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Removal of nonionic surfactant from electroplating wastewater by fluidized zerovalent iron with two oxidants (H_2O_2/$Na_2S_2O_8$)

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ABSTRACT

Removal of nonylphenol polyethoxylate with 9 mol of ethoxylate (NP9EO), a nonionic surfactant, from electroplating wastewater by fluidized zerovalent iron (ZVI) with two oxidants (ZVI/H_2O_2 and ZVI/$S_2O_8^{2-}$) was studied. There are several benefits of using the proposed system: (1) the free radicals that result from the processes can reduce the organic contents and the occurrence of nonylphenol, an endocrine disruptor, (2) the ferric ion, dissoluted from the reaction for ZVI, can act as a coagulant to assist in the following precipitation process and (3) a higher ZVI utilization for the fluidized process due to abrasive motion of the ZVI. For the ZVI/H_2O_2 system, under optimum operating conditions, when the pH is 4.0, and Hydraulic Detention Time (HDT) 1.5 min and H_2O_2 concentration 23.6 mM, NP9EO and TOC removal efficiencies were 99 and 54%, respectively. The removal efficiency were increased with increased H_2O_2 dosage, but became reduced when H_2O_2 dosage was in excess of 23.6 mM. For the ZVI/$S_2O_8^{2-}$ system, when the optimum operating conditions for pH value and HDT were 4.5 and 0.75 min, the removal efficiencies increased with an increase in $S_2O_8^{2-}$ dosage. The removal efficiency of the ZVI/H_2O_2 was better than that of ZVI/$S_2O_8^{2-}$ at the same pH value, HDT and oxidant dosage, but less acidity was required to maintain the constant pH for the ZVI/$S_2O_8^{2-}$ system. In addition, ferrous ion, which was able to be measured quickly, can be used as an indicator for the removal of both TOC and NP9EO.

Keywords: Nonionic surfactant; Nonylphenol polyethoxylate; Fluidized; Zerovalent iron; H_2O_2; $S_2O_8^{2-}$
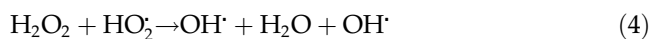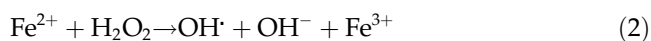
1. Introduction

Nonylphenol polyethoxylate (NPnEO) is a nonionic surfactant that is widely used in the electroplating industry for surface cleaning, but it is also a major organic contaminant and precursor of nonylphenol (NP), which is an endocrine-disrupting chemical affecting the human endocrine system. NP is a hydrophobic material with low water solubility (5.4 mg/L), indicating that bioaccumulation takes place easily in aquatic organisms. Since the biological treatment of NPnEO is questionable due to the generation of NP [1,2], the physicochemical process has to be developed for dealing with the problem of treating NPnEO. Despite many physicochemical applications used for the removal of NPnEO, such as TiO_2 photocatalysis
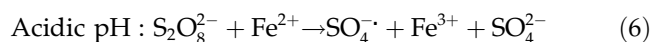
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[3], electrocoagulation and electrochemical Fenton [4], UV photolysis [5], integrated sonochemical and microbial treatment [6], UV-C/H_2O_2, UV-A/TiO_2, photo-Fenton [2], none of them have discussed continuous flow fluidized zerovalent iron (ZVI) system with different oxidants. There are several benefits of using the proposed system: (1) the free radicals that resulted from the processes can reduce the organic contents and the occurrence of NP, (2) the ferric ion, dissolved from the reaction for ZVI, can act as a coagulant to assist in the precipitation process typically utilized, and (3) a higher ZVI utilization for the fluidized process due to the abrasive motion of ZVI. Consequently, fluidized ZVI/H_2O_2 and ZVI/$S_2O_8^{2-}$ processes were designed in this study to reduce the hydrophilicity (ethoxylate chains in NPnEO) and enhance the removal efficiency for nonylphenol polyethoxylate with 9 mol of ethoxylate (NP9EO), since both processes are very easy to incorporate into small-scale electroplating plants. In addition, the benefit of using ZVI to activate these two oxidants is easy to operate without keeping adding the ferrous or ferric ions.

