PRIMARY RESEARCH

Influence of pyrogallol on the catalytic effects of Fe^{3+} during Fe^{2+} oxidation with atmospheric oxygen

S. O. Celik [1], S. Günes Durak [2*], T. Ormanci Acar [3], G. Türkoglu Demirkol [4], Ö. Mutlu Salmanli [5], N. Tüfekci [6]

[1] Corlu Faculty of Engineering, Namik Kemal University, Tekirdǎg, Turkey

[2] Faculty of Engineering-Architecture, Nevsehir Hacı Bektas Veli University, Nevsehir, Turkey

[3, 4, 6] Faculty of Engineering, Istanbul University, Istanbul, Turkey

[5] Faculty of Civil Engineering, Istanbul Technical University, Maslak, Istanbul, Turkey

Abstract— One of the most common methods for the removal of iron from water is oxidation of the ferrous iron to the ferric form by atmospheric oxygen. Ferric hydroxide yielding from hydrolysis of ferric iron precipitates which is settled and filtered out from the water. The oxidation rate of the ferrous iron is affected by several factors such as the concentrations of Fe^{2+}, Fe^{3+}, and oxygen, pH, temperature, organic matter, and other ions present in the solution. Considerable concentrations of dissolved iron can be preserved in aerobic aquatic systems in the presence of organic species of natural origin. Organic species such as tannic acid, gallic acid, and others can completely retard the oxidation of Fe^{2+} for several days, even under an oxygen partial pressure of 0.21 atm. In this study, the effect of Fe3+ on Fe^{2+} oxidation in water containing pyrogallol was simulated and investigated experimentally in two stages. In the first stage, catalytic effect of Fe^{3+} on Fe^{2+} oxidation has been investigated, experimentally. In the second stage, it has been studied how pyrogallol affects the oxidation of Fe^{2+} and the catalytic effect of Fe^{3+}. Without pyrogallol, the oxidation rate of Fe^{2+} was enhanced by increasing Fe^{3+} concentration. The catalytic effect of Fe^{3+} clearly decreased and almost vanished in the presence of pyrogallol. This is considered to be a result of pyrogallol-forming complexes with Fe^{3+}.

© 2017 The Author(s). Published by TAF Publishing.

I. INTRODUCTION

Ground waters in Turkey generally contain Fe^{2+} above the allowed limits for consuming as drinking water. For this reason, it is necessary to remove Fe^{2+} from water. Redox reactions affect the chemical forms of iron in natural waters via photoreduction, thermal reduction of Fe^{3+} or oxidation of Fe^{2+}.

Different kinds of organic matters can be present in water along with Fe^{2+}. These Fe^{2+} oxidation products can be consumed by the other constituents such as Natural Organic Matters (NOM) [1]. NOM in natural waters usually quicken the oxidation reaction at typical ambient pH, which has been attributed to many humic substances that have the high density of carboxylate binding sites [2]. Lee *et al*. [1] conducted a study with Sagami River water samples to investigate the effect of NOM on Fe^{2+} oxidation. They determined the oxidation rate was accelerated up to 3.4-fold with the existence of humic-type NOM. Whereas bioavailability of iron decreases in the presence of humic-type NOM. Besides, some humic acid constituents can form complex with ferrous iron and retard the oxidation [3].

---

*Corresponding author: S. Günes Durak
†Email: ssevgigunes@gmail.com

Pyrogallol is one of the most important phenolic compounds found in different natural or synthetic molecules, crops, and fruits, such as tannic acid, gallic acid, and epicatechin gallate [4, 5]. Pyrogallol can be named one of the fundamental organic matters in the drinking water sources, which has high organic content as a byproduct of the decomposition of humic acid [6]. This compound has high oxygen absorbing capacity due to its ability to react with oxygen. Pyrogallol is a naturally toxic compound but widely used in many industries due to its antibacterial, antiviral, and antioxidant properties [7, 8, 9]. Pyrogallol activates iron released from the ferritin core and reduces ferric iron from ferritin, which makes the cells susceptible to oxidative stress [10, 11]. There are limited studies conducted with pyrogallol in the literature. Theis and Singer [12] determined that pyrogallol can reduce Fe^{3+} to Fe^{2+} when the pH is below 3. Lu *et al.* [13] studied the complexation of pyrogallol with ferrous sulphate. They found that the stoichiometric composition of the formed complex was 1:1. In this study, the complexation reaction was found to be a second-order. Jaen *et al.* [14] investigated the reaction of pyrogallol with metallic iron. It is found in this study that when the pyrogallol concentration is higher than 1%, iron presents in the form of soluble ferric and ferrous polyphenolate complexes; while at lower concentrations (0.1 %), oxyhydroxides are present.

