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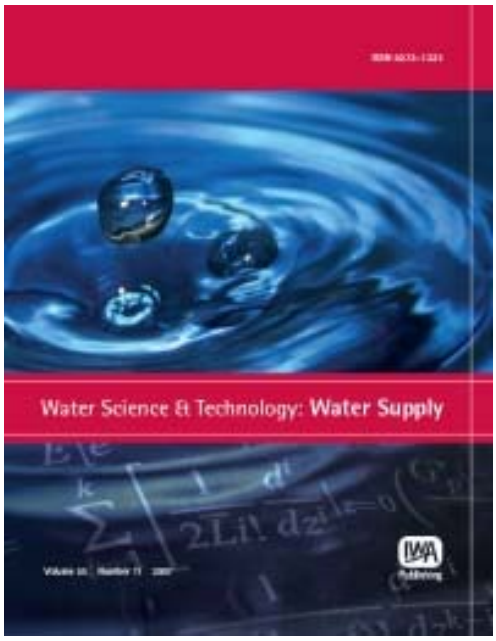

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Impacts of pH-dependent metal speciation on the decomposition of triclosan by sulfate radicals

Prince Nfodzo, Qinhong Hu and Hyeok Choi

ABSTRACT

The presence of triclosan (TCS) in water resources has drawn significant attention due to its endocrine disruption potential. Sulfate radicals (SRs), generated particularly by the metal-mediated activation of peroxymonosulfate (PMS), have been proposed to effectively decompose TCS and many other pharmaceuticals and personal care products. In spite of its significance for understanding the efficiency of SR generation and catalytic/non-catalytic nature of the oxidation reaction, metal speciation has not been adequately highlighted in previous studies. This study investigated the detailed changes in metal speciation in cobalt/PMS and iron/PMS systems and correlated it with TCS decomposition under different pH conditions. A rapid oxidation of Co^{2+} to Co^{3+} and Fe^{2+} to Fe^{3+} generally corresponded with pseudo-steady state decomposition kinetics of TCS after its initial fast decomposition. The presence of potential threshold concentrations of metals to effectively activate PMS was found. A strong catalytic activity was observed for Co/PMS system at pH 3, where most of Co was present in the form of dissolved Co^{2+}. The pH impacts were different for Co/PMS and Fe/PMS. TCS oxidation was fast at pH 5 for Co and pH 3 for Fe. However, long-term mineralization of TCS seemed less dependent on pH.

Key words | advanced oxidation processes, catalytic nature, metal speciation, reaction pH, sulfate radicals, triclosan, water treatment

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INTRODUCTION

Recently, the presence of pharmaceuticals and personal care products (PPCPs) in water resources has raised great attention. Many PPCPs have been classified as emerging chemicals of concern and endocrine disrupting compounds. In particular, triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy)phenol), an antimicrobial agent widely used in PPCPs, has attracted significant concern because of the toxicity and prevalence of its derivatives. Since recent findings about the estrogenic effects of TCS in rats, the US Environmental Protection Agency (EPA) is particularly worried about the potential for antibiotic resistance and endocrine disruption resulting from human exposure to TCS (Zorrilla *et al.* 2009). The EPA is subsequently re-examining the potential health risks of TCS (Erickson 2010).

TCS is not degraded completely in conventional water and wastewater treatment processes. Moreover, TCS destroys some protozoa that facilitate biological treatment processes (Krishnakumar *et al.* 2011). Responding to the growing concerns, recent studies have focused largely on advanced oxidation processes (AOPs), which rely on the generation of transitional reactive free radicals, particularly hydroxyl (HRs, $^{\bullet}OH$) and sulfate (SRs, $SO_4^{\bullet-}$) radicals as strong oxidizing species (Anipsitakis & Dionysiou 2004; Son *et al.* 2007). For the degradation of organic contaminants, including TCS, most research has emphasized HRs-based AOPs. More recently, there has also been a growing interest in the application of SRs-based AOPs. SRs are typically generated by the metal-mediated activation of common oxidants such as peroxymonosulfate (HSO_5^-, PMS) and persulfate ($S_2O_8^{2-}$, PS), as shown in Equations (1) and (2) (Anipsitakis & Dionysiou 2003). In particular, these technologies have been reported to be effective for the

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decomposition of TCS (Nfodzo & Choi 2011a).