The Fenton processes utilizing ferrous ion and H_2O_2 to generate high oxidative power of hydroxyl radical (OH·) were widely reported in the wastewater treatment process, and the modified Fenton processes using ZVI due to the Fe^{2+} salts are particularly advantageous as they can be applied in either the fluidized or the column system without going on adding ferrous ion. In the ZVI/H_2O_2 system, ZVI produces an Fe^{2+} ion, as per Eq. (1), so the concentration of Fe^{2+} can be maintained by the addition of ZVI. The Fe^{2+} ion subsequently reacts with H_2O_2 as in traditional Fenton reactions mentioned in Eqs. (2)–(5). The concentration of Fe^{2+} in the Fenton and Fenton-like processes is crucial for an efficient oxidation of the target organic compounds:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow OH· + OH^- + Fe^{3+} \tag{2}$$

$$H_2O_2 + OH· \rightarrow H_2O + HO_2· \tag{3}$$

$$H_2O_2 + HO_2· \rightarrow OH· + H_2O + OH· \tag{4}$$

$$Fe^{2+} + OH· \rightarrow OH^- + Fe^{3+} \tag{5}$$

In the ZVI/$S_2O_8^{2-}$ system, ZVI is used to activate $S_2O_8^{2-}$ also without going on adding ferrous ion. ZVI produces Fe^{2+}, according to Eq. (1), and since persulfate is a strong chemical oxidant ($E^o = 2.01$ V), it can be

activated by transition metal ions such as Fe^{2+} under acidic pH to form a sulfate radical ($SO_4^-·$), which is an even stronger oxidizing agent ($E^o = 2.60$ V) than the persulfate, as seen in Eq. (7). The hydroxyl radical can also be formed in all pHs, as seen in Eq. (8) [7,8].

$$\text{Acidic pH}: S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^-· + Fe^{3+} + SO_4^{2-} \tag{6}$$

$$\text{All pHs}: SO_4^-· + H_2O \leftrightarrow OH· + H^+ + SO_4^{2-} \tag{7}$$

None of the studies have reported the degradation and mechanism of NP9EO by ZVI to activate these two oxidants, but the Fenton (Fe^{2+}/H_2O_2) and photo-Fenton (UV/Fe^{2+}/H_2O_2) processes for NP9EO treatment have been discussed before [2,4,6,9–11]. Kitis et al. [9] used the Fenton process as a pretreatment before the biological process, and the results showed that a lower oxidant dosage decreases the biodegradable fraction of NP9EO, but the biodegradable fraction was increased at higher dosages, since lower oxidant dosages shortened the EO chain of NPEs primarily, but higher dosages provided adequate hydroxyl radicals to react with hydrophobic NP. De La Fuente et al. [2] used the photo-Fenton system to remove the NP9EO and the result showed that the most efficient NP9EO/H_2O_2/Fe^{2+} molar ratio was 1:1:0.5. Degradation products were also investigated in this study and 4-NP was not found as a byproduct of degradation and a low concentration of aldehydes was observed. Nagarnaik and Boulanger [11] presented the oxidation of APEOs (alkylphenol polyethoxylates) through Fenton's and photo-Fenton's reagents in ultrapure water and in aqueous environmental matrices. The second-order kinetic rate constant for both NPnEO and octylphenol polyethoxylate with OH· was calculated to be $1.1 \times 10^{10}\,M^{-1}\,s^{-1}$. The efficiency of these processes was dependent on the rate of formation of OH· and the scavenging capacity of the matrix.

In the present study, the removal of NP9EO by fluidized ZVI with two oxidants was designed, since the fluidized ZVI process makes pH control and mixing possible through addition of acidity, i.e. controlling pH, and achieve adequate mixing intensity [12] among the fluidized ZVI. Utilization of ZVI for fluidized process would also be higher due to abrasive motion of the ZVI to remove any layer that could possibly be precipitated on ZVI [12]. Due to the above-mentioned advantages, a fluidized ZVI treatment system was proposed to be used to investigate the NP9EO reduction in this study. Therefore, the objectives of this study are to compare the two oxidants for their effects of pH, Hydraulic Detention Time (HDT), and oxidant dosage, and to discuss the speciation and

mechanism of the NP9EO reaction by Gas Chromatography/Mass Spectrometry (GC/MS).

