



Coagulation enhancement of nonylphenol ethoxylate by partial oxidation using zero-valent iron/hydrogen peroxide

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ABSTRACT

Coagulation enhancement of nonionic surfactant nonylphenol polyethoxylate with 9 mol of ethoxylate (NP9EO), was conducted by partial oxidation using zero-valent iron (ZVI)/hydrogen peroxide (H₂O₂) since coagulation is a typical process in many small-scale wastewater treatment plants but it is difficult to remove NP9EO due to micelle formation, and partial oxidation as pretreatment using the proposed process might be adequate and economically feasible. In this study, effects of pH, ZVI dosage, and H₂O₂ concentration were all investigated. The results show, highest NP9EO removal was observed at pH 2 instead of pH 1.5, since the presence of extra ferrous ion in the lower pH consumed the hydroxyl radicals, resulting in low removal efficiency. In addition, ferrous ion was converted to ferric ion for pH higher than 2 which reduced the efficiency of Fenton reaction. NP9EO removal efficiency by coagulation with ZVI/H₂O₂ pretreatment was as high as 99%, which is 40% higher than that without ZVI/H₂O₂ pre-treatment. The optimum dosages for ZVI/H₂O₂ oxidation were about 125 mg/L of H₂O₂ and 3 g/L of ZVI with NP9EO removal higher than 85%. But considering the following coagulation, the optimum dosages were about 125 mg/L of H₂O₂ and 2.5 g/L of ZVI with NP9EO removal efficiency of 95%. Besides, the dissolution of ferric ion from ZVI/H₂O₂ was able to reduce/replace the requirement of the traditional ferric chloride.

Keywords: Coagulation; Partial oxidation; Nonylphenol polyethoxylate; Zero-valent iron; H₂O₂

1. Introduction

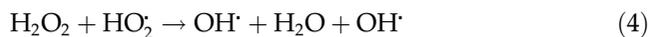
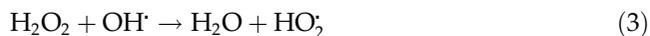
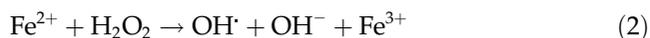
Nonylphenol polyethoxylate with 9 mol of ethoxylate (NP9EO), is widely used as nonionic surfactants, particularly in household detergents as well as surface cleaning for industry. NP9EO is a hydrophobic nonyl-

phenol (NP) structure connected with hydrophilic chain of ethylene oxide. Through traditional aerobic treatment, NP9EO is demonstrated to start with an ethoxylate chain shortening and the effluent contains short-chain NPnEO such as NP1EO or NP2EO. Furthermore, through anaerobic process, the short-chained nonylphenol polyethoxylate complete deethoxylation with the formation of NP, an

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endocrine-disrupting chemical affecting human endocrine system, in nature [1,2]. Therefore, other than traditional biological treatment, some new technology has to be developed for dealing with the problem of NP9EO. In this study, coagulation enhancement of NP9EO by partial oxidation using zero-valent iron (ZVI)/hydrogen peroxide (H_2O_2) was conducted since coagulation is a typical process in many small-scale wastewater treatment plants but it is difficult to remove NP9EO due to micelle formation, and partial oxidation as pretreatment using the proposed process might be adequate and economically feasible. Two major reasons for using ZVI/ H_2O_2 oxidation/coagulation application can be summarized as: (1) ZVI combining with H_2O_2 is capable of generating hydroxyl radical to furthermore destruct polyethoxylate chain and increase the hydrophobicity to benefit the following coagulation and (2) the coagulation dosage is significantly reduced due to the dissolution of ferric ion from the usage of ZVI. Besides, it is easy to incorporate into small-scale industry using NP9EO such as many small-scale electroplating plants in Taiwan.