Catalytic effect of ferric hydroxides on the oxidation of ferrous iron by aeration has been studied by several researchers. It is reported that there is no significant effect of Fe^{3+} concentrations on Fe^{2+} oxidation beyond 600 mg/L [15, 16].

In this study, the effect of pyrogallol on the oxidation of Fe^{2+} and the effect of pyrogallol on the catalytic effect of Fe^{3+} were investigated. Experiments were performed in two steps. In the first step, catalytic effect of Fe^{3+} on Fe^{2+} oxidation has been investigated, experimentally. In the second step, it has been studied how pyrogallol affects the oxidation of Fe^{2+} and catalytic effect of Fe^{3+}.

II. EXPERIMENTAL AND ANALYTICAL METHODS

The oxidation of Fe^{2+} was investigated in batch reactors of 2-liter volume under the conditions of alkalinity: $2x10^{-2}$eq/L, pH:6.7, T:25 ^{o}C, PO_2:0.21 atm, $[Fe^{2+}]^o$:3 mg/L. The experimental setup is illustrated in Figure 1. Chilern Hotplane Magnetik Stirrer HS-31 model of mixer was used to intensely mix the reaction vessel. $NaHCO_3$ was added into the distilled water in order to produce a solution with an alkalinity of $2x10^{-2}$ eq/L. The flow of CO_2 gas was adjusted to be able to control the pH of the solution. HACH HQ40d type of pH meter was used to measure the pH of the solution with sensitivity of ± 0.01 pH unit. Monitoring of the dissolved oxygen levels was done using a WTW oxygen meter. Immersing the reaction vessel into the water bath was done to maintain constant temperature.
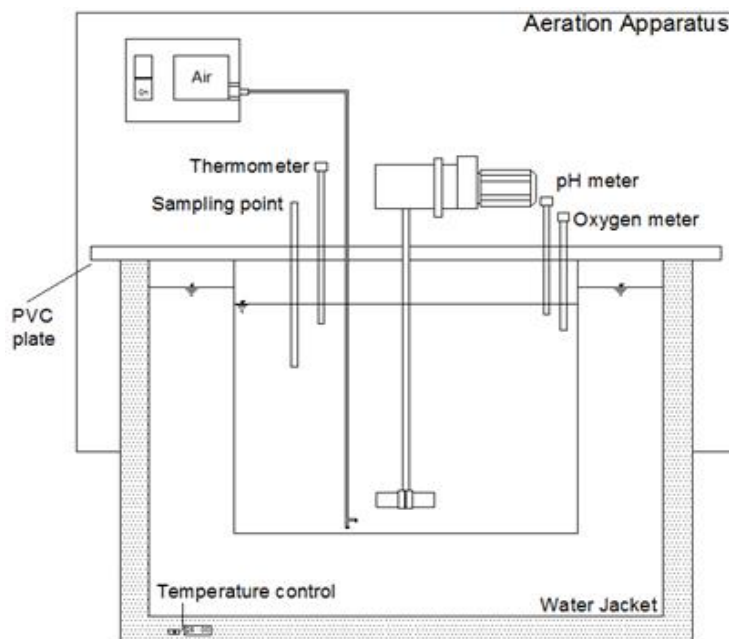

Fig. 1 *.* Experimental setup

The samples were taken at pre-decided times and transferred into the 25 mL flasks containing 1 mL of (1+4) H_2SO_4 (25% H_2SO_4 + 75% demineralized water). In the presence of high concentrations of Fe^{3+}, 1.10 phenanthroline method as given by Tamura *et al.* [17] was followed. In other cases, the PC Instrument T60 model UV/VIS spectrometer was used to determine Fe^{3+}. Relevant calibration curve was prepared at 510 nm wavelength. In this study, Fe^{3+} concentration was kept constant as 3 mg/L and the concentrations of pyrogallol were added into solution as it can be seen from Table 1.