2. Methods

All chemicals used are of reagent grade. Laboratory grade ZVI powder (40 mesh, about 212 µm in diameter, purchased from RDH Chemical Co.) with a surface area of 0.183 m^2/g was measured by the BET analysis. Fig. 1 is a schematic setup of the experimental system. A glass column with a diameter of 30 mm and a length of 500 mm was employed as the reactor. The total volume of 353 ml was controlled by a fluid-level controller. A circulation pump was installed for maintaining the upflow velocity of at least 72 m/h to fluidize the ZVI. The HDT was changed by varying the flow rate of the influent and effluent pumps. The system pH was controlled by a glass electrode and a pH controller, which controls the dosing of sulfuric acid (0.5 N). The effluent that is being withdrawn continuously from the top of the effluent is around 2 cm above that of the circulation pump to avoid the carry over of ZVI.

Research was carried out on a fixed influent concentration of NP9EO (200 mg/L), different influent pH (1.5, 2, 3, and 4), hydraulic detention time (0.75, 1.5, and 3 min), different oxidant concentration (15, 25, and 35 mM), and fixed dosage of ZVI (50 g or 141.6 g/L). All chemicals were of analytical grade and aqueous solutions were prepared with analytical grade Milli-Q water (Millipore). The NP9EO concentration was measured by a high-performance liquid chromatograph (HPLC). The HPLC includes a 20 µL sample loop, a Thermo Scientific Hypersil BDS C18 column (Thermo Fisher Scientific Inc., USA) with 150 mm in length, 4.6 mm in diameter, 5 µm packing diameter with corresponding guard column, and a photo-diode array detector that is operated at a wavelength of 258 nm (Hitachi L-300, Japan). The total iron content was analyzed using the flame atomic adsorption spectroscope (GBC 932, GBC Scientific Equipment, Australia). Ferrous ions were analyzed colorimetrically at 510 nm after forming colored complexes with 1,10-phenanthroline according to the Standard Methods 3500-Fe [13] by a UV–vis spectrophotometer (HACH Model DR-4000). Quantitative analysis of Fe^{3+} was performed by subtracting the Fe^{2+} concentration from the total iron concentration. The total organic carbon (TOC) was measured using the Aurora 1030C TOC Analyzer which was purchased from the O.I. Analytical Corporation in USA. The EDTA byproducts were measured by GC/MS equipped with the DB-5 column by the GC model Agilent 6890N and the MS model Agilent 5973N, respectively.

3. Results and conclusions

3.1. Effects of pH, HDT, and oxidant concentration

Figs. 2 and 3 show the comparison of ZVI/H$_2$O$_2$ and ZVI/S$_2$O$_8^{2-}$ systems on the removal of NP9EO for different pHs for an HDT of 3.0 min, dosages of 23.6 mM, influent NP9EO concentration of 200 mg/L, and a ZVI of 50 g. The results show that, for the ZVI/ H$_2$O$_2$ system, the optimum pH value was around 4.0 in which the NP9EO and TOC removal efficiencies were 99 and 54%, respectively. A lower pH resulted in excess ferrous ion from Eq. (1), contributing to the consumption of the OH radical since any excess ferrous ion could react with the generated OH$^{\cdot}$, which was reported previously [14]. In addition, a higher pH
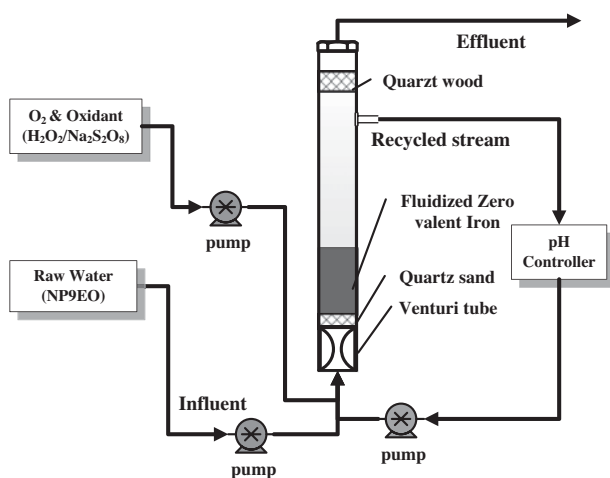

