Degradation of Nonylphenol Ethoxylate-10 (NPE-10) by Mediated Electrochemical Oxidation (MEO) Technology

(Degradasi Nonilfenol Etoksilat-10 (NPE-10) oleh Teknologi Gerak Balas Pengoksidaan Elektrokimia (MEO))

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ABSTRACT

Nonylphenol ethoxylate (NPE-10) is a non-ionic surfactant that is synthesized from alkylphenol ethoxylate. The accumulation of NPE-10 in wastewater will endanger the ecosystem as well as the human being. Nowadays, NPE-10 can be degraded indirectly by using an electrochemical treatment by the advancement of technology. Thus, this study is aimed to evaluate the electro-degradation potential of NPE-10 by MEO using Ce(IV) ionic mediator. In addition, the influence of Ag(I) ionic catalyst in the performance of MEO for the degradation of NPE-10 was also observed. The potency of MEO technology in the NPE-10 degradation was evaluated by voltammetry technique and confirmed by titrimetry and LC-MS analysis. The results showed that in the absence of Ag(I) ionic catalyst, the degradation of NPE-10 by MEO was 85.93%. Furthermore, when the Ag(I) ionic catalyst was applied, the performance of MEO in degradation of NPE-10 was improved to 95.12%. The back titration using $Ba(OH)_2$ confirmed the formation of CO_2 by 46.79%, whereas the redox titration shows the total of degradation organic compounds by 42.50%. It was emphasized by the formation of two new peaks in the LC-MS chromatogram. In summary, our results confirmed the potential of MEO technology for the NPE-10 degradation.

Keywords: Ag(I) catalyst ion; Ce(IV) mediator ion; degradation; mediated electrochemical oxidation; NPE-10

ABSTRAK

Nonilfenol etoksilat (NPE-10) merupakan bahan surfaktan tidak berion yang disintesiskan daripada alkil fenol etoksilat. Pengumpulan NPE-10 dalam air buangan akan membahayakan ekosistem dan juga manusia. Hari ini, NPE-10 dapat digradasikan secara tidak langsung dengan penggunaan rawatan elektrokimia oleh teknologi yang maju. Oleh itu, kajian ini adalah untuk mengkaji potensi degradasi elektro terhadap bahan NPE-10 oleh teknologi MEO dan menggunakan ion Ce(IV) sebagai bahan perantara. Selain itu, pengaruh pemangkin ion Ag(I) dalam prestasinya kepada teknologi MEO untuk degradasi NPE-10 diperhati. Potensi teknologi MEO dalam degradasi NPE-10 telah dinilai daripada teknik voltametri dan disahkan dengan kaedah titrimetri dan analisis LC-MS. Keputusan kajian menunjukkan bahawa dengan ketiadaan pemangkin ion Ag(I), prestasi degradasi NPE-10 melalui teknologi MEO adalah 85.93%. Selain itu, apabila pemangkin ion Ag (I) digunakan, potensi MEO untuk degradasi NPE-10 ditingkatkan kepada 95.12%. Pentitratan balik menggunakan $Ba(OH)_2$ mengesahkan bahawa terdapat penghasilan CO_2 sebanyak 46.79%, sedangkan titrasi redoks menunjukkan jumlah sebatian organik yang digradasi sebanyak 42.50%. Jumlah degradasi ini ditekankan dengan penghasilan dua puncak daripada analisis kromatogram LC-MS. Secara kesimpulannya, keputusan kajian kami sah bahawa potensi teknologi MEO dalam degradasi NPE-10.