As mentioned, since biological treatment of NP9EO is questionable due to generation of NP, physicochemical process has to be developed for dealing with the problem of treating NP9EO. Although many physicochemical applications have been used for the removal of NP9EO, such as photo-Fenton [2], TiO_2 photocatalysis [3], electrocoagulation electrochemical Fenton [4], UV photolysis [5], integrated sonochemical, and microbial treatment [6], none of them have discussed the proposed ZVI/ H_2O_2 system. In ZVI/ H_2O_2 system, ZVI produces Fe^{2+} ion, according to Eq. (1), so the concentration of Fe^{2+} is maintained, and the generated Fe^{2+} ion react with H_2O_2 as reported from Eqs. (2)–(5). The concentration of Fe^{2+} in Fenton and Fenton-like processes is crucial for the effective oxidation of the target contaminants.



Traditional Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and photo-Fenton ($\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$) processes for NP9EO treatment were discussed before [2,4,7–9]. Kitis et al. [7] reported using traditional Fenton process as a pretreatment before biological process, and the results showed that low oxidant dosage was capable of decreasing biodegradable fraction of NP9EO, but biodegradable fraction was increased at higher dosages, since lower oxidant dosages shortened EO-chain of NP9EO primarily but higher dosages provided adequate hydroxyl radicals to react with hydrophobic NP. De La Fuente et al. [2] used photo-Fenton system to remove NP9EO and the result showed that the most effective NP9EO/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio was 1:1:0.5 under UV light. Nagarnaik et al. [9] presented the oxidation of 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 nonylphenol polyethoxylate (NPnEO) and octylphenol polyethoxylate (OPnEO) with OH^\cdot was both calculated to be $1.1 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$. The efficiency of these processes depended on the rate of formation of OH^\cdot and the scavenging capacity of the matrix.

Since one of the benefits of using the ZVI/ H_2O_2 is the capability of generating hydroxyl radical to destruct the micelle, i.e. the inside hydrophobic NP wrapped by outside hydrophilic EO, to assist the following coagulation, the critical factor in this system is to determine the effects of pH and dosage of ZVI/ H_2O_2 on oxidation pretreatment as well as the following coagulation. In addition, byproducts of the NP9EO reaction from oxidation/coagulation were also analyzed by gas chromatography/mass spectrometry (GC-MS) as well.

2. Methods and materials

This study included two stages of experiment. First of all, the ZVI/ H_2O_2 process was used to pretreat NP9EO. Secondly, the samples were coagulated from the residual ferric ion. Parameters such as pH, ZVI dosage, and H_2O_2 concentration were investigated for ZVI/ H_2O_2 oxidation at different pH and coagulation values (pH=8) in this experiment. The reason to set up pH 8 for the coagulation since the coagulated pH is well known and applied in the field. The research was carried out in a fixed influent concentration of NP9EO (1,000 mg/L), different influent pH values (1.5, 2, 3, and 4), different dosages of ZVI (1, 2, 3, and 5 g/L) and H_2O_2 (30, 70, 125, and 250 g/L). In the first step, desired dosages were added into a 1-L beaker

and samples were taken until oxidation reaction was completed. ZVI residual was then removed to perform further iron coagulation. Rapid mixing of 30 s at 100 rpm followed by slow mixing of 20 min at 30 rpm was conducted in which polymer (polyethyleneimine) was added during slow mixing. Samples were then taken after precipitation for 30 min.

All chemicals were of analytical grade and aqueous solutions were prepared with analytical grade Milli-Q water (Millipore). 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 measured by BET analysis. Before usage, a 20-min acid wash (1N sulfuric acid) was conducted on these ZVI powder to remove possible iron oxide layer on the ZVI surface. NP9EO concentration was measured by a high performance liquid chromatography (HPLC). The HPLC includes a 20- μL sample loop, a Thermo BDS Hypersil 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 operated at wavelength of 258 nm (Hitachi L-300, Japan). The total iron content was analyzed using the flame atomic adsorption spectroscopy (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 [10] by a UV-vis spectrophotometer (HACH Model DR-4000). The quantitative analysis of Fe^{3+} was obtained by subtracting Fe^{2+} concentration from total iron concentration. Total organic carbon (TOC) was measured using Aurora 1030C TOC Analyzer purchased from O.I. Analytical Corporation in USA. Byproducts of NP9EO were measured by GC-MS equipped with DB-5 column by GC model Agilent 6890N and MS model Agilent 5973N, respectively.

