Role of Organic Wastewater Constituents in Iron Redox Cycling for Ferric Sludge Reuse in the Fenton-Based Treatment

J. Bolobajev, M. Trapido, A. Goi

Abstract—The practical application of the Fenton-based treatment method for organic compounds-contaminated water purification is limited mainly because of the large amount of ferric sludge formed during the treatment, where ferrous iron (Fe(II)) is used as the activator of the hydrogen peroxide oxidation processes. Reuse of ferric sludge collected from clarifiers to substitute Fe(II) salts allows reducing the total cost of Fenton-type treatment technologies and minimizing the accumulation of hazardous ferric waste. Dissolution of ferric iron (Fe(III)) from the sludge to liquid phase at acidic pH and autocatalytic transformation of Fe(III) to Fe(II) by phenolic compounds (tannic acid, lignin, phenol, catechol, pyrogallol and hydroquinone) added or present as water/wastewater constituents were found to be essentially involved in the Fenton-based oxidation mechanism. Observed enhanced formation of highly reactive species, hydroxyl radicals, resulted in a substantial organic contaminant degradation increase. Sludge reuse at acidic pH and in the presence of ferric iron reductants is a novel strategy in the Fenton-based treatment application for organic compounds-contaminated water purification.

Keywords—Ferric sludge reuse, ferric iron reductant, water treatment, organic pollutant.

I. INTRODUCTION

THE considerable growth of production level in industry inevitably leads to the proportional increase of wastewater produced. The inappropriate treatment of highly polluted water or its direct disposal from industrial sites cause the subsequent spread of toxic substances in water bodies resulting in long-term negative consequences to the aquatic biota. The way to sustainable wastewater management is to use the best available techniques, which tasks consist of providing the highest quality of treated water and the cost efficacy of the process used. Therefore, nowadays the development of new advanced wastewater treatment technologies is of a great importance.

Advanced oxidation processes (AOPs) are efficient wastewater treatment methods aimed to chemically degrade organic pollutants by generation of oxidative species, i.e. hydroxyl radicals (HO•). Among them, the Fenton process deserves special attention as its application in wastewater

J. Bolobajev and A. Goi are with the Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia (phone: +3726204341; fax: +3726202856; e-mail: juri.bolobajev@ttu.ee, anna.goi@ttu.ee).

M. Trapido is with the Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia (phone: +3726202855; fax: +3726202856; e-mail: marina.trapido@ttu.ee

treatment is considered as potentially convenient and inexpensive way to generate HO•. The classical Fenton reaction comprises the catalytic decomposition of H_2O_2 to HO• and OH^- catalyzed by Fe(II) (1) [1]. In the combined AOPs and biological treatment sequences, the Fenton process is usually employed 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.

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO\bullet + OH^- \ (k = 53 \ M^{-1}s^{-1}; [1]) \qquad (1)$$
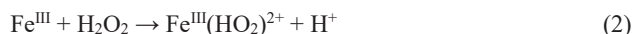
Although the Fenton treatment of wastewater demonstrates high efficacy in degradation of most known organic pollutants, its application on an industrial scale is limited due to the several features of the classical Fenton reaction, e.g. the maximum oxidation efficacy in narrow pH range (pH 2-3) and the precipitation of insoluble ferrioxyhydroxides ($Fe_2O_3 \cdot nH_2O$) as pH is increased from acidic to circumneutral values. The resultant precipitate known as a ferric sludge must be removed from the effluent prior to its disposal to the environment. Therefore, the additional treatment steps such as the separation of sludge from water with its subsequent thickening and utilization are required to provide the better quality of the Fenton treatment.

The use of insoluble or immobilized forms of iron such as iron oxide minerals and iron containing clays [2], zero-valent iron powder [3], [4], iron embedded aluminosilicates (zeolites) [4]-[6] allows overcoming this essential technological drawback. In spite of all these iron forms function well as catalysts of the Fenton-based oxidation, their application on an industrial scale leads to increase of the overall cost of treatment process. The main objective of this study was the complete reuse of ferric sludge as an iron-catalyst in the Fenton-like oxidation. This modification is aimed to solve the main disadvantage related to the Fenton wastewater treatment, i.e. the expenses associated with utilization of solid waste in the form of ferric sludge. It is worthwhile to mention here that iron exists in ferric sludge in its oxidized form (Fe(III)) and the catalysis of H_2O_2 oxidation undergoes according to the Fenton-like oxidation mechanism. The key point in Fenton-like chemistry is the formation of unstable $Fe^{III}(HO_2)^{2+}$ complex (2) with its subsequent reductive decomposition to Fe^{2+} and $HO_2\bullet$ (3).