Fig. 1. Schematic diagram of the fluidized ZVI with H$_2$O$_2$/ S$_2$O$_8^{2-}$ systems.
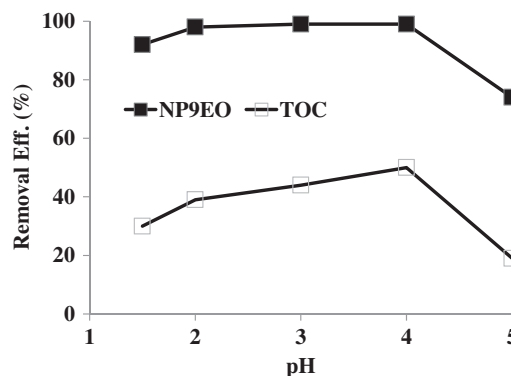

Fig. 2. ZVI/H$_2$O$_2$ on the removal of NP9EO for different pHs (HDT: 3.0 min, H$_2$O$_2$ = 23.6 mM (800 mg/L), [NP9EO] = 200 mg/L and ZVI = 50 g).
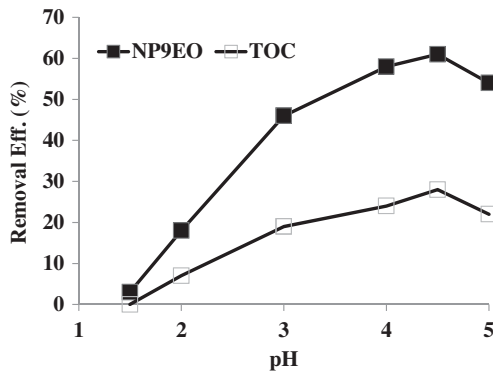
Fig. 3. ZVI/Na$_2$S$_2$O$_8$ on the removal of NP9EO for different pHs (HDT: 3.0 min, Na$_2$S$_2$O$_8$ = 23.6 mM (5,600 mg/L), [NP9EO] = 200 mg/L and ZVI = 50 g).

converted the ferrous ion to a ferric ion, which reduced the efficiency of the Fenton reaction.