$$HSO_5^- + Me^{2+} \rightarrow Me^{3+} + SO_4^{\bullet -} + OH^- \quad (1)$$

$$S_2O_8^{2-} + Me^{2+} \rightarrow Me^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (2)$$

The effectiveness of the metal/oxidant systems to generate such radicals is dependent on the availability of useful metal species in the reaction environment. Since homogeneous systems are much more effective than heterogeneous systems with respect to reaction kinetics, dissolved metal species are preferred to solid state metal species. In particular, the presence of low oxidation state ions, such as Fe^{2+} and Co^{2+}, is important for the activation of oxidants, as demonstrated in Equations (1) and (2). Consequently, the ability of a metal/oxidant system to maintain an adequate amount of useful metal species (i.e. dissolved Fe^{2+} and Co^{2+}) determines the efficiency of SR generation and the catalytic/non-catalytic nature of the overall reaction. In spite of the importance of metal speciation, there have been few studies focusing on measuring metal species over the reaction time and thus correlating the metal speciation with organic decomposition. Measuring metal species in real time poses many analytical challenges. Changes in metal species are radical over time, especially in oxygenated environments (Safarzadeh-Amiri *et al.* 1996), and they are also dependent on pH conditions. Some previous studies reported simply concentration of either total metal or total dissolved metal initially added (Anipsitakis & Dionysiou 2004).

In this study, for the first time, we traced detailed changes in metal species during the decomposition of TCS by SRs at different pH conditions. PMS, which shows a better reactivity than PS, was exclusively focused in this study (Nfodzo & Choi 2011b). The efficiencies of Co/PMS and Fe/PMS systems for the decomposition and mineralization of TCS were correlated with the changes in metal speciation. Among many transition metal activators, Co and Fe were selected because Co is known to be the best metal activator for PMS and Fe is naturally abundant in water resources (Anipsitakis & Dionysiou 2004; Safarzadeh-Amiri *et al.* 1996).

MATERIALS AND METHODS

Chemicals

Triclosan (TCS), potassium peroxymonosulfate ($KHSO_5$), iron(II) sulfate (Fe^{2+}), iron(III) sulfate (Fe^{3+}), and cobalt sulfate (Co^{2+}) were obtained as salts. Iron and cobalt standards, sodium hydroxide, and nitric acid were obtained as volumetric solutions. The chemicals were obtained from Sigma-Aldrich and used as received.

Generation of sulfate radicals and decomposition of triclosan

SRs were generated by the activation of PMS with Co^{2+} and Fe^{2+}. The experiments were conducted in a batch reactor at ambient temperature. Specific aliquot of TCS was transferred into a glass reactor, and appropriate volumes of PMS followed by Co^{2+} or Fe^{2+} stock solutions were added to achieve a 100 mL reaction solution. The initial concentration of TCS was 9 mg/L (0.031 mM, close to its aqueous solubility). In our previous studies on TCS decomposition, PMS:metal molar ratio of 1:1 was the most effective, and TCS:PMS molar ratio of 1:3 when conjugated with Co and TCS:PMS molar ratio of 1:40 when conjugated with Fe resulted in rapid decomposition of TCS (Nfodzo & Choi 2011b). In order to retard the reaction kinetics and effectively monitor changes in the metal species, PMS dosage was reduced in this study to TCS:PMS at 1:2 for Co/PMS and TCS:PMS at 1:10 for Fe/PMS while PMS:metal ratio was fixed at 1:1. Preliminary experiments showed an immediate disappearance of the original molecular form of TCS by self-ionization at pH above 8.1, and thus we focused on experiments exclusively at pH 3.0, 5.0, and 7.0 using phosphate buffers.

Measurement of triclosan and total organic carbon

For the determination of TCS disappearance, sample of 0.5 mL was drawn at 15 min intervals for 2 h, immediately mixed with methanol (a quenching agent for SRs), and filtered through 0.45 μm syringe filters. Samples for total organic carbon (TOC) analysis to determine TCS mineralization were drawn at times of 1, 2, 3, 6, 12, 18 and 24 h, and immediately mixed

with sodium nitrite (an inorganic quenching agent for SRs). The decomposition of molecular TCS was monitored with reversed-phase high performance liquid chromatography (HPLC, 1200 series, Agilent), and TOC was monitored by measuring the non-purgeable organic carbon concentration using a TOC analyzer (TOC-VCSH/CSN, Shimadzu).