Kata kunci: Degradasi; ion perantara Ce(IV); gerak balas pengoksidaan elektrokimia; NPE-10; pemangkin ion Ag(I)

Introduction

NPE is one of a non-ionic surfactant in the class of alkylphenol ethoxylates. NPE is widely used as dispersing agent in household, industrial applications, detergent, as well as emulsifier (Brigden et al. 2012; Fuente et al. 2010; Martins et al. 2006). The toxicity of NPE is relatively low. However, due to the significant increase of usage of this organic pollutant and its potential to produce highly toxic and stable metabolites such as ethylene oxide, as well as its slow biodegradation, NPE can cause serious environmental problems. More importantly, according to a toxicity evaluation, this compound also considered

as an endocrine disrupting compound which may result in functional abnormalities as well as cancer (Forte et al. 2016; Liu et al. 2017; Shufaro et al. 2018). Several approaches have been developed for NPE degradation including biological treatment, as shown by studies of Hernandez-Raquet et al. (2007), Lu et al. (2007), Maki et al. (1994), and Mao et al. (2012) whose results successfully degraded NPE in ranging of 60-100%. However, those biological treatments of NPE may cause other problems as they have the following characteristics: Potential in reducing oxygen transfer, producing foams, disturbing the sedimentation process and disturbing the ecosystem. For the aforementioned reasons, the procedure in the degradation of NPE needs to be established.

Electrochemical based technology offers multiple advantages such as environmental compatibility, versatility, and cost effective. MEO is one of the electrochemical treatments which is commonly used for the degradation of organic pollutants based on the activity of oxidant species (ionic mediators), including Ce(IV), Cl· and $S_2O_8^{2-}$ (Juttner et al. 2000). Due to the nature of NPE as an electro-active organic compound, MEO is possible to be applied for the degradation of NPE. The principle of redox reaction is by electron transfer mechanism (Setiyanto et al. 2015, 2011a, 2011b) was used in this study.

NPE-10 (Figure 1) is one of the most common nonionic surfactant (Cox et al. 1984; Olkowska et al. 2014). The maximum concentration of NPE-10 allowed in the freshwater and saltwater should not exceed 6.6 and 1.7 µg/L (Brooke & Thursby 2005; David et al. 2009). Since no study has been reported about the degradation of NPE-10 by MEO technology, we are interested to evaluate the potential of MEO in the degradation of NPE-10.
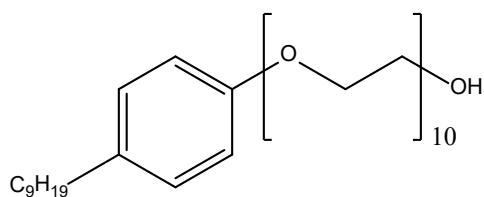

FIGURE 1. Structure of NPE-10

In this paper, the potential of MEO in NPE-10 degradation was evaluated by voltammetry techniques and confirmed by back titration, redox titration, and LC-MS analyses. In addition, we also evaluated the influence of the addition of Ag(I) ionic catalyst in the MEO performance for NPE-10 degradation.

MATERIALS AND METHODS

APPARATUS

The degradation process was carried out by using Potensiostat/Galvanostat eDAQ 410 with Pt wire as the cathode and anode. The degradation product was evaluated by voltammetric techniques using BASi Epsilon Electrochemical Analyzer. The voltammetric detection used three electrodes: Carbon paste electrode (CPE) as the working electrode, Ag/AgCl as the reference electrode, and Pt wire as the auxiliary electrode. The product of the degradation was further analyzed using LC-MS XEVO - Qtof - MS instrument.

CHEMICALS

The cerium sulfate octahydrate (> 99.0%) was purchased from (Sigma Aldrich). Sodium chloride, barium dioxide, potassium permanganate, oxalate acid, hydrochloric acid, Al_2O_3, sulphuric acid, and graphite were from Merck with pro analytical grade. NPE-10 was purchased from a local textile shop with technical grade.

PREPARATION OF THE WORKING ELECTRODE

The working electrode (CPE) was prepared by several steps. First, the mixture of carbon and liquid paraffin (in the ratio of 7:3) was heated at 80 °C in a beaker glass. Then, the mixtures were inserted to a cylindrical electrode holder and cooled in room temperature. For the electrical contact, the carbon paste was connected with a copper wire. The surface of the prepared working electrode was then polished by alumina (Al_2O_3) slurry onto a polishing pad.

