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Removal of nonylphenol ethoxylates by electrochemically-generated coagulants

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Abstract

This study investigated the behaviour of aluminium and carbon steel electrodes in the presence and absence of nonylphenol ethoxylates (NP*n*EO, where *n* is the number of ethoxylate groups in the molecule) and NP*n*EO removal by electrochemically-generated coagulants. The electrode processes were studied by potentiodynamic polarization measurements to determine the influence of surfactant addition (ethylene oxide units and organic load), inorganic composition and pH. The polarization curves showed the extent of the involvement of NP*n*EO in the electrode processes. Their influence appeared clearly in the range of anodic activation, depending on the number of ethoxylate groups. Removal of NP*n*EO from simulated wastewaters was carried out in two electrocoagulation cells with vertical and horizontal electrodes, respectively. The removal efficiencies calculated from the chemical oxygen demand before and after treatment were 30–50% for NP16EO and NP40EO, and 40–80% for NP4EO. The hydrophilic-lipophilic balance number for NP4EO indicated a relative ratio of polar and non-polar groups lower than for the other two surfactants, which was in favour of better NP4EO removal. The experiments showed the processes in the bulk (bridging of electrochemically-generated polymeric species and adsorption of surfactants) were predominant over the involvement of NP*n*EO in the electrode processes, which were only responsible for the electrogeneration of coagulants.

1. Introduction

Nonylphenol ethoxylates (NP*n*EO, where *n* is the number of ethoxylate groups in the molecule) are nonionic surfactants used in various household and industrial detergents. There has been much debate about the environmental fate and the safety of nonylphenol ethoxylates [1–4]. As a result of conventional biological treatment, nonylphenol ethoxylates break down into nonylphenol and shorter chain length ethoxylates, which are more toxic than the parent compounds [5, 6].

Adsorption on coagulants generated in electrochemical cells is an alternative way to decrease the available amount of nonylphenol ethoxylates for biological treatment. The technique involves the anodic dissolution of electrode materials such as aluminium and iron to produce monomeric and polymeric species and hydroxide floc with high adsorption capacity acting as coagulants [7–10]. The formation of highly effective coagulants is made possible by the reaction of aluminium or iron ions resulting from the dissolution of the anode with the hydroxyl ions produced at the cathode. To the best of our knowledge, the removal of surfactants by electrochemical methods has been the aim of only a few previous reports [8, 11–13].

This paper is a continuation of earlier research [14–18] and is aimed at investigating the behaviour of aluminium and carbon steel electrodes in the presence and absence of nonylphenol ethoxylates. In addition, it tackles the *in situ* generation of either aluminium or iron-based coagulants for the removal of the nonylphenol ethoxylates under galvanostatic working conditions in cells with vertical and horizontal electrodes.

2. Experimental details

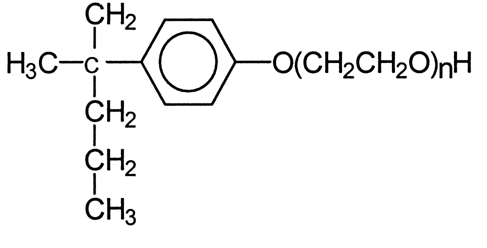
The behaviour of aluminium and carbon steel electrodes in the presence and absence of NP*n*EO was investigated by potentiodynamic polarization measurements. The chemical composition of aluminium was (wt %): Al 99.3; Cu 0.05; Mn 0.05; Fe 0.08; Mg 0.036; Si 0.49; and carbon steel Fe 99.38; C 0.09; Mn 0.49; Si 0.17; P 0.022. The working electrode was cleaned with two-grade emery paper, filter paper, and then degreased with acetone and washed carefully. The cylindrically-shaped working electrode (dia. 2.8 mm) was mounted vertically and had an exposed surface area of 1 cm^2, which allowed the equivalence between current (A) and current density (A cm^{-2}). The counter electrode was made of the same material as the working electrode and it had a surface area of about 50 cm^2. A saturated calomel electrode (SCE) was used as a reference electrode. The cell had no separated anodic and cathodic compartments.

