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 Fe(II) by phenolic compounds (tannic acid, lignin, phenol, catechol, pyrogallol and hydroquinone) added or present as water/wastewater Fe(II) by phenolic compounds (tannic acid, lignin, phenol, catechol, pyrogallol and hydroquinone) added or present as water/wastewater Fe(II) by phenolic compounds (tannic acid, lignin, phenol, catechol, pyrogallol and hydroquinone) added or present as water/wastewater Fe(II) by phenolic compounds (tannic acid, lignin, phenol, catechol, pyrogallol and hydroquinone) added or present as water/wastewater Fe(II) by phenolic compounds (tannic acid, lignin, phenol, catechol, pyrogallol and hydroquinone) added or present as water/wastewater...
Although the formation of Fe(II) and HO• might appear at first glance to be effective in oxidation ability of the process as Fe(II) catalyzes H₂O₂ oxidation via (1) and HO• is the additional oxidizing agent, the Fenton-like reaction is somewhat less potent than the classical Fenton. The reductive decomposition of Fe(III)(HO₂)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 matrices 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 H₂O₂ oxidation a number of organic compounds that possess catecholic, pyrogallolic, and quinone structure were individually tested for their ability to activate HO• 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™, ≥ 30%), ferrous sulfate heptahydrate (FeSO₄·7H₂O, ≥ 99%), deoxyribose (2-deoxy-D-ribose, 97%), tannic acid (puriss), 2-thiobarbituric acid (≥ 98%) were purchased from Sigma-Aldrich, deoxy-D-ribose, 97%), tannic acid (puriss), 2-thiobarbituric acid (≥ 98%) were purchased from Sigma-Aldrich, trichloroacetic acid (≥ 98%), pyrogallol (≥ 98%) was obtained from Merck. Ferric sulfate hydrate [Fe₂(SO₄)₃·xH₂O, 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 Fe₃O₄) was conducted in an automated coagulation apparatus (Kemira, Finland) according to the procedure described in [10]. The coagulant doses (Fe₃O₄) 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 H₂O₂. The weight ratio of H₂O₂: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• 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• 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• generated by Fe(II)/H₂O₂, Fe(III)/H₂O₂, and Fe(III)/H₂O₂ reaction mixture containing any of phenolic compounds (phenol, hydroquinone, catechol, pyrogallol, tannic acid and lignin) suspected to promote HO• formation. The reaction mixture pH was kept at 3.0 using 20 mM H₂PO₄/KH₂PO₄ 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• 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 (Paradisc 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$_2$O$_2$ 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 matrices where Fe(III) reductive interaction with organic substances takes place.

As the pH optimum for the Fenton-based oxidation is near 3 [17], 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$_2$O$_2$ to oxidative species directly on the ferric sludge surface by heterogeneous catalysis. The probable mechanism of oxidative species formation from H$_2$O$_2$ on ferric sludge could be described by (4)-(8) [17].

\[
\begin{align*}
&\text{Fe}^{3+}\text{OH} + \text{H}_2\text{O}_2 \leftrightarrow (\text{H}_2\text{O}_2)\text{H}^+ + \text{HO}_2^- \\
&(\text{H}_2\text{O}_2), \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + \text{HO}_2^- \\
&\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+}\text{OH} + \text{HO}_2^- \\
&\text{HO}_2^- \leftrightarrow \text{H}^+ + \text{O}_2^- \\
&\text{Fe}^{3+}\text{OH} + \text{H}_2\text{O}_2 \leftrightarrow (\text{H}_2\text{O}_2)\text{H}^+ + \text{HO}^- + \text{O}_2 
\end{align*}
\]

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$_2$O$_2$ oxidation catalyzed by soluble iron salts (Fe$^{3+}$/Fe$^{2+}$) or reused ferric sludge](image)

B. Formation of Hydroxyl Radical in Fe(II)/H$_2$O$_2$, Fe(III)/H$_2$O$_2$, and Fe(III)/H$_2$O$_2$ 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

---

### TABLE I

**GENERAL CHEMICAL PROPERTIES OF THE PRE-COAGULATED WASTEWATER SAMPLE**

<table>
<thead>
<tr>
<th>Parameter, unit</th>
<th>Analysis result</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mg L$^{-1}$</td>
<td>3270</td>
</tr>
<tr>
<td>DOC, mg L$^{-1}$</td>
<td>681</td>
</tr>
<tr>
<td>TSS (105 °C), mg L$^{-1}$</td>
<td>255</td>
</tr>
<tr>
<td>Total phenols, mg L$^{-1}$</td>
<td>24.2</td>
</tr>
<tr>
<td>Lignin and tannins, mg L$^{-1}$</td>
<td>215</td>
</tr>
</tbody>
</table>

---

International Scholarly and Scientific Research & Innovation 10(4) 2016 393

ISNI:0000000091950263
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).

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 H2O2 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)/H2O2 and Fe(II)/H2O2 systems were followed (Fig. 3). The Fe(II)/H2O2 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 H2O2 and iron ions according to the reactions (9) and (10) resulting in unproductive consumption of the oxidant.

\[
HO^- + H_2O_2 \rightarrow HO_2^- + H_2O \quad (9)
\]

\[
HO^+ + Fe(II) \rightarrow Fe(III) + HO^- \quad (10)
\]

Fe(III)/H2O2 showed a weak ability of Fe(III) to activate HO• production. That was caused by a rate-limiting step in reductive dissociation of FeIII(HO2)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 H2O2 without supporting side action of organic substrate in reaction mixture, e.g. organic reducing agents, demonstrated unsubstantial amount of HO• formed.

In the presence of the investigated phenolic compounds, except phenol, the substantial growth of HO• amount was observed in Fe(III)/H2O2. 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 fivefold increase in HO• amount comparing to that of Fe(II)/H2O2 was achieved after 1500 min of the reaction in the presence of pyrogallol, i.e. a half of the H2O2 dosage (100 μM) was transformed to HO•. Similar to that, Chen and Piglatafello [27] reported the occurrence of catalytic effect of aromatic compounds in photoassisted-Fenton oxidation, where quinones served also as electron-transfer catalysts between dihydroxyeclohexadienyl 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 H2O2 by reducing Fe(III) to Fe(II) in the other studies [28]. Moreover, similar to the present research Rodriguez et al. [29] found that the addition of catechols increased the organo-halogen 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)/H2O2 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 H2O2 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)/H2O2 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 H2O2. 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)/H2O2 in the presence and in the absence of plant-based phenolic polymers (tannic acid and lignin).](image)

![Fig. 5 The reducing of Fe(III) to Fe(II) by tannic acid and lignin.](image)

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 H2O2 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 H2O2 and obviously, played the dominant role in degradation of wastewater organics by the Fenton-based treatment with the ferric sludge.
The financial support of the Estonian Ministry of Education and Research (Project IUT 1-7) is gratefully acknowledged.

ACKNOWLEDGMENT

The financial support of the Estonian Ministry of Education and Research (Project IUT 1-7) is gratefully acknowledged.

REFERENCES


