Fig. 3. COD and DOC removal versus the COD/H_2O_2 weight ratio by the Fenton treatment of S1.

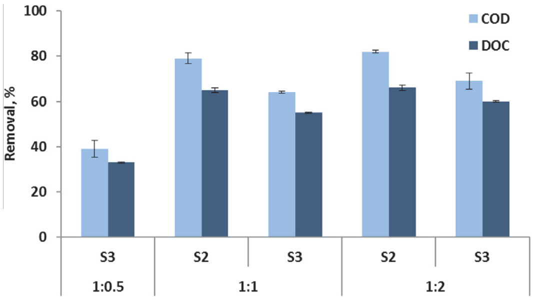

Fig. 4. COD and DOC removal versus the COD/H_2O_2 weight ratio by the Fenton treatment of cS2 and S3.

The oxidative potential of non-catalysed hydrogen peroxide was studied as well. The results of the oxidation of S1 and S3 at a COD/H_2O_2 w/w 1:3.45 and 1:3, respectively, produced a 11% COD removal in both wastewater samples after 24 h of treatment. For cS2, hydrogen peroxide oxidation at a COD/H_2O_2 w/w of 1:1 resulted in more than 50% COD and DOC removal mainly because of the residual iron content (Fe_{total} of 0.09 g L^{-1}) after the coagulation step. However, the addition of an iron catalyst to achieve a H_2O_2/Fe weight ratio 5:1 considerably improved the overall efficacy of the S2 treatment.

3.3. The Fenton-based treatment – sludge reuse

Trials with sludge reused in a 24-h oxidation step and pH of 3 were studied to apply an uniform treatment technique to all the studied samples, to ensure the complete utilisation of hydrogen peroxide and to overcome problems associated with the possible existence of a lengthy lag phase in the ferric sludge catalysed Fenton systems because of iron dissolution. The results indicated almost equal efficacy of both Fe^{2+} and Fe^{3+} catalysed hydrogen peroxide systems in the 24-h treatment of the studied wastewater samples. Therefore, the lower reactivity of ferric ions for initiating the Fenton reaction, as it was observed after 1-h H_2O_2/Fe^{3+} and H_2O_2/Fe^{2+} oxidation (pH 3) for both S1 and S3, could not be considered.

The COD removal remained nearly identical in the four treatment cycles employing the reused iron-containing sludge as presented in Fig. 5. The DOC removal was similar as well throughout the reuse trials. Corresponding to the results of the 24-h Fenton treatment, no residual hydrogen peroxide was observed after the Fenton-based treatment in the reuse systems. Additionally, the concentration of phenols and lignin with tannins was analysed in S2; more than 98% removal of both parameters was observed, which is similar to the results obtained in the Fenton systems catalysed by dissolved iron.

The concentration of dissolved total iron was similar in the reuse trials in the different wastewater samples and resulted in 342 ± 24 mg L^{-1} for S1, 395 ± 42 mg L^{-1} for cS2, and 360 ± 37 mg L^{-1} for S3, which corresponded to H_2O_2/Fe weight ratio of 17.4:1, 7.8:1 and 5.6:1, respectively. In the treatment of S1 by the Fenton-based process, a somewhat lower efficacy can be explained by a lower than the optimal (5:1–6:1) H_2O_2/Fe weight ratio. Moreover, the higher buffering capacity of S1 (when

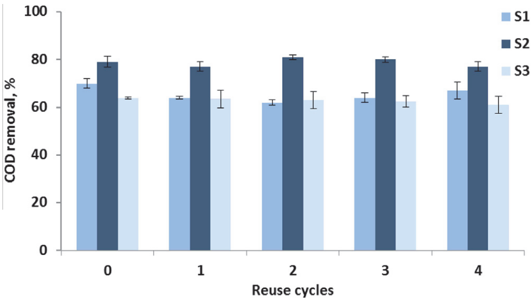

Fig. 5. COD removal by the Fenton treatment using recycled sludge at an optimal COD/H_2O_2 weight ratio.

compared with cS2 and S3) must also be taken into consideration. As a result, the final pH of the oxidised cS2 and S3 samples was lower than 2.6. In the case of landfill leachate sample, no pH decrease was observed.

The possible mechanism of reaction initiated by dissolved Fe^{3+} presented in the ferric sludge catalysed Fenton system may be described as follows [28]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+ \tag{1}$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \tag{2}$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{IV}O^{2+} + HO^{\cdot} \tag{3}$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{V}O^{3+} + OH^- \tag{4}$$

Hydrogen peroxide forms complexes with Fe^{3+}; consequently, a ferric-hydroperoxo intermediate ($Fe(HO_2)^{2+}$) is formed by hydrolysis Eq. (1). According to Ensing et al. [28] this intermediate is able to react directly with organic matter or to decompose into smaller active species in the second reaction step. During the latter scenario, several reaction pathways may be presented: an $Fe(HO_2)^{2+}$ intermediate may decompose forming a $HO_2^{\cdot}$ radical Eq. (2) or $HO^{\cdot}$ radical Eq. (3). Alternatively, the formation of the highly reactive Fe^V species could occur as in Eq. (4).

The heterogeneous catalysis at the surface of ferric-hydroxy complexes may also occur in the H_2O_2/sludge oxidation. The probable mechanism of the heterogeneous Fenton-based reactions, adapted from Lin and Gurol [29], could be described as follows:

$$\equiv Fe^{3+}OH + H_2O_2 \leftrightarrow (H_2O_2)_s \tag{5}$$

$$(H_2O_2)_s \rightarrow \equiv Fe^{2+} + H_2O + HO_2^{\cdot} \tag{6}$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+}OH + {}^{\cdot}OH \tag{7}$$

$$HO_2^{\cdot} \leftrightarrow H^+ + O_2^{\cdot -} \tag{8}$$

$$\equiv Fe^{3+}OH + HO_2^{\cdot}/O_2^{\cdot -} \rightarrow \equiv Fe^{2+} + H_2O/OH^- + O_2 \tag{9}$$

The series of chain reactions is initiated by the formation of a complex of H_2O_2 with the ferric-hydroxy complex surface ($\equiv Fe^{3+}OH$). $(H_2O_2)_s$ represents the hydrogen peroxide attached to the surface of heterogeneous catalyst.

Finally, during the coagulation stage of the Fenton treatment the formed ferric sludge adsorbs organics until the saturation of the sludge sorbing capacity is reached. As a result, the increase in sludge TOC content of up to 25% for all the studied wastewater samples without pre-coagulation and up to 20% for cS2 was observed. The residual organic carbon content was 7.3, 9.1 and 11.6% for S1, S2, and S3, respectively. Notably, the recirculation of sorbed organics with the sludge, whether they are further converted or not, does not alter the overall performance of the process as the sludge will always retain the identical concentration of adsorbed organics. However, after reaching saturation, a certain decrease in the overall treatment efficacy could be observed.

To sum up, all the above-mentioned mechanisms are most likely occurring in the wastewater treatment by the Fenton-based process catalysed by ferric sludge.

A specific feature of S1 was an excessive foam formation immediately after the Fenton oxidation initialisation. Hence, in the case of full-scale landfill leachate treatment by the Fenton process, the addition of a defoaming agent may be required to control foam production through gas evolution, mainly CO_2 and O_2; O_2 is generated during the thermal decomposition of hydrogen peroxide. However, the trials with sludge catalysed hydrogen peroxide oxidation indicated the possibility to overcome this challenge, whereas foam formation was considerably reduced up to a 4-fold volume reduction.

Notably, the continuous reduction in the iron-containing sludge amount (and thus iron concentration; ~5–10% per cycle) during experimental runs was detected; the main reasons to this observation were the loss in ferric precipitate during decantation and centrifugation stages. The correction of test wastewater volume was performed in the reuse trials to ensure the same iron concentration was employed in all treatment steps. In practise, the supplementary Fe^{2+} could be added to correct for the sludge lost in the reuse stage and for faster initiation of the Fenton reaction.

3.4. Biodegradability and toxicity

The direct application of conventional secondary biological treatment to the studied wastewater samples was impossible because of the high level of pollution as indicated in Table 1. Consequently, to assess the options available for subsequent biological treatment of the treated wastewater samples, along with the overall samples' quality improvement, the acute toxicity to *D. magna* and biodegradability of chemically pre-treated samples were evaluated.

The biodegradability of the initial and treated wastewater samples was roughly estimated by the BOD_7/COD ratio and is presented in Fig. 6. The results of the S2 treatment process demonstrated an improvement in biodegradability of up to 65% after the application of ferric pre-coagulation/Fenton process. The Fenton treatment of other studied samples showed moderate increases of up to 20% in the BOD_7/COD ratio. Similar to the COD and DOC reduction in the sludge reuse trials, the BOD_7/COD values remained nearly identical in the four treatment cycles.

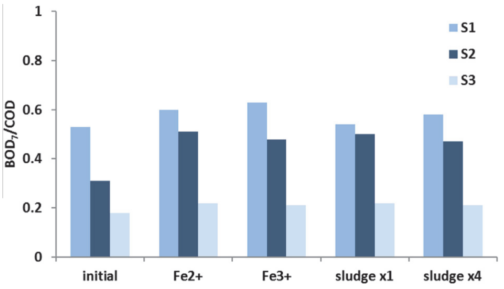

Fig. 6. BOD_7/COD values of the untreated and H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+} and H_2O_2/sludge (1st and 4th reuse) systems (the optimal COD/H_2O_2 w/w ratio, pH 3, 24 h) treated wastewater samples.

Table 2
The acute toxicity to *Daphnia magna* (EC_{50},%) to the initial and treated wastewater samples at the optimal COD/H_2O_2 w/w ratio (pH 3, 24 h).

Sample	Initial	H_2O_2/Fe^{2+} system	H_2O_2/sludge system (1st reuse)	H_2O_2/sludge system (4st reuse)
S1	7.9 ± 1.7	20.6 ± 1.9	18.6 ± 2.2	19.6 ± 2.5
S2	15.3 ± 2.2	80.7 ± 5.5	81.5 ± 4.9	79.2 ± 4.3
S3	19.5 ± 2.9	44.6 ± 4.5	44.9 ± 4.7	40.3 ± 4.2

The results of the acute toxicity to *D. magna* test, presented in Table 2, indicated that the reduction of toxicity in the studied samples after the Fenton treatment was independent of the catalyst applied. Similar to the other studied parameters, the toxicity reduction was steady during the iron-containing sludge reuse steps and nearly identical for the dissolved iron catalysed Fenton system.

As a result, the application of the Fenton-based process to treat wastewater samples was comparable to the classical Fenton process efficacy and could be potentially combined with subsequent biological treatment. Moreover, the reuse of iron-containing sludges, even in a limited number of cycles (not less than 4 times), would substantially minimise the production of hazardous ferric waste and thus reduce the overall cost of the treatment process.

4. Conclusions

The Fenton process both with fresh dissolved catalyst (Fe^{2+}/Fe^{3+}) and reused iron-containing sludge was determined to be an effective technique to treat three different wastewater samples. Two were effectively treated without any pre-treatment and one with a pre-coagulation step. The optimised Fenton treatment resulted in substantial COD and DOC removal in the studied wastewater samples. The application of the Fenton-based process catalysed with ferric sludge behaved similar to the classical Fenton process treatment efficacy during four reuse cycles. According to the results of the biodegradability improvement and the reduction in acute toxicity to *D. magna*, the studied wastewater samples could be potentially subjected to subsequent biological treatment.

The high efficacy of the iron-containing sludge without any regeneration in the Fenton-based treatment of different wastewater samples indicates the possibility to employ the sludge reuse in a wide range of applications. In general, the reuse of iron-containing sludge as an iron source in the oxidation part of the Fenton treatment would substantially minimise the production of hazardous ferric waste and reduce the overall cost of the treatment process.

The proposed technological scheme for the wastewater treatment with the ferric sludge reuse in the Fenton-based process is unique and could provide important information for practical purposes. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Acknowledgments

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PAPER II

Bolobajev, J., Trapido, M., Dulova, N. (2015). Application of different techniques for activation of H_2O_2/Fe^{3+} system: a comparative study. – *Journal of Advanced Oxidation Technologies*, 18(2), 347-352.

Application of Different Techniques for Activation of H_2O_2/Fe^{3+} System: A Comparative Study

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Abstract:

In the present study, the efficacy of L-ascorbic acid (LAA), sodium sulphite (Na_2SO_3), sodium thiosulphate ($Na_2S_2O_3$), and a mixed iron catalyst (Fe^{3+}/Fe^{2+}) to activate Fenton-like (H_2O_2/Fe^{3+}) system was studied and compared. Aqueous solution of a model emerging contaminant (Diuron, DCMU) was used to assess the treatment efficacy of Fenton (H_2O_2/Fe^{2+}) and activated/non-activated Fenton-like systems. The DCMU oxidation in Fenton and Fenton-like systems at a DCMU/H_2O_2/Fe m/m/m of 1/10/1 resulted in more than 99% (in 15 min) and 26% (in 2 h) target compound removal, respectively. The application of inorganic reducing agents (Na_2SO_3 and $Na_2S_2O_3$) to activate the Fenton-like system proved ineffective with a negligible improvement in DCMU degradation as compared to the non-activated Fenton-like system. The application of organic reducing agent (LAA) to activate the Fenton-like system was more promising and demonstrated almost equal DCMU removal efficacy for both the Fenton system at a DCMU/H_2O_2/Fe^{2+} m/m/m of 1/10/1 and LAA-activated Fenton-like system at a DCMU/H_2O_2/Fe^{3+}/LAA m/m/m/m of 1/10/1/1. The DCMU degradation in $H_2O_2/(Fe^{3+}/Fe^{2+})$ system was slower than in the Fenton system, but nevertheless, complete DCMU removal was observed after 2 h of oxidation at a DCMU/$H_2O_2/Fe^{2+}/Fe^{3+}$ m/m/m/m of 1/10/0.2/0.8. The highest mineralisation was observed in the classical Fenton system followed by the mixed catalyst-activated Fenton-like process. The activation of Fenton-like system by mixed iron catalyst (Fe^{3+}/Fe^{2+}) proved to be more feasible for the application in the water or wastewater treatment using un-regenerated ferric sludge catalysed Fenton process.

Keywords: advanced oxidation; Fenton oxidation; mixed iron catalyst; L-ascorbic acid; water treatment

Introduction

Advanced oxidation technologies (AOTs) have been extensively used for the degradation of various organic pollutants found in contaminated water or wastewater (Klavarioti et al. 2009; Benitez et al. 2011; Martins et al. 2011; Dulov et al. 2013; Ghatak 2014). The AOTs can be broadly categorised into chemical, photochemical, photocatalytic, and electrochemical processes. The efficacy of all these AOTs relies on the generation of non-selective and extremely reactive hydroxyl radicals ($HO^{\bullet}$). Among the various AOTs, the Fenton process is one of the most promising methods for water/wastewater treatment (Trapido et al., 2006; Bautista et al. 2008; Jiang et al. 2010; Dulov et al. 2011; Babuponnusami and Muthukumar 2014; Ghatak 2014). In the Fenton process, the $HO^{\bullet}$ is generated from hydrogen peroxide (H_2O_2) when catalysed by ferrous ion (Fe^{2+}) at acidic pH (Eq. 1). The oxidized catalyst (ferric ion, Fe^{3+}) is then reduced as shown in Eqs. 2 and 3, or through the reaction with organic radicals ($R^{\bullet}$) as shown in Eq. 4 (Bautista et al. 2008).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \quad (3)$$

$$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^{+} \quad (4)$$

During the Fenton treatment of the water/wastewater samples, both oxidation and neutralisation processes with subsequent precipitation of ferric-hydroxy complexes contribute to the efficacy of the target contaminants removal. However, the main disadvantages of the Fenton process include the continuous formation of ferric sludge and the necessity of its further handling. Thus, many studies have comprehensively investigated the possibility of sludge recycling or reuse in order to minimize this limitation. In general, all the proposed methods to reduce sludge formation can be divided into three approaches: (i) reuse of sludge as a coagulant for water/wastewater pre-treatment (Yoo et al. 2001); (ii) use of heterogeneous catalysts (Garrido-Ramírez et al. 2010; Dulova et al. 2011; Le-Tuan Pham et al. 2012; Segura et al. 2013; Ramirez et al. 2014; Vaiano et al. 2014); and (iii) the thermal, chemical, or electrochemical regeneration of the iron-containing sludge for

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subsequent use as a catalyst in the Fenton reaction (Kavitha and Palanivelu 2004; Kishimoto et al. 2013; Rossi et al. 2013). The latter was proven to be the most promising solution, but it increased the overall cost of the wastewater treatment due to the consumption of energy and chemicals in the sludge regeneration stage.

Thus, the aim of this research was to study the efficacy of activated Fe^{3+} to catalyze the Fenton reaction and thus, simulate the condition presented in H_2O_2/sludge system. According to Eqs. 2-4, the Fenton reaction could be indirectly initiated by the Fe^{3+}, although this process is usually characterized by a lengthy lag phase and lower efficiency as compared to the classical Fenton system. In order to overcome these limitations, various reducing agents were tested to facilitate faster Fe^{2+} formation in H_2O_2/Fe^{3+} system. Additionally, a partial substitution of Fe^{3+} by Fe^{2+} was studied. The latter simulated the condition of continuous loss of the certain part of iron during the sludge separation procedure and the subsequent addition of fresh ferrous catalyst to replace the lost iron amount. A broad-spectrum and widely used residual herbicide/algaecide Diuron (DCMU) was used as a model micropollutant in order to assess and compare the degradation efficacy of H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}, H_2O_2/Fe^{3+}/(reducing agent), and $H_2O_2/(Fe^{3+}/Fe^{2+})$ systems. The data obtained within this study gives valuable knowledge for further implementation in water/wastewater treatment by means of un-regenerated ferric sludge catalyzed Fenton process.