TABLE 1
THE CONCENTRATION OF PYROGALLOL AND FE(OH)$_3$

Pyrogallol, mg/L	Fe(OH)$_3$, mg/L
0	0
1	5
5	25
7.5	50
10	

Fe^{2+} stock solution was produced by dissolving ferric ammonium sulfate in 1 liter demineralized water with 2 ml of concentrated H_2SO_4. Dissolved reagent grade pyrogallol was used to prepare 1000 mg/L pyrogallol stock solution supplied by Merck in deionized water. All experiments were performed at least three times. The results of the experiments under same conditions were generally found to be very close to each other. This shows that the experiments are iterated while experimental conditions have been kept constant.

III. RESULTS AND DISCUSSION

A. The Effect of Pyrogallol on Fe^{2+} Oxidation

It is known that iron exists associated with organic matters in natural waters. In this part of the study, the effects of pyrogallol on the oxidation of Fe^{2+} were analyzed. The results of the experiments are given in Figure 2 as a graph. In these experiments, Fe^{2+} has been kept constant as 3 mg/L and pyrogallol has been changed between 0 and 10 mg/L. Temperature, pH, and alkalinity have been kept at 25°C, 6.7, and $2x10^{-2}$eq/L, respectively. As it can be seen from the Figure 2, the results have been very close to each other and oxidation was slowing down as the concentration of pyrogallol increased. Before the addition of pyrogallol to the medium, the reaction completion time was 78 minute.

When pyrogallol was 1 mg/L, the completion time of the reaction was increased to 81 minute. The reaction completion time reached maximum level (91 min.) when pyrogallol concentration was 10 mg/L.

Oxidation of iron can be inhibited or retarded by humic substances. In fact, it was reported that pyrogallol can reduce Fe^{3+} to Fe^{2+} when the pH is below 3. Iron can be kept in soluble form in the presence of pyrogallol due to chelate formation that made Fe^{2+} species unavailable for oxidation [12]. In this study, pyrogallol has retarded the oxidation and retardation time increased in parallel with increasing pyrogallol concentration. Findings of the study are consistent with the literature. Jaen *et al.* [15] also reported that when pyrogallol concentration is higher than 1%, iron is present in the form of soluble ferric and ferrous complexes.
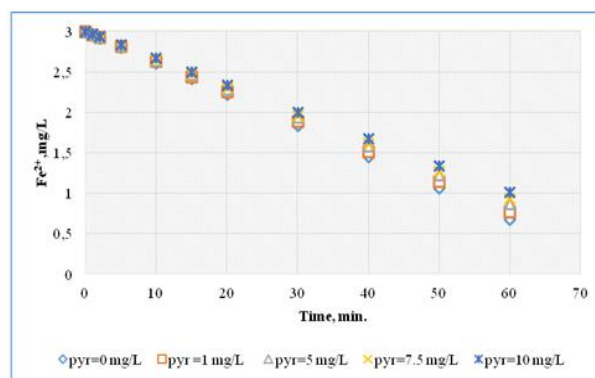

Fig. 2 . The effect of pyrogallol on Fe^{2+} oxidation (Fe^{2+} = 3 mg/L, T = 25°C, pH = 6.7, PO$_2$ = 0.21 atm)

B. The Effect of Fe(OH)$_3$ on Fe^{2+} Oxidation

The concentration of Fe(OH)$_3$ has been studied at low values (0-50 mg/L), and the effect of Fe(OH)$_3$ has been carefully controlled by analysis in the batch reactor. Initial concentration of Fe^{2+}, pH, alkalinity, and temperature have been kept constant at 3 mg/L, 6.7, $2x10^{-2}$eq/L, and 25°C, respectively. Afterwards, the experiments have been repeated by changing the concentration of Fe(OH)$_3$. The results of the experiments are shown in Figure 3. The heterogeneous rate constant ($k$cat) was determined as shown in Figure 4 by calculating the reaction equation linearly. The increase in the concentration of Fe(OH)$_3$ increased the oxidation rate significantly up to 50 mg/L. Before the addition of Fe(OH)$_3$ into the medium, the reaction completion time was 78 minute and the k value was 0.0386. When Fe(OH)$_3$ was 50 mg/L, the heterogeneous rate constant ($k$cat) was found as 0.1274 and the completion time of the reaction

was 27 minute. The reaction speed reached the maximum value at $Fe(OH)_3$ concentration of 50 mg/L.