Measurement of metal species

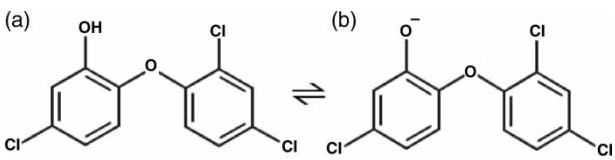
The concentrations of the various metal species were monitored for 2 h. Measurements of the ionic species were performed with an ion chromatograph (IC) (LC 20, Dionex), while total metal and total dissolved metal concentrations were determined with a quadruple inductively coupled plasma–mass spectrometry (ICP–MS) system (PerkinElmer/SCIEX, Sheldon, CT) after acid digestion. Comparing the results from IC and ICP-MS analyses enabled us to confirm the detailed metal speciation in the complex systems.

RESULTS AND DISCUSSION

The effects of pH at 3, 5, and 7 on the speciation of Co and Fe and consequently on the kinetics of TCS degradation were examined. It has been reported that at pH values of above 8.1 (pKa of TCS), TCS exists primarily in its ionic form (Lindström *et al.* 2002) as shown in Scheme 1. At pH 9.0 and 11, no evidence of the presence of initial molecular TCS added in solution was observed at all times. Since our focus was on the transformation of the original molecular form of TCS over time at different pHs, reactions at pH 9 and 11 were excluded from further investigation.

Cobalt speciation and triclosan decomposition

The decomposition of aqueous TCS by the Co-mediated system was significantly affected by pH, as shown in Figure 1(a). The decomposition of TCS within 2 h ranged from 60 to 95% and was more effective at pH 5 compared to pH 7 and 3. It has been reported that SRs have the potential to react with H_2O under neutral conditions and with hydrogen ions under acidic conditions, as shown in Equations (3) and (4) (Buxton & Greenstock 1988; Spinks & Woods 1990). As a result, SRs generated are immediately transformed to less effective species, which hinders the decomposition of TCS. Other studies also suggested near pH 5 as an optimal pH for organic decomposition by Co/PMS system (Anipsitakis & Dionysiou 2003).



Scheme 1 | Molecular and ionized structures of TCS with acid dissociation constant pK_a of 8.1: (a) phenolic form at pH <8.1 and (b) phenolate form at pH >8.1.

$$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + OH^- + H^+ \quad (3)$$

$$SO_4^{\bullet -} + H^+ + e^- \rightarrow HSO_4^{\bullet -} \quad (4)$$

The kinetics of TCS decomposition is somewhat interesting. A non-catalytic reaction evidenced by an initial rapid decomposition followed by a pseudo-steady state was observed at pH 5 and 7, while a catalytic-like activity was seen at pH 3, showing slow but continuous decomposition of TCS over time. Considering that the heterogeneous activation of oxidants by solid state metals is not as effective as the homogeneous activation by dissolved metal ions, determining fractional changes of the solid state and ionic state metals was of particular interest. As shown in Figure 1(b), although a small amount of Co precipitates were found at pH of 7 and 5, a high level of dissolved Co species was always maintained at all pH values. The dissolved Co species at above 2.7 mg/L is considered to be enough to activate PMS, according to the concept of a cobalt threshold concentration (Anipsitakis & Dionysiou 2003). Due to the similar behavior of the dissolved Co fraction over time under different pHs, it did not explain well the unique TCS decomposition kinetics shown in Figure 1(a). Some of the dissolved Co species may not be effective to activate PMS. As a result, we focused on tracing the oxidation state of dissolved Co ions in order to elucidate the catalytic/non-catalytic behavior of the oxidation reaction. Figure 1(c) shows changes in the ionic Co species during the reaction. As expected from Equation (1), maintaining a high concentration of Co^{2+} is important for inducing the catalytic behavior of the overall reaction in order to