For the ZVI/S$_2$O$_8^{2-}$ system in the same operating condition, the optimum pH value was around 4.5 in which the NP9EO and TOC removal efficiencies were 60 and 30%, respectively. The removal efficiency was gradually increased up to pH 4.5, but leveled off when the pH was higher than 4.5. The results can be explained again that at low pH, the efficiency was lower since the excess ferrous ion can react with the OH· generated from Eq. (8), but when the pH was above 4.5, the ferrous ion became less and the overall sulfate radicals were also less based on Eq. (7). Comparing the ZVI/H$_2$O$_2$ and ZVI/S$_2$O$_8^{2-}$ systems, the removal efficiency of ZVI/H$_2$O$_2$ was better than that of ZVI/S$_2$O$_8^{2-}$ on the same pH value, HDT, and oxidant dosage, contributing to one more hydroxyl radical being generated for ZVI/H$_2$O$_2$ than for ZVI/S$_2$O$_8^{2-}$ on the stoichiometric base. However, the benefit of using ZVI/S$_2$O$_8^{2-}$ is that almost no acid was added
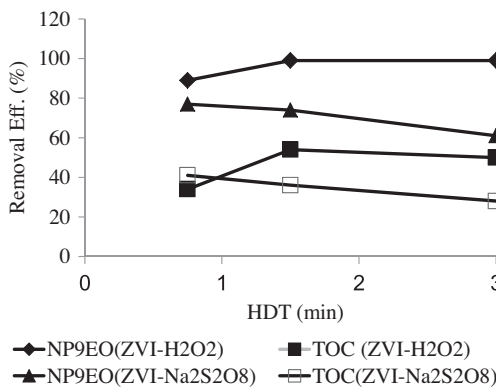
Fig. 4. ZVI/H$_2$O$_2$ vs. ZVI/S$_2$O$_8^{2-}$ for the removal of NP9EO under different HDTs for H$_2$O$_2$ of pH 4.0, Na$_2$S$_2$O$_8$ of pH 4.5, oxidant: 23.6 mM, [NP9EO] = 200 mg/L, and ZVI = 50 g (141.6 g/L).
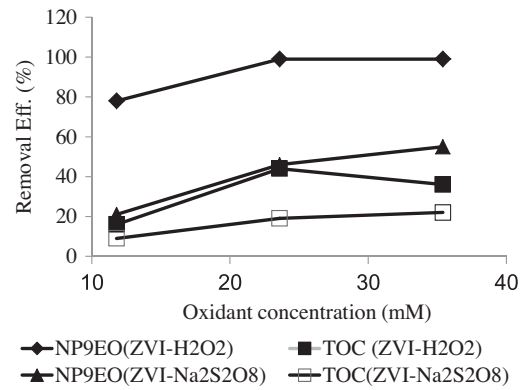

Fig. 5. ZVI/H$_2$O$_2$ vs. ZVI/S$_2$O$_8^{2-}$ for the removal of NP9EO under different oxidant concentration for HDT = 3.0 min, pH: 3.0, [NP9EO] = 200 mg/L, and ZVI = 50 g (141.6 g/L).

since the hydrogen ion was generated according to Eq. (8). Therefore, controlling pH is easier for the ZVI/S$_2$O$_8^{2-}$ compared to the ZVI/H$_2$O$_2$ system. In addition, the rejection of TOC was way less than the rejection of NP9EO, indicating some of the byproducts
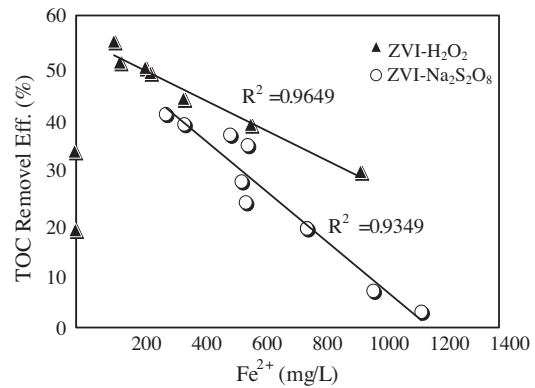

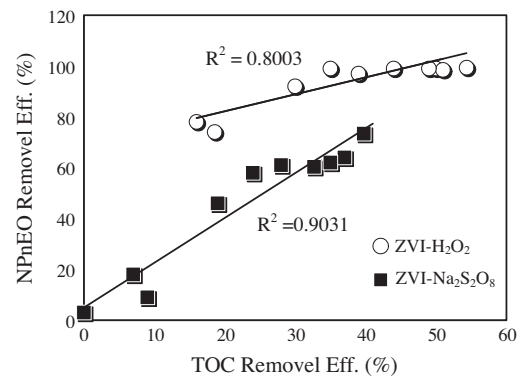Fig. 6. TOC removal efficiency vs. ferrous ion concentration for ZVI/H$_2$O$_2$ and ZVI/S$_2$O$_8^{2-}$ system.

