Mediated electrochemical oxidation (MEO) process: a study on nonylphenol ethoxylates (NPE) oxidation in batch mode using cerium (IV) oxidant

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Abstract. Nonylphenol ethoxylate (NPE-10) is one type of non-ionic surfactants from the class of alkylphenol ethoxylate (APE). This compound is already tightened their use in European Union countries. However, these surfactants are still used widely in Indonesia because the price is relatively cheap. Consequently, these compounds can accumulate in aquatic environments. NPE-10 can disrupt aquatic ecosystems. This study aimed to describe the electro-oxidation process of NPE-10 based on the parameters of a potential difference, concentration of NPE-10, concentration of Ce (III), and oxidation time. The result of oxidation NPE-10 was measured by the amount of current generated from voltammetry technique. Studies of cyclic voltammetry using carbon paste electrodes illustrates the potential value of the oxidation of Ce (III) / Ce (IV) of 1.25 V and the reduction potential value of Ce (IV) / Ce (III) of 1.192 V. NPE-10 are electroactive irreversible because it only provides the potential value of oxidation at 1.44 V. Percent of total degradation of 84.96% was obtained at electro-oxidation of 500 ppm NPE-10 by the addition of 0.015 M Ce (III) for 90 minutes at 0.2 M H2SO4 and the use of potential of 6 V.

1. Introduction

Surfactant is one of organic pollutants in water for utilization in various fields as a raw material for detergents, emulsifiers and dispersants. Surfactants are divided into three groups, namely anionic surfactant (Linear Alkylbenzene sulfonate/ LAS), a cationic surfactant (Cetyl Trimethyl Ammonium Bromide/ CTAB), and nonionic surfactant (alkylphenol ethoxylate/ APE). Nonionic surfactant nonylphenol ethoxylate (NPE) is a synthetic surfactant types of alkylphenol ethoxylates that used in the chemical industry, paint, varnish, metal processing, industrial cleaning, paper and agricultural products such as biocides [1]. The extent of the use of NPE cause probability accumulation of these compounds in the river water becomes higher. In European Union countries, the use of NPE has been tightened which should be lower than 0.01%, or 100 mg / kg of textile material. NPE and tributyl phosphate waste pollution of more than 800 textile companies in Indonesia are estimated to be around 450.000.000 m3/y [2]. The impact of NPE in the flow of the river is the disruption of aquatic ecosystems because it can disrupt the organism reproductive system and the ecosystem cycles. Additionally, NPE may also affect the endocrine work system in the human body [3].

There are several methods of degradation that has been used to degrade NPE surfactants. In a study this studi [3] electrode Fe and Al were used to form a coagulant Al(OH)3 and Fe(OH)3 which serves to...
precipitate the NPE. The weakness of this method is the secondary waste production of coagulants. Biodegradation method using Fe (III) has also been used to degrade NPE for 3 days with 60% of percent maximum of degradation [4]. The weakness of this method is that it takes a relatively time consuming. The oxidation and photo degradation method is a method that utilizes advanced radical and ultraviolet (UV) to break bonds in molecules NPE [5]. The downside of this method is fairly high energy consumption in the use of UV light and the use of H$_2$O$_2$ relatively much to produce hydroxyl radicals.

One method that has not been published to degrade NPE is an electrochemical method. Electrochemical methods have been widely used for a wide range of purposes including reaction mechanisms, reactivity, micro analysis and degradation [6-9]. This method utilizes the electron transfer reaction to a reduction / oxidation of an analyte. This method can be used to degrade (oxidize) an organic pollutant directly or indirectly (mediated). Mediated electrochemical oxidation (OET) is a method that utilizes oxidizing agent from the results of electro oxidation to degrade (oxidize) of organic pollutants. Products to be produced is a product that more simple, if the perfect degradation will turn into CO$_2$ and water. The main advantages of this method is the repeatable use of the oxidant when the degradation process carried out by the ex-cell system. Another advantage is that this methods do not pollute the environment and can be done at room temperature and atmospheric pressure and also oxidizer optimum strength under acidic [10].