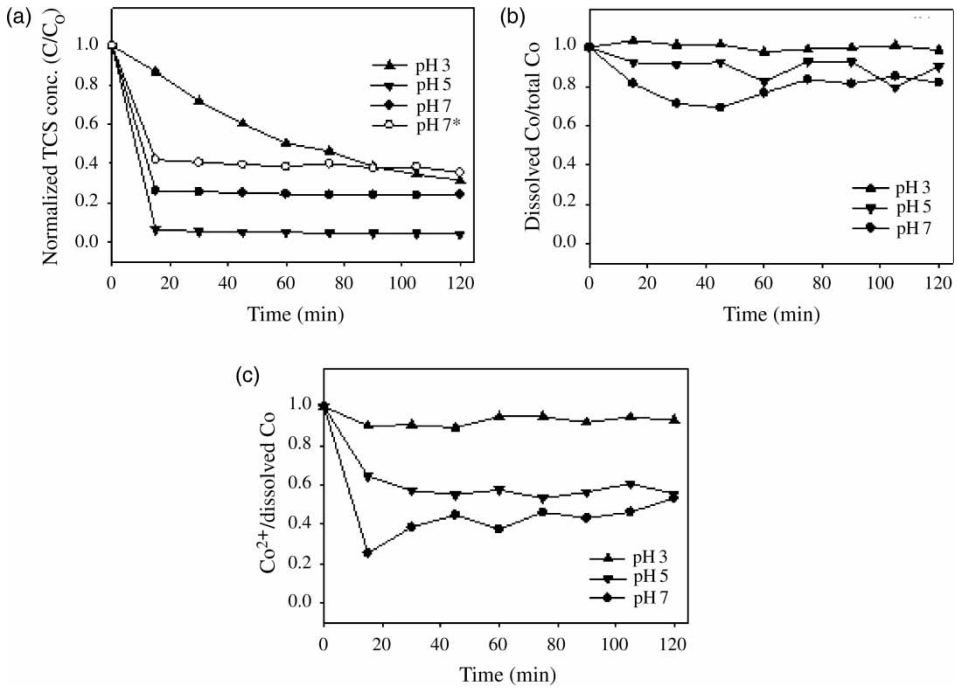


Figure 1 | Effects of pH in a Co/PMS system on (a) TCS decomposition, (b) fraction of dissolved Co/total Co, and (c) fraction of Co^{2+}/dissolved Co. For all reactions, chemicals were added in order of TCS, PMS, and Co, except for pH 7*, chemicals were added in order of PMS, Co, and TCS. $[TCS]_o = 9$ mg/L, $[Co^{2+}]_o = 3.66$ mg/L, and $[PMS]_o = 19.14$ mg/L.

continuously generate SRs and thus decompose TCS. At pH 3, the steady-state high concentration of Co^{2+} at above 3.5 mg/L could explain the continuous decomposition of TCS over time observed in Figure 1(a).

$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{\bullet -} + H^+ \quad (5)$$

During the production of SRs, Co^{2+} is converted to Co^{3+} (note Equation (1)). The generated Co^{3+} can also react with PMS to transform back to Co^{2+} (note Equation (5)). However, the reduction of Co^{3+} to Co^{2+} is generally slower than the oxidation of Co^{2+} to Co^{3+} (Equations (1) and (2)), resulting in accumulation of Co^{3+} in the reaction solution. This is one of possible explanations on why many Fenton-like reactions show non-catalytic behavior in organic oxidation. However, the Co regeneration process is known to be somewhat enhanced under certain conditions. The Co/PMS system at pH 3 seemed successful in regenerating Co^{2+} at all times. On the other hand, a rapid oxidation of Co^{2+} to Co^{3+} was observed at pH 5 and 7. The initial fast decomposition of TCS can be explained by the initial prompt conversion of Co^{2+} to Co^{3+} at pH 5 and 7. Although a certain level of Co^{2+} was continuously maintained, TCS decomposition was almost idle. Similar results showing an initial sharp drop followed by no further reaction were reported by other researchers (Anipsitakis & Dionysiou 2004; Rastogi *et al.* 2009). One notable explanation for this behavior is the presence of a potential threshold concentration of Co^{2+} minimally required to activate PMS. Anipsitakis and Dionysiou reported a minimum concentration of 0.72 mg/L of Co for the effective degradation of 2,4-dihlorophenol (Anipsitakis & Dionysiou 2003). Threshold concentrations might vary depending on the ratio of oxidant and metal added as well as target contaminants. For all the experiments, reactants were added in the order of TCS, PMS and Co^{2+}. PMS alone does not decompose TCS and thus addition of Co^{2+} initiates the decomposition of TCS. Co^{2+} is, however, converted to Co^{3+} while TCS is decomposed. In a separate test, we first added PMS and Co^{2+} before TCS injection. As shown in Figure 1(a), there was a substantial decrease in TCS decomposition when TCS was added later. Significant amount of Co^{2+} added was already converted to Co^{3+} during its instantaneous reaction with PMS before TCS addition. The results so far suggested the importance of

the presence of dissolved Co^{2+} ions for activating PMS to generate SRs and catalytically decompose TCS.