Fig. 7. NP9EO removal efficiency vs. ferrous ion concentration for ZVI/H$_2$O$_2$ and ZVI/S$_2$O$_8^{2-}$ system.
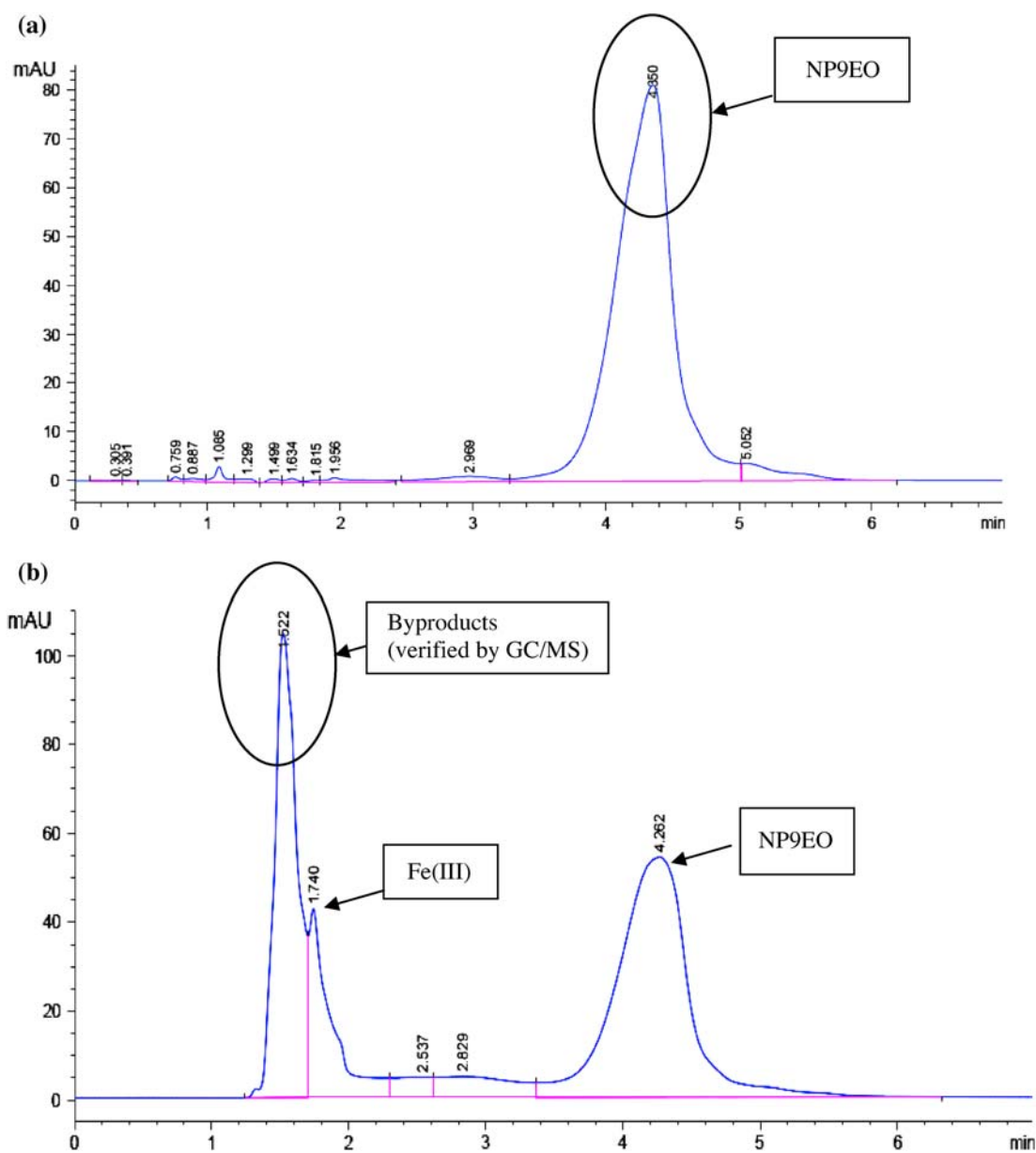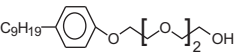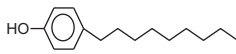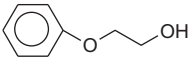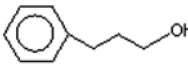
Fig. 8. Chromatography of HPLC for (a) raw water containing 200 mg/L NP9EO and (b) treated after fluidized ZVI/ H_2O_2 system experimental condition of pH 4, detention time of 1.5 min, and ZVI 50 g (141.6 g/L).
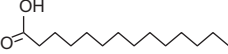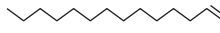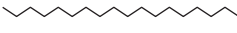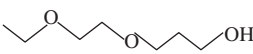
were formed, instead of the mineralization to CO_2. Therefore, the byproducts were analyzed conducted and are presented in the later section.