$$Fe^{III} + H_2O_2 \rightarrow Fe^{III}(HO_2)^{2+} + H^+ \qquad (2)$$

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{II} + HO_2\bullet \qquad (3)$$

Although the formation of Fe(II) and $HO_2\bullet$ might appear at first glance to be effective in oxidation ability of the process as Fe(II) catalyzes H_2O_2 oxidation via (1) and $HO_2\bullet$ is the additional oxidizing agent, the Fenton-like reaction is somewhat less potent than the classical Fenton. The reductive decomposition of $Fe^{III}(HO_2)^{2+}$ complex in Fe(III)-catalyzed oxidation undergoes with the reaction rate constant of 2.7×10^{-3} s^{-1} [7] that is several orders of magnitude lower than that of the classical Fenton reaction ((1), $k = 53$ M^{-1} s^{-1}, [1]). Therefore, it constitutes the rate-limiting step of Fenton-like process.

There are other pathways for reduction of Fe(III) to Fe(II) that may occur by ferric sludge reuse. Emphasis should be placed on the reactions between organic compounds to be oxidized and Fe(III). Possible interactions include the formation of stable complexes with iron ions that solubilize iron at circumneutral pH, or more importantly, the reduction of Fe(III) to Fe(II) that may occur either on the sludge surface or in aqueous media. Therefore, the organic wastewater constituents could be essential contributors to the catalytic behavior of ferric sludge.

In this study, the wood-soaking basin effluent from a plywood manufacturing plant was subjected to the heterogeneous Fenton-based treatment using non-regenerated ferric sludge as a catalyst. The wood processing water effluents are usually rich in phenols, plant-based phenolic polymers (tannins and lignin) and extractives such as terpenes, resin acids, triglycerides, and fatty acids [8], [9]. As the study on the interaction of organic compounds with Fe(III) in the wastewater samples is limited due to the complexity of matrixes investigated, the experiments on the interaction of organic constituents with Fe(III) were conducted. Therefore, to understand the role of phenols and other organic pollutants in the Fenton-mediated H_2O_2 oxidation a number of organic compounds that possesses catecholic, pyrogallolic, and quinone structure were individually tested for their ability to activate $HO\bullet$ formation via Fe(III) reduction to Fe(II).

This study is on the influence of water constituents on Fe(III) to Fe(II) reduction. It contributes substantially to Fenton-based treatment efficacy and creates a hypothesis for subsequent studies on organic pollutants activating behavior in the Fenton-based oxidation.

II. MATERIALS AND METHODS

A. Materials

Hydrogen peroxide (PERDROGEN™, $\geq$ 30%), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, $\geq$ 99%), deoxyribose (2-deoxy-D-ribose, 97%), tannic acid (puriss), 2-thiobarbituric acid ($\geq$ 98%) were purchased from Sigma-Aldrich, trichloroacetic acid ($\geq$ 98%), pyrogallol ($\geq$ 98%) was obtained from Merck. Ferric sulfate hydrate [$Fe_2(SO_4)_3 \cdot xH_2O$, 21-23% of Fe] was purchased from Ridel-de Häen. All the other chemicals were of analytical grade and used without purification.

B. Methods

The wastewater coagulation with ferric sulfate (KEMIRA PIX-322, 12.5% w/w of Fe_{total}) was conducted in an automated coagulation apparatus (Kemira, Finland) according to the procedure described in [10]. The coagulant doses (Fe_{total}) varied in the range 100-1000 mg L^{-1}. After coagulation, the supernatant was separated from precipitate and collected for the further experiments.

The following Fenton/Fenton-based oxidation was performed in a batch reactor. 500 mL of pre-coagulated wastewater were treated in a 1-L cylindrical glass reactor using a continuous agitation of reaction mixture. After the addition of catalyst (iron salts or ferric sludge) the oxidation was initiated by the addition of appropriate dose of H_2O_2. The weight ratio of H_2O_2/Fe(II) or Fe(III) was maintained at 5/1. In case of ferric sludge reuse experiments the pH of wastewater was regulated to 3. The oxidation was stopped by pH increase with NaOH (10 M) to an approximate value of 9. Insoluble ferric sludge formed as a result of neutralization was settled during 24 h and then the supernatant was collected for further analyses. Ferric sludge separated from supernatant was used as an iron source in the following Fenton-based treatment of wastewater without any chemical or thermal regeneration

