Study of Membrane Ageing and Grafting Mechanisms Using Electron Paramagnetic Resonance

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Abstract:

An important setback for a wider use of membrane processes in industry is fouling, caused by aggregation of biomolecules at membrane surface and pores. Two important approaches to reduce this effect are the use of chemical cleaning procedures and the functionalisation of the membrane surface. However, both processes may lead to membrane degradation and structure alteration due to free radical formation or radical interaction with membrane polymer chains.

In this work, electron paramagnetic resonance (EPR) was used to evaluate and quantify radical formation in both chemical cleaning and membrane functionalisation by UV grafting, allowing for a better understanding of free radical formation processes and their influence on membrane characteristics. Studies under different cleaning and grafting conditions, such as, cleaning agent concentration and pH, light intensity and irradiation were also performed showing the potential of EPR as a technique for monitoring both procedures.

The information provided by EPR may contribute significantly to the development of new cleaning strategies which minimise the effect of membrane ageing and to the implementation of new and more efficient grafting procedures.

Keywords: Membrane ageing; Membrane chemical cleaning; Membrane grafting;EPR; ESR.

1. Introduction

Fouling of membranes caused by the adsorption and deposition of organic or/and inorganic material on the membrane surface and within the membrane porous structure is a major drawback of pressure-driven membrane processes, leading to the decrease of membrane flux and selectivity.

Chemical cleaning is used to remove organic and inorganic foulants from membrane surface and pores, being the most common procedure for fouling control in membrane processes. However, cleaning agents used to remove foulants are usually aggressive and their successive contact with membrane materials may lead to a decrease of membrane lifetime and, eventually, to membrane replacement [1-2].

Several solutions and protocols are used for membrane cleaning though, the most commonly used in reverse osmosis systems, consist in the usage of hypochlorite solutions [2]. These solutions are known to originate free radicals [3] that not only, oxidise the organic material present on the membrane surface, but may also interact with the membrane polymer affecting its structure and lifetime. This interaction between free radicals and membrane polymer may lead to the formation of free radicals in the membrane material [4-6] which causes scission of the membrane polymer chains and subsequent degradation of the membrane. In order to develop improved cleaning protocols, which are effective in fouling reduction but simultaneously minimise membrane ageing, it is necessary to understand the mechanisms behind the formation of the referred free radicals and their role in the oxidation of the membrane polymers. Most of the work reported in the literature on membrane ageing, is focused in studying the alterations induced in membrane performance and membrane morphology [7-9]. Fewer studies focus their attention in the mechanisms responsible for the molecular alterations occurring in the membrane polymer.

Mitigation of the membrane fouling problems has been attempted through application of different strategies. In particular, membrane functionalisation has deserved a special attention during the last decade [10-13]. The objective of membrane functionalisation is to change the membrane surface chemistry without altering substantially the membrane bulk properties, guaranteeing high physical and fouling resistant membranes. Among membrane functionalisation techniques, graft techniques present themselves as an attractive surface modification method. In these techniques, membranes are exposed to an irradiation source which can be a low temperature plasma, electron-beam or UV irradiation, among others, in the presence of a selected monomer [10,14]. Due to various advantages, such as rapid reaction, simple operation and low cost, UV grafting procedures are one of the most used to selectively alter membrane surface characteristics [10,13]. When using this functionalisation technique, two main approaches can be taken. The first one consists in the use of photoinitiators or photosensitizers acting as connectors between the membrane polymer and the desired monomer. The second approach consists in the use of membranes composed of UV-light sensitive polymers. Commonly, in the second approach membranes are exposed to UV-light producing radical sites that act as polymerization initiators and onto which the desired monomer can graft [10-13]. Due to its easy applicability this was the technique employed in this study.

Current studies are focused on the selection of the most adequate initial conditions in order to obtain membranes with the final desired characteristics. Small attention has been given to the mechanisms involved in membrane grafting. Knowledge of the mechanisms involved in membrane functionalisation through UV grafting techniques is crucial for further optimisation of membrane grafting procedures. It is expected, that optimisation will lead to higher grafting degrees while causing minimum membrane degradation.

Understanding the molecular mechanisms responsible for membrane oxidation during, membrane cleaning and membrane grafting will lead to the development of methodologies capable of minimising membrane fouling and ageing, contributing to the optimisation of membrane processes. In order to achieve this understanding it is crucial to identify and characterise the formation and decay of free radicals in the membrane polymers and contacting media, during cleaning and grafting procedures. This fundamental information can be acquired with electron paramagnetic resonance (EPR).