The oxidant commonly used is the species that has the oxidation state not stable (oxidizing agent) so easily back into species in a state of reduction. Some of redox system from transition metal ions has been reported to be used in the method of MEO: Mn$^{2+}$/Mn$^{3+}$, Co$^{2+}$/Co$^{3+}$, Cr$^{3+}$/Cr$^{6+}$, Ti$^{3+}$/Ti$^{4+}$, Ce$^{3+}$/Ce$^{4+}$, V$^{4+}$/V$^{5+}$, Pd$^{2+}$/Pd$^0$, Sn$^{2+}$/Sn$^{3+}$, Ag$^{+}$/Ag$^+$, Cu$^{2+}$/Cu$^+$ and Ru$^{4+}$/Ru$^{8+}$ [11]. Cerium (IV) Oxidants has advantages over other transition metal oxidants in terms of regeneration, stability and selectivity, especially in the synthesis reaction [12]. Cerium (IV) Oxidants were used in the synthesis reaction of organic compounds and degradation of organic pollutants. As in aniline [13] benzoic acid [14], phenol [15], EDTA [16], acetaminophen [17], dioxins and dibenzofuran [14]

2. Methods

2.1. Materials
Ce$_2$SO$_4$. 8H$_2$O (Sigma Aldrich), NaCl (Merck), K$_3$Fe(CN)$_6$ (Merck), K$_4$Fe(CN)$_6$ (Merck), H$_2$SO$_4$ (Merck), Na$_2$CO$_3$ (Merck), Ba(OH)$_2$ (Merck), HCl (Merck), phenolfialein indicator (Merck), NPE-10, graphite powder, liquid paraffin, and demin water. All chemicals were used as received.

2.2. Instruments
Magnetic stirrer, motor rotary, working electrode (paste carbon electrode) homemade, Ag/AgCl reference electrode homemade, Ag/AgCl reference electrode BAS (Bioanalytical System), Pt wire and Potensiostat/Galvanostat eDAQ 410, Power Supply DC ATTEN dan instrumen LC/ESI-MS.

2.3. Methods

2.3.1. Determination of potential oxidation of Ce (III) and NPE-10. The determination of the redox potential of Ce (III) / Ce (IV) and NPE-10 systems was performed by comparing the cyclic voltamgram of 4 solutions i.e. 0.2 M H$_2$SO$_4$; 0.01 M Ce (III) solution in 0.2 M H$_2$SO$_4$; 1000 ppm NPE-10 in 0.2 M H$_2$SO$_4$ and the mixture of 0.01 M Ce (III) solution and 1000 ppm NPE-10 in 0.2 M H$_2$SO$_4$. Cyclic voltammetric technique was performed in the range 200-1800 mV.

2.3.2. Determination of optimum concentration of supporting electrolyte (H$_2$SO$_4$) for the oxidation of Ce (III) solution. Determination of optimum concentration of supporting electrolyte solution to oxidize Ce (III) solution was done by using cyclic voltammetric technique. The concentration of supporting electrolyte solution was varied in the range of 0.1-0.4 M for oxidation of 0.01 M. Ce (III) solutions, and 0.05-0.4 M for oxidation of 0.02 M Ce (III) solutions.
2.3.3. Comparison of H2SO4, Ce (III) and NPE-10 voltammograms. This was done to determine the effect of adding NPE-10 to a 0.01 M Ce (III) solution mixture in H2SO4 0.2 M. NPE-10 is a non-ionic surfactant to be degraded.

2.3.4. Studies of Degradation. The optimized parameters were oxidation/reduction potential, concentration of NPE-10, concentration Ce (III) solution and degradation time.

Optimization of potential: the degraded solution was 25 mL of 750 ppm NPE-10 in 0.02 M H2SO4 with and without 0.01 M Ce (III) solution. The comparison of NPE-10 oxidation current values before and after degradation was determined by SWV measurement technique.

Optimization of NPE-10 concentration: degradation of NPE-10 was performed using NPE-10 solution in 0.2 M H2SO4 at concentration range of 500-1750 ppm.

Optimization of Ce (III) concentration: The variation of Ce (III) concentration used was in the range of 0.05-0.02 M.

Optimization of degradation time: Optimization of degradation time parameters was performed using optimum parameters of potential, NPE-10 concentration, and Ce (III) concentration obtained from previous optimizations. Variation of degradation time was done in the range of 15 to 90 minutes. The comparison of NPE-10 oxidation current values before and after degradation have been determined by SWV measurement technique.

3. Results and Discussion

3.1. Determination of oxidation/reduction potential of Ce (III) / Ce (IV) system.

The cyclic voltammetric measurement technique was used to determine the oxidation and reduction potential of the Ce (III) / Ce (IV) redox system.