Iron speciation and triclosan decomposition

Similarly to the Co/PMS system, the decomposition of aqueous TCS by the Fe/PMS system was significantly affected by pH conditions, as shown in Figure 2(a). The transformation of TCS ranged from 35 to 60%. The highest TCS decomposition occurred at pH 3. Other studies also reported pH 3 as the best condition of Fe/PMS systems for the decomposition of organic compounds, such as polychlorinated biphenyls (PCBs) (Rastogi *et al.* 2009). Their study showed that decreasing reaction pH in a Fe/PMS system generally increased the oxidation kinetics of PCBs. In this present study, pH 7 was marginally better than pH 5. The slightly different observation might be related to the selective nature of SR attack to specific target organic molecules.

At pH 5, Fe was mainly present in solid form, as shown in Figure 2(b). This was consistent with the lowest TCS decomposition observed at pH 5. On the other hand, a significant amount of dissolved Fe ions were maintained at pH 3 and 7. As mentioned previously, the amount of reactive dissolved species such as Fe^{2+} is more important than total dissolved Fe. However, measuring Fe^{2+} concentration in real time is challenging especially under oxygenated environments since Fe^{2+} readily oxidizes to Fe^{3+} in the presence of any measurable amount of dissolved oxygen in water (Snoeyink & Jenkins 1980). Figure 2(c) shows the fraction of Fe^{2+} ions/total dissolved Fe over time. Fe^{3+} ions were found to be dominant at pH 3 and 7. The initial fast oxidation of Fe^{2+} to Fe^{3+} resulted in a pseudo-steady state TCS decomposition, as observed in Figure 2(a). The result is in agreement with previous studies on Fenton reaction, where the slow Fe regeneration kinetics from Fe^{3+} back to Fe^{2+} is a major drawback of the technology for organic decomposition (Klamerth *et al.* 2010). Although a fairly high concentration of Fe^{2+} was still maintained in the solution (4 mg/L at pH 3 and 5 mg/L at pH 7), TCS decomposition did not progress promptly, suggesting the presence of a potential threshold concentration of Fe to effectively activate PMS. The importance of maintaining high concentration of Fe^{2+} was also examined by changing the order of chemical addition, as shown in Figure 2(a). There was a substantial reduction in the efficiency of the PMS/Fe system when TCS was added