Experimental

Chemicals and Materials

Diuron ($C_9H_{10}Cl_2N_2O$, ≥ 98%, DCMU), hydrogen peroxide (PERDROGEN™, ≥ 30%), ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, ≥ 99%), ferric sulphate nonahydrate ($Fe_2(SO_4)_3{\cdot}9H_2O$, ≥ 98%), L-ascorbic acid ($C_6H_8O_6$, ≥ 99%, LAA), deoxyribose ($C_5H_{10}O_4$, 97%, DR), trichloroacetic acid ($C_2HCl_3O_2$, ≥ 99%, TCA), thiobarbituric acid ($C_4H_4N_2O_2S$, ≥ 98%, TBA), sodium sulphite (Na_2SO_3, ≥ 98%), and sodium thiosulphate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$, ≥ 99.5%) were purchased from Sigma-Aldrich. All other chemicals were of reagent grade and used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System).

Oxidation Experiments

The H_2O_2/Fe^{2+} and $H_2O_2/Fe^{3+}(Fe^{3+}/Fe^{2+})$ systems are hereinafter referred to as the Fenton and Fenton-like processes, respectively. All the Fenton and Fenton-like process trials were performed in the batch mode and non-buffered solutions at an ambient room temperature (21 ± 1 °C). The DCMU solutions (100 μM, 30 mL) were treated in 50 mL amber glass reactor at a permanent agitation speed for a pre-determined period. The pH of the samples was adjusted to 3 using sulphuric acid (H_2SO_4, 0.5 M). The catalyst ($FeSO_4{\cdot}7H_2O$, $Fe_2(SO_4)_3{\cdot}9H_2O$ or $Fe_2(SO_4)_3{\cdot}9H_2O/FeSO_4{\cdot}7H_2O$) was added, and after its complete dissolution, the Fenton reaction was initiated by adding H_2O_2. The molar ratio of $H_2O_2/Fe^{2+}(Fe^{3+}$, $Fe^{3+}/Fe^{2+})$ was maintained at 10:1, which was found to be an optimal ratio in our previous study (Dulova and Trapido 2011), if not specified otherwise. In the case of H_2O_2/Fe^{3+}/(reducing agent) systems, the reducing agent was added simultaneously with H_2O_2. The oxidation was terminated by the addition of sodium hydroxide (NaOH, 10 M) to achieve a pH > 9. The experiments on DCMU oxidation with non-catalysed H_2O_2 were conducted in identical reactors and treatment conditions for the respective Fenton oxidation trials. All experiments were duplicated, and the results of the analysis were presented as mean with a standard deviation less than 5%.

Rate Constant Determination Experiments

The second-order rate constant for DCMU reaction with $HO^{\bullet}$ was determined according to the method adapted from Halliwell et al. (1987). This technique was based on the competitive reactions of DR and DCMU with $HO^{\bullet}$ generated by the Fenton reagent. All the experiments were conducted in 20 mM H_3PO_4/KH_2PO_4 buffer solution at a pH of 3.0. The reaction mixture (1 mL) consisted of DR (2.8 mM), DCMU (0–250 μM), H_2O_2 (2.0 mM), and Fe^{2+} (200 μM). After 30 min of oxidation, the reaction was stopped by the addition of 1.25 mL of 2.8% (w/v) TCA. Then 1.25 mL of 1% (w/v) TBA was added, and the reaction mixture was heated at 100 °C for 20 min. The chromophore formed was then spectrophotometrically analysed at λ = 532 nm using a Heλios-β UV/VIS spectrophotometer (Thermo Electron Corporation).

Analytical Methods

The concentration of DCMU in filtered (0.45 μm, Whatman™) samples was quantified using a high-performance liquid chromatography combined with diode array detector (HPLC-PDA, Prominence SPD-M20A, Shimadzu) equipped with a Phenomenex Gemini (150 × 2.0 mm, 1.7 μm) NX-C18 (110 Å, 5 μm) column. The isocratic method involving the application of a solvent mixture of 50% acetonitrile and 50% acetic acid aqueous solution (0.1%) was carried out. The flow rate was kept at 200 µL/min. Samples were scanned at 190–800 nm and analyzed at λ = 248 nm. The concentration of DCMU was determined by using the standard chemical to fit the retention time. The pH was measured using a digital pH meter (Schott CG-840). The initial H_2O_2 concentration in the stock solutions was measured spectrophotometrically at λ = 254 nm (the molar extinction coefficient of H_2O_2 at 254 nm is 19.6 L/(mol cm) as suggested by Baxendale and Wilson (1957)) using a Heλios-β UV/VIS spectrophotometer (Thermo Electron Corporation). The total organic carbon (TOC) was measured by a TOC analyzer multi N/C® 3100 (Analytik Jena).

Results and Discussion

First, the second-order rate constant for the reaction between DCMU and $HO^{\bullet}$ was determined in order to prove the feasibility of DCMU as a model micropollutant for assessing the efficacy of Fenton and activated Fenton-like systems. For this, the method based on competitive reactions of DR and DCMU with $HO^{\bullet}$ generated by the Fenton reagent was used. The reaction rate of DR with $HO^{\bullet}$ in the presence of DCMU could be expressed through the absorbance of light (*A*) after 30 min of oxidation (Eq. 5). The absorbance (A_0) is a measure of reaction rate in the absence of DCMU (Eq. 6).

$$A = k_{DR}[HO\,\cdot][DR] \tag{5}$$

$$A_0 = k_{DR}[HO\,\cdot][DR] + k_{DCMU}[HO\,\cdot][DCMU] \tag{6}$$

The rearrangement and combination of the above equations yield the linear dependence between *1/A* and DCMU concentration as presented in Eq. 7. The slope of the line, initial concentration of DR, reaction constant of DR oxidation (k_{DR}=3.1 · 10^9 L/(mol s) (Halliwell et al. 1987)), and A_0 characterizes the second-order rate constant of DCMU oxidation (k_{DCMU}) (Eq. 8).

$$\frac{1}{A} = \frac{1}{A_0}\left(1 + \frac{k_{DCMU}[DCMU]}{k_{DR}[DR]}\right) \tag{7}$$

$$k_{DCMU} = slope \cdot k_{DR} \cdot [DR] \cdot A_0 \tag{8}$$

According to the data obtained from the experiments on $HO^{\bullet}$ scavenging by DCMU, the rate constant for the reaction of $HO^{\bullet}$ with DCMU was 3.3 · 10^9 L/(mol s), which is similar to the value obtained in a previous study conducted by Gallard and De Laat (2001). This demonstrates that DCMU is a good model compound for assessing and comparing the degradation efficacy of Fenton and activated/non-activated Fenton-like systems.

Furthermore, the effect of H_2O_2 dosage on DCMU degradation efficacy in the Fenton oxidation was investigated. The results of the DCMU oxidation at different H_2O_2 to DCMU molar ratios are presented in Figure 1. A faster DCMU degradation was observed with higher H_2O_2 amount in the Fenton's reagent. Thus, the 15-min oxidation of DCMU solution at a DCMU/H_2O_2/Fe^{2+} m/m/m of 1/10/1 resulted in more than 99% DCMU removal, whereas oxidation at a DCMU/H_2O_2/Fe^{2+} m/m/m of 1/5/0.5 resulted in complete DCMU removal only after 2 h of the reaction. The blank oxidative potential of non-catalyzed H_2O_2 was also studied. The results of the oxidation of DCMU aqueous solution at a DCMU/H_2O_2 m/m of 1/10 showed no DCMU degradation during the 2-h treatment. In order to assess the potential of Fenton-like (H_2O_2/Fe^{3+}) system in DCMU degradation, the most effective DCMU/H_2O_2 molar ratio and acidic conditions of the reaction (pH 3) were used. The latter was chosen to reach the maximum rates of the Fe^{3+} activated Fenton reactions (Pignatello et al. 2006). Thus, the indirect initiation of the Fenton reaction by Fe^{3+} was studied at a DCMU/H_2O_2/Fe^{3+} m/m/m of 1/10/1 (Figure 1). The DCMU degradation in Fenton-like system was characterized by a lengthy lag phase (0% DCMU removal in ≥ 15 min) and overall lower efficiency compared to the classical Fenton system with only 26% DCMU degradation after 2 h of oxidation. The possible mechanism of Fenton oxidation initiated by dissolved Fe^{3+} could be described as follows (Ensing et al. 2003; Pignatello et al. 2006):

$$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+ \tag{9}$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \tag{10}$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{IV}O^{2+} + HO^{\bullet} \tag{11}$$

Accordingly, at first, a $Fe(HO_2)^{2+}$ intermediate was formed by hydrolysis as shown in Eq. 9, which was hypothetically able to react directly with the target organics presented in the solution or to decompose forming a $HO_2^{\bullet}$ radical (Eq. 10) or $HO^{\bullet}$ radical (Eq. 11).

In order to improve the efficacy of Fenton-like oxidation of DCMU in aqueous solution, the lag phase, which is intrinsic to the H_2O_2/ Fe^{3+} system, was required to be eliminated or substantially reduced. For this, two inorganic (Na_2SO_3 and $Na_2S_2O_3$) and one organic (LAA) reducing agents were used. Both inorganic reluctant, which were applied to activate the H_2O_2/Fe^{3+} system, demonstrated negligible improvement in DCMU degradation at DCMU/H_2O_2/Fe^{3+}/(reducing agent) molar ratios ranging from 1/10/1/0.1 to 1/10/1/1 compared to the Fenton-like treatment, which had DCMU/H_2O_2/Fe^{3+} m/m/m of 1/10/1. In

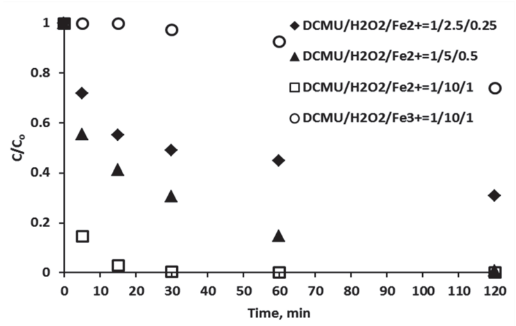

Figure 1. DCMU degradation as a function of time in the Fenton and non-activated Fenton-like oxidation at different reagents molar ratios.

general, the only purpose of using inorganic activators was to reduce Fe^{3+} to Fe^{2+} for facilitating the classic Fenton reaction. In the case of organic activator, the mechanism of activation was expected to be more complex. The LAA was chosen as a mild reducing agent and a good electron donor to promote the free radical reactions. The LAA could potentially be oxidized by the reactive oxygen species (e.g. $HO^{\bullet}$) presented in the Fenton/Fenton-like systems to form a radical ion:

$$HO^{\bullet} + C_6H_8O_6 \rightarrow C_6H_7O_6^{\bullet} + H_2O \qquad (12)$$

Thus, the promotion of Fenton reaction could be attained not only through the direct Fe^{3+} reduction but also in Fe^{3+} reaction with the organic radicals (Eq. 4). The application of LAA in the Fenton-like system considerably improved the overall DCMU degradation efficacy as compared to the non-activated H_2O_2/ Fe^{3+} system (Figure 2). Accordingly, even at a DCMU/ H_2O_2/Fe^{3+}/LAA m/m/m/m of 1/10/1/0.1, a complete DCMU degradation was observed after 2 h of oxidation. A further increase in LAA concentration at the same oxidation conditions resulted in faster DCMU removal and a DCMU degradation profile that was similar to the classical Fenton oxidation (Figure 2). Thus, the DCMU removal efficacy was almost equal for both the H_2O_2/Fe^{2+} system at a DCMU/ H_2O_2/Fe^{2+} m/m/m of 1/10/1 and H_2O_2/Fe^{3+}/LAA system at a DCMU/H_2O_2/Fe^{3+}/LAA m/m/m/m of 1/10/1/1.

The high efficacy of the studied LAA activation of the Fenton-like system was most likely due to the simultaneous oxidation of LAA and DCMU by the Fenton reagent. This resulted in the effective organic radicals induced reduction of Fe^{3+} (Eqs. 4 and 12). Moreover, the negligible efficacy of inorganic reducing agent to activate the Fenton-like system indicated the marginal impact of direct Fe^{3+} reduction to promote the Fenton reaction. Accordingly, in the case of Fenton-like treatment of more complex matrix (e.g. wastewater), the H_2O_2/Fe^{3+} system could be activated by the organic reducing agents or organic species presented in the effluents; the target contaminant may also play the role of such activators. Alternatively, an organic reducing agent may be added simultaneously with the ferric catalyst (e.g. reused ferric sludge) to the treatment system.

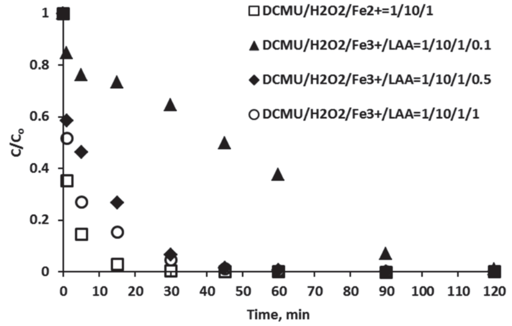

Figure 2. DCMU degradation as a function of time in the Fenton and LAA-activated Fenton-like oxidation at different reagents molar ratios.

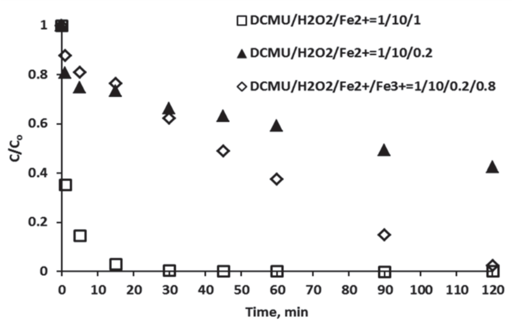

Figure 3. DCMU degradation as a function of time in the Fenton and mixed iron catalyst-activated Fenton-like oxidation at different reagents molar ratios.

In practice, the reuse of ferric sludge occurred with continuous loss of the certain part of iron during the sludge separation procedure. In order to solve this problem, fresh Fe^{2+} could be added not only to compensate for the catalyst lost in the reuse stage but also to facilitate the faster initiation of the Fenton reaction. Thus, the partial substitution of Fe^{3+} with Fe^{2+} was studied in order to simulate the situation that could occur in a full-scale wastewater H_2O_2/sludge treatment. The results of Fenton-like oxidation with mixed catalyst at a Fe^{2+}/Fe^{3+} m/m of 1/4 indicated slower DCMU degradation as compared to the Fenton

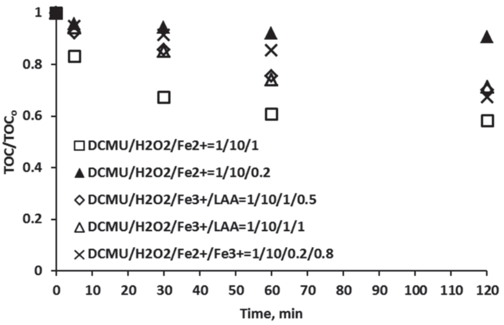

Figure 4. TOC removal as a function of time in the Fenton and activated Fenton-like oxidation at different reagents molar ratios.

system at a DCMU/H_2O_2/Fe^{2+} molar ratio of 1/10/1 (Figure 3). On the other hand, during the oxidation of DCMU with H_2O_2 catalyzed by mixed iron, the complete target compound removal was observed within 2 h of oxidation. The oxidation of DCMU at a DCMU/H_2O_2/Fe^{2+} molar ratio of 1/10/0.2 was also studied, and the result indicated lower efficacy compared to the mixed iron catalyzed system, with more than 40% residual DCMU observed in solution even after 2 h of treatment.

For a detailed comparison between the two H_2O_2/Fe^{3+} system activation techniques, the TOC removal was studied as an indicator of mineralization during DCMU oxidation by Fenton/Fenton-like systems (Figure 4). The highest mineralization was observed in the classical Fenton system followed by the mixed catalyst-activated Fenton-like process. The latter fact makes the oxidation by H_2O_2 activated with the mixed catalyst more favourable than the LAA-activated Fenton-like process, which contrarily resulted in higher residual TOC value of the treated solution due to the organic nature of the activator. Notably, TOC removal was similar at the beginning of the Fenton reaction irrespective of the LAA dose added, indicating a higher residual TOC value for a higher activator dose added. The lowest mineralization was observed in H_2O_2/Fe^{3+} system after 2-h treatment and resulted in less than 5% target compound removal.

Conclusions

The oxidation of organic contaminants by H_2O_2 catalyzed with Fe^{3+} could be activated both by the addition of organic reducing agent and the partial substitution of Fe^{3+} with Fe^{2+}. Both of these activation techniques behaved similar to the classical Fenton process treatment in terms of target compound degradation after 2 h of oxidation. In terms of mineralization, the mixed catalyst addition to the Fenton-like system was more practical than the LAA activation and resulted in lower residual TOC.