Fig. 4 presents the effects of different HDTs on the removal of NP9EO for both systems in the same operating conditions, except pH 4.0 for ZVI/H_2O_2 and pH 4.5 for ZVI/$S_2O_8^{2-}$, obtained from Figs. 2 and 3. The results show that, under HDT of 3 min, degradation of NP9EO can reach above 80% for both systems, representing a very small space that is required to utilize both the processes. However, for a ZVI/$S_2O_8^{2-}$ system,

longer HDT did not have benefits on the removal efficiencies, possibly due to the short lifetime of a sulfate radical. Fig. 5 shows the removal of NP9EO for these two systems under different oxidant concentration for an HDT of 3.0 min, influent NP9EO concentration of 200 mg/L, and ZVI of 50 g (141.6 g/L). The results show that the removal efficiency was increased with oxidant dosage, but it was reduced when the oxidant dosage was in excess of 23.6 mM, but the removal efficiencies increased with an increase of $S_2O_8^{2-}$ dosage up to 35 mM.

Table 1
Byproduct analysis from GC/MS

NP2EO	NP	2-Phenoxyethanol	Benzenepropanol
64	88	96	59

Tetradecanoic acid	1-Tetradecene	Octadecane	2-(2-ethoxyethoxy)-
93	97	95	72

3.2. Byproducts and speciation for ZVI/H_2O_2 and $ZVI/Na_2S_2O_8$ reaction

Since low pH is controlled in these fluidized systems, ferrous ion is the predominant species for dissolved iron species. Ferrous ion was reported as an indicator to represent the contaminant removal efficiency in the fluidized ZVI system [15]. Consequently, Fig. 6 presents the TOC removal vs. the ferrous ion concentration and the results show TOC removal efficiency is inversely correlated to the presence of ferrous ion, indicating that the consumption of ferrous is critical for the removal of TOC. Since the removal of NP9EO and TOC is proportional as indicated in Fig. 7, ferrous ion, which was able to measure quickly, can be used as an indicator to represent both TOC and NP9EO removal.

Furthermore, from previous results, TOC is consistently lower than the removal efficiency of NP9EO, indicating other than mineralization to CO_2, some of the intermediates were also generated. Chromatography of HPLC result was presented for (a) raw 200 mg/L NP9EO and (b) treated after fluidized ZVI/H_2O_2 system for experimental condition of pH 4, detention time of 1.5 min, and ZVI 50 g (141.6 g/L). Comparing these two figures, other than a NP9EO peak, two peaks representing Fe(III) and byproducts are observed in Fig. 8(b). Therefore, these byproducts were analyzed by the GC/MS and are presented in Table 1, and the quality numbers are also listed below for reference. These byproducts include NP2EO, NP, 2-phenoxyethanol, benzenepropanol, tetradecanoic acid, 1-tetradecene, octadecane, and 2-(2-ethoxyethoxy). Although there was still some NP observed in these byproducts, it should be removed by further coagulation since NP is more hydrophobic species and is easier to remove by the coagulation process.

4. Conclusion

Removal of NP9EO from electroplating wastewater by fluidized ZVI with two oxidants (ZVI/H_2O_2 and ZVI/$S_2O_8^{2-}$) was studied. The results showed, for the ZVI/H_2O_2 system, when the oxidant concentration was 23.6 mM, the pH value was 4.0, and the HDT was 1.5 min, and the NP9EO and TOC removal efficiencies were 99 and 54%, respectively. The removal efficiency increased with H_2O_2 dosage, but became reduced when H_2O_2 was in excess of 23.6 mM. For the ZVI/$S_2O_8^{2-}$ system, the optimum operating conditions for pH value and HDT were 4.5 and 0.75 min, and the removal efficiencies were also increased with an oxidant of the $S_2O_8^{2-}$ dosage. The removal efficiency of ZVI/H_2O_2 was better than that of ZVI/$S_2O_8^{2-}$ on the same pH value, HDT, and oxidant dosage, but less acidity was required to maintain a constant pH for the ZVI/$S_2O_8^{2-}$ system. In addition, ferrous ion, which was able to measure quickly, can be used as an indicator for both TOC and NP9EO removal.