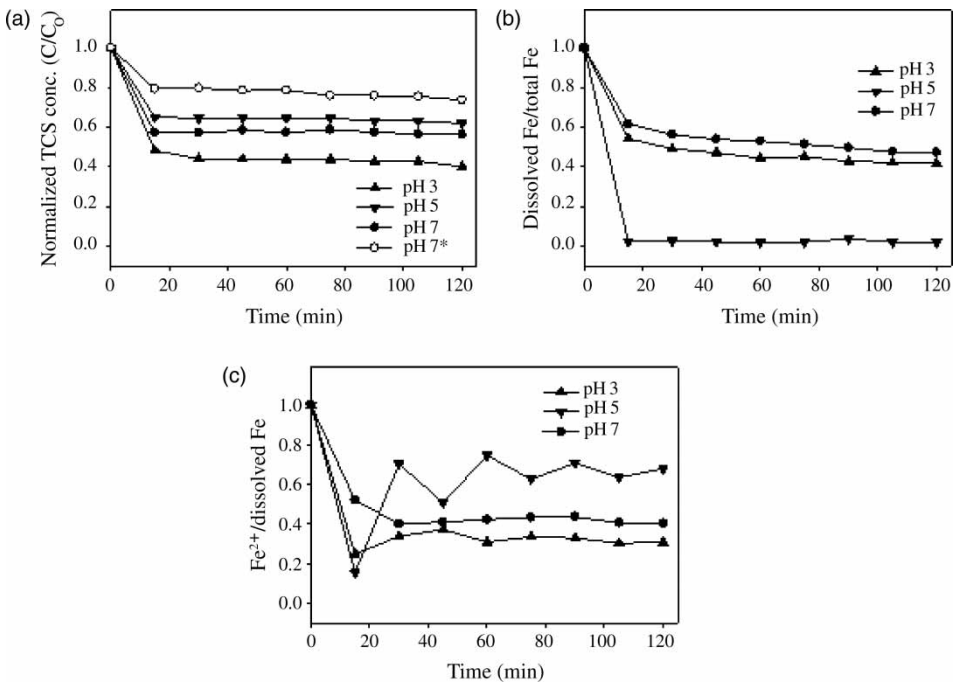


Figure 2 | Effects of pH in a Fe/PMS system on (a) TCS decomposition, (b) fraction of dissolved Fe/total Fe, and (c) fraction of Fe^{2+}/dissolved Fe. For all reactions, chemicals were added in the order of TCS, PMS, and Fe except for pH 7*, chemicals were added in order of PMS, Fe, and TCS. $[TCS]_o = 9$ mg/L, $[Fe^{2+}]_o = 17.36$ mg/L, and $[PMS]_o = 94.69$ mg/L.

later after Fe^{2+} ions pre-reacted with PMS and thus some of them already transformed to Fe^{3+}.

Comparison of Co/PMS and Fe/PMS systems

Although both Co- and Fe-mediated systems effectively generated SRs and decomposed TCS, different impacts of pH on the metal speciation and TCS disappearance were exhibited. Co was mostly dissolved at all pH values tested whereas a fairly high amount of Fe was precipitated and thus not available for the homogeneous activation of PMS. TCS disappearance ranged from 45 to 95% in the Co/PMS system and was more effective at pH 5, while it ranged from 35 to 60% in the Fe/PMS system (even with much higher Fe concentration than Co) and was more effective at pH 3. The large amount of Fe^{2+} required to activate PMS suggests a high threshold concentration of Fe^{2+}, which accounts for the non-catalytic nature of the Fe/PMS system. On the other hand, the steady-state high concentration of Co^{2+} resulting from the effective Co regeneration from Co^{3+} back to Co^{2+} enhanced the catalytic-like activity of the Co/PMS system at pH 3. A potential threshold concentration of Co^{2+} was much lower than Fe^{2+}.

Triclosan mineralization

Mineralization of TCS is another important parameter to evaluate the effectiveness of the metal/PMS systems. Reduction of TOC by Co/PMS and Fe/PMS systems was monitored over 24 h, as shown in Figure 3. Generally, pH conditions did not significantly affect the mineralization of TCS, except for Co/PMS at pH 7. The Co/PMS was much more effective than Fe/PMS, considering a lower dose of Co (TCS/PMS/Co of 1:2:2) was used than Fe (TCS/PMS/Fe of 1:10:10), which is consistent with the observation on the disappearance of original molecular TCS. The disappearance rate of molecular TCS reached a pseudo-steady state within 15 min in most cases, while the mineralization of TCS continuously progressed over the prolonged time. This suggests that SRs might attack preferentially some reaction intermediates rather than the original molecular TCS at some point during the reaction.

CONCLUSIONS

This study has demonstrated the detailed changes in metal speciation in Co/PMS and Fe/PMS systems over time and correlated it with TCS decomposition under different pH regimes. We proved that a rapid oxidation of Co^{2+} to Co^{3+} and Fe^{2+} to Fe^{3+} deteriorates the effective decomposition of TCS and the potential threshold concentration of Fe is much higher than that of Co. A strong catalytic activity was also observed for a Co/PMS system in particular under pH 3, where Co^{3+} seemed to be effectively regenerated back to Co^{2+}. The pH effects on the metal speciation and reactivity were quite different for Co and Fe. Overall, it was concluded that SRs generated from the Co/PMS and Fe/PMS systems are effective to mineralize TCS under various pH conditions. This study contributes towards taking an important first step in understanding the catalytic/non-catalytic nature of the metal-mediated activation of PMS. Our ongoing research studies are targeted at addressing the following question:

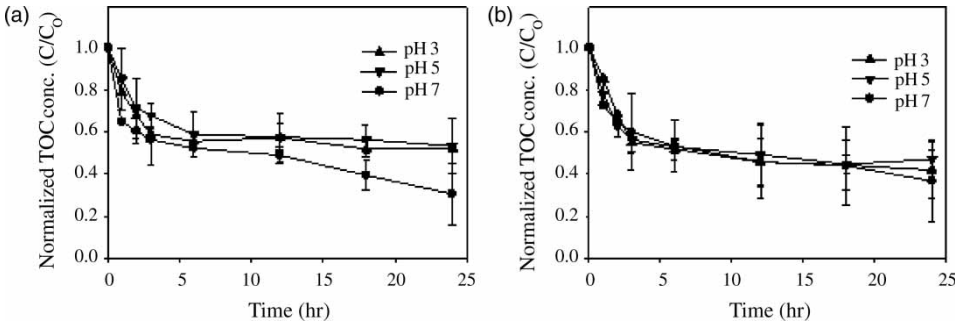


Figure 3 | Effect of pH on TCS mineralization: (a) Co/PMS system at $[Co^{2+}]_o = 3.66$ mg/L, $[PMS]_o = 19.14$ mg/L, and $[TCS]_o = 9$ mg/L and (b) Fe/PMS system at $[Fe^{2+}]_o = 17.36$ mg/L, $[PMS]_o = 94.69$ mg/L, and $[TCS]_o = 9$ mg/L.

are the findings in this study universal and thus applicable to other organic chemicals?

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REFERENCES

Anipsitakis, G. P. & Dionysiou, D. D. 2003 Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt. *Environ. Sci. Technol.* **37** (20), 4790–4797.

Anipsitakis, G. P. & Dionysiou, D. D. 2004 Radical generation by the interaction of transition metals with common oxidants. *Environ. Sci. Technol.* **38** (13), 3705–3712.

Buxton, G. V., Greenstock, C. L., Helman, W. P. & Ross, A. B. 1988 Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/^{\bullet}O^{-}$) in aqueous solutions. *J. Phys. Chem. Ref. Data* **17** (2), 513–886.

Erickson, B. 2010 Targeting triclosan. *Chem. Eng. News* **88** (16), 8.

Klamerth, N., Malato, S., Maldonado, M. I., Aguera, A. & Fernandez-Alba, A. R. 2010 Application of photo-fenton as a tertiary treatment of emerging contaminants in municipal wastewater. *Environ. Sci. Technol.* **44** (5), 1792–1798.

Krishnakumar, B., Anupama, V. N., Anju, S. & Rugminisukumar, M. 2011 Effect of triclosan on protozoa in wastewater treating bioreactors. *Water Sci. Technol.* **63** (4), 754–760.

Lindström, A., Buerge, I. J., Poiger, T., Bergqvist, P. A., Müller, M. D. & Buser, H. R. 2002 Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environ. Sci. Technol.* **36** (11), 2322–2329.

Nfodzo, P. & Choi, H. 2011a Sulfate radicals destroy pharmaceuticals and personal care products. *Environ. Eng. Sci.* **28** (8), 605–609.

Nfodzo, P. & Choi, H. 2011b Triclosan decomposition by sulfate radicals: effects of oxidant and metal doses. *Chem. Eng. J.* **174** (2–3), 629–634.

Rastogi, A., Al-Abed, S. R. & Dionysiou, D. D. 2009 Sulfate radical-based ferrous–peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems. *Appl. Catalysis B: Environm.* **85** (3–4), 171–179.

Safarzadeh-Amiri, A., Bolton, J. R. & Cater, S. R. 1996 The use of iron in advanced oxidation processes. *J. Adv. Oxidation Technol.* **1**, 18–26.

Snoeyink, V. L. & Jenkins, D. 1980 *Water Chemistry*, John Wiley and Sons, New York.

Son, H. S., Chol, S. B., Zoh, K. D. & Khan, E. 2007 Effects of ultraviolet intensity and wavelength on the photolysis of triclosan. *Water Sci. Technol.* **55** (1–2), 209–216.

Spinks, J. W. T. & Woods, R. J. 1990 *An Introduction to Radiation Chemistry*, Wiley-Interscience.

Zorrilla, L. M., Gibson, E. K., Jeffay, S. C., Crofton, K. M., Setzer, W. R., Cooper, R. L. & Stoker, T. E. 2009 The effects of triclosan on puberty and thyroid hormones in male Wistar rats. *Toxicol. Sci.* **107** (1), 56.

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