SAMPLE PREPARATIONS AND VOLTAMMETRIC MEASUREMENT

The oxidation potential of Ce(III) and NPE-10 were investigated by using voltammetric method. Four solutions were prepared in 0.2 M H_2SO_4: (1) background solution (0.4 M H_2SO_4); (2) 0.04 M Ce (III); (3) 1000 ppm NPE-10; (4) the mixture of 0.04 M Ce(III) and 1000 ppm NPE-10. The measurement was recorded in the scan range of -200 - 2000 mV with the scan rate of 100 mV/s using cyclic voltammetry.
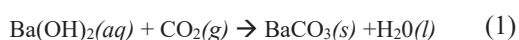
For measurement optimization, four solutions were prepared in a 0.4 M H_2SO_4 containing: (a) 1500 ppm NPE-10; (b) 0.04 M Ce(III) and 1500 ppm NPE-10; (c) 0.04 M Ce(III), 0.009 M Ag(I), and 1500 ppm NPE-10. The duration of degradation was varied from 5 to 55 min. The solution after degradation was further evaluated by voltammetric techniques.

LC-MS ANALYSIS

LC-MS analysis was performed by the LC-MS XEVO - Qtof - MS instrument. The column used was ACQUITY UPLC BEH C18 (1,7 μm × 2,1 mm × 100 mm). The flow rate was 0.3 mL/min with the injection volume of 5 μL. For the separation of degradation products, the following solvents were used: 2 mM ammonium acetate in water (A) and 2 mM ammonium acetate in acetonitrile (B).

INDIRECT DETERMINATION OF CARBON DIOXIDE BY BACK TITRATION

The content of CO_2 gas formed during degradation of NPE-10 by MEO was evaluated by back titration using $Ba(OH)_2$ solution. The amount of $Ba(OH)_2$ is equivalent with CO_2 according to (1):

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l) \qquad (1)$$
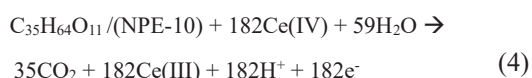
The protocol for indirect determination of CO_2 is as follows: The CO_2 gas formed during degradation of NPE-10 by MEO was fed into an Erlenmeyer flask containing $Ba(OH)_2$ solution ($Ba(OH)_2$ total at 0.9588 mmol). After the degradation process finished, the $Ba(OH)_2$ solution containing CO_2 was then titrated with a 0.0282 mmol HCl. The mmol of $Ba(OH)_2$ remained was assumed as the amount of $Ba(OH)_2$ that did not react with the CO_2 formed from the NPE-10 degradation and can be shown from (2):

$$[Ba(OH)_2] \text{ (mmol)} = [Ba(OH)_2] \text{ total (mmol)} - [Ba(OH)_2] \text{ titration (mmol)} \quad (2)$$

The percentage of CO_2 formed can be calculated by the following formula in (3):

$$\% CO_2 = \frac{mmol\ of\ Ba(OH)2}{mmol\ CO2\ theoretical} \times 100\% \qquad (3)$$

where the amount of mmol CO_2 theoretical is according to the prediction of mmol CO_2 from the propose NPE-10 complete degradation reaction on anode and can be shown from equation (4) (Balaji et al. 2007; Chung & Park 2000):

$$C_{35}H_{64}O_{11}/(NPE-10) + 182Ce(IV) + 59H_2O \rightarrow$$
$$35CO_2 + 182Ce(III) + 182H^+ + 182e^- \qquad (4)$$

DETERMINATION OF PERMANGANATE VALUE BY REDOX TITRATION

The percentage of degraded organic compound from NPE-10 degradation by MEO was confirmed by redox titration. Prior to the redox titration, the samples were prepared by these following steps: The solution of NPE-10 before and after degradation were diluted for 25 times. About 100 mL of NPE-10 solution was put into a 300 mL Erlenmeyer flask and added with a few drops of 0.01 N $KMnO_4$ until the color of the solution becomes pink. The solution was further added with 5 mL of an 8 N sulfuric acid and heated to 105 °C, then cooled in room temperature. About 10 mL of prepared sample was then pipetted and transferred into an Erlenmeyer flask. Subsequently, the sample was re-heated for 10 min. After 10 min, the solution was added with 10 mL of a 0.01 N oxalic acid. The excess oxalic acid was titrated with 0.01 N $KMnO_4$. The permanganate value was calculated using (5):

$$KMnO_4(mg/L) = \frac{[(10 - a) \times b - (10 \times c)] \times 1 \times 31.6 \times 1000}{d} \times \quad (5)$$

where, 'a' is the required volume of $KMnO_4$ in the titration, 'b' is the actual $KMnO_4$ normality, 'c' is the normality of oxalic acid, 'd' is the volume of the sample, and 'f' is the dilution factor (Suslova et al. 2014).