EPR is a spectroscopic technique used in the detection of chemical species that have unpaired electrons, such as free radicals, inorganic complexes and transition metals, spin traps and spin labels. EPR has been the standard technique in quantification and characterisation of radical species, their stability and decay kinetics. For this reason, it is currently the main experimental technique used for understanding and comparing the effect of different phenomena, such as, alkaline treatment and gamma irradiation of polymers [15-18]. EPR allows the study of the internal structure of samples in great detail, since EPR spectra depend on the magnetic moments of the unpaired electrons which are very sensitive to local magnetic fields within the sample.

The aim of this paper is to introduce EPR as a powerful technique for following membrane ageing and monitoring membrane UV grafting. The possibility of using EPR in the detection of free radicals formed in polymeric membrane materials will be demonstrated. The detection of these radicals gives important information on molecular and structural changes that may occur in polymeric membranes, when they are exposed to oxidation conditions, such as membrane cleaning, and irradiation conditions.

Parameters that influence membrane ageing such as hypochlorite concentration and pH, will be evaluated as well as the possibility of detecting radicals in cleaning

solutions. Additionally, EPR spectra of membranes irradiated under different irradiation exposure times and intensities will be also obtained, in order to determine the influence of different grafting irradiation conditions.

2. Materials and Methods

2.1. Preparation of membrane samples for ageing studies with EPR

The membrane used for the ageing studies was a commercial supported polyamide membrane (Dow, Filmtec NF270). A polyamide membrane was chosen because polyamide membranes present high sensitivity to chlorine degradation. In this paper two different ageing processes were addressed: ageing due to membrane cleaning with hypochlorite and due to sunlight exposure, which may occur during deficient membrane storage conditions.

In order to simulate membrane ageing due to cleaning, membrane pieces of 5 x 10 cm were submerged for 24h in bleach solutions (commercial available bleach contains proximally 3% of NaOCl). Different concentrations of hypochlorite (NaOCl) were tested (20, 50 and 80% of commercial bleach), as well as different pHs, in order to study the influence of cleaning agent concentration and cleaning solution pH, in the formation of membrane radicals. After 24h of contact, the membrane pieces were dried, using paper tissue and nitrogen gas, and transferred to the EPR quartz tube for analysis. Three replicas were performed for each study. The concentration of hypochlorite in the cleaning solutions was determined by titration with potassium iodine and sodium thiosulfate.

Ageing of membranes due to sunlight exposure was simulated by exposing membrane pieces of 5 x 5 cm to direct sunlight for 1 hour, with and without the presence of water.

After exposure, the membranes were analysed with EPR; sample preparation was the same as previously described for membrane cleaning.

2.2. Membrane UV grafting protocol

An UV illumination system (UV point source LQ-400, Dr. Gröbel UV-Elektronik GmbH, Germany) equipped with a liquid light guide and a medium-pressure mercury lamp ($\lambda >$ 280 nm) was used. UV intensity measurements where performed using an ILT 393 uniformity view (Nist traceable light measurements systems)

Commercial poly(ether sulfone) (PES) membrane (Millipore, Biomax PBTK02510) with a 30-kDa cut off were used due to its UV-light sensitivity.

Membrane pieces of 7 x 10 mm where transferred to and EPR quartz tube filled with 3 ml of grafting solution. The presence of oxygen influences negatively the membrane grating efficiency since it competes with the monomer for radical binding along polymerisation process. In order to minimize the presence of oxygen during membrane grafting process a degassing protocol was applied to the grafting solution. This degassing procedure involved bubbling the grafting solution with an argon stream for 10 minutes.. After this procedure, the quartz tube was immediately sealed and transferred to the EPR cavity. Membrane irradiation under different conditions were performed inside the EPR cavity and the ERS acquisition was performed online. Each EPR spectra acquisition takes approximately 20 seconds, consequently the EPR signal acquired in each 20 sec. period correspond to the average of the radical concentration present in the membrane in this time frame. Tests under different intensities (60 mW/cm^2 and $30mW/cm^2$), irradiation time (180, 300 and 600 seconds) and grafting solutions (pure hexane solution or a 1% N-Vinylpyrrolidone (NVP) hexane solution) were performed.