The experiments on $HO\bullet$ concentration estimation in the Fenton-type reaction mixtures were conducted using the deoxyribose method [11]. This method is based on the selective reaction of $HO\bullet$ with 2-deoxy-D-ribose (DR) to produce an oxidation by-product, malondialdehyde (MDA), which then reacts with 2-thiobarbituric acid (TBA). A 2.8 mM DR solution was oxidized by $HO\bullet$ generated by Fe(II)/H_2O_2, Fe(III)/H_2O_2, and Fe(III)/H_2O_2 reaction mixture containing any of phenolic compounds (phenol, hydroquinone, catechol, pyrogallol, tannic acid and lignin) suspected to promote $HO\bullet$ formation. The reaction mixture pH was kept at 3.0 using 20 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, USA). The amount of $HO\bullet$ formed was quantified using MDA standards prepared via hydrolysis of 1,1,3,3-tetraethoxypropane in 0.1 N HCl.

The Fe(II) concentration was measured photometrically at 492 nm using the o-phenanthroline method [12]. The chemical oxygen demand (COD) and total suspended solids (TSS) were determined according to [13]. The total concentrations of tannins, lignin and phenols were measured photometrically by using tyrosine method adapted from Kloster [14] and 4-aminoantipyrine method according to ISO 6439 [15], respectively. The dissolved organic carbon (DOC) was measured in filtered (Puradisc Aqua, 0.45 µm, CA membrane) wastewater samples by a TOC analyzer multi N/C® 3100 (Analytik Jena, Germany).

III. RESULTS AND DISCUSSION

A. Wastewater Treatment

An important background for successful application of the Fenton treatment is the preliminary removal of total suspended solids (TSS) from water, as they tend to increase iron-catalyst and H_2O_2 dosages required for the effective Fenton-based process performance. Therefore, the coagulation using a KEMIRA PIX-322 commercial formulation of coagulant was applied for the treatment of the plywood manufacturing plant effluent. This pre-treatment method allowed for the substantial elimination of TSS ($\geq$ 90%), total phenols ($\geq$ 50%), and high molecular weight phenolic polymers such as tannins and lignin ($\geq$ 60%). The high treatment efficacy by pre-coagulation served as the basis for the following successful Fenton-based treatment.
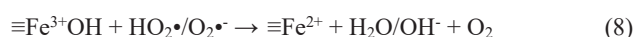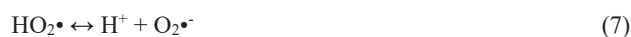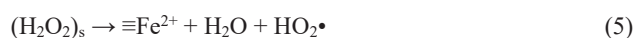
The Fenton oxidation of the pre-coagulated wastewater (Table I) was conducted using either soluble iron salts in the form of sulfates or the ferric sludge precipitated in the final stage of the Fenton treatment where pH of water was increased to the values close to 9. The treatment efficacy using soluble iron catalysts was independent of added iron form (Fe(II) or Fe(III)). This is consistent with the assumption of Pignatello et al. [16] that the differentiation of the Fenton catalyzing effect by Fe(II) and Fe(III) action is "meaningless from mechanistic standpoint" because the initially added Fe(II) is rapidly oxidized to Fe(III), and the system is consequently independent of the initial form of iron. One should note here that this assumption is valid only in those matrixes where Fe(III) reductive interaction with organic substances takes place.

TABLE I
GENERAL CHEMICAL PROPERTIES OF THE PRE-COAGULATED WASTEWATER SAMPLE

Parameter, unit	Analysis result
COD, mg L^{-1}	3270
DOC, mg L^{-1}	681
TSS (105 °C), mg L^{-1}	255
Total phenols, mg L^{-1}	24.2
Lignin and tannins, mg L^{-1}	215

As the pH optimum for the Fenton-based oxidation is near 3 [16], the pre-acidification of water to that pH values was necessary in the ferric sludge reuse experiments. Contrary to that, oxidation catalyzed by soluble iron salts was conducted without pH pre-adjusting as in the beginning of the oxidation a fast pH decrease caused by the hydrolysis of added acidic Fe(II)/Fe(III) sulfates was observed. Besides the optimal oxidation conditions supported the formation of HO•, the acidic media of water facilitated the iron leaching process from ferric sludge to aqueous phase. The further analysis indicated the presence of total dissolved iron in treated wastewater at concentrations of 340-400 mg L^{-1}. Therefore, in the presence of ferric sludge, the Fenton oxidation mechanism can be initiated by Fe(III) or Fe(II) in aqueous phase (1)-(3), or by the decomposition of H_2O_2 to oxidative species directly on the ferric sludge surface by heterogeneous catalysis. The probable mechanism of oxidative species formation from H_2O_2 on ferric sludge could be described by (4)-(8) [17].