The findings of the present study indicated that the reuse of iron-containing sludge as an iron source in the oxidation part of the Fenton treatment could be effectively employed for water and wastewater purification, and as a result could substantially minimize the production of undesirable ferric waste and reduce the overall cost of the treatment process.

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PAPER III

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Improvement in iron activation ability of alachlor Fenton-like oxidation by ascorbic acid

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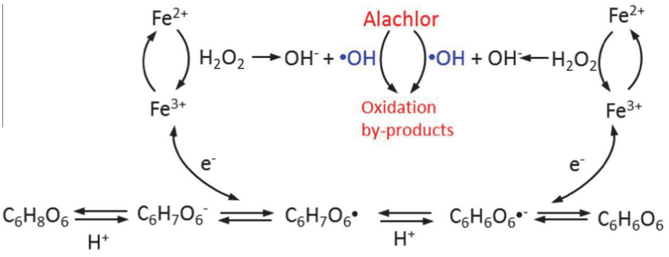
HIGHLIGHTS

- Ascorbic acid reductant with Fe^{3+}/H_2O_2 is a novel treatment method.
- Fe^{3+}/H_2O_2/ascorbic acid and Fenton reagent had similar alachlor oxidation efficacies.
- H_2O_2/ascorbic acid resulted in hydroxyl radical formation and alachlor degradation.
- Oxidation by Fe^{3+}/H_2O_2/ascorbic acid proceeded via hydroxyl radicals.
- Oxidation intermediates were phenylacetamide structure compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

The addition of a strong reductant, L-ascorbic acid (AA), to Fe^{3+}/hydrogen peroxide (H_2O_2) improved alachlor degradation substantially. AA in the form of ascorbate monoanion undergoes a two-step oxidation to yield dehydroascorbic acid through the formation of intermediate semidehydroascorbate and ascorbyl radicals that are responsible for the autocatalytic transformation of Fe^{3+} to Fe^{2+}. The ability of AA to reduce Fe^{3+} to Fe^{2+} and propagate the formation of hydroxyl radicals was confirmed by the indirect measuring of hydroxyl radicals. Hydroxyl radicals production and alachlor degradation by H_2O_2/AA resulted. Alachlor degradation rate by Fe^{3+}/H_2O_2/AA was similar to that obtained by Fe^{2+}/H_2O_2, although a much lower alachlor degradation and mineralization by Fe^{3+}/H_2O_2 was achieved. The kinetics of alachlor removal by Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2/AA were characterized by a rapid decay (0–1 min) because of a higher formation of hydroxyl radicals and then by a slower decay (1–120 min). The determination of a second-order reaction rate constant of hydroxyl radicals with alachlor relied on the competitive reactions of deoxyribose and alachlor with hydroxyl radicals. A rate constant of $6.9 \times 10^9\ M^{-1}\ s^{-1}$ (correlation coefficient of 0.997) implies that the reaction rate is close to that of diffusion-controlled reactions in water, and indicates that the hydroxyl radicals play a predominant role during oxidation. Phenylacetamide compounds that were primary by-products of alachlor degradation allowed for the prediction of the general reaction pathway. This study highlights the ability of AA to reduce Fe^{3+} making a presumption for non-regenerated ferric oxyhydroxide sludge reuse for activation of H_2O_2 oxidation in wastewater treatment at acidic pH.

1. Introduction

Despite the fact that the Fenton process has existed for more than 100 years, its mechanism is not clear and is still under

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discussion, because many factors such as pH, temperature, organic substrate to be oxidized and hydrogen peroxide (H_2O_2) and iron concentrations influence the reaction pathway. The most cited mechanism of the classical Fenton reaction (referred to as the Fenton) was first proposed by Haber and Weiss [1] and then modified by Barb et al. [2] and Walling [3] and consists of a sequence of reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

$$^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (3)$$

$$^{\cdot}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \quad (5)$$

$$Fe^{2+} + HO_2^{\cdot} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (7)$$

Fe^{2+} plays a major role in activation of the Fenton, and promotes the formation of highly reactive species, as hydroxyl radicals ($^{\cdot}OH$). Despite Pignatello et al. [4] reporting that a differentiation of “ferrous-” and “ferric-” type Fenton reactions is meaningless from a mechanistic standpoint because Fe(II) and Fe(III) species are present simultaneously in the chain (Eqs. (1)–(7)), some studies [5] suggest that the effect of Fe^{3+} activation on H_2O_2 oxidation is lower compared with that of Fe^{2+}. In strongly acidic solution without H_2O_2 and complexing agents Fe(III) exist as hexaaquo ion $Fe(H_2O)_6^{3+}$. As the pH increases, the hexaaquo ion of Fe^{3+} (Eq. (8)) undergoes extensive hydrolysis with amorphous ferric oxyhydroxide precipitation [6].

$$Fe^{3+} \leftrightarrow FeOH^{2+} \leftrightarrow Fe(OH)_2^+ \leftrightarrow Fe_2(OH)_2^{4+} \\ \leftrightarrow \text{other polynuclear species} \leftrightarrow Fe_2O_3 \cdot nH_2O(s) \quad (8)$$

Fe^{2+} in the presence of H_2O_2 is oxidized to Fe^{3+} according to Eq. (1) and after H_2O_2 decomposition undergoes a similar reaction pathway described by Eq. (8). Fe^{2+} also tends to co-precipitate with Fe(III) oxyhydroxides if the two ions are present together and the pH is raised above 3. This results in the main disadvantage of the Fenton process on an industrial scale, which is a continuous accumulation of ferric oxyhydroxide sludge formed in clarifiers as a result of coagulation and precipitation in the final stage of wastewater treatment. Nowadays, several modifications of the Fenton, such as solar-, ultraviolet (UV)- or electro-Fenton processes allow for a minimization of the amount of iron in the reaction mixture. However, more complicated reactors are used and the additional energy cost [7,8] for the UV- and electro-Fenton limit the application of these methods.

Sludge recirculation and reuse was proposed as an alternative solution to this problem. Three main methods exist for sludge reuse: (1) thermal treatment of sludge at 300–400 °C to eliminate organic residue and use of the sludge as an activator in the Fenton process [9], (2) use of the sludge as an additive to improve coagulation [10] and (3) electrochemical reduction of sludge Fe^{3+} to Fe^{2+} with its reuse as an activator in H_2O_2 oxidation [11].

Our previous study [12] on the treatment of landfill leachate, wood soaking basin effluent and effluent collected from a semicoke landfill area was based on the reuse of non-regenerated sludge as the activator in Fenton-like oxidation and a substantial reduction in treated wastewater chemical oxygen demand (COD) resulted. However, the study on activation mechanism of the organic substrate oxidation was not performed.

A substantial reduction in pH achieved with high dosages of H_2O_2 required for optimization of the ratio of COD-to-H_2O_2 may change the added sludge iron chemistry (Eq. (8)) with the iron ion leaching into the solution. Based on studies [13–15] of antioxidant and prooxidant action in biological systems (living organisms), Fe^{3+} can be reduced to Fe^{2+} by compounds that possess catecholic, pyrogallolic or quinone structures and as a result, according to Chen and Pignatello [16], Lu et al. [17] and Ortiz de la Plata et al. [18], activate $^{\cdot}OH$ formation from oxygen-derived species such as superoxide and H_2O_2. These organic compounds react with $^{\cdot}OH$ (Eq. (9)) and lead to the formation of intermediate carbon-centered organic radicals ($R^{\cdot}$) [19]. These may then produce the autocatalytic transformation of Fe^{3+} to Fe^{2+} (Eq. (10)).

$$^{\cdot}OH + RH \rightarrow H_2O + R^{\cdot} \quad (9)$$

$$Fe^{3+} + R^{\cdot} \rightarrow Fe^{2+} + R^+ \quad (10)$$

Some reductive compounds can achieve the autocatalytic transformation of Fe^{3+} to Fe^{2+} without H_2O_2. The presence of these compounds or compounds that can be oxidized by H_2O_2 with organic radical formation, in wastewater, or their addition to wastewater may result in an improved iron activation ability of the Fenton oxidation. Knowledge transfer from biological systems to wastewater/water treatment will allow for the effective reuse of non-regenerated sludge for the Fenton treatment of wastewater without any supplementary Fe^{2+}. Thus, a study of the ability of the reductant to reduce Fe^{3+} to Fe^{2+}, and activate the Fenton reaction, presents a high-impact contribution to water/wastewater treatment technology that may result in an increased treatment efficacy and a substantial decrease in treatment cost.

Under various conditions, L-ascorbic acid (AA) can act as a chelating agent, pro-oxidant, oxygen scavenger or Fe^{3+} reductant. These AA reactions have been studied extensively in biological systems [20–22] mainly because of their physiological role. The industrial and commercial use of AA in environmental technology is limited mainly to chemical cleaning and decontamination of oils from metal surfaces as a component in the solvent used [23]. Several scientific studies on the application of AA in soil treatment as an iron chelating agent [24], as an iron reductant that binds to the metal oxide (goethite) surface and results in the iron-reductive dissolution reaction with enhanced 2-chlorophenol oxidation by H_2O_2 [17] and as a chlorinated solvent reduction reagent under alkaline conditions in the presence of iron minerals [25] have been conducted. However, no studies exist on the application of AA with the Fenton reagent for organic contaminant oxidation in aqueous solution.

Studies of the catalytic behavior of Fe^{3+} in wastewater are limited because of the complexity of the matrices investigated [26]. Thus, alachlor-spiked water was used to understand the role and behavior of Fe^{3+} and the reductant in the oxidation of organic substrate with H_2O_2. The applied contaminant, alachlor, (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetanilide, $C_{14}H_{20}ClNO_2$, molecular mass 269.77 g mol^{-1} and CAS No. 15972-60-8) enters water and water bodies as a result of its application as a herbicide. It is moderately persistent in water, is highly mobile and is toxic to aquatic organisms [27]. It has even been detected in drinking water at concentrations below 2 μg L^{-1} [28]. Directive 2013/39/EU includes alachlor as a priority compound related to aquatic ecosystems [29]. The Directive updates the water framework policy and highlights the need to develop new water treatment technologies to deal with this problem. Several modifications of the Fenton treatment, such as photo-Fenton with citrate solution [30], electro-Fenton with boron-doped diamond anode [31] and ultrasound with the

Fenton [32,33] showed a high efficacy in alachlor degradation and supported the pollutant choice in this study.

The main objective of this study was to evaluate the effect of AA to promote iron cycling in ferric iron-activated H_2O_2 oxidation of alachlor. The production of $^{\cdot}OH$ and alachlor degradation and mineralization in $Fe^{3+}/H_2O_2/AA$, $Fe^{2+}/H_2O_2/AA$, AA/H_2O_2 and alachlor/H_2O_2 systems, as well as the autocatalytic transformation of Fe^{3+} to Fe^{2+} in AA/Fe^{3+} and alachlor/Fe^{3+} systems were followed. The second-order rate constant for the reaction of $^{\cdot}OH$ with alachlor was measured by competitive kinetics. By-products of alachlor oxidation were identified by gas chromatography-mass spectrometry and the pathway was proposed. The increase of wastewater treatment efficacy by the presence of Fe^{3+} reducing additives represents an important contribution in the field.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade. Alachlor (PESTANAL® analytical standard 99.2%), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, ⩾99%), H_2O_2 (PERDROGEN®, ⩾30%, w/w), deoxyribose (2-deoxy-D-ribose, ⩾99%), 2-thiobarbituric acid (TBA, ⩾98%), trichloroacetic acid (⩾99%), 1,1,3,3-tetraethoxypropane (⩾96%), AA (⩾99%) and ferric sulfate nonahydrate ($Fe_2(SO_4)_3{\cdot}9H_2O$, ⩾99%) were purchased from Sigma–Aldrich. Solutions were prepared using ultrapure water obtained from a Millipore ultrapure water UV-system (Simplicity®, Billerica, MA, USA, EMD Millipore Corporation). AA solution was prepared using deaerated ultrapure water.

2.2. Alachlor-spiked water treatment

Alachlor-polluted water treatment was performed in a 50 mL batch reactor at ambient temperature (21 ± 1 °C). Alachlor solution (30 mL, 100 μM) was treated with Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$, H_2O_2/AA and H_2O_2. The initial concentration of H_2O_2 was 2.0 mM. The molar ratio of H_2O_2/Fe^{n+} was maintained at 10/1. An equimolar ratio of Fe^{3+} to AA was used. The solution pH was adjusted to 3.0 using a 0.5-M sulfuric acid. The oxidation process was initiated by the addition of H_2O_2 to alachlor solution with the previously added (if required) Fe^{3+} or Fe^{2+}. AA (if required) was added simultaneously with the H_2O_2. The reaction mixture was mixed continuously using a multiple magnetic stirrer. The oxidation process was stopped by increasing the pH above 11 using a 10-M sodium hydroxide solution. All the water treatment experiments were duplicated. The standard deviation of the results was less than 5%.

2.3. Analyses

A $^{\cdot}OH$ concentration was estimated using the deoxyribose method [34] that is based on the reaction of $^{\cdot}OH$ with deoxyribose (DR) to produce the oxidation by-product, malondialdehyde (MDA), which then reacts with TBA.

A 2.8 mM DR solution was oxidized by $^{\cdot}OH$ generated by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, H_2O_2/AA or $Fe^{3+}/H_2O_2/AA$. The pH of the reaction mixture was kept at 3.0 using a 40-mM H_3PO_4/KH_2PO_4 buffer solution. The reaction was stopped by addition of 1.25 mL of a 2.8% (w/v) trichloroacetic acid solution. Then TBA (1.25 mL, 1% (w/v)) was added to react with MDA and the reaction mixture was heated to 90–100 °C for 20 min. The absorbance of resultant pink chromophore (TBA-MDA reaction product) was determined in a 1-cm pathlength cuvette at 532 nm using a Heλos UV–visible spectrophotometer (Beverly, MA, USA, Thermo Electron Corporation). The concentration of $^{\cdot}OH$ was equated with TBA-MDA reaction product using extinction coefficient of 1.56×10^5 M^{-1} cm^{-1} [35]. The $^{\cdot}OH$ production was controlled in the reaction mixtures that containing any one of the components, such as AA, H_2O_2, Fe^{2+} or Fe^{3+}.

The second-order reaction rate constant of $^{\cdot}OH$ with alachlor was estimated according to the calculation procedure proposed by Halliwell et al. [34]. The deoxyribose method was used to measure $^{\cdot}OH$ consumption in alachlor oxidation by the Fenton reaction. The presence of alachlor with the initial concentration varying from 2.0×10^{-4} to 5.0×10^{-4} M resulted in competitive reactions of $^{\cdot}OH$ with alachlor and DR. The estimated time was 30 min.

Total iron and Fe^{2+} concentrations in the Fe^{3+}/AA and Fe^{3+}/alachlor systems were measured photometrically (Heλos UV–visible spectrophotometer, Beverly, MA, USA, Thermo Electron Corporation) at wavelength of 492 nm using the *o*-phenanthroline method [36].

The concentration of alachlor in spiked water was measured using a Shimadzu liquid chromatograph mass spectrometer (LC-MS2020, Japan) equipped with a Phenomenex Gemini (150 mm × 2.0 mm inner diameter) NX-C18 (110 Å pore size, 5 μm particle size) column. Gradient elution was achieved with eluent A, 0.1% CH_3COOH in ultrapure water, and eluent B, acetonitrile at 0.2 mL min^{-1}. The total analysis time was 45 min. The injected sample volume was 20 μL. The gradient elution started at 0% eluent B with a continuous increment to 100% in 30 min. After 5 min at this level, the percentage of eluent B was reduced to 0% and remained isocratic. Mass spectra were scanned over a m/z range of 50–500 with a scan speed of 938 amu s^{-1}. Ionization was performed using an electrospray ionization positive-ion mode, a probe voltage of 4.5 kV and nebulizer and drying gas flow rates of 1.5 and 15 L min^{-1}, respectively. The desolvation line heater temperature and heated block temperature were 250 °C and 400 °C, respectively. The detection limit was 0.1 μM alachlor. Samples for LC-MS analysis were filtered using Millipore cartridge filters (0.45 μm).

The total organic carbon (TOC) was measured using an Analytic Jena TOC analyzer (multi N/C 3100, Germany). TOC analyses were performed without sample pre-filtration.

Liquid–liquid extraction with the three-step addition of dichloromethane to the sample (1/1, v/v) was used to determine the oxidation intermediates. The extract was dried with Na_2SO_4 and filtered through a Millipore Millex-FH cartridge filter (hydrophobic PTFE, 0.45 μM). The extract was concentrated (1/10, v/v) and analyzed using a Shimadzu gas chromatograph mass spectrometer (GC–MS, QP2010, Japan). Samples (2 μL) were injected splitless into a ZB-5MS capillary column (30 m × 0.32 mm inner diameter with a film thickness of 0.25 μm). The injection port temperature was 250 °C. The carrier gas (nitrogen) velocity was 1 mL min^{-1}. The GC column oven was programmed to remain at 80 °C for 2 min, increase from 80 °C to 180 °C at 20 °C min^{-1} and increase to 280 °C at 5 °C min^{-1} and remain at this temperature for 3 min. Mass spectra were obtained using an electron-impact ionization mode and scanned over a m/z range of 40–340 with a scan speed of 1666 amu s^{-1}. An anion source temperature of 230 °C and an interface temperature of 250 °C were applied.