2.3. EPR experiments for determination of radical species

The identification of free radicals was performed by using a Bruker EMX 6/1,EPR Spectrometer. EPR analyses of membranes were performed in quartz tubes with 8 mm diameter at room temperature and a modular frequency of 100 kHz.

In order to identify radicals in cleaning solutions a spin trap had to be used in order to capture the extremely reactive radicals present in the solutions. The 5,5-dimethyl-pyrroline N-oxide (DMPO) was used with this propose. The EPR measurements of cleaning solutions were performed in a WG-812-S-Q, Wilmad LabGlass Quatz cell.

EPR ageing protocol measurements were performed using a microwave power of 6.33 mW and a modulation amplitude of 10 G, while in the EPR study of the UV grafting measurements were performed using a microwave power of 2 mW and a modulation amplitude of 4 G. The time necessary for aged membrane sample preparation, between radical generation and measurement, was equal for all the samples (5 min), to uniform the initial measurement conditions, preventing different initial free radical decays.

3. Results and discussion

3.1. EPR as a technique for characterisation of membranes submitted to ageing protocols

As explained, ageing is caused by the oxidation of membrane polymers due to the formation and reaction of free radicals during chemical cleaning or during radiation exposure. The reactions of these radicals result in scissions of the membrane polymer chains and/or alterations in chain structure, leading to membrane degradation. Therefore, knowledge on the mechanisms responsible for membrane free radical formation is crucial for identifying ways to prevent their formation and reducing membrane ageing and degradation.

The membrane ageing studies aimed at demonstrating the potential of using EPR for detection of free radicals during two different ageing situations: membrane cleaning and exposure to irradiation.

3.1.1. Ageing of polymeric membranes due to membrane cleaning

Different parameters that influence the cleaning of membranes were studied, such as hypochlorite concentration and pH. Membrane pieces of 5 x 10 cm were submerged in bleach solutions with different concentrations of hypochlorite during 24h, in order to determine the influence of its concentration in the formation of radicals in the membrane polymer. Figure 1 represents the EPR spectra of the radicals formed in the membrane, under these conditions, while Figure 2 depicts the influence of the hypochlorite concentration in the peak-to-peak amplitude of the EPR spectra. The peak-to-peak amplitude is a measure of EPR signal intensity which depends on the concentration of free radicals formed in the membrane polymer. The results obtained show that the EPR radical signal is directly proportional to the bleach (hypochlorite)

solution concentration where the membranes were submerged. This behaviour implies that the concentration of the cleaning agent is directly responsible for the number of radicals formed in the membrane polymer.

As reported by Kang et al., [2], and Causserand et al., [6], the degradation of membranes during cleaning depends not only on the concentration of hypochlorite but also on the pH of the cleaning solution. In order to study the influence of pH in the formation of radicals in the membrane, pieces of membrane with 5 x 10 cm were submerged in solutions of 20% of bleach at pH of 8 and 9. As shown in Figure 3 and Table 1, even a small difference in the pH of the cleaning solutions causes an increase in the concentration of free radicals formed in the membrane. This result is consistent with the results obtained by Kang et al., [2], and Causserand et al., [6], that reported a high influence of the cleaning solution pH in the degradation of the membrane polymer and a larger effect in membranes exposed to cleaning solutions at lower pH values.

The identification of the free radicals formed in the membrane polymer during cleaning, Figures 1 and 3 is unfeasible, due to the absence of hyperfine structures in the obtained EPR spectra. Hyperfine structures give information on interactions between magnetic moments of unpaired electrons in free radicals with nearby nuclear spins, this information allows to determine the position of unpaired electrons and identify the free radicals.

3.1.1.2. Detection of radicals present in the cleaning solutions

As reported by Causserand et al., [6], the degradation of the membranes, due to ageing, is a result of the action of radicals present in the cleaning solution. These radicals react with the membrane polymer to form the membrane radicals that were detected by EPR and shown in Figure 1. The majority of radicals expected to be