The percentage degraded organic compound can be referred to (6):

$$\frac{[KMnO4\ value]before\ degradation - [KMnO4\ value]after\ degradation}{[KMnO4\ value]before\ degradation} \times 100\% (6)$$

RESULTS AND DISCUSSION

VOLTAMMETRIC STUDY OF CE(III)/CE(IV) AND NPE-10

The voltammetric behavior of Ce(III) and NPE-10 were observed by using cyclic voltammetry (CV) in H_2SO_4 as the supporting electrolyte (Paulenova et al. 2002; Ren & Wei 2011). The measurement of CV was aimed to determine whether the reaction is reversible or irreversible. As shown in Figure 2, two reduction peaks were observed at the potential value of 0.786 and 0.444 V, respectively. Those peaks were assumed as the reduction peaks of H_2SO_4, as suggested by the following prediction reduction reaction in (7) and (8):

$$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2(aq) + 2H_2O \qquad (7)$$

$$SO_2(aq) + 4H^+ + 4e^- \rightleftharpoons S(s) + 2H_2O \qquad (8)$$

As can also be seen in Figure 2, the voltammogram of Ce(III)/Ce(IV) (black line) showed oxidation and reduction peak current (Ipa and Ipc) at 1.322 and 1.148 V, respectively, indicating reversible reaction. Meanwhile, the voltammogram of NPE-10 (red line) only showed oxidation peak current at 1.400 V, indicating irreversible reaction of NPE-10. As also depicted in Figure 2 (blue line), in the mixture of Ce(III) and NPE-10 solution, the nett of NPE-10 peak oxidation current (ΔIp) decreased, indicating the oxidation of NPE-10 due to the reduction reaction of Ce(IV) into Ce(III).
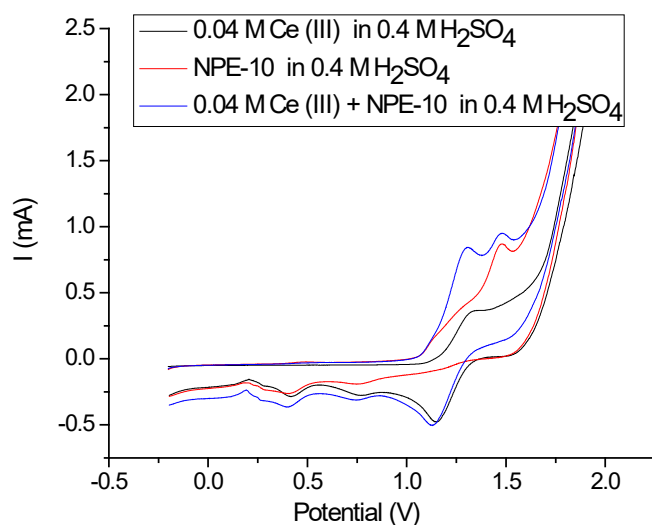
FIGURE 2. The cyclic voltammogram of (a) 0.04 M Ce(III), (b) NPE-10, and (c) 0.04 M Ce(III) and NPE-10 in 0.4 M H_2SO_4 by CPE as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the auxiliary electrode