3. Results and discussion

3.1. Formation of hydroxyl radical in Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$ and H_2O_2/AA reaction mixtures

The formation of $^{\cdot}OH$ was followed to estimate the activation efficiency of the Fe^{2+} and Fe^{3+} ions and the influence of AA on $^{\cdot}OH$ propagation in the Fe^{3+}/H_2O_2 reaction mixture (Fig. 1). Hydroxyl radicals formed in Fe^{2+}/H_2O_2 where a maximum concentration was achieved after 10 s. Fe^{2+} added to the Fenton system is oxidized easily to Fe^{3+} by $^{\cdot}OH$ (Eq. (1), reaction rate constant 53 $M^{-1}\,s^{-1}$, [2]) within the first minute of the reaction. The additional formation of $^{\cdot}OH$ was not observed because of the slow reduction of Fe^{3+} to Fe^{2+} followed by Eq. (2) (reaction rate constant 0.02 $M^{-1}\,s^{-1}$, [37,38]). The iron reducing agent, AA, in the $Fe^{3+}/H_2O_2/AA$ system allows for an increase in the formation of $^{\cdot}OH$. However, some delay in $^{\cdot}OH$ production was observed in the $Fe^{3+}/H_2O_2/AA$ within the first min. This delay can be explained by Fe^{3+} reduction to Fe^{2+} in the presence of AA, which leads to deprotonation with dehydroascorbic acid formation (Fig. 2). AA has two ionizable —OH groups, and a dissociation constant in water of 7.94×10^{-5} ($pKa_1 = 4.25$, [39]). At pH 3.0, ascorbic acid is partly presented as ascorbate monoanion (AH^-), which undergoes a two-step oxidation to yield dehydroascorbic acid through the formation of an intermediate semidehydroascorbate and ascorbyl radicals that are responsible for the autocatalytic transformation of Fe^{3+} to Fe^{2+}.

The ascorbate monoanion supports the production of cytotoxic $^{\cdot}OH$ [20], when oxidized by H_2O_2 in the presence of copper or iron activators in biological systems. The ascorbate monoanion has an active hydroxyl group and it is an effective free radical consumer (Eqs. (11) and (12)). It is known, for example, that AA reacts rapidly ($k = 1.6 \times 10^{-4}$ $l\,mol^{-1}\,s^{-1}$; [40]) with perhydroxyl radicals ($HO_2^{\cdot}$). An unreactive ascorbyl radical ($A^{-\cdot}$) is formed with a delocalized unpaired electron [41].

$$AH^- + HO_2^{\cdot} \rightarrow H_2O_2 + A^{-\cdot} \tag{11}$$

$$AH^- + {}^{\cdot}OH \rightarrow H_2O + A^{-\cdot} \tag{12}$$

The immediate and complete reduction of Fe^{3+} to Fe^{2+} after AA addition without H_2O_2 occurred at an equimolar ratio of Fe^{3+} to AA and a pH of 3. A rapid reducing ability of AA related to ferric iron allows forming of $^{\cdot}OH$ according to the Fenton mechanism, where Fe^{2+} plays the role of electron donor. In the mechanism of Fe^{3+} transformation to Fe^{2+} by AA (Fig. 2), the molar ratio of AA-to-Fe^{3+} for the complete reduction of Fe^{3+} could be 1/2. However, the higher ratio of AA-to-Fe^{3+} (1/1) was applied because of AA oxidation by the H_2O_2.

Besides its Fe^{3+} reductive ability (Fig. 2) AA was found [24] to be an effective iron chelating agent that allowed the soluble iron content to be maintained (Fe(III)/AA = 0.8, 1.6 and 3.2, w/w) at neutral pH in water. AA was a very effective organic chemical dechlorinative reduction reagent under alkaline conditions [25]. Therefore, the total effect of AA in the Fenton system will depend on many factors, such as pH and concentration of iron ions and H_2O_2.

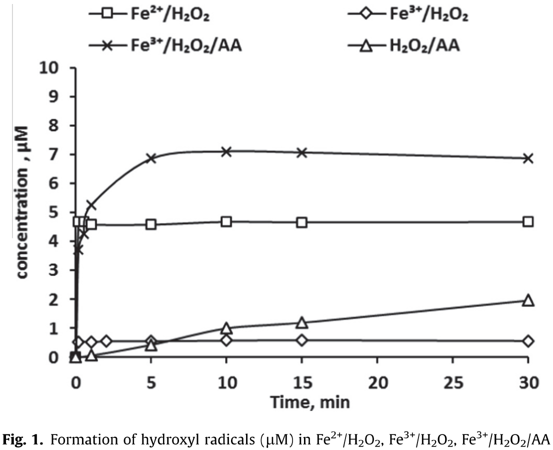


Fig. 1. Formation of hydroxyl radicals (µM) in Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$ and H_2O_2/AA over 30 min. $[H_2O_2]$ = 2.0 mM, $[Fe^{2+}] = [Fe^{3+}] = [AA]$ = 200 µM.

The Fe^{3+}/H_2O_2 showed a weak ability of Fe^{3+} to activate $^{\cdot}OH$ production. According to Eqs. (13) and (14), H_2O_2 forms complexes with Fe^{3+} [42].

$$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+ \tag{13}$$

$$FeOH^{2+} + H_2O_2 \rightarrow Fe(OH)(HO_2)^+ + H^+ \tag{14}$$

However, the rate-limiting step in the Fe(III)-catalyzed decomposition of H_2O_2 is usually the reductive dissociation of the Fe(III)-peroxide complex (Eqs. (15) and (16), [43]) that is the source of Fe(II) involved in the production of $^{\cdot}OH$ according to Eq. (1).

$$Fe(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \tag{15}$$

$$Fe(OH)(HO_2)^+ \rightarrow Fe^{2+} + HO_2^{\cdot} + OH^- \tag{16}$$

Hydroxyl radicals production also occurred in the H_2O_2/AA system (Fig. 1). According to Eq. (17) that was presented by Nappi and Vass [44] in the study of a reaction mechanism to account for cytotoxic activity in some cellular environments, H_2O_2 reacts with the ascorbate monoanion to produce $A^{-\cdot}$ and $^{\cdot}OH$. However, the $^{\cdot}OH$ production in the H_2O_2/AA system was substantially lower than that in the Fe^{3+}-mediated H_2O_2/AA system. In addition, whereas the production of $^{\cdot}OH$ in the iron-mediated systems (Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$) was mostly observed at the beginning of the reaction and then remained constant, $^{\cdot}OH$ in the H_2O_2/AA system was formed within the assay time (up to 30 min). This may also account for the higher $^{\cdot}OH$ formation in the $Fe^{3+}/H_2O_2/AA$ than that in the Fenton. Thus, the synergism of Fe^{3+} reduction and $^{\cdot}OH$ production because of AA addition to the Fe^{3+}/H_2O_2 reaction system can possibly affect contaminant degradation.

$$AH^- + H_2O_2 \rightarrow A^{-\cdot} + H_2O + {}^{\cdot}OH \tag{17}$$

Hydroxyl radicals were not detected in reaction mixtures containing AA, H_2O_2, Fe^{2+} or Fe^{3+}.

3.2. Alachlor oxidation and mineralization by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$, H_2O_2/AA and H_2O_2

The path integral analyses of the alachlor concentration curves versus reaction time indicated that the decomposition rate of alachlor by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$ and H_2O_2/AA followed a pseudo-first order kinetic law and may be described with regard to the alachlor concentration [Ala] by Eq. (18) [45].

$$\frac{d[\mathrm{Ala}]}{dt} = -k_1[\mathrm{Ala}] \tag{18}$$

where, k_1 is the pseudo first-order rate constant. The k_1 was calculated from the slopes of the straight lines by plotting $\ln(Ala_0/Ala)$ as a function of time t, through linear regression. $[Ala]_0$ is the initial concentration of alachlor.

Although $^{\cdot}OH$ formation by $Fe^{3+}/H_2O_2/AA$ was higher than that by Fe^{2+}/H_2O_2, the degradation rate of alachlor by $Fe^{3+}/H_2O_2/AA$ was close to that from Fe^{2+}/H_2O_2 (Table 1), which indicates a fast reduction of Fe^{3+} to Fe^{2+}. Some unsubstantial delays in the degradation of alachlor by $Fe^{3+}/H_2O_2/AA$ (Fig. 3, inset; Table 1) as well as in the $^{\cdot}OH$ formation (Fig. 1) compared to that of the Fe^{2+}/H_2O_2 were observed during the first min of the oxidation that is explained by the time required for the reduction of ferric iron by AA (Fig. 2). The kinetics of alachlor removal by Fe^{2+}/H_2O_2 and

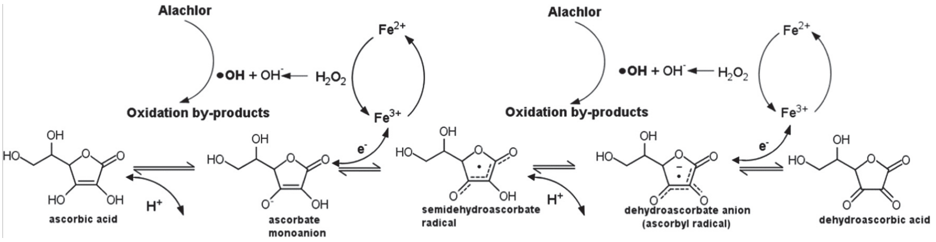


Fig. 2. Proposed mechanism of Fe^{3+} reduction to Fe^{2+} by ascorbic acid that is presented partly as ascorbate monoanion yielding dehydroascorbic acid through the formation of intermediate semidehydroascorbate and ascorbyl radicals, with the propagation of hydroxyl radical production from H_2O_2 and ensuing alachlor oxidation.

Fe^{3+}/H_2O_2/AA was characterized by a rapid (0–1 min) and then a slower decay (1–120 min). This can be explained by a higher concentration of $^{\cdot}OH$ within the first minute of reaction in both treatment systems (Fig. 1), which resulted in more than 90% alachlor degradation. Thus, Fe^{2+} added to the Fenton system or formed by the reductive reaction of Fe^{3+} with AA was easily oxidized to Fe^{3+} by $^{\cdot}OH$ within the first minute of the reaction. The retardation of the reaction can be explained by the slow reduction of Fe^{3+} to Fe^{2+}, which results in the predominant oxidation by $HO_2^{\cdot}$ (Eqs. (2) and (5)–(7)). A rapid reducing ability of AA related to ferric iron allows forming of $^{\cdot}OH$. The formation of $^{\cdot}OH$ in the case of Fe^{3+}/H_2O_2/AA was higher than that in the Fenton within 1–5 min of the treatment time (Fig. 1). This indirectly indicates that AA was not degraded completely prior to alachlor 90% degradation by $^{\cdot}OH$ and the recycling of iron with the oxidation process activation in the Fe^{3+}/H_2O_2/AA system proceeded at least within the first min of the reaction. However, the procedure of AA measurement using HPLC equipped with UV-detector at a wavelength of 265 nm presented by Lin and Liang [25] should be adopted for direct following of AA concentration.

Higher concentration of $^{\cdot}OH$ in the Fe^{3+}/H_2O_2/AA starting from 1 min of the treatment did not result in the improved degradation of the target compound. The $^{\cdot}OH$ formed in excess were probably consumed for the competitive reactions of $^{\cdot}OH$ with AA and by-product of AA and alachlor. The TOC removal in the system alachlor/Fe^{3+}/H_2O_2/AA was close to that of the Fenton; however, taking into account higher TOC content due to the presence of AA in the alachlor/Fe^{3+}/H_2O_2/AA the TOC removal is considered as more effective (Fig. 4). Dehydroascorbic acid, which is formed by the two-step oxidation of AA (Fig. 2), is unstable and breaks down rapidly into diketo-L-gulonic acid, which produces oxalic and L-threonic acids [25,47].

Alachlor degradation by Fe^{3+}/H_2O_2 was slow (Table 1), but continuous during all the treatment time tested achieving only 30% after 120 min (Fig. 3). In spite some low $^{\cdot}OH$ formation in the Fe^{3+}/H_2O_2 without alachlor has been observed already in 10 s of the reaction (Fig. 1), this instantaneous production of $^{\cdot}OH$ at the earlier stage of the treatment is not actually consistent with the rate-limiting step in Fe(III)-catalyzed decomposition of H_2O_2. This is usually reductive dissociation of the Fe(III)-peroxide complex (Eqs. (16) and (17)) formed in the reaction of H_2O_2 with aqueous Fe(III) in acidic media (Eqs. (14) and (15)). Thus, some compounds (the solution became of yellow color) formed in the deoxyribose assay probably interfere with TBA-MDA reaction product in spectrophotometric measurement of $^{\cdot}OH$ concentration using the deoxyribose method proposed by Halliwell et al. [34]. This is complicated the calculation of a true concentration of $^{\cdot}OH$ in the Fe^{3+}/H_2O_2 system. However, small but continuous degradation of alachlor during 120 min of the treatment time suggesting that the production of $^{\cdot}OH$ takes place. Prolonging the time from 30 min to 24 h showed some increase in the measured value calculated as $^{\cdot}OH$ concentration from 0.6 to 1.4 μM, respectively.

The alachlor degradation (Fig. 3) and $^{\cdot}OH$ formation (Fig. 1) by the H_2O_2/AA system were slightly higher than that by the Fe^{3+}/H_2O_2, however, negligible TOC removal (Fig. 4) by the H_2O_2/AA and the Fe^{3+}/H_2O_2 was obtained. The alachlor degradation and $^{\cdot}OH$ formation (Fig. 1) by the H_2O_2/AA indicates that AA in the Fe^{3+}/H_2O_2 system may be involved not only in Fe^{3+} reduction, but also in $^{\cdot}OH$ formation, which results in improved contaminant degradation. Alachlor degradation and TOC removal by unaccompanied H_2O_2 treatment were not observed.

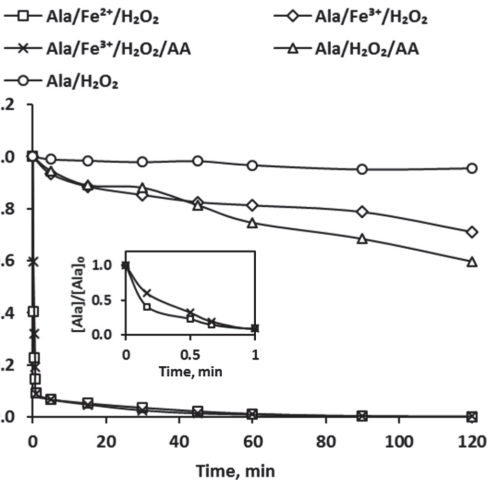


Fig. 3. Degradation of alachlor ($[Ala]/[Ala]_0$, where [Ala] is the alachlor concentration after a certain reaction time and $[Ala]_0$ is the initial concentration of alachlor) by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2/AA and Fe^{3+}/H_2O_2 within 120 min treatment. $[Ala]_0$ = 100 μM, $[H_2O_2]$ = 2.0 mM; $[Fe^{2+}] = [Fe^{3+}]$ = [AA] = 200 μM (inset is the enlargement of alachlor degradation by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2/AA within 1 min treatment).

Table 1
Pseudo-first order reaction rate constant (k_1, min^{-1}) of alachlor degradation by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2/AA, Fe^{3+}/H_2O_2 and H_2O_2/AA measured at different treatment times.

Process	k_1 (min^{-1}), (treatment time, min)	*R^2
Alachlor/Fe^{2+}/H_2O_2	2.7 (0–1 min)	0.906
	3.6×10^{-2} (1–120 min)	0.988
Alachlor/Fe^{3+}/H_2O_2/AA	2.4 (0–1 min)	0.995
	3.0×10^{-2} (1–120 min)	0.978
Alachlor/Fe^{3+}/H_2O_2	2.2×10^{-3} (0–120 min)	0.979
Alachlor/H_2O_2/AA	4.0×10^{-3} (0–120 min)	0.942

* R - correlation coefficient.

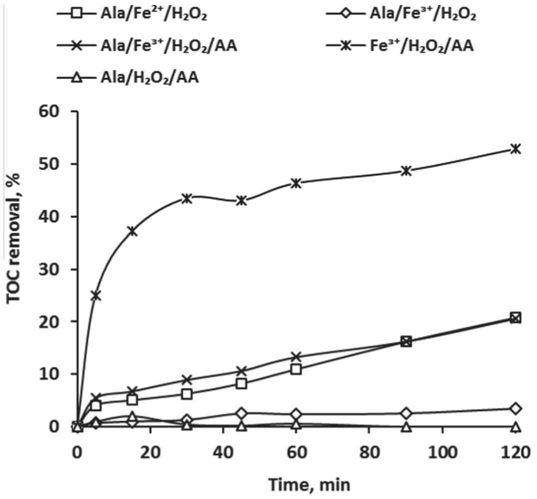


Fig. 4. Removal of TOC (% of initial) during alachlor (Ala) degradation by Fe^{2+}/H_2O_2, $Fe^{3+}/H_2O_2/AA$, Fe^{3+}/H_2O_2, H_2O_2/AA and AA without alachlor by Fe^{3+}/H_2O_2. $[Ala]_0$ = 100 µM, $[H_2O_2]$ = 2.0 mM; $[Fe^{2+}]$ = $[Fe^{3+}]$ = [AA] = 200 µM.