formed in solution are ClO•, OH•, and organic free radicals resulting from the oxidation of organic matter. Therefore, additionally to the detection of radicals formed in the membrane polymers, crucial information can be obtained by analysing the nature of the radicals that are formed in the cleaning solutions. The radicals present in solution are extremely reactive and can only be detected with the addition of a spin trap. A spin trap is a molecule that reacts with the short life time radical to form a more persistent radical that can be detected by EPR. Figure 4 shows an example of a radical detected using the spin-trap 5,5-dimethyl-pyrroline N-oxide (DMPO) in a solution of 10% of bleach. The addition of DMPO to the cleaning solution results in the formation of a nitroxide-based persistent radical, within the solution, that is detected by EPR (Figure 4), the detected radical spectra is consistent with the 5,5-dimethyl-2-pyrrolidone-N-oxyl radical (DMPO-X), a radical usually detected in NaOCl solutions were DMPO is used as spin-trap [19]. The possibility of detecting radicals in the cleaning solution using EPR may provide information about the reactions occurring during membrane cleaning, between the radicals in solution and the formed radicals in the membrane.

3.1.2. Ageing of membranes due to solar exposition

Ageing of membranes can also be caused by deficient storage conditions. Exposure to humidity and light during long periods of storage may increase the degradation of polymeric membranes. To simulate an accelerated ageing due to membrane exposition to light and humidity, membrane pieces of 5 x 5 cm were exposed to direct sunlight, for about one hour, with and without the presence of deionised water. Radical signals were detected in all the samples exposed to sunlight: $1.04 \cdot 10^5$ peak-to-peak amplitude/g of membrane for the dried membrane and $2.25 \cdot 10^5$ peak-to-peak amplitude/g of membrane for the membrane under water. This indicates that the exposition of a membrane to sunlight creates membrane radicals. These radicals are

formed due to oxidation of the polymer caused by UV radiation. These radicals may propagate through the membrane polymers, causing cleavage of polymer bounds and eventuality diminishing membrane performance. The EPR spectra, obtained for the water submerged membrane samples exposed to sunlight is two times stronger than the signal obtained for the membranes exposed to the sunlight in dry conditions. This behaviour occurs because water acts as a free radical propagation medium within the membrane polymer. Additionally, a solution of water under irradiation is also a source of OH• radicals, which may also react with the membrane polymer, causing further membrane radicals and bound cleavage. Therefore, the higher amount of radicals formed in the membrane submerged in water is a combination of two phenomena: radical propagation and reaction with water radicals.

3.2. EPR as a technique for monitoring membrane functionalisation using UV irradiation

As discussed in the introduction a possible strategy for the minimisation of membrane fouling consists in the functionalisation of the membrane surface, enhancing its fouling resistance. This can be achieved by using UV irradiation grafting methods, where radical sites, acting as polymerization initiators, are produced in the membrane by UV irradiation. In order to optimise the membrane functionalisation methodology, deeper knowledge about the mechanisms influencing radical formation and monomer grafting is necessary.

The work performed regarding membrane grafting, aimed at showing the potentialities of EPR as a technique to optimise and monitor radical formation under different conditions, during the grafting phase.

3.2.1. Influence of UV irradiation intensity in EPR spectra

UV Irradiation intensity can play a very important role in membrane grafting. Higher intensities are generally related with higher membrane grafting degrees [20], but also with higher membrane degradation. As showed by Georges Belfort et al., [20], higher UV light intensities and irradiation times cause a higher degradation of the membrane structure, creating a membrane with lower selectivity and higher permeability. This happens because in UV grafting radicals are formed due to polymer chains cleavage. For this reason, the cleavage of polymer chains and thus the formation of membrane radicals increase with the increase of the intensity and energy of the irradiation light. Therefore, lower UV light intensities and shorter irradiation times are normally preferred when using UV grafting techniques. This strategy benefits the maintenance of membrane bulk characteristics while guaranteeing that only the membrane surface is modified, but limits the achievement of higher grafting degrees.

To evaluate the influence of UV irradiation intensity in the formation of membrane radicals, two PES membranes where irradiated for 300 second in pure hexane under different intensities (30 mW/cm^2 and 60 mW/cm^2). Both EPR spectra are shown in Figure 5.

As expected, radical concentration increases with increasing light intensity. The highest radical concentration was achieved when an intensity of 60 mW/cm^2 was used.

By using the EPR as a monitoring technique, a direct relationship between radical concentration, irradiation intensity and membrane degradation can be found, which allows for determination of the optimum irradiation intensity.

As reported for the membrane cleaning studies the absence of hyperfine structures in the obtained EPR spectra Figure 5 prevents the identification of the free radicals formed in the membrane polymer.