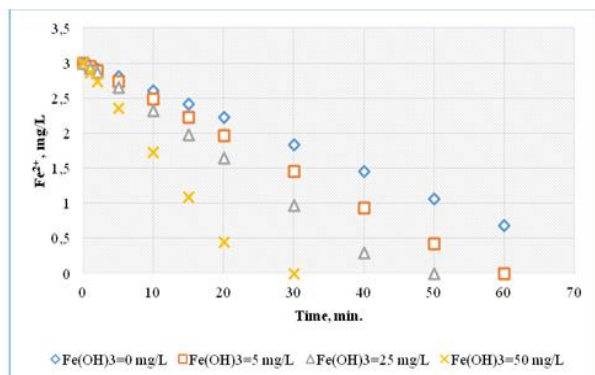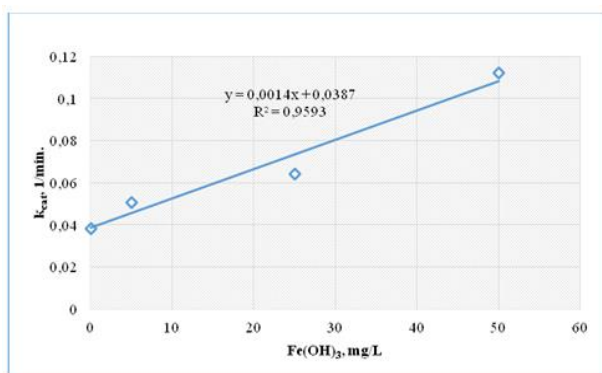Fig. 3 . The effect of $Fe(OH)_3$ on Fe^{2+} oxidation (Fe^{2+} = 3 mg/L, T = 25°C, pH = 6.7, PO_2 = 0.21 atm)

Fig. 4 . Change in "k_{cat}" with $Fe(OH)_3$

C. The Effect of Pyrogallol- Fe(OH)$_3$ on Fe^{2+} Oxidation

In this part of the study, the effects of oxidation on the different pyrogallol concentrations (0-10 mg/L) were investigated by keeping the concentration of Fe^{2+} and $Fe(OH)_3$ constant. In this section, 50 mg/L of $Fe(OH)_3$ concentration was selected to conduct the experiment which helped to obtain the maximum oxidation rate. As it can be seen from Figure 5, the rate of oxidation decreased with increasing pyrogallol concentration as found in the first section.

The heterogeneous rate constant (k) was determined as shown in Figure 6 by calculating experiment equation linearly. Before the addition of pyrogallol into the medium, the reaction completion time was 27 minute and k value was 0.1274. When pyrogallol was 1 mg/L, the completion time of the reaction was found as 33.5 minute and k value was 0.1150. The reaction completion time reached

the minimum value (38 min.) when pyrogallol concentration was 10 mg/L and k value was 0.0842. It was observed that pyrogallol reduced the reaction rate in both cases with and without $Fe(OH)_3$. In this study, it was observed that pyrogallol almost totally prevented the oxidation of Fe^{2+}.