The experimental set-up included an Autolab 20 potentiostat/galvanostat controlled by a PC operating the General Purpose Electrochemical System software from Eco Chemie B.V. The overall electrode processes were studied by voltammetric techniques: cyclic voltammetry (linear scan) and linear sweep voltammetry in two variants: potentiostatic (current integration) and galvanostatic, that is, current was swept and potential observed. The potential ranged from -2 to $+2$, V vs SCE in potentiostatic measurements and the current ranged from -0.020 A (cathodic current) to $+0.020$ A in galvanostatic ones. The scan rates were 0.02 V s^{-1} and 0.0001 A s^{-1}, respectively. The static working electrode was cathodically prepolarized for 3 min to provide conventionally reproducible conditions.

The supporting electrolytes were aqueous solutions of 0.1 M Na_2SO_4 (supporting electrolyte 1, SE1 in Figure captions) and 0.1 M Na_2SO_4 plus 0.01 M NaCl as activator (supporting electrolyte 2, SE2 in Figure captions). Chemically pure salts and doubly distilled water were used for preparation. Three nonylphenol ethoxylates (technical grade products) with chain lengths of 4, 16 and 40 ethoxy units were considered for experiments (see Structure 1).

The concentration of nonylphenol ethoxylates (NP4EO, NP16EO and NP40EO) in the solution was 0.1 g L^{-1} to simulate surfactant-containing industrial wastewater and the temperature was 22 ± 1 °C for all experiments.

The removal of NP*n*EO by electrochemically-generated coagulants was carried out in two types of electrocoagulation cell to compare the removal efficiencies for two electrode configurations. The first type of cell had vertical plate electrodes. Four anodes and five cathodes having equally exposed surface areas of 300 cm^2 and electrode gap of 0.5 cm were connected in a monopolar arrangement. Batches of 0.3 L aqueous solution (0.1 g L^{-1} surfactant and 0.6 g L^{-1} sodium chloride at initial pH of 6–7) were run into the cell. The effective anodic surface area/effective cell volume ratio was 100 m^2 m^{-3}.



Structure 1. Molecular structure of nonylphenol ethoxylates.

The other type of cell had horizontal electrodes. A grid of stainless steel wires (dia. 3 mm) with active surface area of 40 cm^2, acting as a cathode, was placed over a rectangular plate anode of 60 cm^2 surface area at a gap of 0.5 cm. The arrangement was placed at a slight tilt on the bottom of the cell. Batches of 0.7 L aqueous solution (0.1 g L^{-1} surfactant and 0.6 g L^{-1} sodium chloride at initial pH of 6–7) were run into the cell. The effective anodic surface area/effective cell volume ratio was 8.6 m^2 m^{-3}.

Both vertical and horizontal electrode configurations operated under galvanostatic working conditions. The current densities were set up by preliminary experiments with the provision that the same volumetric current density (A m^{-3}) would be applied for both electrode configurations. Finally, a volumetric current density of 1000 A m^{-3} resulted as the best option for practical and operational reasons.

3. Results and discussion

3.1. *Polarization curves*

Figure 1 shows the behaviour of aluminium and carbon steel electrodes in two supporting electrolytes and in the absence of nonylphenol ethoxylates. In 0.1 M Na_2SO_4 solution, the aluminium electrode (curve 1) remained passive over a wide range of potential, while the carbon steel electrode (curve 3) displayed a shorter potential sector where passivation occurred. However, the active dissolution of the carbon steel electrode occurred rather