SELECTION OF VOLTAMMETRY TECHNIQUE FOR EVALUATION OF NPE-10 DEGRADATION

Prior to the evaluation of NPE-10 degradation, we selected the most suitable voltammetry techniques as suggested by the highest nett current. In this study, four voltammetry techniques were evaluated for NPE-10 degradation: Linear sweep voltammetry (LSV), cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV). The NPE-10 solution used in this study was prepared at 5000 ppm in 0.4 M H_2SO_4. The value of nett current was presented in Figure 3.
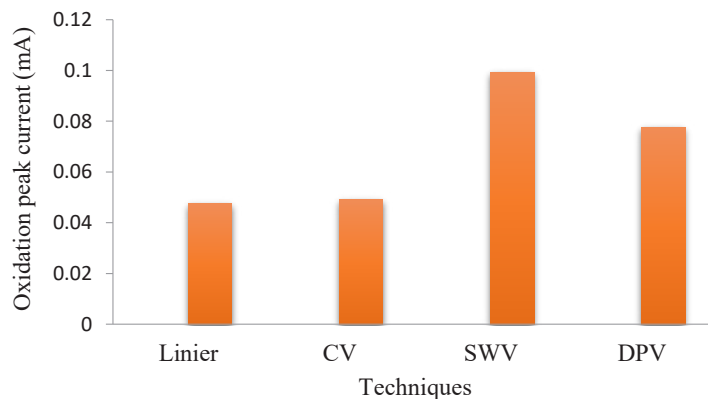

FIGURE 3. The nett current of NPE-10 using various voltammetry technique

As depicted in Figure 3, the nett current values of NPE-10 were 0.0477, 0.0491, 0.0777, and 0.0990 mA for LSV, CV, DPV, and SWV, respectively. Comparison between nett current value of NPE-10 using SWV and other techniques showed that SWV is the most sensitive technique. It has been reported that the limit detection of DPV and SWV were in nanomolar range which are superior than LSV and CV (Hussain & Silvester 2018). In DPV

technique, only forward current was measured. Whereas in SWV technique, both the forward and reverse current are measured, hence the higher nett current value was observed by SWV. Our results were in agreement Wang (2000), which reported that SWV was 3.3 times more sensitive than DPV for detection of irreversible compounds.

THE OPTIMIZATION OF NPE-10 DEGRADATION TIME

In waste treatment, degradation time plays an important role particularly in cost effectiveness. In general, the longer degradation time, the more compound or organic pollutants are degraded and the higher cost is required. However, when the steady state condition is reached, no more compounds will be degraded. Thus, it is very important to optimize the degradation time of NPE-10. In our previous report, we have successfully electro-degraded NPE-10 by MEO at potential value of 5.5 V (Muslim et al. 2018). The percentage degradation value of NPE-10 was ~80%. In this study, the percentage degradation of NPE-10 as function of time was presented in Figure 4. As shown, the percent degradation of NPE-10 tends to increase at min of 5 to 35. Whereas at min of 35 to 55, the percent degradation of NPE-10 is relatively constant. The percent degradation value of NPE-10 at min of 35 was 85.51%. Accordingly, we suggest applying 35 min of degradation time for degradation of 1500 ppm NPE-10 by MEO.
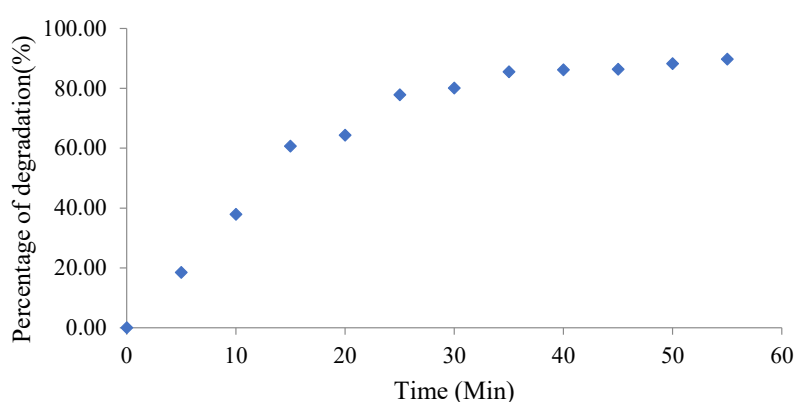