$$\equiv Fe^{3+}OH + H_2O_2 \leftrightarrow (H_2O_2)_s \tag{4}$$

$$(H_2O_2)_s \rightarrow \equiv Fe^{2+} + H_2O + HO_2\bullet \tag{5}$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+}OH + HO\bullet \tag{6}$$

$$HO_2\bullet \leftrightarrow H^+ + O_2\bullet^- \tag{7}$$

$$\equiv Fe^{3+}OH + HO_2\bullet/O_2\bullet^- \rightarrow \equiv Fe^{2+} + H_2O/OH^- + O_2 \tag{8}$$

As a result, the reuse of iron-containing sludge during four Fenton-based treatment cycles showed nearly identical to the classical Fenton treatment (utilized soluble iron ion catalysts) COD and DOC removal (Fig. 1). The high efficacy of the heterogeneous Fenton process with the ferric sludge reuse led to the consideration of the proposed novel and cost-effective method for the application on a technological level. Therefore, the obtained knowledge represents an important contribution to the field of the Fenton-based treatment implementation on an industrial scale.
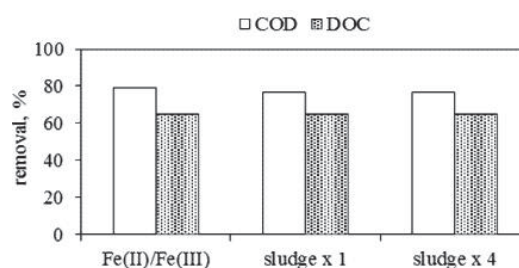

Fig. 1 COD and DOC removal of pre-coagulated wastewater treated by H_2O_2 oxidation catalyzed by soluble iron salts (Fe^{3+}/Fe^{2+}) or reused ferric sludge

B. Formation of Hydroxyl Radical in Fe(II)/H₂O₂, Fe(III)/H₂O₂, and Fe(III)/H₂O₂ in the Presence of Phenolic Compounds and Plant-Based Polyphenols

Although the ferric sludge reuse for the catalyzing of the Fenton-based process resulted in a substantial reduction of COD and DOC of the treated wastewater, the Fe(III) catalytic behavior and interaction with organic constituents relied in these experiments only on theoretical basis, and therefore, continued to engage attention. As the reduction of Fe(III) to Fe(II) is the main "driving force" of the Fenton oxidation process, emphasis should be placed on the identification of organic wastewater constituents that possess Fe(III) reducing ability. For example, the quinone structure compounds (hydroquinone, catechol) are known to participate in iron redox reactions by cycling between quinone, semiquinone, and benzoquinone with its subsequent donation of electrons to Fe(III) (Fig. 2 (b)). At acidic and neutral conditions, quinones (hydroquinone, catechol) occur in the non-dissociated form ($pK_a > 9$, [18]), whereas quinones radicals most probably in the dissociated form [19]. Most quinones form stable complexes with transition metal ions, especially with trivalent

ions such as Fe(III). Therefore, the electron transfer undergoes within the Fe(III)-quinone complex. Pyrogallol [20] and gallic acid [21], precursor of pyrogallol, possess similar metal reducing and complexing behavior. Gallic acid is a monomer of tannic acid where gallic acid monomers are attached to each

other by depside bonds, or to central polyol (such as glucose) by ester bonds [22]. Tannins are also known to be strong metal-chelating [23] and -reducing [24] agents. Therefore, all mentioned phenol-structure compounds should promote HO• generation in the presence of transition metals such as Fe(III).