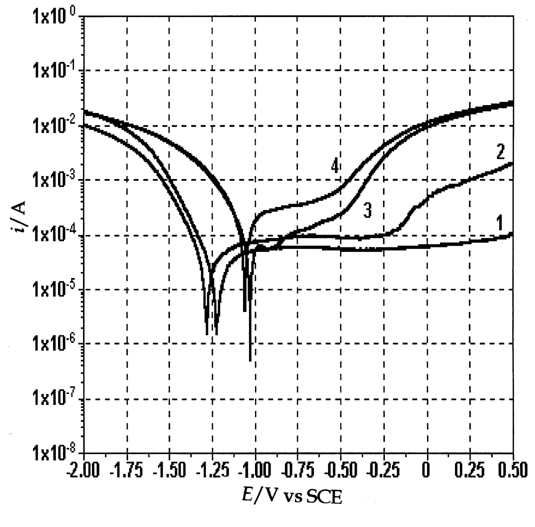


Fig. 1. Potentiostatic polarization curves for aluminium electrode in (1) SE1 (supporting electrolyte 1); (2) SE2 (supporting electrolyte 2); carbon steel electrode in (3) SE1; (4) SE2 at 0.02 V s^{-1}; pH 7.0.

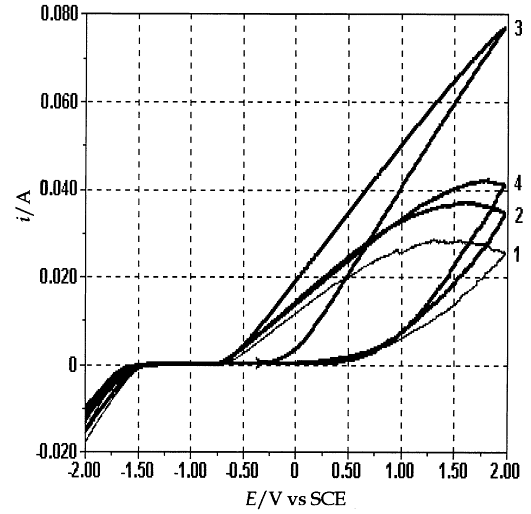


Fig. 2. Potentiostatic cyclic voltammograms for aluminium electrode in (1) SE2; (2) NP4EO + SE2; (3) NP16EO + SE2; (4) NP40EO + SE2 at 0.02 V s^{-1}; pH 7.0.

easily beyond −0.50 V vs SCE. The use of the second supporting electrolyte (0.1 M Na_2SO_4 plus 0.01 M NaCl) determined the active dissolution of the aluminium electrode (curve 2) and a slight increase in current from −1.00 to 0 V vs SCE for the carbon steel electrode (curve 4).

The cyclic voltammograms in Figure 2 show the influence of NP*n*EO on the behaviour of the aluminium electrode in the presence of the second supporting electrolyte. The most striking influence was recorded for nonylphenol with 16 ethoxylate groups. When the potential was swept back the currents remained higher than for the forward sweep over a wide potential range, which was considered as a supplementary activation at 0.02 V s^{-1}.

The cyclic voltammograms for the carbon steel electrode (Figures 3 and 4) were almost the same for both supporting electrolytes and in the presence of nonylphenol ethoxylates. However, in 0.1 M Na_2SO_4 solution as supporting electrolyte, the active dissolution began at a slightly more positive potential. The peaks on the backward curves in the region from −1.1 to −1.2 V vs SCE reflected the possible reduction of iron ions within the precipitate formed on the surface of the electrode. The polarization curves did not show the behaviour of the nonylphenol ethoxylates as organic corrosion inhibitors [19] in the context of generating iron-based coagulants.

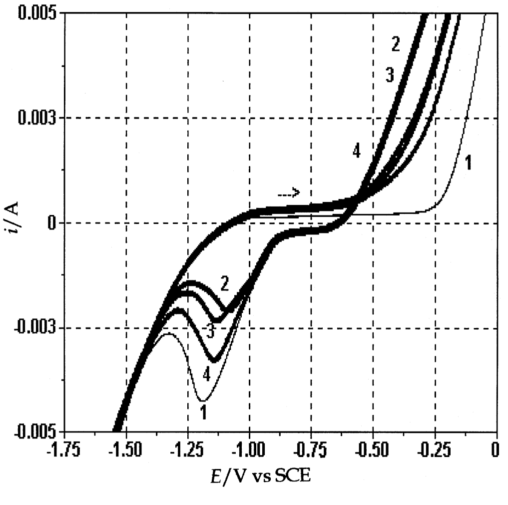


Fig. 3. Potentiostatic cyclic voltammograms for carbon steel electrode in (1) SE1; (2) NP4EO + SE1; (3) NP16EO + SE1; (4) NP40EO + SE1 at 0.02 V s^{-1}; pH 7.0.