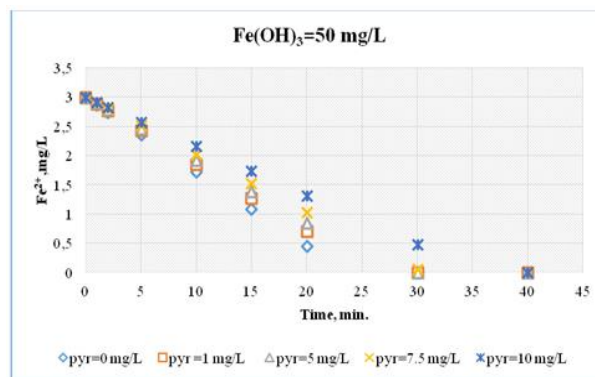Fig. 5 . The effect of $Fe(OH)_3$ on Fe^{2+} oxidation (Fe^{2+} = 3 mg/L, $Fe(OH)_3$ = 50 mg/L, T = 25°C, pH = 6.7, PO_2 = 0.21 atm)
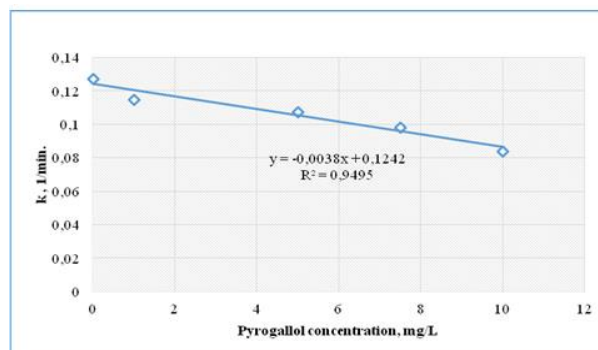

Fig. 6 . Change in "k" with pyrogallol

IV. CONCLUSION

In this study, the effect of $Fe(OH)_3$ on the oxidation of Fe^{2+} by different concentrations of pyrogallol was investigated experimentally. $Fe(OH)_3$ formation increased the rate of Fe^{2+} oxidation in the absence of pyrogallol due to catalytic effect. This catalytic effect increased when 50 mg/L concentration of $Fe(OH)_3$ was used. When pyrogallol was added, the catalytic effect of $Fe(OH)_3$ clearly decreased with increasing pyrogallol concentration. This is considered to be an indication that pyrogallol has a high oxygen scavenging ability in alkaline environments. Also, pyrogallol has an ability to keep iron in soluble form. It is thought that this is due to the probability of chelate formation by pyrogallol and making Fe^{2+} unavailable for oxidation.

In this study, pyrogallol has retarded the oxidation and retardation time increased in parallel with increasing concentration of pyrogallol. The inhibition effect of pyrogallol on the oxidation of Fe^{2+} is dependent on the pyrogallol concentration. Without pyrogallol, it is found that the reaction completion time was 78 minute. Even pyrogallol concentration was 1 mg/L, the completion time of the reaction was increased up to 81 minute. The reaction completion time reached the maximum value (91 min.) when pyrogallol concentration was 10 mg/L. When pyrogallol was present in the medium, the catalytic effect of $Fe(OH)_3$ was reduced. Catalytic effect of $Fe(OH)_3$ was found as significant without pyrogallol in the medium. In this situation, the reaction completion time was found as 27 minute and *k* value as 0.1274. But, when pyrogallol was 1 mg/L, the completion time of the reaction increased to 33.5 minute and *k* value was reduced to 0.1150. The reaction completion time reached a minimum (38 min.) at pyrogallol concentration of 10 mg/L and *k* value was 0.0842. The catalytic effect of Fe3+ clearly decreased and was almost insignificant in the presence of pyrogallol. It is observed that pyrogallol reduces the reaction rate in both cases with and without $Fe(OH)_3$.

REFERENCES

[1] Y. P. Lee, M. Fujii, K. Terao, T. Kikuchi and Chihiro Yoshimura, "Effect of dissolved organic matter on Fe (II) oxidation in natural and engineered waters," *Water Research*, vol. 103, pp. 160-169, 2016.
DOI: 10.1016/j.watres.2016.07.033

[2] A. L. Rose and T. D. Waite, "Effect of dissolved natural organic matter on the kinetics of ferrous iron oxygenation in seawater," *Environmental Science and Technology*, vol. 37, no. 21, pp. 4877-4886, 2003.
DOI: 10.1021/es034152g

[3] T. Ormancı Acar, S. Güneş Durak and N. Tüfekci, "Effects of fulvic acid and ferric hydroxide on removal of Fe^{2+} and Mn^{2+} by oxidation and aerated/submerged ultrafiltration membrane system," *Water Science and Technology-Water Supply*, vol. 12, pp. 145-152, 2017.
DOI: 10.2166/ws.2017.033