However, alachlor oxidation by Fe^{3+}/H_2O_2 was very slow compared with that by the Fe^{2+}/H_2O_2 (Table 1). In addition, higher alachlor mineralization with Fe^{2+}/H_2O_2 than with Fe^{3+}/H_2O_2 occurred all treatment time (Fig. 4). The mineralization may proceed by reaction (19) assuming that H_2O_2 is the oxidative reactant for the global stoichiometry.

$$2C_{14}H_{20}ClNO_2 + 31H_2O_2 \rightarrow 2NO_3^- + 28CO_2 + 4H_2O + 2Cl^- + 94H^+ \quad (19)$$

Only 3.5% TOC removal was achieved by the Fe^{3+}/H_2O_2 after 120 min of treatment, whereas the Fenton removed 20% of the TOC. The mineralization of AA was 53% in 2 h of the Fenton oxidation. These compounds can mineralize to carbon dioxide and water. Taking into account the substantial dependence of the Fenton oxidation rate on the organic constitutes presented in the reaction mixture, the mathematical differentiation between the TOC of AA and alachlor in the alachlor/Fe^{3+}/H_2O_2/AA using the data from the separate experiments on mineralization of alachlor and AA in Fe^{3+}/H_2O_2 could not give reliable results. Although the presence of AA complicated the estimation of alachlor mineralization by the Fe^{3+}/H_2O_2/AA system, the improvement in alachlor degradation by Fe^{3+}/H_2O_2 with AA addition (Fig. 3) occurred.

3.3. Determination of a second-order reaction rate constant of hydroxyl radicals with alachlor

The second-order rate constant for the reaction of ·OH with alachlor was calculated using the method presented by Halliwell et al. [34] to estimate the role of ·OH to induce the H_2O_2 oxidation. The determination of a second-order reaction rate constant of ·OH with alachlor relies on the competitive reactions of DR and alachlor with ·OH.

The rate (r) of the reaction of ·OH with alachlor, or DR can be described by the following general rate equation [34]:

$$r = \frac{d[^{\cdot}OH]}{dt} \quad (20)$$

where [·OH] is the concentration of ·OH that was equated with TBA-MDA reaction product light absorbance (A) in the presence of alachlor obtained at wavelength of 532 nm in a 1-cm pathlength (l) cuvette using extinction coefficient (ε) of $1.56 \times 10^5\ M^{-1}\ cm^{-1}$ [35] according to Eq. (21).

$$[^{\cdot}OH] = \frac{A}{\varepsilon \cdot l} \quad (21)$$

Substituting [·OH] in Eq. (20) with that of Eq. (21) the rate (r) of the reaction of ·OH with alachlor can be expressed as follows:

$$r = \frac{d(\frac{A}{\varepsilon \cdot l})}{dt} \quad (22)$$

Taking into account that ε and l are constant values, the reaction rate can be expressed as follows:

$$r = \frac{dA}{\varepsilon \cdot l \cdot dt} \quad (23)$$

In a similar way the rate of the reaction of ·OH with DR in the absence of alachlor can be expresses as follows:

$$r_0 = \frac{dA_0}{\varepsilon \cdot l \cdot dt} \quad (24)$$

where A_0 is the absorbance of light in the absence of alachlor.

Then the rate of ·OH with DR in the absence of alachlor is:

$$r_0 = \frac{dA_0}{\varepsilon \cdot l \cdot dt} = k_{DR}[^{\cdot}OH][DR] + k_{Ala}[^{\cdot}OH][Ala]_0 \quad (25)$$

where (k_{DR}) is a reaction rate constant of deoxyribose oxidation by ·OH, [DR] is the initial concentration of deoxyribose, [·OH] is the ·OH concentration, $[Ala]_0$ is the alachlor initial concentration and K_{Ala} is the second-order reaction rate constant.

The rate of ·OH with DR in the presence of alachlor is as follows:

$$r = \frac{dA}{\varepsilon \cdot l \cdot dt} = k_{DR}[^{\cdot}OH][DR] \quad (26)$$

The time of 30 min was fixed for either of the experiment of ·OH reaction with DR in the presence and the absence of alachlor. A linear dependence between 1/A and alachlor initial concentration $[Ala]_0$ can be established (Fig. 5) by transforming Eqs. (25) and (26) to Eq. (27) by dividing of r_0 by r and then to Eq. (28). A plot of 1/A versus $[Ala]_0$ gave a straight line whose slope (Eq. (29)) allows for the calculation through linear regression of the second-order reaction rate constant (k_{Ala}) as given by Eq. (30).

$$\frac{r_0}{r} = \frac{A_0}{A} = 1 + \frac{k_{Ala}[Ala]_0}{k_{DR}[DR]} \quad (27)$$

$$\frac{1}{A} = \frac{1}{A_0}\left(1 + \frac{k_{Ala}[Ala]_0}{k_{DR}[DR]}\right) \quad (28)$$

$$\text{slope} = \frac{k_{Ala}}{A_0 k_{DR}[DR]} \quad (29)$$

$$k_{Ala} = slope \cdot k_{DR} \cdot [DR] \cdot A_0 \quad (30)$$

The slope of a linear function of consumption of ·OH for alachlor oxidation varying $[Ala]_0$ from 2.0×10^{-4} to 5.0×10^{-4} M was calculated based on five duplicated experiments through a linear regression (correlation coefficient of 0.997) (Fig. 5.). The second-order reaction rate constant of ·OH with alachlor was $6.9 \times 10^9\ M^{-1}\ s^{-1}$, using $k_{DR} = 3.1 \times 10^9\ M^{-1}\ s^{-1}$ from Halliwell et al. [34]. This value is consistent with $k_{Ala} = 7 \times 10^9\ M^{-1}\ s^{-1}$ calculated by Haag and Jao [46]. The second-order reaction rate constant of ·OH with alachlor was close to that of a diffusion-controlled rate constant $k_d = 7 \times 10^9\ M^{-1}\ s^{-1}$, which was calculated using Fick's first law of diffusion and the

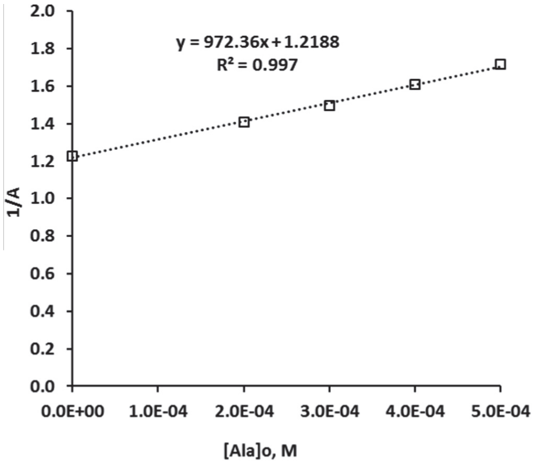


Fig. 5. Consumption of hydroxyl radicals expressed as 1/*A* (*A* is light absorption at 532 nm) for alachlor oxidation by Fe^{2+}/H_2O_2. Initial concentration of alachlor $[Ala]_0$ varied from 2×10^{-4} to 5×10^{-4} M. Dots and line represent experimental results and trend, respectively.

Stokes–Einstein equation. This implies that the reaction rate of $^{\cdot}OH$ with alachlor was close to that of the diffusion-controlled reactions in water, which demonstrates a predominant role of $^{\cdot}OH$ among the other oxidative species in the alachlor oxidation. Thus, the alachlor degradation rate may be limited by the rate of $^{\cdot}OH$ generation and competitive reactions of $^{\cdot}OH$ with other consumers such as AA, iron species and H_2O_2.

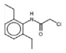
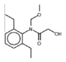
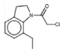
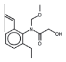
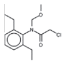
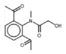
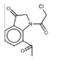
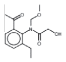
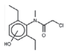
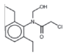
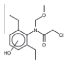
3.4. Alachlor oxidation by-products

An analysis of the MS spectra obtained from the GC–MS and their comparison with the NIST database allowed for the identification of primary intermediates of alachlor oxidation (Table 2, Fig. 6). $^{\cdot}OH$ can attack organic compounds by abstracting H from C–H and O–H bonds or H–N bonds and by addition to C–C bonds, or by conjugating aromatic rings, and the alachlor oxidation pathway can therefore occur in six main ways: (1) hydroxylation, (2) cleavage of hydrogen atoms, (3) scission of the C—N bond, (4) attack of the ether bond, (5) addition reaction to the aromatic ring and (6) cyclization.

Hydroxylation proceeds by substituting –Cl with –OH, whereas alachlor reacts with $^{\cdot}OH$ to form 2-chloro-N-(2,6-diethyl-4-hydroxyphenyl)-N-(methoxymethyl)acetamide (A). The presence of this intermediate in the reaction mixture was also found in the other studies on alachlor degradation by photo-Fenton [30], ozonation [47] and hydrodynamic cavitation [48].

Two compounds on the chromatograms were similar to the mass spectra of compound (A) ($m/z = 251$), but their m/z values differed by 2 units ($m/z = 249$). Thus, cleavage of hydrogen atoms and the appearance of double bonds between carbon atoms may result in the formation of N-(2-ethenyl-6-ethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide (B). This by-product of alachlor degradation was also found by Katsumata et al. [30]. N-(2,6-diacetylphenyl)-2-hydroxy-N-methylacetamide (C) had similar mass spectra with an m/z value of 249, which is identical to (B). The presence of by-product (C) has not been reported previously. The mass spectra of another intermediate N-(2-acetyl-6-ethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide (D) was obtained at a retention time (Rt) of 10.2 min and it is the probable precursor of (C).

Table 2
Alachlor oxidation by-products (m/z values, retention time and structure) identified by GC–MS.

Compound	m/z value	Retention time (min)	Structure
E	225	7.7	
A	251	9.0	
M	223	9.2	
B	249	9.3	
Alachlor	269	9.6	
C	249	9.9	
L	251	10.1	
D	265	10.2	
K	255	10.3	
F	255	11.1	
G, H	285	13.0, 13.8	

2-Chloro-N-(2,6-diethylphenyl)acetamide (E) was formed by C–N bond scission. This compound was one of the major metabolites of alachlor in mammalian organisms, human liver microsomes and urine [49].

Attack of the ether bond led to the formation of 2-chloro-N-(2,6-diethylphenyl)-N-(hydroxymethyl)acetamide (F).

Hydroxyl radicals are prone to aromatic ring and C—C bonds addition. Thus, two isomers (G, H) with an —OH group bound to an aromatic ring, or ethyl groups and m/z values of 285 were identified. Some isomers were degraded to compound (K) with an m/z value of 255 by abstracting the hydroxymethyl group. Cyclisation reactions, which are typical for alachlor oxidation by $^{\cdot}OH$ [30,46], proceeded by intermediate L ($m/z = 251$) and M ($m/z = 223$) formation. However, the precursors of compound L did not exist on the GC-chromatograms.

The oxidation by-products of alachlor can result in organic radical formation (Eq. (9)) and in the competitive AA reduction of Fe^{3+} to Fe^{2+} by electron transfer (Eq. (10)); however, because of their relatively low concentration, this effect is negligible.

Existing and characterized primary by-products allow for the prediction of general reaction pathway (Fig. 6) and secondary reaction intermediates. All primary oxidation intermediates should be degraded to more benign by-products such as chloroacetic acid, acetic acid and methanol, or mineralized to chlorides, nitrates, CO_2 and H_2O. 2,6-Diethylaniline and other aniline derivatives can also be considered to be oxidation by-products, but because of their rapid oxidation, they were not detected.

4. Conclusions

Hypotheses of the improved Fe^{3+} activation ability of the H_2O_2 oxidation of the organic pollutant, alachlor, in aqueous solution

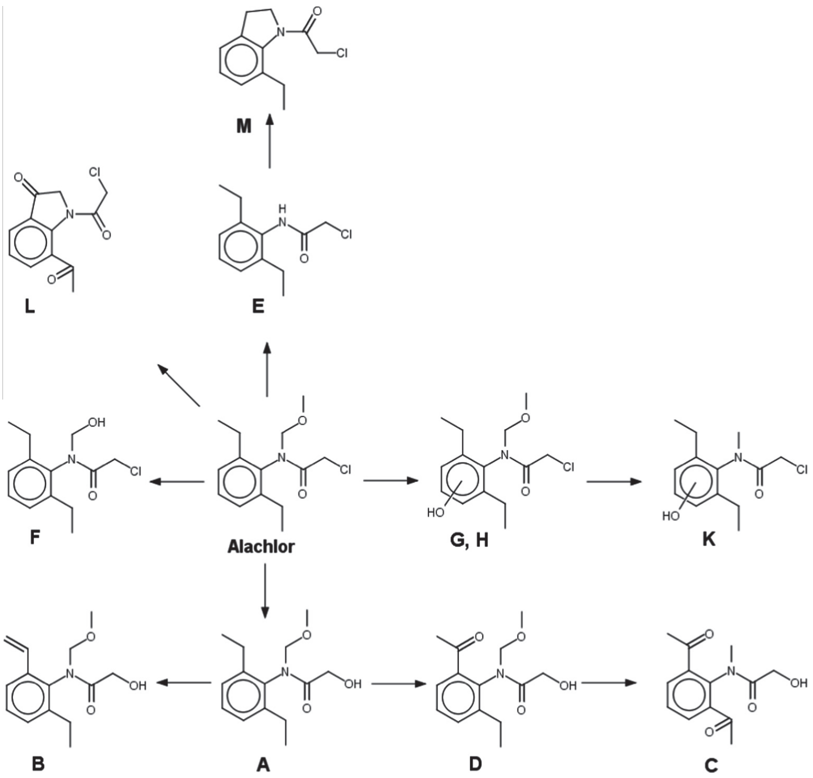


Fig. 6. Proposed mechanism of alachlor degradation.

by organic reductant, AA, was confirmed. The formation of $^{\cdot}$OH and the degradation of alachlor were much lower in the Fe^{3+}/H_2O_2 system than in Fe^{2+}/H_2O_2. AA addition to the Fe^{3+}/H_2O_2 system reduced the Fe^{3+} to the Fe^{2+} immediately by electron transfer with AA deprotonation and dehydroascorbic acid formation. Alachlor degradation in addition to $^{\cdot}$OH production in the H_2O_2/AA indicated that AA in the Fe^{3+}/H_2O_2 system was involved not only in Fe^{3+} reduction, but also in $^{\cdot}$OH production, which resulted in an improved contaminant degradation. However, $^{\cdot}$OH production by Fe^{3+}/H_2O_2/AA was higher than that by Fe^{2+}/H_2O_2 (treatment time of 1–120 min), and alachlor degradation by Fe^{3+}/H_2O_2/AA was similar to that obtained by Fe^{2+}/H_2O_2. Thus, the primary benefit of reductant addition or their availability in wastewater is the autocatalytic transformation of Fe^{3+} to Fe^{2+} that allows for the recycling of non-regenerated ferric oxyhydroxide sludge for the Fenton treatment without any supplementary Fe^{2+}.

A second-order reaction rate constant of $^{\cdot}$OH with alachlor ($6.9 \times 10^9\ M^{-1}\ s^{-1}$) obtained in this study demonstrates the dominant role of $^{\cdot}$OH among other oxidative species in alachlor oxidation.

The proposed oxidation pathways of alachlor include eleven primary intermediates (2-chloro-N-(2,6-diethyl-4-hydroxyphenyl)-N-(methoxymethyl)acetamide, N-(2-ethenyl-6-ethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide, N-(2,6-diacetylphenyl)-2-hydroxy-N-methylacetamide, N-(2-acetyl-6-ethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide, 2-chloro-N-(2,6-diethylphenyl)acetamide, 2-chloro-N-(2,6-diethylphenyl)-N-(hydroxymethyl)acetamide and products with m/z value of 223, 251, 255 (two compounds) and 285) and are followed mainly by hydroxylation, hydrogen atom cleavage, C–N bond scission, ether bond attack, addition to the aromatic ring and cyclization.

The study on the ability of reductants to reduce Fe^{3+} to Fe^{2+} and activate the Fenton reaction, presents a high-impact contribution to water/wastewater treatment technology using non-regenerated ferric oxyhydroxide sludge. This technique may result in an increased treatment efficacy and substantial decrease in treatment cost.

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PAPER IV

Bolobajev, J., Trapido, M., Goi, A. (2016). Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalytic decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment. – *Applied Catalysis B: Environmental*, 187, 75-82.

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Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalytic decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment

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A B S T R A C T

A comprehensive study of the catalytic behaviour of Fe^{3+} in the presence of tannic acid during the Fenton-based treatment of chlorophenols-contaminated water was performed. The ability of the iron-containing sludge to catalyse the Fenton-based process was assessed and the mechanistic behaviour of tannic acid in the iron dissolution was evaluated.