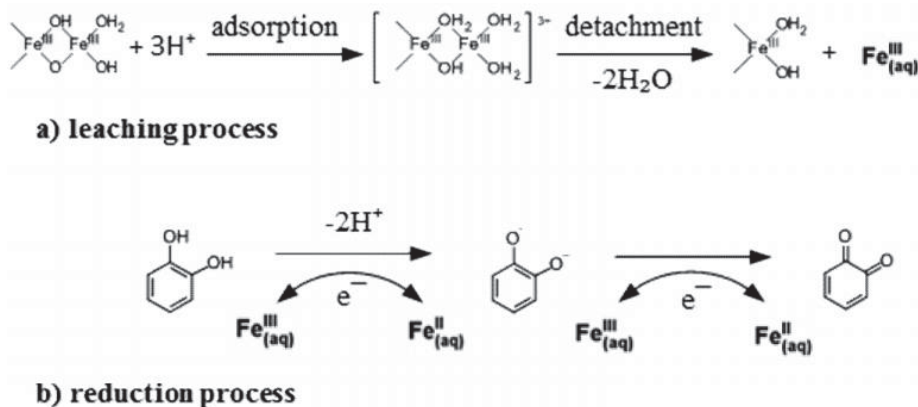a) leaching process

b) reduction process

Fig. 2 Iron dissolution mechanism from ferric sludge with its subsequent reduction in wastewater in the presence of catechol as the example (modified from [25] and [19])

The iron leaching was observed in the Fenton-based experiments utilized ferric sludge and the reduction of Fe(III) could occur either in the aqueous solution, or on the ferric sludge surface.

Acidic reaction media favored iron dissolution by protonation of ferric oxyhydroxide with the subsequent release of Fe(III) into aqueous media. The mechanism of that relies on protons (H^+) binding with OH-group on the hydrated substrate surface (Fig. 2 (a)). This reaction then weakens Fe-O bond in ferric oxyhydroxide with slow detachment of surface Fe(III) species into solution [25]. The subsequent reduction of Fe(III) affected by quinones undergoes in aqueous solution. Contrary to that, Kung and McBride [26] suggested that Fe(III)-sites on the ferric oxyhydroxide surface may gain an electron from the hydroquinone through a ligand exchange to form an inner sphere Organic-Fe(III) complex. Electron transfer within the complex then forms structural Fe(II), which dissociates into solution.

As both Fe(II) and Fe(III) may exist in the bulk solution, the formation of HO• from H_2O_2 to estimate the activation efficiency of the Fe(II) and Fe(III) ions and the influence of phenolic wastewater constituents on HO• propagation in the Fe(III)/H_2O_2 and Fe(II)/H_2O_2 systems were followed (Fig. 3). The Fe(II)/H_2O_2 system was characterized by rapid HO• formation where a maximum concentration was achieved after 10 s. Fe(II) is known to be easily oxidized to Fe(III) (1) with the reaction rate constant of 53 M^{-1} s^{-1}. This reaction is followed by immediate burst of HO•. Some produced HO• remained unconsumed by organic compound to be oxidized and was scavenged then by H_2O_2 and iron ions according to the reactions (9) and (10) resulting in unproductive consumption of the oxidant.

$$HO• + H_2O_2 \rightarrow HO_2• + H_2O \qquad (9)$$

$$HO• + Fe(II) \rightarrow Fe(III) + HO^- \qquad (10)$$
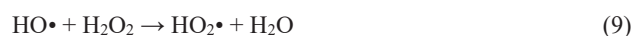
Fe(III)/H_2O_2 showed a weak ability of Fe(III) to activate HO• production. That was caused by a rate-limiting step in reductive dissociation of $Fe^{III}(HO_2)^{2+}$ complex (2), (3) which is known to be several orders of magnitude slower than the classical Fenton process (see the Introduction section). Therefore, the proposed Fe(III)-mediated HO• generation from H_2O_2 without supporting side action of organic substrate in reaction mixture, e.g. organic reducing agents, demonstrated unsubstantial amount of HO• formed.
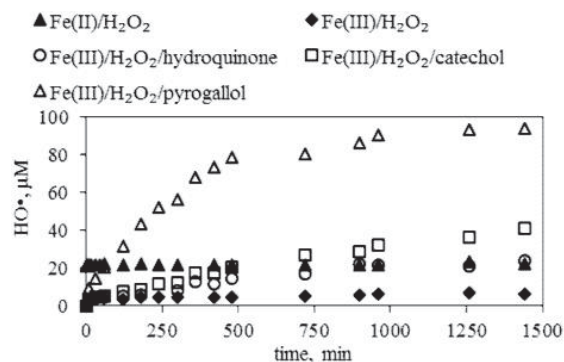

Fig. 3 Formation of hydroxyl radicals (μM) in Fe(II)/H_2O_2, Fe(III)/H_2O_2, and Fe(III)/H_2O_2 in the presence of one of the investigated phenolic compound (hydroquinone, catechol, and pyrogallol). [H_2O_2] = 2.0 mM, [Fe(II)] = [Fe(III)] = 200 μM. Concentration of phenolic compound was 200 μM