[4] J. Chen and J. Bai, "Chemiluminescence flow sensor with immobilized reagent for the determination of pyrogallol based on potassium hexacyanoferrate (III) oxidation," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 71, no. 3, pp. 989–992, 2008. **DOI:** 10.1016/j.saa.2008.02.022

[5] K. Zhan, H. Ejima and N. Yoshie, "Antioxidant and adsorption properties of bioinspired phenolic polymers: A comparative study of catechol and gallol," *ACS Sustainable Chemistry and Engineering*, vol. 4, no. 7, pp. 3857–3863, 2016.
DOI: 10.1021/acssuschemeng.6b00626

[6] E. Zeiger, "*Pyrogallol–review of toxicological literature,*" North Carolina, NC: National Institute of Environmental Health, 1998.

[7] K. K. Gaikwad and Y. S. Lee, "Novel natural phenolic compound-based oxygen scavenging system for active packaging applications," *Journal of Food Measurement and Characterization*, vol. 10, no. 3, pp. 533–538, 2016.
DOI: 10.1007/s11694-016-9332-1

[8] P. Feng, S. Wang, W. Su and S. Cheng, "Electrochemical oxidation and sensitive determination of pyrogallol at preanodized screen-printed carbon electrodes," *Journal of the Chinese Chemical Society*, vol. 59, no. 2, pp. 231–238, 2012. **DOI:** 10.1002/jccs.201100384

[9] Y. Uemura, T. Shimasaki, N. Teramoto and M. Shibata, "Thermal and mechanical properties of bio-based polymer networks by thiol-ene photopolymerizations of gallic acid and pyrogallol derivatives," *Journal of Polymer Research*, vol. 23, no. 10, pp. 216-220, 2016.
DOI: 10.1007/s10965-016-1105-3

[10] R. Agrawal, P. K. Sharma and G. S. Rao, "Release of iron from ferritin by metabolites of benzene and superoxide radical generating agents," *Toxicology*, vol. 168, no. 3, pp. 223–230, 2001.
DOI: 10.1016/s0300-483x(01)00412-7

[11] M. Bauer and I. Bauer, "Heme oxygenase-1: Redox regulation and role in the hepatic response to oxidative stress", *Antioxidants and Redox Signaling*, vol. 4, no. 5, pp. 749–758, 2002.
DOI: 10.1089/152308602760598891

[12] T. L. Theis and P. C. Singer, "The stabilization of Ferrous Iron by organic compounds in natural waters." In P. C. Singer, ed. *Trace metals and metal-organic interactions in natural waters*, 2nd, California, CA: Ann Arbor Science Publishers, pp. 303-320, 1974.

[13] L. L. Lu, Y. H. Li and X. Y. Lu, "Kinetic study of the complexation of gallic acid with Fe (II)," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 74, no. 3, pp. 829-834, 2009.
DOI: 10.1016/j.saa.2009.08.025

TAF Publishing

[14] J. A. Jaén, L. González, A. Vargas and G. Olave, "Gallic acid, ellagic acid and pyrogallol reaction with metallic iron," *Hyperfine Interactions*, vol. 148, no. 1–4, pp. 227–235, 2003. **DOI:** 10.1023/b:hype.0000003784.88539.d4

[15] N. Tufekci and H. Z. Sarikaya "Catalytic fffects of high Fe (3) concentration on Fe (II) oxidation," *Journal of Water Science and Technology*, vol. 34, no. 7-8, pp. 389-396, 1996. **DOI:** 10.1016/s0273-1223(96)00770-6

[16] N. Tufekci and H. Z. Sarikaya, "An experimental study on iron removal with ferric sludge recycle," *Journal of Water Science and Technology*, vol. 42, no. 1-2, pp. 387-392, 2000.

[17] H. Tamura, K. Goto, T. Yotsuyanagi and M. Nagayama, "Spectrophotometric line in the presence of large amounts of Iron(III)," *Talanta*, vol. 21, no. 4, pp. 314–318, 1974.
DOI: 10.1016/0039-9140(74)80012-3

— This article does not have any appendix. —

TAF
Publishing