References

[1] N. Brand, G. Mailhot, M. Bolte, Degradation photoinduced by Fe(III): Method of alkylphenol ethoxylates removal in water, Environ. Sci. Technol. 32 (1998) 2715–2720.

[2] L. De La Fuente, T. Acosta, P. Babay, G. Curutchet, R. Candal, M.I. Litter, Degradation of nonylphenol ethoxylate-9 (NPE-9) by photochemical advanced oxidation technologies, Ind. Eng. Chem. Res. 49 (2010) 6909–6915.

[3] E. Pelizzetti, C. Minero, V. Maurino, A. Sclafani, H. Hidaka, N. Serpone, Photocatalytic degradation of nonylphenol ethoxylated surfactants, Environ. Sci. Technol. 23 (1989) 1380–1385.

[4] A.F. Martins, M.L. Wilde, T.G. Vasconcelos, D.M. Henriques, Nonylphenol polyethoxylate degradation by means of electrocoagulation and electrochemical Fenton, Sep. Purif. Technol. 50 (2006) 249–255.

[5] L. Chen, H.-y. Zhou, Q.-y. Deng, Photolysis of nonylphenol ethoxylates: The determination of the degradation kinetics and the intermediate products, Chemosphere 68 (2007) 354–359.

[6] G. Cravotto, S. Di Carlo, A. Binello, S. Mantegna, M. Girlanda, A. Lazzari, Integrated sonochemical and microbial treatment for decontamination of nonylphenol-polluted water, Water Air Soil Pollut. 187 (2008) 353–359.

[7] S.-Y. Oh, S.-G. Kang, P.C. Chiu, Degradation of 2,4-dinitrotoluene by persulfate activated with zero-valent iron, Sci. Total Environ. 408 (2010) 3464–3468.

[8] C. Liang, Z.-S. Wang, C.J. Bruell, Influence of pH on persulfate oxidation of TCE at ambient temperatures, Chemosphere 66 (2007) 106–113.

[9] M. Kitis, C.D. Adams, G.T. Daigger, The effects of Fenton's reagent pretreatment on the biodegradability of nonionic surfactants, Water Res. 33 (1999) 2561–2568.

[10] G. Lofrano, S. Meric, M. Inglese, A. Nikolau, V. Belgiorno, Fenton oxidation treatment of tannery wastewater and tanning agents: Synthetic tannin and nonylphenol ethoxylate based degreasing agent, Desalination and Water Treatment 23 (2010) 173–180.

[11] P.M. Nagarnaik, B. Boulanger, Advanced oxidation of alkylphenol ethoxylates in aqueous systems, Chemosphere 85 (2011) 854–860.

[12] Y.-M. Chen, C.-W. Li, S.-S. Chen, Fluidized zero valent iron bed reactor for nitrate removal, Chemosphere 59 (2005) 753–759.

[13] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard methods for the examination of water and wastewater, in: American Public Health Association, American Water Work Association and Water Environment Federation, 20th ed., American Public Health Association, Washington, DC, 1998.

[14] C.S. Chiou, C.F. Chang, C.T. Chang, J.L. Shie, Y.H. Chen, Mineralization of Reactive Black 5 in aqueous solution by basic oxygen furnace slag in the presence of hydrogen peroxide, Chemosphere 62 (2006) 788–795.

[15] S.S. Chen, C.Y. Cheng, C.W. Li, P.H. Chai, Y.M. Chang, Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process, J. Hazard. Mater. 142 (2007) 362–367.