![Figure 1. Cyclic voltammogram of 0.2 M H2SO4 solution and Ce (III) solution in 0.2 M H2SO4 with a scan rate of 100 mV/sec using a carbon paste electrode](image)

Voltammogram showed that H2SO4 species has two reduction peaks at potential regions of 0.746 and 0.414 V. H2SO4 has no oxidation peak because it is already at the highest oxidation value that is the oxidation number of atom S = + 6. Addition of Ce (III) into H2SO4 solution resulted in the formation of 2 new peaks of oxidation of 1.25 V and a reduction peak of 1.192 V versus Ag/AgCl electrodes. Both peaks are the redox peak of the Ce (III)/Ce (IV) system. This results corresponds to a theoretical study in which the standard oxidation potential of Ce (III/ IV) system is +1.24 V with respect to the Ag/AgCl electrode in the use of 1.0 M H2SO4 solution.
3.2. Determination of optimum concentration of supporting electrolyte (H$_2$SO$_4$) for the oxidation of Ce (III) solution

![Figure 2](image)

**Figure 2.** Cyclic voltammogram of 0.01 M Ce(III) in 0.1-0.4 M H$_2$SO$_4$ with a scan rate of 100 mV/sec using a carbon paste working electrode

Voltammogram showed that the increased use of H$_2$SO$_4$ concentration as a support solution causing capacitive current also increased. The peak value of oxidation current of the Ce (III) to Ce (IV) is highest in the use of 0.2 M H$_2$SO$_4$ solution of 0.0384 mA. The higher use of H$_2$SO$_4$ concentration causes the oxidation peak value of Ce (III) to decrease (influence of capacitive current).

3.3. Comparison of H$_2$SO$_4$, Ce (III) and NPE-10 voltammograms

The comparison of cyclic voltammogram of H$_2$SO$_4$, Ce (III) and NPE-10 can be seen in the Figure 3.

![Figure 3](image)

**Figure 3.** Comparison of cyclic voltammogram of 0.2 M H$_2$SO$_4$, 0.01 M Ce(III) and 1000 ppm NPE-10 in 0.2 M H$_2$SO$_4$ with a scan rate of 100 mV/sec using a carbon paste working electrode.

Voltammogram provides the peak potential values for each species as presented in table 1.
Table 1. The peak potential values of H$_2$SO$_4$, Ce (III) and NPE-10

| Spesi   | $E_p$ (V) | $E_p$ (V) |
|---------|-----------|-----------|
| H$_2$SO$_4$ | - | 0.746 and 0.414 |
| Ce(III)/Ce(IV) | 1.25 | 1.192 |
| NPE-10   | 1.44      | -         |

Based on the data, NPE-10 belongs to an irreversible electroactive compound because it can provide an oxidation peak value but not for reduction peak. Comparison of NPE-10 voltammogram with and without addition of Ce (III) can prove that Ce (IV) formed can oxidize NPE-10. This is evidenced by the peak of oxidation current of NPE-10, lower in NPE-10 voltammogram with the addition of Ce (III).

3.4. Studies of Degradation

The NPE-10 degradation was performed using an electrolysis system. There are 4 types of parameters that are optimized to obtain optimum percent of degradation ie potential, NPE-10 concentration, Ce (III) concentration and degradation time. Percent of degradation is calculated based on the formula:

$$\% \text{ Degradation} = \frac{i_{\text{initial}} - i_{\text{final}}}{i_{\text{initial}}} \times 100\%$$

(1)

The optimum percent of degradation were found on potential of 6 V; 500 ppm of NPE-10 concentration; 0.015 M of Ce(III) concentration and 90 minutes degradation time.

![Figure 4. Relation of NPE-10 degradation to time for 500 ppm NPE-10 with 0.015 M Ce (III) addition in 0.2 M H$_2$SO$_4$](image)

The data shows the percent value of degradation is proportional to the time spent. Maximum degradation in the range is obtained in degradation for 90 minutes. The maximum percentage of degradation values for direct and mediated were 87.95 and 84.96%, respectively.

4. Conclusion

In this research, NPE-10 electrodegradation has been performed using a batch oxidation electrochemical method with a Ce (IV) oxidizer. The maximum degradation percentage of 84.96% was generated from 500 ppm NPE-10 -mediated electrodegradation with additions of 0.015 M Ce (III) over 90 min at a potential of 6 V.

5. References

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