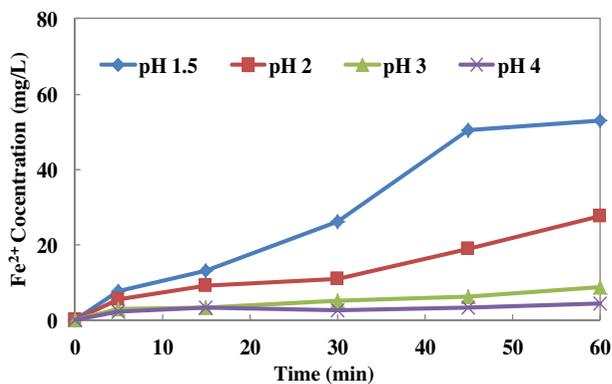


Fig. 1. Ferrous concentration vs. time for different pH values (NP9EO 1,000 mg/L, ZVI 3 g/L, H_2O_2 70 mg/L).

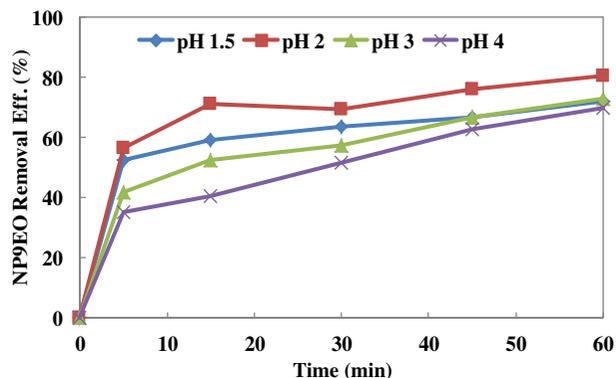


Fig. 2. NP9EO removal vs. time for different pH values (NP9EO 1,000 mg/L, ZVI 3 g/L, H_2O_2 70 mg/L).

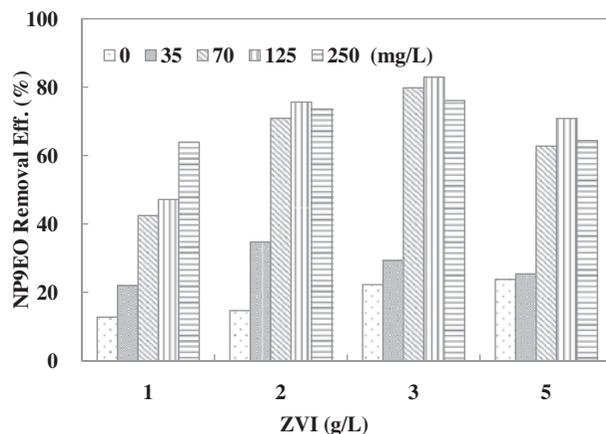


Fig. 3. Effects of dosage of ZVI and H_2O_2 on NP9EO removals at pH 2.

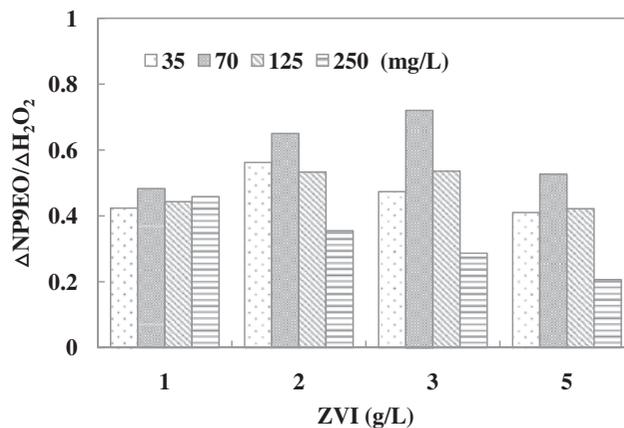


Fig. 4. Effects of dosage of ZVI and H_2O_2 on $\Delta\text{NP9EO}/\Delta\text{H}_2\text{O}_2$ at pH 2.