In the presence of the investigated phenolic compounds, except phenol, the substantial growth of HO• amount was observed in Fe(III)/H_2O_2. The delay in HO• formation can be explained by the additional step of Fe(III) reduction to Fe(II)

induced by benzenediols or benzenetriols (Fig. 2 (b)). A five-fold increase in HO• amount comparing to that of $Fe(II)/H_2O_2$ was achieved after 1500 min of the reaction in the presence of pyrogallol, i.e. a half of the H_2O_2 dosage (100 μM) was transformed to HO•. Similar to that, Chen and Pignatello [27] reported the occurrence of catalytic effect of aromatic compounds in photoassisted-Fenton oxidation, where quinones served also as electron-transfer catalysts between dihydroxycyclohexadienyl radical and Fe(III) by way of a semiquinone radical. Catechols have been also found to enhance the degradation of organic pollutants in the presence of Fe(III) and H_2O_2 by reducing Fe(III) to Fe(II) in the other studies [28]. Moreover, similar to the present research Rodríguez et al. [29] found that the addition of catechols increased the organo-halogens fraction removal in the wood processing effluent treatment by the Fenton-based method. However, the proposed approach relied on catechols addition to enhance the Fenton efficiency should inevitably lead to the increase of organic load in water. Contrary to that, in the present study wastewater constituents were found to propagate HO• formation without the addition of supplementary organic activators.

The activation effect of monobasic phenols (benzenols) on iron redox cycling was insufficient. No any remarkable increment of HO• in $Fe(III)/H_2O_2$ in the presence of phenol was observed. (The data was not included in Fig. 3.)

Plant-based polymers such as tannic acid and lignin known to be the constituents of wood processing wastewater can also yield oxidative species from H_2O_2 by a way of electron transfer in iron redox cycling. Among them, tannic acid deserves special attention, as its polymeric structure constitutes gallic acid monomers known to be strong complexing and reducing agent. Besides that, pyrogallol, the product of gallic acid decarboxylation, showed the maximum ability to activate the HO• formation among the studied phenolic compounds (Fig. 3). On the other hand, some monomers of lignin, monolignols, such as coniferyl and sinapyl alcohols [30] can hypothetically participate in Fe(III) reductive transformation to Fe(II) as they possess benzenediol and benzenetriol structures found to be effective in propagation of HO• formation. That encourages to propose the participation of polyphenols along with previously reported phenolic compounds in activation of the Fenton-based oxidation.

Expected HO• formation was observed in $Fe(III)/H_2O_2$ with the addition of either tannic acid or lignin (Fig. 4). Tannic acid demonstrated superior to lignin activation properties, as it consists of gallic acid monomers. Gallic acid possesses similar to pyrogallol benzenetriol-structure that allowed for a rapid Fe(III) reduction, i.e. for the formation of HO• in Fenton-mediated reactions.

The reduction of Fe(III) to Fe(II) in the presence of tannic acid or lignin was also confirmed experimentally (Fig. 5). One should note here that the theoretical stoichiometric ratio of Fe(III)/polyphenol for the complete reduction of Fe(III) cannot be calculated due to the uncertain number of bounded phenolic monomers, or their unknown composition in case of lignin.

Therefore, the mass ratio of Fe(III)/TN was used and varied from 1/2 to 1/4 for tannic acid and lignin, respectively. The rapid reduction of Fe(III) by tannic acid provided the necessary source of Fe(II) involved as the catalyst in the following substantial HO• formation from H_2O_2. As the reduction of Fe(III) in studied wastewater was foremost responsible for effective Fenton-based treatment, in the following studies on ferric sludge reuse emphasis should be placed on the role of wastewater organic constituents in iron redox cycling in Fenton-mediated reactions.
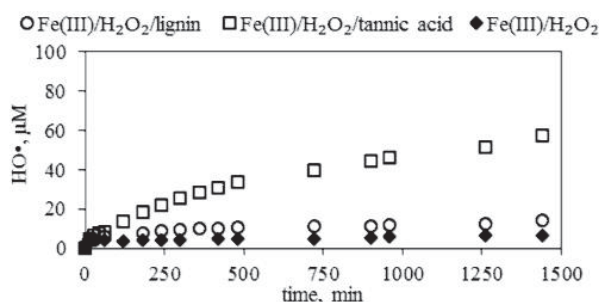