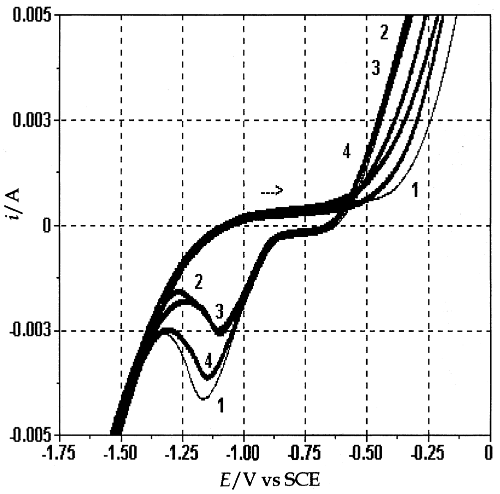


Fig. 4. Potentiostatic cyclic voltammograms for carbon steel electrode in (1) SE2; (2) NP4EO + SE2; (3) NP16EO + SE2; (4) NP40EO + SE2 at 0.02 V s^{-1}; pH 7.0.

The first supporting electrolyte (0.1 M Na_2SO_4 solution) was not considered further because aluminium remained totally passivated, even in the presence of nonylphenol ethoxylates. Preliminary work showed that a third supporting electrolyte (0.1 M NaCl solution) would have been undesirable because its excessively activating effect masked the influence of nonylphenol ethoxylates. Moreover, such a high sodium chloride concentration would not typically be found in wastewater.

The galvanostatic polarization measurements aimed at investigating the galvanostatic operating conditions in the cells for the removal of nonylphenol ethoxylates. For the aluminium electrode, variation of pH from 4 to 7 resulted in a different influence of nonylphenol ethoxylates. As the pH increased, the polarisation decreased more for nonylphenol with 16 and 40 ethoxy units than for that with four ethoxy units (Figures 5 and 6).

The same pH variation did not cause a significant change in polarisation for the carbon steel electrode according to the number of ethoxy groups (Figures 7 and 8). However, there was a lower polarization in the presence of nonylphenol ethoxylates compared to the supporting electrolyte up to 0.005 A.

It is well known that because of the negative difference effect [20], hydrogen evolution does not decrease with increase in anodic polarization of aluminium in the presence of sodium chloride. Consequently, the possibility of simultaneous oxidation of chloride ion at the aluminium electrode and, as a result, the production of

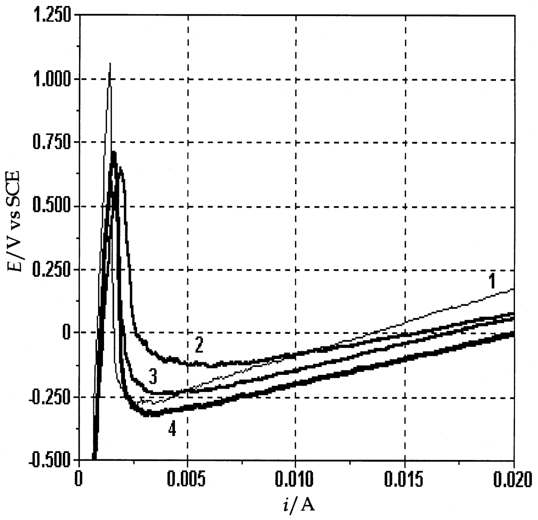


Fig. 5. Galvanostatic polarization curves for aluminium electrode in (1) SE2; (2) NP4EO + SE2; (3) NP16EO + SE2; (4) NP40EO + SE2 at 0.0001 A s^{-1}; pH 4.0.