Tannic acid, a constituent of pulp and paper industry water effluent and natural water, enhanced the 2,4,6-trichlorophenol catalytic decomposition in Fe^{3+}-activated H_2O_2 oxidation system by reducing of the Fe^{3+}. The Fe^{3+} reductive mechanism by tannic acid incorporated tannic acid–Fe^{3+} complex formation and decay through an electron transfer reaction to form Fe^{2+}. An indirect measurement of hydroxyl radical ($HO^{\bullet}$) by the deoxyribose method indicated a considerable increase in $HO^{\bullet}$ by Fe^{3+}/H_2O_2 in the presence of tannic acid. A pseudo-first reaction rate constant of 2,4,6-trichlorophenol degradation by Fe^{2+}/H_2O_2 was high and close to that of Fe^{3+}/H_2O_2 with tannic acid. Degradation of tannic acid along with that of 2,4,6-trichlorophenol required optimization of H_2O_2 and Fe^{3+} dosages to balance $HO^{\bullet}$ formation and scavenging.

Acidic reaction media (pH 3.0) and the presence of tannic acid favoured 2,4,6-trichlorophenol degradation by H_2O_2 oxidation induced by iron dissolved from ferric oxyhydroxide sludge. The reuse of ferric oxyhydroxide sludge as a catalyst source in the Fenton–based process can minimise the production of hazardous solid waste and the overall cost of the treatment.

This study highlights the ability of tannic acid-Fe^{3+} complexes to participate in Fe^{3+} reductive pathway and, as a result, to allow reuse of non-regenerated ferric oxyhydroxide sludge for activation of H_2O_2 oxidation in wastewater treatment at acidic pH.

1. Introduction

Degradation by many advanced oxidation processes involves the oxidative reactions of highly reactive hydroxyl radicals ($HO^{\bullet}$) with target organic compounds. In Fenton treatment, transition metals ions, such as the ferrous ion (Fe^{2+}), play a key role in the activation of hydrogen peroxide (H_2O_2) oxidation of organic contaminants to promote the formation of $HO^{\bullet}$ (Eqs. (1)–(7)) [1–3].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad (k = 53\,M^{-1}\,s^{-1}; [4]) \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{2}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{3}$$

$$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{4}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2H^+ \tag{5}$$

$$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2 \tag{6}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{7}$$

In general, the reaction of ferric iron (Fe^{3+}) with H_2O_2 (Eq. (2)) is several orders of magnitude slower than Reaction (1), and thus Reaction (2) can become the rate-limiting step. However, other important reactions with iron ions in Fenton chemistry influence the overall degradation rate substantially. In these reactions, organic compounds may act as ligands (L) to form complexes with iron ions, or act as redox agents resulting in the autocatalytic transformation of iron catalyst. Possible interactions include (1) photolysis of Fe^{3+}–L complexes, (2) formation of reactive high valent iron-oxo or iron-peroxo complexes that are stabilized by

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L, (3) reduction of Fe^{3+} by neutral organic molecules or organic radicals, and (4) oxidation of Fe^{2+} by radicals or carbo-cations [5].

A number of variations of the Fenton reaction has been studied, including those using Fe^{2+} and Fe^{3+} with the supplementary addition of complexing ligands (Interaction (2)) [6,7] or reductants (Interaction (3)) [8,9]. Little is known, however, about the influence of target compounds (treated water constituents) or their degradation by-products [10] on the reactivity of iron.

Chlorophenols are listed as priority pollutants [11] and have been found to be toxic to aquatic environments [12]. They are formed as undesirable by-products of many industrial processes—such as, disinfection of drinking water, production of paper, waste incineration, cooking process and coal pyrolysis—that involve organic compounds and chlorine. Studies on the state of environmental pollution confirm the presence of chlorophenols in surface and ground water, bottom sediments, atmospheric air and soil [13]. Tannins are plant-based polyphenolic compounds that are found in natural water and are known to be bioresistant [14] and toxic to bacteria and fish [15,16]. Chlorophenols and tannins are both found in pulp and paper industrial effluent [17] and natural water [13,18].

Studies on the effective treatment of chlorophenol-containing effluent are significant since large volumes of wastewater are produced. The most widely used treatment method, bio-oxidation, is unable to remove toxic organic pollutants such as chlorophenols completely from wastewater [19]. Based on the principle of best available technique, the use of additional treatment steps is usually required to provide the highest effluent quality. Fenton treatment is applied successfully in sequential mode as a preliminary step in pulp and paper industrial effluent treatment followed by a biological process [20]. This strategy relies on the principle that recalcitrant pollutants tend to be more reactive chemically than biologically, whereas the opposite is typical for their degradation by-products. The Fenton-based process was found to be effective for chlorophenol- [21–24] and tannin-contaminated water [25] and pulp and paper industry effluent [20,26] treatment.

Despite Perez et al. [26] findings that Fenton and photo-Fenton reactions were highly effective for pulp and paper water effluent treatment, practical applications of Fenton-based treatment processes may be limited by sludge generation. Fe^{3+} formed in Reactions (1), (4), and (6) is known to precipitate as amorphous ferric oxyhydroxide (undesirable (ferric) sludge in technological applications) with increases in pH from strongly acidic to neutral. In our previous study [27], wastewater from different industrial sites, including tannins-containing wood-soaking basin effluent from a plywood manufacturing plant was subjected to Fenton-based treatment using non-regenerated ferric sludge as activator. Although the application of this method resulted in a substantial reduction in treated wastewater chemical oxygen demand, a study of activation mechanism of the H_2O_2 oxidation with ferric sludge was not performed. Studies of the catalytic behaviour of Fe^{3+} in wastewater are usually limited because of the matrixes complexity. In a study that tested the ability of ascorbic acid to improve Fe^{3+} activation of alachlor Fenton-like oxidation [9], it was assumed that some wastewater constituents and their degradation by-products are similar to ascorbic acid in organic radical formation and in the reduction of Fe^{3+} to Fe^{2+} by electron transfer. The effect of reductive agent, hydroxylamine, in assistance of Fe(III)/Fe(II) redox cycle on the iron-loaded natural zeolite surface and enhancement the generation of $HO^•$ via decomposition of H_2O_2 was observed in the study of Fukuchi et al. [8]. Non-regenerated ferric sludge may therefore be reused for the activation of H_2O_2 oxidation in wastewater treatment at acidic pH.

Tannins are strong transition metal-chelating [28] and -reducing [29] agents. They exhibit antioxidation (act as $HO^•$ scavengers) [30] and pro-oxidation (promote $HO^•$ generation in the presence of transition metals) [31] properties in biological systems (living organisms). Thus, the presence of tannins in the reaction mixture may hypothetically influence the efficacy of Fenton treatment by promoting the ability of iron ions by Interactions ((2), (3)) to activate oxidation. In the study of Rodriguez et al. [32], the supplementary addition of catechols, compounds that possess similar transition metal-reducing properties [33] to those of tannins, to pulp-bleaching effluent increased the fraction of organo-halogen compounds that was removed in the Fenton-based process. Chlorophenols degradation by-products as quinone- and hydroquinone-structure compounds [33–35] may assist the Fenton oxidation by reducing Fe^{3+} to Fe^{2+} or acting in the form of semiquinone radicals as electron-transfer catalysts between the dihydroxycyclohexadienyl radical ($HO^•$ adduct of phenol) and Fe^{3+} [5].

Although the Fenton-based process is an essential contributor to chlorophenol oxidative transformation in natural water [13], its mechanism is still under discussion, since many factors in the natural environment, such as matrix composition, pH, and temperature influence the reaction pathway. Iron is among the most abundant elements of natural water that is involved in many redox reactions including with H_2O_2 and organic compounds. The effect of tannins that are also found among constituents of natural water on the Fe^{3+} reduction and the Fenton-based process efficacy is of notable interest. Nevertheless, studies on mechanistic behaviour of tannic acid in the Fenton-based processes have not been reported.

In this research, the ability of tannic acid (TN) to interact with Fe^{3+}, promote the activation of H_2O_2 oxidation of 2,4,6-trichlorophenol (TCP), and assist reuse of ferric sludge as a source of iron catalyst in wastewater Fenton-based treatment was assessed. TCP degradation, the dechlorination, $HO^•$ production, and H_2O_2 consumption in Fe^{3+}/H_2O_2 in the presence and absence of TN and Fe^{2+}/H_2O_2 were studied. The mechanistic behaviour and ability of TN to form complexes and to reduce Fe^{3+} at pH 3.0 were evaluated. This study on the influence of water constituents on Fe^{3+} to Fe^{2+} reduction contributes substantially to Fenton-based treatment efficacy and creates a hypothesis for studies on chlorophenols transformation routes in the presence of TN in natural water. The novelty of the study is the understanding of the mechanism of the sludge reuse for the Fenton oxidation in the presence of the reductive agents as TN a major constituent of the wastewater.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical grade. TCP ($Cl_3C_6H_2OH$, ≥97%), TN ($C_{76}H_{52}O_{46}$, ASC grade reagent), ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, ≥99%), ferric sulphate nonahydrate ($Fe_2(SO_4)_3{\cdot}9H_2O$, ≥99%), hydrogen peroxide (H_2O_2, ≥30% w/w), 2-deoxy-D-ribose ($C_5H_{10}O_4$, ≥99%), 2-thiobarbituric acid ($C_4H_4N_2O_2S$, ≥98%), trichloroacetic acid (Cl_3CCOOH, ≥99%), and 1,1,3,3-tetraethoxypropane ($(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2$, ≥96%) were purchased from Sigma–Aldrich. Solutions were prepared using ultrapure water obtained from a Millipore ultrapure water UV-system (Simplicity®, EMD Millipore Corporation, Billerica, MA, USA).

2.2. TCP-spiked water treatment

Treatment of a 10 μM TCP aqueous solution (1 L) with Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, ferric sludge/H_2O_2, and H_2O_2 was performed in a batch reactor at ambient temperature (21 ± 1 °C) and under acidic conditions (pH 3.0). The initial concentrations of H_2O_2

were 100 and 400 μM, which corresponds to a TCP/H_2O_2 molar ratio of 1/10 and 1/40, respectively. The molar ratio of Fe^{n+}/H_2O_2 was maintained at 1/10, which is close to that of 1/11 predicted theoretically for 2,4-dichlorophenol degradation by Tang and Huang [21]. Two initial concentrations of 10 and 50 mg L^{-1} TN were tested. These concentrations were indicative of TCP and TN concentrations found in pulp and paper (bleached kraft) mill effluent [36]. Solution pH was adjusted using a 0.5 M sulfuric acid or 0.1 M sodium hydroxide solution. The oxidation process was initiated by simultaneous addition of Fe^{n+}, or ferric sludge and H_2O_2 to TCP solution with the previously added TN (if required). The reaction mixture was mixed continuously using a multiple magnetic stirrer. Oxidation was stopped by 0.1 M Na_2SO_3 solution addition (1/2, v/v). Ferric sludge was synthesized by mixing sodium hydroxide and ferric sulphate solutions with further filtration and washing out of sodium sulphate from precipitate. Dried sludge (50 mg) was added to the treated solution (1 L). The treatment times were 120 min and 300 min for soluble iron/H_2O_2 and ferric sludge/H_2O_2, respectively. For evaluation of the adsorption of TCP to the hydroxide surface the solution of TCP was mixed with ferric sludge for 300 min and the TCP concentration in bulk solution was measured. All samples after ferric sludge/H_2O_2 treatment were filtered using Millipore (Express® plus, EMD Millipore Corporation, Billerica, MA, USA) membrane filters. All water treatment experiments were duplicated. The standard deviation of the results was less than 5%.

2.3. Analyses

The $HO^\bullet$ concentration was estimated using the deoxyribose method [37]. This method is based on the reaction of $HO^\bullet$ with 2-deoxy-D-ribose to produce an oxidation by-product, malondialdehyde (MDA), which then reacts with 2-thiobarbituric acid (TBA). A 2.8 mM 2-deoxy-D-ribose solution was oxidized by $HO^\bullet$ generated by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, and Fe^{3+}/H_2O_2/TN. The reaction mixture pH was kept at 3.0 using a 40 mM H_3PO_4/KH_2PO_4 buffer solution. The reaction was stopped by addition of 1.25 mL of a 2.8% (w/v) trichloroacetic acid solution. TBA (1.25 mL, 1% w/v) was added and the reaction mixture was heated to 90–100 °C for 20 min. The absorbance of resultant pink chromophore (TBA-MDA reaction product) was determined in a 1-cm-pathlength cuvette at 532 nm using a Heλos ultraviolet-visible spectrophotometer (Thermo Electron Corporation, Beverly, MA, USA). The $HO^\bullet$ concentration was equated to the TBA-MDA reaction product using an extinction coefficient of 1.56×10^{-5} M^{-1} cm^{-1} [38]. $HO^\bullet$ production was controlled in the reaction mixtures that contained any of the components, such as TN, H_2O_2, Fe^{2+} or Fe^{3+}.

Chloride ion (Cl^-) was detected using an ion chromatograph (761CompactIC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm × 4.0 mm inner diameter) analytical column.

Total iron and Fe^{2+} concentrations in the Fe^{3+}/TN and Fe^{3+}/TN/H_2O_2, and Fe^{2+}/H_2O_2 systems were measured photometrically at 492 nm using the *o*-phenanthroline method [39]. H_2O_2 in the reaction mixture was analysed photometrically at 410 nm as a complex of H_2O_2 with Ti^{4+} [40]. Absorption spectra of TN, Fe^{3+}, and the TN-Fe^{3+} complex in solutions prepared under identical conditions to those of the water treatment experiments were recorded between 250 and 700 nm. The TCP concentration in spiked water was measured using a high performance liquid chromatograph (YL-Instrument 9300, Young Lin Instrument Corporation, Hogye-dong, Anyang, Korea) equipped with a Waters Bridge (150 mm × 3.0 mm inner diameter) C18 (3.5 μm particle size) column. Light absorbance was measured by ultraviolet-visible photometric detector at 295 nm. Isocratic elution was achieved with 40% eluent A (0.1% CH_3COOH in ultrapure water), and 60% eluent B (acetonitrile) at 0.2 mL min^{-1}. The total analysis time was 22 min. The injected sample volume was 20 μL. The detection limit was 0.1 μM TCP.

Table 1
Pseudo-first order reaction rate constant (k_1, min^{-1}) of TCP degradation by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, and ferric sludge/H_2O_2 with and without TN.

Process	k_1 (min^{-1}), (Treatment time, min)	R^2
TCP/Fe^{2+}/H_2O_2 = 1/1/10	6.3×10^{-2} (0–120)	0.987
TCP/Fe^{3+}/H_2O_2 = 1/1/10	2.1×10^{-3} (0–120)	0.970
TCP/Fe^{3+}/H_2O_2 = 1/1/10	7.2×10^{-3} (0–60)	0.989
$[TN]_0$ = 50 mg L^{-1}	4.1×10^{-3} (60–120)	0.993
TCP/Fe^{3+}/H_2O_2 = 1/1/10	4.0×10^{-2} (0–60)	0.995
$[TN]_0$ = 10 mg L^{-1}	1.7×10^{-2} (60–120)	0.998
TCP/Fe^{3+}/H_2O_2 = 1/4/40	5.8×10^{-3} (0–40)	0.960
	2.1×10^{-1} (60–90)	0.997
TCP/Fe^{3+}/H_2O_2 = 1/4/40	1.4×10^{-1} (0–30)	0.997
$[TN]_0$ = 50 mg L^{-1}	5.1×10^{-2} (30–90)	0.992
TCP/H_2O_2 = 1/10 [ferric sludge]$_0$ = 50 mg L^{-1} $[TN]_0$ = 10 mg L^{-1}	1.2×10^{-2} (0–300)	0.997
TCP/H_2O_2 = 1/40 [ferric sludge]$_0$ = 50 mg L^{-1} $[TN]_0$ = 50 mg L^{-1}	8.7×10^{-3} (0–300)	0.991
TCP/H_2O_2 = 1/40 [ferric sludge]$_0$ = 50 mg L^{-1}	2.7×10^{-3} (0–300)	0.965

R–correlation coefficient.

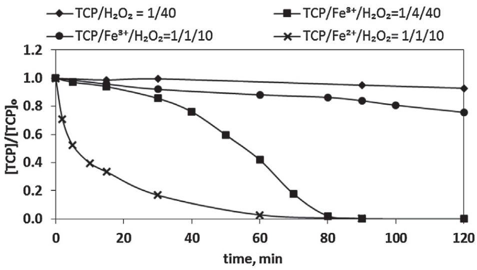

Fig. 1. TCP degradation by Fe^{3+}/H_2O_2 ($[TCP]_0$ = 10 μM, $[Fe^{2+}]_0$ = 10 μM, $[Fe^{3+}]_0$ = 10 or 40 μM, $[H_2O_2]_0$ = 100 or 400 μM) within 120 min treatment.

3. Results and discussion

3.1. TCP degradation by Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 in the absence of TN

A kinetic study accomplished by path integral analyses of TCP concentration curves versus time indicated that TCP degradation in the Fenton-based processes followed a pseudo-first order kinetic law. The pseudo-first order reaction rate constant (k_1) according to Eq. (8) is calculated from the slope of the straight line by plotting ln($[TCP_0]$/[TCP]) as a function of time (t) by linear regression.

$$ln\left(\frac{[TCP]_0}{[TCP]}\right) = k_1 \cdot t \tag{8}$$

Kinetic analyses of TCP degradation curves indicated a multiple-step Fenton-like reaction pathway in some cases, where each step can be characterized by an individual reaction rate constant (Table 1). TCP degradation profiles analysed without suggested multiple-step reaction pathway fit to pseudo-first or pseudo-second kinetics with substantially lower correlation coefficient values.