3. Results and conclusions

3.1. Effects of pH and dosage of ZVI/H₂O₂ for partial oxidation

Fig. 1 presents the ferrous ion concentration for ZVI 3 g/L and H₂O₂ 70 mg/L for different pH values, and higher ferrous ion concentration was observed at the lowest pH (pH 1.5) due to low pH favoring dissolution of ferrous ion according to Eq. (1). However, in Fig. 2, highest NP9EO removal was observed at pH 2 instead of pH 1.5, since the presence of extra ferrous ion in the lower pH could consume the hydroxyl radicals according to Eq. (5), resulting in low removal efficiency [11]. In addition, ferrous ion was converted to

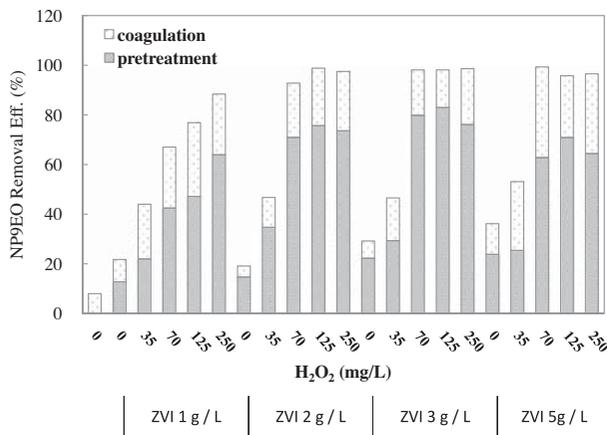


Fig. 5. NP9EO removals by ZVI/H₂O₂ oxidation and coagulation (pH 2 for oxidation and pH 8 for chemical coagulation).

ferric ion for pH higher than 2 which reduced the efficiency of Fenton reaction.

Fig. 3 shows effects of dosage of ZVI and H₂O₂ on NP9EO removals at pH 2. Apparently, without the addition of H₂O₂, removal efficiencies were lower than 24% regardless of ZVI dosage. As H₂O₂ dosage increases, removal efficiencies increased to higher than 80% for H₂O₂ dosage of 125 mg/L at ZVI 3 g/L, resulting from the generation of hydroxyl radicals. But the removal efficiencies were reduced for H₂O₂ higher than 125 mg/L, since the hydroxyl radicals were consumed by excess H₂O₂. Therefore, the optimum dosage of H₂O₂ is determined as 125 mg/L. In addition, as ZVI dosage increased, removal efficiencies also increased to higher than 80% from 1 to 2 g/L with the presence of H₂O₂, resulting also from the generation of hydroxyl radicals. But the removal efficiencies were reduced for dosage of H₂O₂ higher than 3 g/L, since hydroxyl radical was consumed by excess ferrous ion as well, as mentioned previously. Furthermore, molar ratio of $\Delta\text{NP9EO}/\Delta\text{H}_2\text{O}_2$ was also considered to determine effective H₂O₂ dosage. Fig. 4 shows the effects of dosage of ZVI H₂O₂ on molar ratio of $\Delta\text{NP9EO}/\Delta\text{H}_2\text{O}_2$ at pH 2. The results proved to be economically wise, for ZVI dosage of 3 g/L, 1 mol of H₂O₂ reduced 0.75 mol of NP9EO for a dosage of 70 mg/L of H₂O₂, and NP9EO was reduced 80% as seen in Fig. 3.