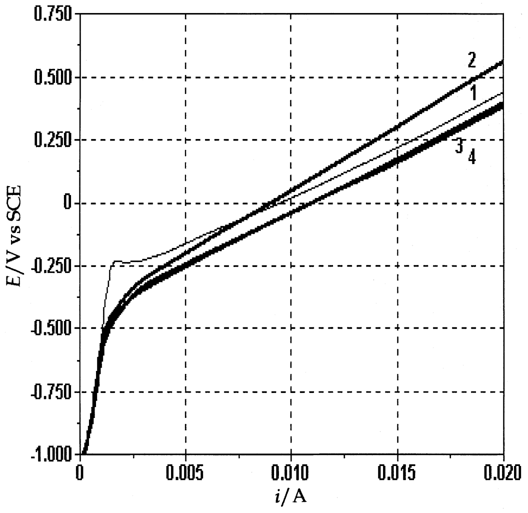


Fig. 7. Galvanostatic polarization curves for carbon steel electrode in (1) SE2; (2) NP4EO + SE2; (3) NP16EO + SE2; (4) NP40EO + SE2 at 0.0001 A s^{-1}; pH 4.0.

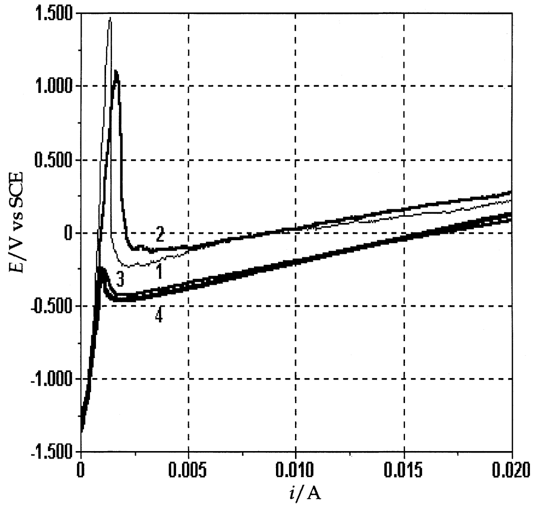


Fig. 6. Galvanostatic polarization curves for aluminium electrode in (1) SE2; (2) NP4EO + SE2; (3) NP16EO + SE2; (4) NP40EO + SE2 at 0.0001 A s^{-1}; pH 7.0.

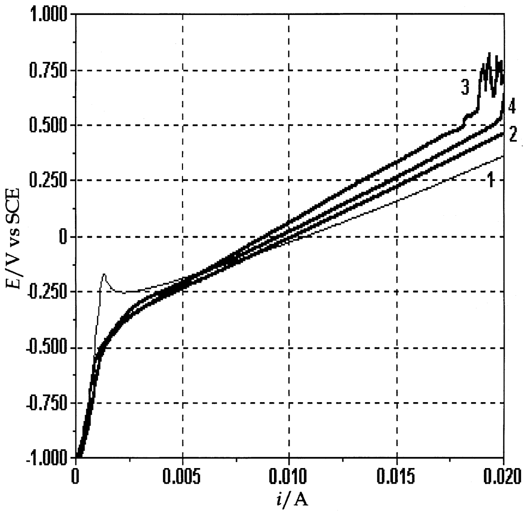


Fig. 8. Galvanostatic polarization curves for carbon steel electrode in (1) SE2; (2) NP4EO + SE2; (3) NP16EO + SE2; (4) NP40EO + SE2 at 0.0001 A s^{-1}; pH 7.0.

chlorinated compounds was unlikely to occur in the potential range −0.25 to +0.10 V vs SCE (Figures 5 and 6), which corresponded to the working current densities (10 and 116 A m^{-2}, respectively) in the electrocoagulation cells. At the carbon steel electrode (Figures 7 and 8), the same current densities shifted potentials to more negative values. Chlorine evolution occurred even on electrocatalytic materials (e.g., RuO_2–TiO_2/Ti) and in the presence of high sodium chloride concentration at potentials beyond +1.0–1.1 V vs SCE [21, 22].