FIGURE 4. Percent degradation of NPE-10 by MEO as function of time

THE EFFECT OF AG(I) CATALYST ION FOR NPE-10 DEGRADATION BY MEO USING CE(IV) IONIC MEDIATOR

The influence of Ag(I) ionic catalyst addition in the NPE-10 degradation by MEO was presented in Table 1. As presented, the degradation of NPE-10 by MEO in acidic solution of without Ce(III), with Ce(III) and combination of Ce(III):Ag(I) were 61.44, 85.93 and 95.12%, respectively. From Table 1, it is obvious that, the presence of Ce(III) and Ag(I) increased the NPE-10 degradation by MEO. It should be noted that in an acidic solution containing Ce(III), the Ce(IV) can be produced as the result of redox reaction. The produced Ce(IV) will continuously oxidize NPE-10 (Figure 5) hence resulting degradation products including CO_2 (Martinez-Huitle & Ferro 2006; Raju & Basha 2005).
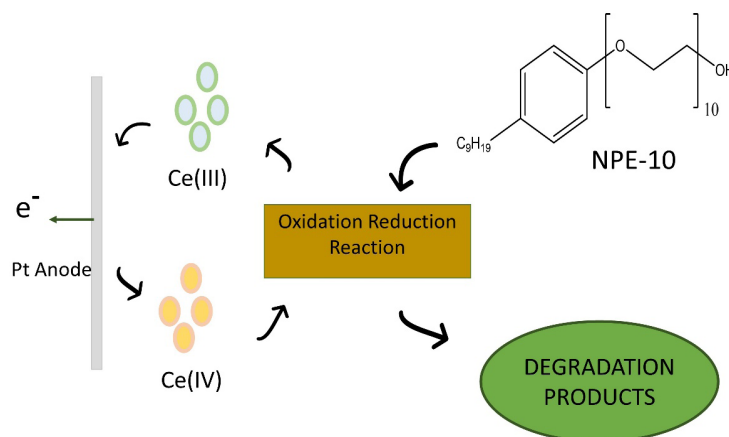

FIGURE 5. The mechanism process of NPE-10 degradation by using Ce(IV) as mediator ion

In an acidic solution, Ag(I) will be oxidized as Ag(II). Ag(II) is an unstable ion and can act as an oxidator. Therefore, the presence of Ag(II) in a solution containing Ce(III) supports the oxidation of Ce(III) to Ce(IV). According to the results of NPE-10 degradation in the presence of Ag(I), we showed that the performance of NPE-10 by MEO was improved. Furthermore, our data were in the line with previous studies which have reported that the presence of Ag(I) in a solution containing Ce(III) will increase the oxidation peak current of Ce(III) (Fawzy & Al-Jahdali 2016; Matheswaran et al. 2007; Sumathi et al. 2010). Based on these explanation, Ag(I) has the potential as an ionic catalyst in the redox reaction of Ce(III)/Ce(IV). Therefore, we suggest to add Ag(I) in acidic solution of Ce(III) for the electro-degradation of NPE-10 by MEO to achieve a better result.

TABLE 1. The percent degradation of NPE-10 in acidic solution

Condition of NPE-10 degradation	Percentage of degradation (%)
Without 0.04 M Ce(III)	61.44
Containing 0.04 M Ce(III)	85.93
With 0.04 M Ce(III) and 0.009 M Ag(I)	95.12

DEGRADATION OF NPE-10 BY MEO RESULTING CO_2

In anode, the degradation of NPE-10 was predicted to form CO_2 (see the propose reaction 2). We confirmed that the formation of CO_2 is from NPE-10 degradation according to the precipitation of white sediment as the results of reaction $Ba(OH)_2$ with CO_2. This result was also emphasized by the calculation of CO_2 formed by back titration. It shows that NPE-10 resulted in 46.79% CO_2 formation. The results from back titration obviously showed the incomplete degradation of NPE-10 by MEO. It should be noted that the results from degradation of organic pollutants are not always in the form of CO_2 as their final product. An organic pollutant may also produce more simple compounds as its degradation product (Brillas 2014; Setiyanto et al. 2016). In respect to the result of CO_2 analysis concentration, we therefore suggest that the remaining content were other organic compounds with smaller molecules.

