



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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ABSTRACT

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 $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of tannic acid. A pseudo-first reaction rate constant of 2,4,6-trichlorophenol degradation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was high and close to that of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ 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.

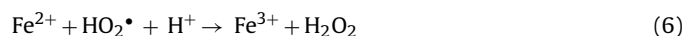
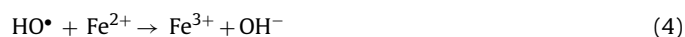
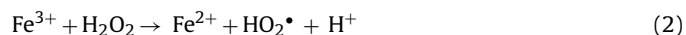
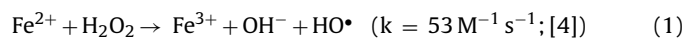
Acidic reaction media (pH 3.0) and the presence of tannic acid favoured 2,4,6-trichlorophenol degradation by H_2O_2 oxidation induced by iron dissolved from ferric oxyhydroxide sludge. The reuse of ferric oxyhydroxide sludge as a catalyst source in the Fenton-based process can minimise the production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

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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].



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 bioreistant [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^\bullet 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^\bullet

scavengers) [30] and pro-oxidation (promote HO^\bullet 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^\bullet 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^\bullet production, and H_2O_2 consumption in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence and absence of TN and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ 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 ($\text{Cl}_3\text{C}_6\text{H}_2\text{OH}$, $\geq 97\%$), TN ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$, ASC grade reagent), ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99\%$), ferric sulphate nonahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99\%$), hydrogen peroxide (H_2O_2 , $\geq 30\%$ w/w), 2-deoxy-D-ribose ($\text{C}_5\text{H}_{10}\text{O}_4$, $\geq 99\%$), 2-thiobarbituric acid ($\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$, $\geq 98\%$), trichloroacetic acid (Cl_3CCOOH , $\geq 99\%$), and 1,1,3,3-tetraethoxypropane ($(\text{C}_2\text{H}_5\text{O})_2\text{CHCH}_2\text{CH}(\text{OC}_2\text{H}_5)_2$, $\geq 96\%$) 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 $10\ \mu\text{M}$ TCP aqueous solution (1 L) with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, ferric sludge/ H_2O_2 , and H_2O_2 was performed in a batch reactor at ambient temperature ($21 \pm 1\ ^\circ\text{C}$) and under acidic conditions (pH 3.0). The initial concentrations of H_2O_2

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