Because of the complicated molecular structure of NP*n*EO, the direct anodic oxidation was also unlikely to occur at aluminium or carbon steel electrodes. Direct anodic oxidation of phenol requires high anodic potentials, even at electrode materials with good electrocatalytic properties (e.g., bismuth-doped lead dioxide [23]) or large potential windows (e.g., boron-doped diamond [24]). On the other hand, easily oxidizable phenolic compounds (e.g., flavonoids used as antioxidants) required 0.15–0.35 V vs SCE for oxidation at glassy carbon [25], whereas the working potentials on the aluminium and carbon steel electrodes were not higher than 0 V vs SCE (Figures 5–8).

3.2. *Water treatment*

Prior to water treatment experiments, the calculation of the hydrophilic–lipophilic (hydrophobic) balance (HLB) number according to [26] returned 9, 15 and 18 for NP4EO, NP16EO and NP40EO, respectively. Given a scale from 1 (oil soluble) to 20 (water soluble) for the HLB number, this indicated that NP16EO and NP40EO were soluble in water unlike NP4EO, which was moderately soluble in water. This finding was sustained by turbidity measurements, which showed 6.9, 0.3 and 0.15 NTU (nephelometric turbidity units) for the solutions containing 0.1 g L^{-1} NP4EO, NP16EO and NP40EO, respectively and 0.6 g L^{-1} NaCl. Thus, NP4EO was a hydrophobic colloid in solution rather than a micellar solution.

Two electrode configurations were compared to see whether the accommodation of large electrode areas in a small cell volume influenced removal efficiencies and power consumption. Moreover, the vertical configuration consisted of either aluminium/aluminium electrodes or aluminium/carbon steel electrodes, and the horizontal arrangement had either an aluminium anode/stainless steel cathode or a carbon steel/stainless steel pair.

Table 1 shows working conditions and results for the treatment with electrochemically-generated coagulant for nonylphenol ethoxylate removal in a vertical electrode cell. Both the anodes and the cathodes were aluminium.

The higher the number of ethoxylate units in the molecular structure, the more hydrophilic the surfactant [27]. NP16EO and NP40EO were mostly hydrophilic, had little tendency to adsorb on the electrochemically-generated flocs and remained in solution in a greater proportion. On the other hand, NP4EO was more hydrophobic, as indicated by its HLB number. Because of this hydrophobic character, NP4EO showed a greater tendency for adsorption [28]. These aspects explain the difference in removal efficiencies expressed as chemical oxygen demand.

Another experimental approach used the same vertical electrode arrangement, but the anodes and the cathodes were carbon steel. Table 2 shows the working conditions and results. The cell voltage (1.6 V as against 2.1–2.2 V on aluminium) reflected the main difference between the two configurations. This aspect influenced the energy consumption, which was lower for carbon steel than for aluminium. The lower cell voltage for the carbon steel electrode arrangement could be predicted from the galvanostatic plots. At lower current densities (e.g., 10 A m^{-2}) the difference in cathodic polarization for aluminium and carbon steel was about 0.25–0.30 V. The trend for nonylphenol ethoxylate removal remained the same (i.e., higher removal efficiencies for low content of ethoxy units), which showed the predominant role of HLB.

Other experiments for removal of nonylphenol ethoxylates with electrochemically-generated coagulant were carried out in a cell with horizontal electrodes. First, the anode was aluminium and the cathode stainless steel. Table 3 shows other working conditions and the result of nonylphenol ethoxylate removal. The processes were more intense because of a higher current density (116 A m^{-2} as against 10 A m^{-2} in the cell with vertical electrodes), but the removal efficiencies remained almost unchanged for the same charge passed.