CHARACTERIZATION OF DEGRADATION PRODUCTS USING LC - MS

Results from Table 1 obviously showed the potential of MEO for electro-degradation of NPE-10 and in producing smaller molecules. For this reason, we further analyse the degradation products of NPE-10 by LC-MS analysis. The LC-MS spectrum of NPE-10 before and after degradation is presented in Figure 6. As it can be seen, before degradation process, the NPE-10 shows peaks at retention time of 5.00; 5.41; 5.75; 9.72; 11.07; and 15.05 min. This is due to the type of NPE-10 used in this study. The type is a technical grade, thus showing its impurities. However, the impurities of NPE-10 used in this study did not interfere. The degradation products were detected in Figure 6, as suggested by the two new peaks present in the LC-MS chromatogram of NPE-10 after degradation process (Figure 6) at retention time of 6.970 and 13.618 min. The ion chromatograms and characterization of those compounds can be seen in Figures 7 and 8. As shown in Figure 7, for compound at retention time of 6.970 min, the most significant ion is produced at m/z of 413.29, corresponding to the combination of benzylic cleavages $[M-71]^+$ and the shortened of polyethoxy chain $[M-176]^+$. Whereas in Figure 8, for compound at retention time of 13.618 min, the most significant ion is produced at m/z of 603.92, corresponding to benzylic cleavage of $[M-57]^+$. The benzylic cleavages and the shortened of polyethoxy chains are common for degradation of NPE compounds (Karci 2014; Li et al. 2018; Namara et al. 2012). According to the ion at m/z of 603.92, it seems that the terminal atom carbon of hydrophobic part of NPE-10 was firstly oxidized. And subsequently, the polyethoxylate chain which was continuously oxidized. Hence, resulting smaller molecules. Although the ion chromatograms in Figures 7 and 8 are not very informative in terms of structure elucidation, however, they provide an indication of the products of NPE-10 degradation and created a landscape for the future development of NPE-10 degradation process.
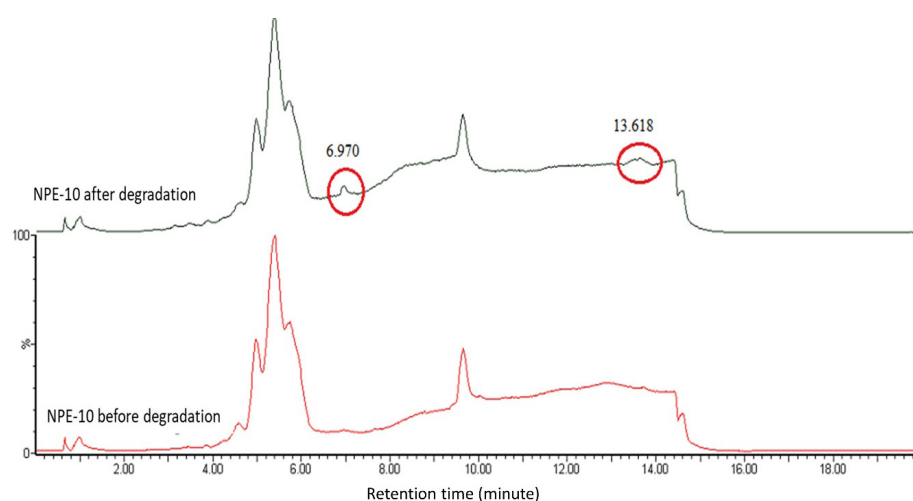
FIGURE 6. LC-MS chromatogram of NPE-10 before and after degradation by MEO
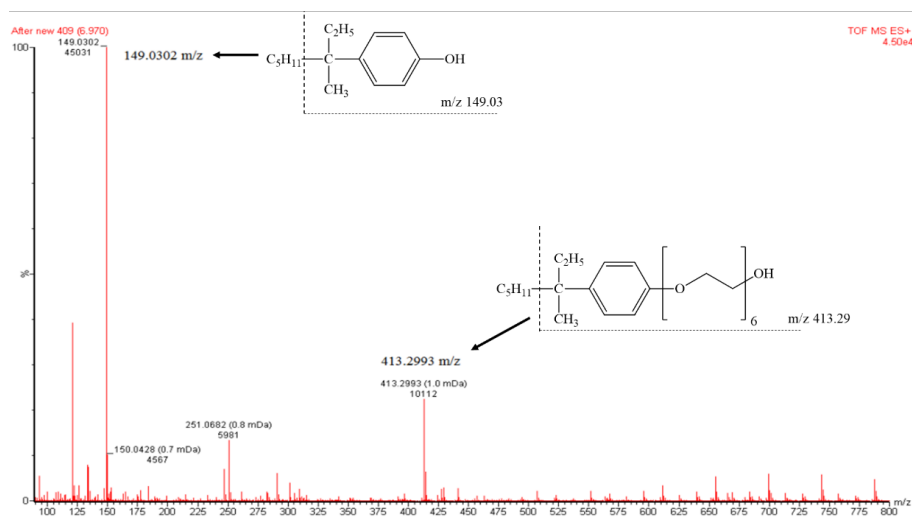