The degradation of TCP by Fe^{3+}/H_2O_2 = 1/40 (M/M) was followed by a lag-phase (Table 1, Fig. 1). Fe^{3+}/H_2O_2 is known as a Fenton-like system and is able to oxidize organic compounds. The detailed investigation of Fenton-like system general reaction (Eq. (2)) indicated the formation of H_2O_2-Fe^{3+} complexes (Eqs. (9) and (10)) with their decomposition to hydroperoxyl radicals ($HO_2^\bullet$) and Fe^{3+} reduction (Eqs. (11) and (12)) [41]. Besides $HO_2^\bullet$, $HO^\bullet$ can be formed according to the classical Fenton pathway (Eq. (1)).

$$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+ \quad (9)$$

$$Fe(OH)^{2+} + H_2O_2 \rightarrow Fe(OH)(HO_2)^+ + H^+ \quad (10)$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \quad (11)$$

$$Fe(OH)(HO_2)^+ \rightarrow Fe^{2+} + HO_2^\bullet + OH^- \quad (12)$$

The Fe^{3+}/H_2O_2 process is known to be less reactive than Fe^{2+}/H_2O_2 [42] because of a rate-limiting step of the reductive dissociation of the Fe(III)-peroxo complex (Eqs. (11) and (12)) in the Fe(III)-catalysed decomposition of H_2O_2. While in Fenton-like treatment only the highest molar ratio of $TCP/Fe^{3+}/H_2O_2/ = 1/4/40$ results in complete TCP degradation in 90 min treatment time (Fig. 1), the kinetics of TCP removal by Fe^{2+}/H_2O_2 is characterized by a more rapid decay without any lag-phase at a four-times lower ratio of $TCP/Fe^{2+}/H_2O_2/ = 1/1/10$ (Table 1).

The organic substrate to be oxidized and its degradation by-products (intermediates) may influence the efficacy of the Fenton-based oxidation process substantially. For example, quinone-structure compounds formed as phenol intermediates and its derivative oxidation shuttles electrons from the $HO^\bullet$ adduct of the starting aromatic compound to Fe^{3+}, thereby facilitating the degradation of starting aromatic compounds [5]. Hydroquinones and catechols are known to reduce Fe^{3+} to Fe^{2+} under acidic conditions and therefore accelerate the production of $HO^\bullet$ by the classical Fenton reaction (Eq. (1)) [5,33]. An estimation of initial Fe^{2+} oxidation rate in the reported conditions using a rate constant value of $53\,M^{-1}\,s^{-1}$ [4] for Reaction (1) yields a half-life of about 2 min, which is not consistent with a prolonged depletion in the Fe^{2+}concentration profile of the Fe^{2+}/H_2O_2 system (Fig. 2). In addition, slow but remarkable increase of Fe^{2+} was observed after 30 min. Both findings led to the assumption of Fe^{3+} reducing process by TCP degradation intermediates reflecting therefore on Fe^{2+} concentration profile in reaction mixture.

Several researchers have indicated the formation of quinone-, hydroquinone-, and catechol-structure intermediates, as 2,6-dichloro-1,4-benzoquinone, 2,6-dichloro-1,4-dihydroxybenzene, and 3,5-dichlorocatechol, during TCP degradation by the advanced oxidation (in particular, the Fenton-like process) [34,35,43]. Thus, it is reasonable to assume the multiple-step oxidation mechanism of TCP by Fe^{3+}/H_2O_2 with an initial oxidation step characterized by a slow TCP degradation rate (lag-phase) (Eqs. (1) and (9)–(12)) and a subsequent acceleration (Table 1) provided by the reaction (Fe^{3+} reduction and electron transport) of intermediates.

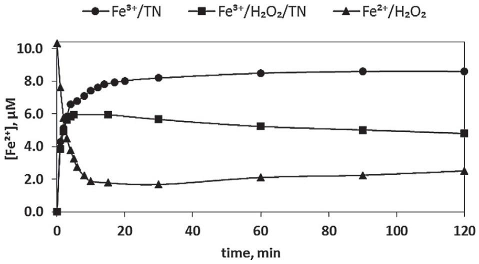

Fig. 2. Concentration profile of Fe^{2+} (µM) during degradation of TCP by Fe^{3+}/TN, Fe^{3+}//H_2O_2/TN, and Fe^{2+}/H_2O_2. $[TCP]_0 = [Fe^{2+}]_0 = [Fe^{3+}]_0 = 10\,\mu M$, $[H_2O_2]_0 = 100\,\mu M$, $[TN]_0 = 10\,mg\,L^{-1}$.

No TCP degradation by unaccompanied H_2O_2 treatment resulted.

3.2. Formation and reactivity of Fe^{3+}-TN complexes in catalytic decomposition of TCP by Fenton-based process

The addition of TN, a major constituent of the real wastewater, to the reaction mixture increased the degradation rate of TCP by the Fe^{3+}/H_2O_2 system substantially (Table 1). The role of TN in activation of the H_2O_2 oxidation by Fe^{3+} can be explained by its molecular structure (Fig. 3), which consists of several monomers of gallic acids attached to each other by depside bonds, or to a central polyol (such as glucose) by ester bonds [44]. Gallic acid is known to form unstable complexes with Fe^{3+}, which then decay by electron transfer. In aqueous solutions, $Fe(OH)^{2+}$ (Eq. (13)) is a dominant species of Fe^{3+}-hydroxo complexes at pH 3.0 [45].

$$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+ \quad (pK_a = 2.54) \quad (13)$$

According to the investigation of Hynes and Coinceanainn [46] on the kinetics and mechanism of gallic acid reactions with Fe^{3+}, two complexes of Fe^{3+} with gallic acid, protonated $[Fe(LH)]^{2+}$ and deprotonated $[Fe(L)]^+$, are formed from pH 1.0 to 3.0. These complexes then decay through an electron transfer reaction to form Fe^{2+}

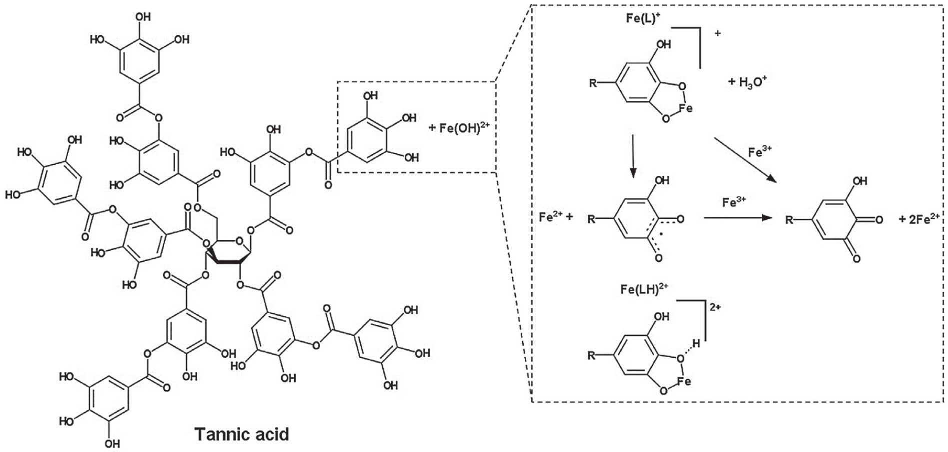

Fig. 3. Proposed mechanism of Fe^{3+} reduction by TN. $Fe(LH)^{2+}$ and $Fe(L)^+$ are protonated and deprotonated complexes, respectively.

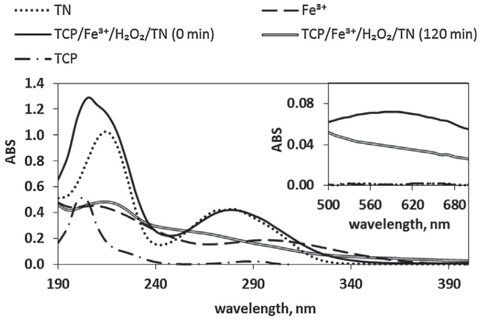

Fig. 4. Light absorption spectra of Fe^{3+}, TCP, TN, and TCP/Fe^{3+}/H_2O_2/TN reaction system (inset is the enlargement of Fe^{3+}-TN complex absorbance in the Fe^{3+}/H_2O_2 treatment system at pH 3.0 in the beginning of the reaction and after 120 min). $[TCP]_0 = [Fe^{3+}]_0 = 10\ \mu M$, $[H_2O_2]_0 = 100\ \mu M$, $[TN]_0 = 10\ mg\ L^{-1}$.

and the quinone group. Spectrophotometric studies on the complexity of TN with Fe^{3+} at pH 3.0 demonstrated an absorption area of a TN-Fe(III) complex with its maximum at 580–600 nm (inset of Fig. 4) and TN maximum absorbance at 215 and 280 nm (Fig. 4). In the study by Sungur and Uzar [28], a maximum absorbance of the TN-Fe(III) complex at pH < 3.0, pH 3.0–7.0, and pH > 7.0 was recorded at 620, 600, and 500 nm, respectively.

The reduction of Fe^{3+} in the Fe^{3+}/H_2O_2 system in the presence of TN was also confirmed experimentally (Fig. 2). The mass ratio of Fe^{3+}/TN was 1/18 in these experiments. The theoretical stoichiometric ratio of Fe^{3+}/TN for the complete reduction of Fe^{3+} cannot be calculated because of the polymeric structure of TN and the uncertain number of bounded gallic acid monomers. According to the spectrophotometric investigations, Fe^{3+} was at least partially complexed by TN at the beginning of the treatment and was still present in the solution at lower concentration after 120 min treatment (the absorbance of the Fe(III)-TN complex was reduced; see inset of Fig. 4). The Fe^{2+} concentration profile in Fe^{3+}/H_2O_2/TN indicated the competitive reactions of Fe^{3+} reduction by TN and H_2O_2 oxidation of Fe^{2+} mediated by the Fenton chemistry (Eqs. (1), (4), and (6)). The concentration of Fe^{2+} was reduced from 5.9 to 4.8 μM within 15–120 min. In addition, competitive reactions of Fe(III)-TN complex formation and TN oxidation occurred. Spectrophotometric analysis showed a substantial decrease in TN absorbance (Fig. 4) and TN-Fe^{3+} complex (500–700 nm) absorbance after 120 min of H_2O_2 oxidation (inset of Fig. 4). Some extension of TN peak (λ to 400 nm) absorbance indicated structural changes of TN molecules attacked by oxidative species ($HO^\bullet$, $HO_2{}^\bullet$). Kalyanaraman et al. [25] found that TN was degraded effectively by the Fenton treatment with the formation of low molecular weight compounds. Fragments of gallocatechin, gallic acid, catechin, $C_8H_8O_2$, and $C_9H_{12}O$ were observed in gas chromatographic spectrometric analysis. This also explains the difference in concentration of Fe^{3+} reduced by TN in the presence and absence of H_2O_2 (Fe^{3+}/TN/H_2O_2 and Fe^{3+}/TN, Fig. 2).

In addition to TN degradation, which was confirmed indirectly by spectrophotometric studies, an increased consumption of H_2O_2 in the TCP/Fe^{3+}/H_2O_2/TN reaction mixture was observed (Fig. 5). A 120 min treatment time was required for near-complete degradation of TCP by applying higher dosages of H_2O_2 ($[H_2O_2]_0 = 400\ \mu M$) and TN ($[TN]_0 = 50\ mg\ L^{-1}$) and lower dosages of H_2O_2 ($[H_2O_2]_0 = 100\ \mu M$) and TN ($[TN]_0 = 10\ mg\ L^{-1}$) (Fig. 6). This indicates an excessive consumption of H_2O_2 with regards the target compound. Although elevated dosages of H_2O_2 are of necessity in case of higher concentration of TN, the reciprocal removal of TN (toxic constituent of water) and H_2O_2 (toxic oxidising chemical) is of a practical importance.

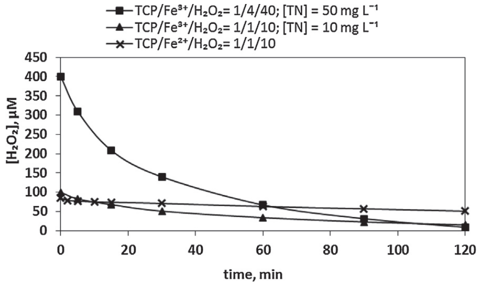

Fig. 5. H_2O_2 consumption during TCP treatment by Fe^{3+}/H_2O_2/TN and Fe^{2+}/H_2O_2. $[TCP]_0 = 10\ \mu M$, $[H_2O_2]_0 = 100$ or $400\ \mu M$, $[Fe^{3+}]_0 = 10$ or $40\ \mu M$, $[Fe^{2+}]_0 = 10\ \mu M$, $[TN]_0 = 10$ or $50\ mg\ L^{-1}$.

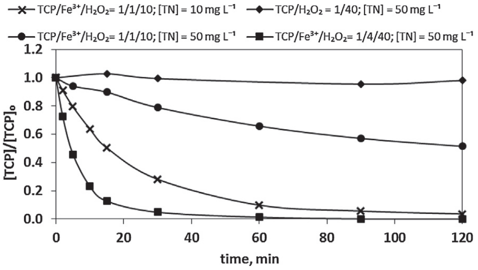

Fig. 6. TCP degradation by Fe^{3+}/H_2O within 120 min treatment in the presence of TN. $[TCP]_0 = 10\ \mu M$, $[Fe^{3+}]_0 = 10$ or $40\ \mu M$, $[H_2O_2]_0 = 100$ or $400\ \mu M$, $[TN]_0 = 10$ or $50\ mg\ L^{-1}$.

Thus, similar to that found in biological systems [30,31] TN in Fenton-based contaminated water treatment possesses antioxidant properties—as a hydroxyl radical scavenger that is autocatalytically degraded—and pro-oxidant properties—as a Fe^{3+} reductant. That should result in the effective purification of pulp and paper industry effluent, where, besides chlorophenols, TN is among the major constituents requiring degradation.

3.3. TCP degradation by Fe^{3+}/H_2O_2 in the presence of TN

TCP degradation in the presence of TN followed pseudo-first order reaction kinetics with a multiple-step reaction mechanism. Contrary to results obtained in the kinetic study of the Fe^{3+}/H_2O_2 system, the degradation of TCP in the presence of TN proceeded without any lag phase in the first step with a higher pseudo-first order reaction rate constant of TCP degradation than in the second one (Table 1). TCP degradation was only slightly slower by Fe^{3+}/H_2O_2 in the presence of TN than by the classical Fenton (Fe^{2+}/H_2O_2 = 1/10).

Contrary to our previous study [9], where ascorbic acid—another Fe^{3+} reductant—was able to degrade the target pollutant by $HO^\bullet$ (generated from H_2O_2 through direct electron transfer and proton donation from the ascorbate anion to H_2O_2 with its subsequent decomposition to $HO^\bullet$) independent of mediation by transition metals, TN addition to H_2O_2 alone resulted in no TCP oxidation (Fig. 6).

Expected $HO^\bullet$ formation was observed in Fe^{3+}/H_2O_2 with the addition of TN. Instantaneous formation of $HO^\bullet$ in Fe^{2+}/H_2O_2 (Fig. 7) and the relatively fast release of reduced Fe^{2+} in Fe^{3+}/H_2O_2/TN (Fig. 2) implied an unexpected decrease in $HO^\bullet$ concentration by Fe^{3+}/H_2O_2 in the presence of TN. The unsubstantial delay in TCP degradation by Fe^{3+}/H_2O_2/TN (Table 1) and the decrease in $HO^\bullet$ concentration compared to Fe^{2+}/H_2O_2 (Fig. 7) could be explained

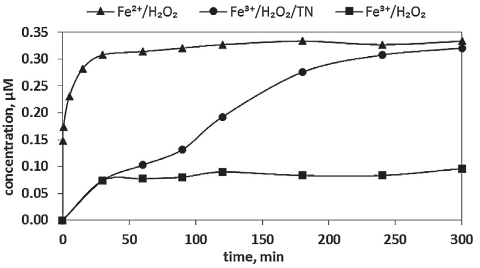

Fig. 7. Formation of hydroxyl radicals in $Fe^{3+}/H_2O_2/TN$, Fe^{3+}/H_2O_2, and Fe^{2+}/H_2O_2. $[Fe^{3+}]_0 = [Fe^{2+}]_0 = 10\,\mu M$, $[H_2O_2]_0 = 100\,\mu M$, $[TN]_0 = 10\,mg\,L^{-1}$.

by the $HO^{\bullet}$ scavenging properties of TN. Although TN scavenged $HO^{\bullet}$ and resulted in the considerable H_2O_2 consumption (Fig. 5), the degradation of TN is among the benefits of the treatment, as TN is a major constituent of the water requiring degradation.