Table 1. Water treatment by electrochemically-generated coagulants for NP*n*EO removal in a vertical electrode (aluminium) cell (A: Al; C: Al; i_A=10 A m^{-2}; c_i = 0.1 g L^{-1}; COD_i: 52 mg O_2 L^{-1} (NP4EO), 241 mg O_2 L^{-1} (NP16EO), 191 mg O_2 L^{-1} (NP40EO); pH_i 6–7; NaCl 0.6 g L^{-1}; at 22 °C)

Q /Ah m^{-3}	*U* /V	pH_f	*COD* removal/% NP4EO	NP16EO	NP40EO	W_{sp} /kWh m^{-3}
100	2.8	7.6	41	12	11	0.28
200	2.2	7.9	52	37	21	0.50
300	2.1	8.4	63	46	29	0.71
400	2.1	8.6	67	53	39	0.92
500	2.0	8.8	75	58	44	1.12

Key: (A) anode; (C) cathode; (Al) aluminium; (CS) carbon steel; (SS) stainless steel; (Q) quantity of electricity; (*U*) cell voltage; (i_A) current density; (c_i) initial surfactant concentration; (*COD*) chemical oxygen demand; (pH_i, pH_f) initial and final pH; (W_{sp}) specific energy consumption Percentage $COD_{\mathrm{removal}} = \frac{COD_{\mathrm{initial}} - COD_{\mathrm{actual}}}{COD_{\mathrm{initial}}} \times 100$.

Table 2. Water treatment by electrochemically-generated coagulants for NP*n*EO removal in a vertical electrode (carbon steel) cell (A: CS; C: CS; i_A = 10 A m^{-2}; c_i = 0.1 g L^{-1}; COD_i: 52 mg O_2 L^{-1} (NP4EO), 241 mg O_2 L^{-1} (NP16EO), 191 mg O_2 L^{-1} (NP40EO); pH_i 6–7; NaCl 0.6 g L^{-1}; at 22 °C)

Q /Ah m^{-3}	*U* /V	pH_f	*COD* removal/% NP4EO	NP16EO	NP40EO	W_{sp} /kWh m^{-3}
100	1.4	7.0	42	29	12	04.14
200	1.5	8.4	48	36	17	0.29
300	1.6	8.9	48	37	18	0.45
400	1.6	9.3	56	41	29	0.61
500	1.6	9.5	63	44	37	0.77

Key: see Table 1.

Table 3. Water treatment by electrochemically-generated coagulants for NP*n*EO removal in a horizontal electrode (aluminium anode) cell (A: Al; C: SS; i_A=116 A m^{-2}; c_i = 0.1 g L^{-1}; *COD*$_i$: 52 mg O_2 L^{-1} (NP4EO), 241 mg O_2 L^{-1} (NP16EO), 191 mg O_2 L^{-1} (NP40EO); pH$_i$ 6–7; NaCl 0.6 g L^{-1}; at 22 °C)

Q /Ah m^{-3}	*U* /V	pH$_f$	*COD* removal/% NP4EO	NP16EO	NP40EO	W_{sp} /kWh m^{-3}
100	3.4	7.9	42	21	16	0.34
200	3.3	8.1	50	32	29	0.67
300	3.3	8.3	75	39	32	1.00
400	3.2	8.3	83	46	38	1.32
500	3.1	8.6	92	53	45	1.63

Key: see Table 1.

Table 4. Water treatment by electrochemically-generated coagulants for NP*n*EO removal in a horizontal electrode (carbon steel anode) cell (A: CS; C: SS; i_A = 116 A m^{-2}; c_i = 0.1 g L^{-1}; *COD*$_i$: 52 mg O_2 L^{-1} (NP4EO), 241 mg O_2 L^{-1} (NP16EO), 191 mg O_2 L^{-1} (NP40EO); pH$_i$ 6–7; NaCl 0.6 g L^{-1}; at 22 °C)

Q /Ah m^{-3}	*U* /V	pH$_f$	*COD* removal/% NP4EO	NP16EO	NP40EO	W_{sp} /kWh m^{-3}
100	3.1	8.5	41	31	21	0.31
200	3.3	9.3	58	36	32	0.64
300	3.5	9.4	62	42	35	0.99
400	3.6	9.5	62	49	43	1.35
500	3.7	9.5	62	56	51	1.72

Key: see Table 1.