FIGURE 7. Ion chromatogram of degradation compound from NPE-10 at retention
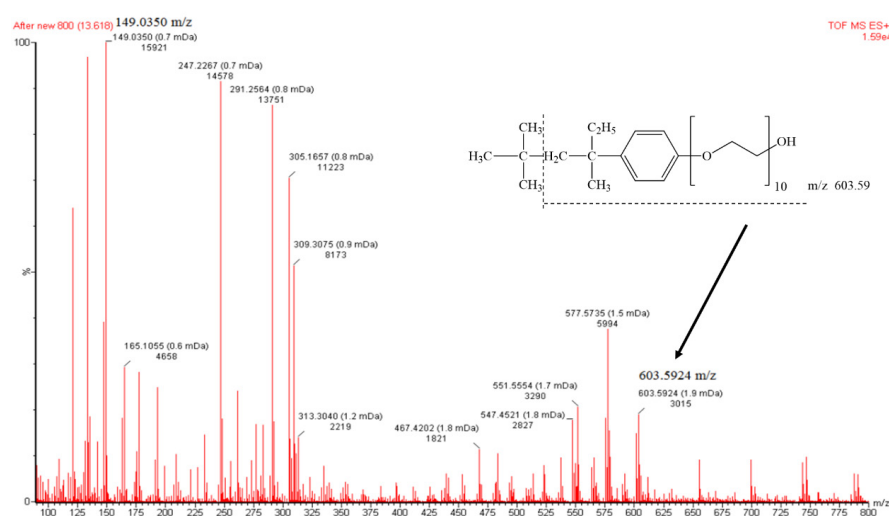time of 6.97 min

FIGURE 8. Ion chromatogram of degradation compound from NPE-10 at retention
time of 13.61 min

DETERMINATION OF ORGANIC MATTER CONTENT USING PERMANGANATE VALUE

The permanganate value denotes the number of milligrams of $KMnO_4$ required in the oxidation of organic substances as suggested by the following reaction in (9) (Suslova et al. 2014):

$$C + MnO_4^- + 4H^+ + e \rightarrow CO_2 + Mn^{2+} + 2H_2O \qquad (9)$$

Our results showed that before and after degradation of NPE-10 the $KMnO_4$ value were 445.56 and 256.18 mg/L, respectively. The percent degradation of the organic compound was determined as 42.50%. By summarizing the percentage value of CO_2 and degradation organic compound, about 88% of NPE-10 was assumed to be degraded. This result is almost similar with the calculation of NPE-10 degradation by voltammetry technique as suggested by the degradation of 95.1% NPE-10. It is not surprising that the result of NPE-10 degradation by MEO using voltammetry technique is higher than the value resulted from back and redox titration. Because in voltammetry technique, the value recorded was based on the reaction on the electrode surface. Meanwhile in the back and redox titration, the values were obtained by using bulk solution. In addition, the more complex reaction may be occurred in a bulk solution results in lower value. In reverse, on the surface of electrode, the simpler and certain reaction occur as proposed in Figure 5, results in higher value. The results from voltammetry technique and titration mutually supports each other.

CONCLUSION

In conclusion, NPE-10 can be degraded by using MEO technology. About 88-95% of 1500 ppm of NPE-10 can be degraded by MEO within 35 min. The presence of Ag(I) ionic catalyst improves the performance of MEO technology for degradation of NPE-10. Thus, we suggest that the MEO technology is a promising method for degradation of organic pollutant in waste water.

ACKNOWLEDGEMENTS

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