Structure of TN hypothetically can yield organic radical species. According to the study of Fukushima and Tatsumi [24] such organic radical formation can result in the incomplete dechlorination of TCP, because the chlorinated species from TCP are able to bind to TN. Therefore, dechlorination of TCP after 120 min of the treatment by Fe^{3+}/H_2O_2, Fe^{2+}/H_2O_2 and $Fe^{3+}/H_2O_2/TN$ was evaluated. Both treatment systems, Fe^{2+}/H_2O_2 and $Fe^{3+}/H_2O_2/TN$, resulted in close dechlorination of 82 and 78% (of theoretical maximum formed Cl^-), respectively, while the treatment with Fe^{3+}/H_2O_2 allow to achieve only 2% of dechlorination. 24.6, 23.3 and 0.5 µM of Cl^- in Fe^{2+}/H_2O_2, $Fe^{3+}/H_2O_2/TN$ and Fe^{3+}/H_2O_2 were formed, respectively. This indicated that the addition of TN to Fe^{3+}/H_2O_2 was effective for dechlorination in TCP degradation.

After 300 min, the $HO^{\bullet}$ production level was equal to that of Fe^{2+}/H_2O_2, which indicates that the Fe^{3+}-reducing properties of TN propagate $HO^{\bullet}$ formation. $HO^{\bullet}$ production in $Fe^{3+}/H_2O_2/TN$ was substantially higher than that in the Fe^{3+}-mediated H_2O_2 system without TN, which supports the assumption that TN is able to boost the Fenton reaction. $HO^{\bullet}$ was not detected in reaction solutions that contained sole TN, H_2O_2, Fe^{2+} or Fe^{3+}.

Thus, the observed reduction of Fe^{3+}, $HO^{\bullet}$ formation along with H_2O_2 consumption, and rapid TCP degradation with high dechlorination support the ability of TN, despite its radical scavenging properties, to boost the Fenton-based process utilising Fe^{3+} as a catalyst of H_2O_2 oxidation. A similar chlorophenol transformation route may occur in the natural environment since (1) chlorophenols [13] and tannins [18] are formed by natural transformation routes and exist in natural water; (2) transition metal-reductive properties of tannins in natural water have been observed [18]; and (3) H_2O_2 and Fe^{2+} found in natural water [47,48] may initiate Fenton-based processes.

The results demonstrated TN participation in the iron ion redox cycling and as the consequence improved Fenton-based oxidation of contaminants in water.

3.4. Ferric sludge for catalytic decomposition of TCP by Fenton-based process in the presence of TN

Under strongly acidic conditions without H_2O_2 and complexing agents, Fe(III) exist as the hexaaquo ion $Fe(H_2O)_6{}^{3+}$. With increase in pH, the hexaaquo ion of Fe^{3+} (Eq. (14)) undergoes extensive hydrolysis with amorphous ferric oxyhydroxide precipitation [49].

$$Fe^{3+} \leftrightarrow FeOH^{2+} \leftrightarrow Fe(OH)_2{}^{+} \leftrightarrow Fe_2(OH)_2{}^{4+} \leftrightarrow \text{otherpolynuclearspecies} \leftrightarrow Fe_2O_3{\cdot}nH_2O(s) \quad (14)$$

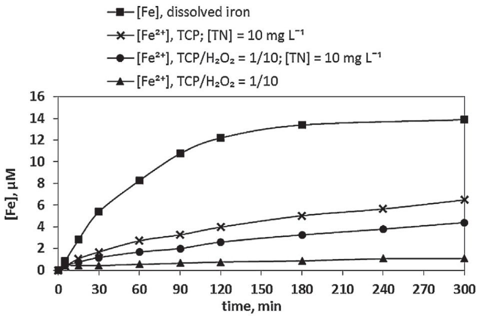

Fig. 8. Effect of TN on iron dissolution in 50 mg L^{-1} ferric sludge suspension and on Fe^{3+} reduction of sludge in H_2O_2 treatment of TCP. $[TCP]_0 = 10\,\mu M$, $[H_2O_2]_0 = 100$ or 400 µM.

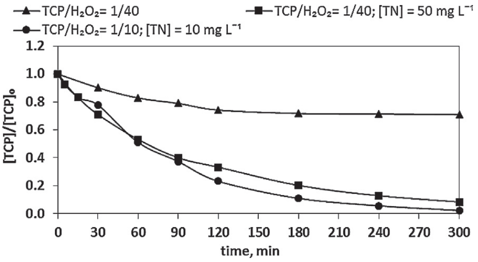

Fig. 9. Degradation of TCP by H_2O_2 in 50 mg L^{-1} ferric sludge suspension within 300 min of H_2O_2 treatment in the presence and absence of TN. $[TCP]_0 = 10\,\mu M$, $[H_2O_2]_0 = 100$ or 400 µM.

TCP removal by H_2O_2 oxidation with ferric sludge similarly to the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 systems followed pseudo-first order reaction kinetics (Table 1). TCP degraded slower by H_2O_2 oxidation activated by ferric sludge than by Fe^{3+} because of the additional reaction of iron dissolution in aqueous media (Fig. 8). The reaction rate was accelerated substantially in the presence of TN (Table 1) resulting in a near-complete degradation of TCP in 300 min (Fig. 9). This confirmed the need for organic reductants in water treated by the Fenton with ferric sludge reuse. A lower dosage of TN (10 mg L^{-1}) and H_2O_2 ($TCP/H_2O_2 = 1/10$) favoured TCP degradation by the H_2O_2-ferric sludge system. A higher dosage of TN required a higher addition of H_2O_2 because of the competitive oxidation reactions of TCP and TN. Thus, H_2O_2 dose and ferric sludge load for water treatment in the presence of TN should be optimized to balance Fe^{3+} reduction to boost the Fenton reaction and $HO^{\bullet}$ scavenging to remove TN from water.

Acidic reaction media (pH 3.0) and the presence of TN (solute) with chelating and reducing properties may result in three main iron dissolution mechanisms: protonation, complexation, and reduction [6,50–53].

Acidic media favoured iron dissolution by protonation. This mechanism relies on protons (H^+) binding with an OH-group on the hydrated substrate surface (step 1, Fig. 10a). This reaction then weakens the Fe—O bond in ferric oxyhydroxide with slow detachment of surface Fe(III) species into solution (step 2, Fig. 10a).

Dissolution by complexation involves the attachment of a chelating compound (TN) onto the ferric oxyhydroxide crystal surface (step 1, Fig. 10b). Deprotonation is required prior to adsorption, since strongly complexing ligands (TN) in the solution exchange for a protonated OH-group bound to the substrate (ferric oxyhydroxide). The surface ion–ligand complex ultimately detaches into the

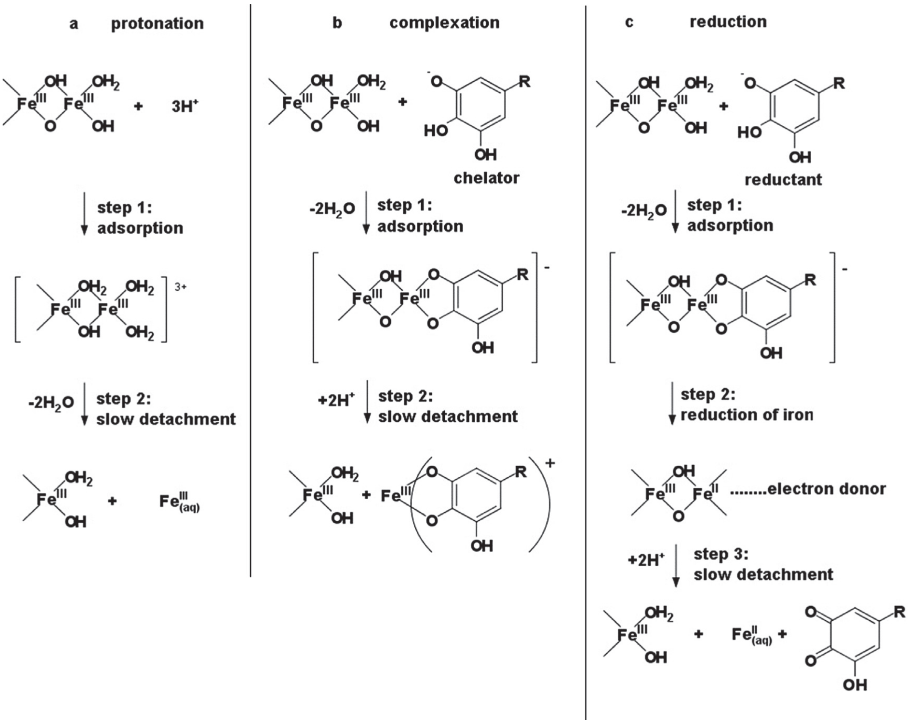

Fig. 10. Iron dissolution mechanisms from ferric sludge: (a) protonation under acidic conditions, (b) complexation, and (c) reduction in the presence of gallic acid (monomer of TN) (R is a rest structure of TN).

aqueous phase (step 2, Fig. 10b). In ferric oxyhydroxide, the high polarity of the surface complex leads to a decrease in bond strength between the surface iron and its neighbouring atoms that facilitates iron dissolution.

Dissolution by reduction implies that the Fe(III) sites on the substrate (ferric oxyhydroxide) surface gain an electron from the adsorbed solute (electron donor) and are reduced to Fe(II) (step 2, Fig. 10c). The newly formed Fe(II) at the substrate surface has a less stable bond with oxygen than its predecessor Fe(III), thus the Fe(II) is more easily detached from the surface than Fe(III) (step 3, Fig. 10c).

Since protons in the phenolic OH-groups of gallic acid (TN monomer) have pKa of 8.7, 11.4, and above 13 [54], the extent of TN dissociation at pH 3.0 was small and TN was mostly present in solution in undissociated form. Since TN deprotonation is required prior to complexation (Fig. 10b) and reduction (Fig. 10c), the probability of iron dissolution from ferric sludge by these mechanisms is very small. Thus, the most evident mechanism of iron dissolution at pH 3.0 is ferric oxyhydroxide protonation with Fe(III) release to aqueous solution (Fig. 10a) followed by Fe(III) reduction to Fe(II) by TN through Fe(III)-TN complex formation with decay by electron transfer reaction mechanism (Fig. 3). The enhanced release of Fe^{2+} from ferric sludge to solution in the presence of TN was observed (Fig. 8). A slightly lower concentration of Fe^{2+} in the ferric sludge/H_2O_2/TN system (Fig. 8) existed because of the utilization of Fe^{2+} for the activation of H_2O_2 oxidation (Eq. (1)) with an effective degradation of TCP (Fig. 9). Adsorption of TCP on the surface of ferric sludge was not observed after 300 min of the solution mixing at pH 3.0.

A study of chlorophenol-contaminated soil treatment [55] showed that organic substances in soil produced by plants and microorganisms may dissolve iron from natural soil iron minerals, reduce it to Fe^{2+}, and boost the reactivity of H_2O_2 oxidation. These findings support results obtained in this study on H_2O_2 oxidation activation by ferric sludge reuse. In soil, Fe^{2+} addition was unnecessary for H_2O_2 decomposition if a considerable amount of reduced metal ions was present; the reductant availability in wastewater allows for the reuse of non-regenerated ferric sludge for Fenton-based oxidation without any supplementary Fe^{2+}.

4. Conclusions

H_2O_2 oxidation activated by Fe^{2+} resulted in a considerably higher degradation rate of TCP than that catalysed by Fe^{3+}. The addition of TN accelerated the degradation rate of TCP and substantially improved the dechlorination by the Fe^{3+}/H_2O_2 system substantially. TN exhibited Fe^{3+}-reductive properties and boosted the reactivity of the Fenton-based process towards TCP degradation by improving iron redox cycling and as a result enhanced activation of H_2O_2 oxidation. Along with the degradation of TCP the scavenging of the hydroxyl radicals by TN was observed. This is not a limitation, since TN is a major constituent in water to be degraded. Among the benefits is that TN degradation proceeded along with the removal of unconsumed by TCP H_2O_2. Thus, H_2O_2 and Fe^{3+} dosages should be optimized to maintain both properties of TN to reduce ferric iron and to scavenge the $HO^{\bullet}$. Iron dissolution from ferric sludge and its reduction by TN to Fe^{2+} was observed under acidic conditions. This improved the reactivity of the Fenton-based process with ferric sludge as the catalyst source of the H_2O_2 oxidation.

The study indicated that natural water or wastewater constituent, TN, is involved in the Fenton chemistry and supports the reuse of ferric sludge as a catalyst source of H_2O_2 oxidation. As a result, expenses of Fe^{2+} addition and sludge utilization can be minimized. The study demonstrated tannic acid participation in the iron ion redox cycling and as a consequence the improved Fenton-based oxidation of contaminants in water with the effective ferric sludge reuse. This presents a high-impact contribution to Fenton-based treatment of wastewater that may result in increased treatment efficacy, and decrease in solid waste accumulation and treatment cost.

Acknowledgement

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APPENDIX B. CURRICULUM VITAE

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi: Juri Bolobajev
Sünniaeg ja -koht: 03.09.1984, Tallinn
Kodakondsus: määratlemata
E-posti aadress: juri.bolobajev@gmail.com

2. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2012	Tehnikateaduste magistrikraad
Tallinna Tehnikaülikool	2008	Tehnikateaduste bakalaureusekraad
Tallinna 53. Keskkool	2003	Keskharidus

3. Keelteoskus

Keel	Tase
Eesti keel	Kõrgtase
Inglise keel	Kõrgtase
Vene keel	Kõrgtase
Saksa keel	Kesktase

4. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2012-2014	Tallinna Tehnikaülikool	Insener
2009-2012	Põllumajandusuuringute keskus	Väetiseanalüüside sektori juhataja
2008-2009	Aeroc AS	Kvaliteediteenistuse juht

5. Kaitstud lõputööd

Tehnikateaduste magistrikraad: Chemical treatment of chlorophene-contaminated soil in columns (Klorofeeniga saastatud pinnase keemiline töötlemine kolonnides). Tallinna Tehnikaülikool, 2012, juhendajad: Anna Goi ja Marika Viisimaa

6. Teadustöö põhisuunad

   1. Bio- ja keskkonnateadused, 1.9. Keskkonnaohtlikke aineid käsitlevad uuringud, P305 Keskkonnakeemia (Mikrosaasteainete lagundamine süvaoksüdatsiooniprotsessidega)

7. Uurimisprojektid

IUT-7 Keemiatehnikapõhine lähenemisviis prioriteetsete saasteainete ja uute esilekerkivate mikrosaasteainete kõrvaldamisele veest/reoveest ja pinnasest: täiustatud oksüdatsioonitehnoloogiate kasutamine ja optimeerimine
ETF8186 Esiletulevate orgaaniliste mikrosaasteainete eemaldamine veest/reoveest täiustatud Fenton-protsessidega
ETF7812 Klooritud süsivesinikega saastatud pinnase taastamine peroksüdeerimisega
AR12017 Bioloogiliselt raskesti lagunevate ainete kõrvaldamine reoveest füüsikalis-keemiliste ja bioloogiliste meetoditega vesikeskkonna saastekoormuse vähendamiseks (CHEMBIO)

8. Juhendatud väitekirjad

Irina Repeshova, magistrikraad, 2015, (juh) Juri Bolobajev, Doksütsükliini lagundamine Fenton-tüüpi reaktsioonidega ning ultraviolettkiirgusega: võrdlev uuring

Deniss Pastuhhov, magistrikraad, 2015, (juh) Juri Bolobajev, Mikrosaasteaine alakloori lagundamine Fenton-protsessidega: kineetika, reaktsiooni mehhanismid ja laguproduktid

CURRICULUM VITAE

1. Personal data

Name: Juri Bolobajev
Date and place of birth: 03.09.1984, Tallinn
Citizenship: Undefined
E-mail: juri.bolobajev@gmail.com

2. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2012	M.Sc. in Engineering
Tallinn University of Technology	2008	B.Sc. in Engineering
Tallinn Secondary 53th School	2003	High school education

3. Language competence/skills

Language	Level
Estonian	Fluent
English	Fluent
Russian	Fluent
German	Moderate skills

4. Professional employment

Period	Organization	Position
2012-2014	Tallinn University of Technology	Engineer
2009-2012	Agricultural Research Center	Head of fertilizers analyses sector
2008-2009	Aeroc AS	Quality manager

5. Defended theses

M.Sc. thesis: Chemical treatment of chlorophene-contaminated soil in columns. Tallinn University of Technology, 2012. Supervisors: Anna Goi and Marika Viisimaa

6. Main areas of scientific work

4. Natural Sciences and Engineering, 4.11. Chemistry and Chemical technology, P305 Environmental chemistry (Advanced oxidation processes for water/wastewater treatment)

7. Research projects

   IUT-7 Chemical engineering approach to removal of priority pollutants and emerging micropollutants from water/wastewater and soil: implementation and optimization of advanced oxidation technologies
   ETF8186 Removal of emerging organic micropollutants from water and wastewater by application of advanced Fenton-based processes
   ETF7812 Peroxidation for remediation of chlorinated hydrocarbons contaminated soil
   AR12017 Degradation of persistent organic pollutants in wastewater with physico-chemical and biological treatment for reduction of pollution load to water bodies (CHEMBIO)

8. Supervised dissertations

   Irina Repeshova, M.Sc. degree, 2015, (sup) Juri Bolobajev, Fenton-type and UV-assisted reactions for the degradation of doxycycline in water: a comparative study

   Deniss Pastuhhov, M.Sc. degree, 2015, (sup) Juri Bolobajev, Degradation of micropollutant alachlor by Fenton processes: kinetics, mechanisms of reaction and by-products

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and Destruction of Polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase Transformations in Hydrothermal Sintering Processing of Phosphate Rock. 1995.

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