Table 5. Comparison between a vertical electrode cell (VEC) and a horizontal electrode cell (HEC) during water treatment by electrochemically-generated coagulants for NP4EO removal (c_i=0.1 g L^{-1}; *COD*$_i$: 52 mg O_2 L^{-1}; pH$_i$ 7.2; NaCl 0.6 g L^{-1}; at 22 °C)

Q	**VEC** [A: Al; C: SS; i_A=10 A m^{-2}]				**HEC** [A: Al; C: SS; i_A=116 A m^{-2}]			
/Ah m^{-3}	*U* /V	pH$_f$	*COD* removal /%	W_{sp} /kWh m^{-3}	*U* /V	pH$_f$	*COD* removal /%	W_{sp} /kWh m^{-3}
100	1.9	7.5	25	0.19	3.4	7.9	42	0.34
200	1.8	7.6	42	0.37	3.3	8.1	50	0.67
300	1.8	7.6	58	0.55	3.3	8.3	75	1.00
400	1.8	7.9	65	0.73	3.2	8.3	83	1.32
500	1.8	8.2	83	0.91	3.1	8.6	92	1.63

Key: see Table 1.

The increase in current density determined the increase in energy consumption by 30–40%.

A second horizontal electrode arrangement consisted of a carbon steel anode and a stainless steel cathode. The other operating conditions were identical to those in the cell equipped with horizontal electrodes of aluminium and stainless steel. The results are displayed in Table 4. The same trends were recorded for the removal efficiencies of nonylphenol ethoxylates. By comparison between the two horizontal electrode configurations (aluminium/stainless steel and carbon steel/stainless steel), the same cell voltages were observed: these values were different than those from the vertical arrangements (aluminium electrodes as against carbon steel).

Table 5 shows a comparison between a vertical and a horizontal electrode arrangement. The electrodes were made of the same materials, aluminium anodes and stainless steel cathodes. The treatment referred only to the removal of nonylphenol with four ethoxylate units. Under these circumstances, the removal efficiencies were higher for the horizontal arrangement. The current density and cell voltage were also higher for the horizontal electrode cell and consequently, the power consumption almost doubled in comparison with the vertical arrangement.

In addition to the electrode processes (described by polarization curves), the hydrophilic–lipophilic balance influenced the processes occurring at the adsorption surface of the electrochemically-generated coagulant. It had an amorphous structure and special adsorption properties [9,10]. A few seconds after generation, the coagulant underwent structuring processes and it would have been difficult to study NP*n*EO adsorption outside the cells.

4. Conclusion

The effect of nonylphenol ethoxylates (NP*n*EO) on aluminium and carbon steel electrodes was studied by plotting polarization curves under various conditions.

The involvement of NP*n*EO in the electrode processes was more significant on aluminium than on carbon steel in a solution of 0.1 M Na_2SO_4 plus 0.01 M NaCl as supporting electrolyte. On the other hand, the carbon steel electrode could be activated moderately by NP*n*EO in 0.1 M Na_2SO_4 solution as supporting electrolyte, while the aluminium electrode remained passivated over a wide range of potential.

With galvanostatic polarization and in the presence of NP*n*EO, the anodic activation was more evident on aluminium than on carbon steel. The influence of NP*n*EO depended on ethoxylate chain length.

The water treatment experiments for *in situ* generation of either aluminium or iron-based coagulants to remove the nonylphenol ethoxylates underlined the role of the ethoxy groups. The higher the number of ethoxylate units in the molecular structure, the more hydrophilic the surfactant, which had little tendency to adsorb on the electrochemically-generated flocs and remained in solution in a greater proportion. These aspects explained removal efficiencies of 30–50% for NP16EO and NP40EO as against 40–80% for NP4EO.

On the whole, the water treatment experiments showed the predominant role of processes in the bulk (bridging of electrochemically-generated polymeric species and adsorption of surfactants) as compared to the involvement of NP*n*EO in electrode processes, which were only responsible for the electrogeneration of coagulants.

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