Fig. 4 Formation of hydroxyl radicals (μM) in $Fe(III)/H_2O_2$ in the presence and in the absence of plant-based phenolic polymers (tannic acid and lignin). $[H_2O_2]$ =2.0 mM, [Fe(III)] = 200 μM. Concentration of tannic acid or lignin was 50 mg L^{-1}
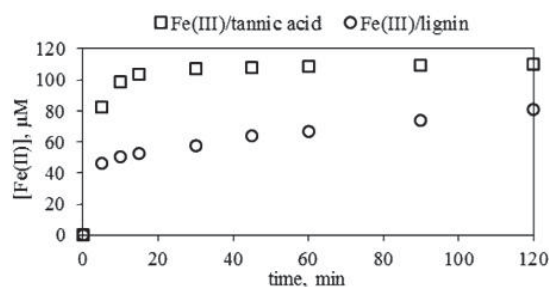

Fig. 5 The reducing of Fe(III) to Fe(II) by tannic acid and lignin. [Fe(III)] = 200 μM. The initial concentration of tannic acid and lignin was 25 and 50 mg L^{-1}, respectively

IV. CONCLUSION

In the present research, the heterogeneous Fenton-based oxidation catalyzed by ferric sludge in acidic media was used to minimize the accumulation of undesirable solid wastes in the Fenton wastewater treatment technology. The application of proposed strategy in the treatment of plywood manufacturing plant effluent demonstrated efficacy similar to the classical Fenton. As the catalytic behavior of ferric sludge relied only on theoretical basis, the following experiments on the Fe(III)-mediated formation of HO• from H_2O_2 in the presence of phenolic compounds, constituents of wastewater, were performed. As a result, benzenetriol-structure wastewater constituents (tannic acid, pyrogallol), whether they were bounded in polymeric structure or not, were able to induce the substantial formation of HO• from H_2O_2, and obviously, played the dominant role in degradation of wastewater organics by the Fenton-based treatment with the ferric sludge

reuse.

REFERENCES

[1] W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, "Reactions of ferrous and ferric ions with hydrogen peroxide. Part I. – The ferrous ion reaction," *Trans. Faraday Soc*., vol. 47, pp. 462-500, Jan. 1951.

[2] E. G. Garrido-Ramírez, B. K. G. Theng, and M. L. Lora, "Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions – A review," *Appl. Clay Sci*., vol. 47, no. 3-4, pp. 182-192, Feb. 2010.

[3] Y. Segura, F. Martínez, and J. A. Melero, "Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron," *Appl. Catal. B Environ*., vol. 136-137, pp. 64-69, June 2013

[4] W. Wang, M. Zhou, Q. Mao, J. Yue, X. Wang, "Novel NaY zeolite-supported nanoscale zero-valent iron as an efficient heterogeneous Fenton catalyst," *Catal. Commun*., vol. 11, no. 11, pp. 937-941, June 2010.

[5] M. Aleksić, H. Kušić, N. Koprivanac, D. Leszczynska, A. Lončarić Božić, "Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water – The application of zeolite assisted AOPs," *Desalination*, vol. 257, no. 1-3, pp. 22-29, July 2010.

[6] S. Fukuchi, R. Nishimoto, M. Fukushima, Q. Zhu, "Effects of reducing agents on the degradation of 2,4,6-tribromophenol in a heterogeneous Fenton-like system with an iron-loaded natural zeolite," *Appl. Catal. B Environ.*, vol. 147, pp. 411-419, Apr. 2014.

[7] J. De Laat and H. Gallard, "Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modelling," *Environ. Sci. Technol*., vol. 33, no. 16, pp. 2726-2732, July 1999.

[8] I. Levchuk, J. J. Rueda-Márquez, S. Suihkonen, M. A. Manzano, M. Sillanpää, "Application of UVA-LED based photocatalysis for plywood mill wastewater treatment," *Sep. Purif. Technol.*, vol. 143, pp. 1-5, Mar. 2016.

[9] D. Pokhrel and T. Viraraghavan, "Treatment of pulp and paper mill wastewater – a review," *Sci. Total Environ.*, vol. 333, no. 1-3, pp. 37-58, Oct. 2004.

[10] A. Goi, Y. Veressinina, M. Trapido, "The Fenton process for landfill leachate treatment: evaluation of biodegradability and toxicity," J. Environ. Eng-ASCE, vol. 136, no. 1, pp. 46-53, Jan. 2010.