3.2. Effects of coagulation

Fig. 5 compares the difference between ZVI/H₂O₂ oxidation pretreatment at pH 2 (shaded) and coagula-

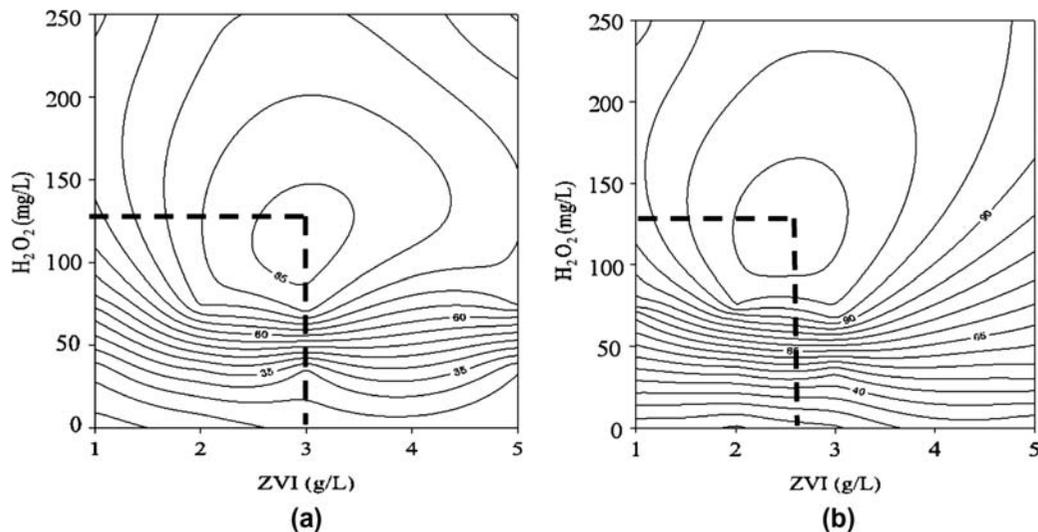


Fig. 6. Dosage of ZVI and H₂O₂ for NP9EO removal by (a) ZVI/H₂O₂ oxidation and (b) combination of ZVI/H₂O₂ oxidation and coagulation.

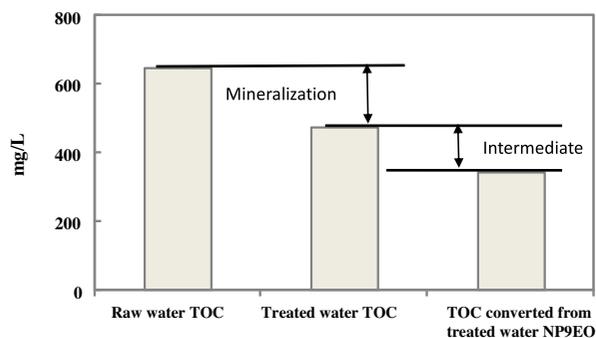
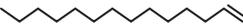
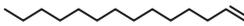
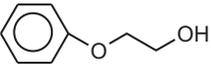
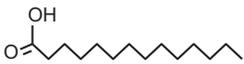
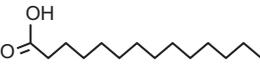
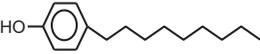
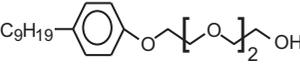
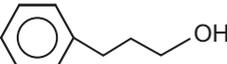


Fig. 7. Comparison of raw water TOC, treated water TOC, and treated water TOC converted from NP9EO (NP9EO 1,000 mg/L, ZVI 1 g/L, H₂O₂ 125 mg/L, pH 2).