[11] B. Halliwell, J. M. C. Gutteridge, and O. I. Aruoma, "The deoxyribose method: a simple test tube assay for determination of rate constants for reactions with of hydroxyl radicals, Anal. Biochem., vol. 165, no. 1, pp. 215-219, Aug. 1987.

[12] E. Merck, *The testing of water*, Merck, Darmstadt, 1994.

[13] *Standard Methods for the Examination of Water and Wastewater,* 21th ed., A. D. Eaton, L. S. Clesceri, E. W. Rice, A. E. Greenberg, Eds., Washington, DC: APHA-AWWA-WEF, 2005.

[14] M. B. Kloster, "Determination of tannin and lignin," J. Am. Water Works Assoc., vol. 66, no. 1, 44-51.

[15] ISO 6439, Water quality – Determination of phenol index – 4-Aminoantipyrine spectrometric methods after distillation, Geneva: International Organization for Standardization, 1990.

[16] J. J. Pignatello, E. Oliveros and A. MacKay, "Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry," *Crit. Rev. Env. Sci. Tec.*, vol. 36, no. 1, pp. 1-84, Jan. 2007.

[17] S. S. Lin and M. D. Gurol, "Catalytic decomposition of hydrogen peroxide on iron oxide: kinetics, mechanisms, and implications," *Environ. Sci. Technol.*, vol. 32, no. 10, pp. 1417-1423, Apr. 1998.

[18] W. P. Jencks and J. Regenstein, "Ionization constants of acids and bases," in Handbook of Biochemistry and Molecular Biology, 4th ed., R. R. Lundblad and F. M. Macdonald, Eds., Oxford: CRC Press, 2010, ch. 67.

[19] J. Magdalena Santana-Casiano, M. Gonzáles-Dávila, A. G. Gonzáles, F. J. Millero, "Fe(III) reduction in the presence of catechol in seawater," *Aquat. Geochem.*, vol. 16, pp. 467-482, Jan. 2010.

[20] T. L. Theis and P. C. Singer, "Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation," *Environ. Sci. Technol.,* vol. 8, no. 6, pp. 569-573, June 1974.

[21] M. J. Hynes and M. Ó. Coinceanainn, "The kinetics and mechanisms of the reaction of iron(III) with gallic acid, gallic acid methyl ester and catechin," *J. Inorg. Biochem.*, vol. 85, no. 2-3, pp. 131-142, June 2001.

[22] I. Mueller-Harvey, "Analysis of hydrolysable tannins," *Anim. Feed Sci. Technol.*, vol. 91, no. 1-2, pp. 3-20, May 2001.

[23] S. Sungur and A. Uzar, "Investigation of complexes tannic acid and myricetin with Fe(III), Spectrochim. Acta A, vol. 69, no. 1, pp. 225-229, Jan. 2008.

[24] J. D. Hem, "Complexes of ferrous iron with tannic acid," *U.S. Geological Survey Water-Supply Paper, 1459-D*, Washington: U. S. Government Printing Office, 1960, pp. 75-94.

[25] B. Sulzberger, D. Sutter, C. Siffert, S. Bannwart, W. Stumm, "Dissolution of iron(III) (hydr)oxides in natural waters, laboratory assessment on the kinetics controlled by surface coordination," *Mar. Chem.,* vol. 28, no. 1-3, pp. 127-144, Dec. 1989.

[26] K.-H. Kung and M. B. McBride, "Electron transfer processes between hydroquinone and iron oxides," *Clay Clay Miner.*, vol. 36, no. 4, pp. 303-309, 1988.

[27] R. Chen and J. J. Pignatello, "Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds," *Environ. Sci. Technol.,* vol. 31, no. 8, pp. 2399- 2406, July 1997.

[28] H. Iwanashi, H. Morishita, T. Ishii, R. Sugata, R. Kido, "Enhancement by catechols of hydroxyl-radical formation in the presence of ferric ions and hydrogen peroxide, *J. Biochem*., vol. 105, no. 3, pp. 429-434, Mar. 1989.

[29] J. Rodríguez, D. Contreras, C. Parra, J. Freer, J. Baeza, N. Durán, "Pulp mill effluent treatment by Fenton-type reactions catalysed by iron-complexes," Water Sci. Technol., vol. 40, no. 11-12, pp. 351-355, Dec. 1999.

[30] K. V. Sarkanen and C. H. Ludwig, *Lignins: Occurrence, Formation, Structure and Reactions*, Wiley-Interscience, New-York, 1971.