tion at pH 8 (clear) for different dosages of ZVI and H₂O₂, and the first data are the ones without any pretreatment (0 g/L of ZVI and H₂O₂). Therefore, the clear parts are the effects of coagulation enhancement. The results show, without pretreatment, only less than 10% removal of NP9EO was achieved, indicating coagulation alone is not effective on the hydrophilic structure of NP9EO. Besides, the dosages increases of both ZVI and H₂O₂ were effective on the removal of NP9EO up to almost 100%. For clarification, Fig. 6(a) and (b) show the isopleths of NP9EO removal efficiency vs. dosage of H₂O₂ and ZVI for ZVI/H₂O₂ oxidation pretreatment (Fig. 6(a)) and coagulation (Fig. 6(b)). The optimum dosages for ZVI/H₂O₂ oxidation

Table 1
Byproduct analysis (a) oxidation pretreatment (b) coagulation of ZVI/H₂O₂

| Oxidation pretreatment | Quality | Coagulation | Quality |
|---|---------|--|---------|
|  | 97 |  | 93 |
| 1-Tetradecene | | 1-Tetradecene | |
|  | 96 |  | 90 |
| 2-Phenoxyethanol | | Tetradecanoic acid | |
|  | 95 |  | 83 |
| Octadecane | | Octadecane | |
|  | 93 |  | 54 |
| Tetradecanoic acid | | 1,2-Diethoxyethane | |
|  | 88 | | |
| NP | | | |
|  | 64 | | |
| NP2EO | | | |
|  | 59 | | |
| Benzenepropanol | | | |

were about 125 mg/L of H₂O₂ and 3 g/L of ZVI with NP9EO removal of higher than 85%. But with following coagulation, the optimum dosages for coagulation were about 125 mg/L of H₂O₂ and 2.5 g/L of ZVI with NP9EO removal efficiency of 95%. These results indicate that NP9EO can be removed by low dosage of ZVI together with chemical coagulation.

3.3. Byproduct analysis

Fig. 7 presents comparison of raw water TOC, treated water TOC, and TOC converted from the treated water NP9EO for the raw water NP9EO of 1,000 mg/L, dosages of ZVI 1 g/L and H₂O₂ 125 mg/L at pH 2. The difference between raw water TOC and treated water TOC is mineralization by converting carbon to CO₂, and the difference between raw water TOC and TOC converted from treated water NP9EO is the byproducts. The results show that TOC converted from treated water NP9EO is consistently lower than treated water TOC, indicating some of the intermediates were also generated. Therefore, these byproducts were analyzed by GC/MS and are presented in Table 1 for oxidation pretreatment and coagulation, and the quality numbers from high to low are also listed for reference. The results show 1-Tetradecene, 2-Phenoxyethanol, Octadecane, Tetradecanoic acid, NP, NP2EO, and Benzenepropanol were seen after oxidation and 1-Tetradecene, Tetradecanoic acid Octadecane, and 1,2-Diethoxyethane were seen after coagulation, indicating most of the hydrophobic (aromatic) group were removed after the coagulation process.

4. Conclusion

Coagulation enhancement of NP9EO was achieved by partial oxidation using ZVI/H₂O₂. Highest NP9EO removal was observed at pH 2 instead of pH 1.5, since the presence of extra ferrous ion in the lower pH could consume the hydroxyl radicals, resulting in low removal efficiency. In addition, ferrous ion was converted to ferric ion for pH > 2 which reduced the efficiency of Fenton reaction. Furthermore, NP9EO removal efficiency by coagulation with ZVI/H₂O₂ pretreatment was as high as 99%, which is 40% higher than that of without ZVI/H₂O₂ pretreatment. Highest NP9EO removal for ZVI/H₂O₂ pretreatment was

observed at pH 2. The optimum dosages for ZVI/H₂O₂ oxidation were about 125 mg/L of H₂O₂ and 3 g/L of ZVI with NP9EO removal of higher than 85%. But with following coagulation, the optimum dosages for coagulation were about 125 mg/L of H₂O₂ and 2.5 g/L of ZVI with NP9EO removal efficiency of 95%. Besides, the dissolution of ferric ion from ZVI/H₂O₂ was able to reduce/replace the requirement of the traditional ferric chloride.

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