3.2.2. Influence of different irradiation times in the EPR spectra

Another important parameter of the membrane UV grafting technique is the irradiation time. Longer irradiation times are normally associated with higher grafting degrees [20].

To study the change of radical concentration during irradiation time, a PES membrane was irradiated with an intensity of 30 mW/cm^2 in pure hexane. EPR measurements where performed online while the membrane was irradiated. EPR spectra are shown in Figure 6, while the spectra peak-to-peak amplitude variation over time is shown in Figure 7.

As can be seen in Figure 6 and 7, radical concentrations increase with irradiation time. However, at longer irradiation times the radical concentration variation tends to a plateau. This may reflect the presence of a steady state stage, due to the establishment of an equilibrium between radicals formation and decay. The existence of a plateau at longer irradiation times, may indicate that although longer times are always associated to higher grafting degrees, an optimal grafting irradiation time should exist and its value is lower than the steady state phase exposure time.

The use of EPR to monitor the changes of radical concentration during irradiation, contributes to a better understanding of the effects of irradiation time on the grafting procedure, ultimately leading to an optimum irradiation time.

3.2.3. EPR signal variation in the presence of monomer

The previous experiences were performed in the absence of monomer to demonstrate that EPR could give solid information regarding the variation of radical concentration during grafting. However, the presence of monomers is expected to interfere in the mechanisms of radical formation and fading during grafting. For this reason, a

comparison between membranes in the absence and presence of monomer was performed.

Two PES membranes, one immersed in a 1% v/v N-Vinylpyrrolidone NVP hexane solution and the other in a pure hexane were irradiated, separately, during 300 seconds using a light intensity of 30 mW/cm^2. NVP was chosen since it presents high grafting degrees [10]. Both EPR spectra are shown in Figure 8.

As can be seen in Figure 8, the membrane irradiated in the presence of NVP presents a significantly lower radical concentration than the one irradiated in pure hexane. Several phenomena may explain this observation, such as the reaction of the formed membrane radicals with the monomer present in solution or the absorption of part of UV light by the monomer. According to Georges Belfort et al., [10] both phenomena may occur when NVP is used as monomer. However, since NVP presents a strong absorption in wavelengths below 290 nm, and in this work a medium pressure mercury lamp irradiating with wavelengths superior to 280 nm was used, the reduction of radical concentration due to absorption of light by the monomer solution should be minimum.

This may indicate that, when the membrane is irradiated in the presence of NVP, the EPR spectra intensity diminishes essentially due to grafting reactions between the formed radicals and the NVP present in solution. The higher variation of EPR signals, in the presence and absence of NVP, may indicate that a significant amount of the radicals formed during irradiation reacted with the monomer and a higher monomer grafting degree was obtained.

These preliminary results suggest that the EPR technique may allow to obtain a correlation between the radical concentration profiles in the absence and presence of monomers, with the degree of membrane grafting achieved. It is also expected that these studies may conduce to further optimisation of NVP grafting procedures.

3.2.4. Study of the decay of the EPR signal

It is commonly considered that grafting processes occur essentially during the irradiation stage, being less important during the radical decay stage, i.e., after irradiation. However, the study of the membrane radical decay after irradiation may not only provide insights on radicals dynamics and life time, but also gives relevant information regarding the importance of this phase.

To study the membrane radical decay phase, a PES membrane was irradiated for 600 seconds, in pure hexane applying a light intensity of 30 mW/cm^2. EPR measurements were performed at different times during radical decay. EPR spectra are shown in Figure 9, while the variation of the spectra peak-to-peak amplitude over radical decay time is shown in Figure 10.

As depicted in Figure 10, a decrease of the radical concentration over time, after irradiation, was observed. These results suggest that when irradiation of the membrane is ceased, annealing reactions between radicals are dominant, causing a decrease in radical concentration.

In Figure 10 it can be seen, that most of the EPR signal variation occurs in the first 50 seconds, while in the following 250 seconds the radical concentration variation is less abrupt. This may be explained by the higher initial radical concentration which causes frequent annealing reactions and faster initial signal decay. The radical concentration diminishes over time, causing a decrease of the annealing reactions and consequently a decrease in the velocity of radical concentration decay.

It is expected that by studying decay profiles of different grafting systems, crucial information regarding grafting mechanisms and reactions is obtained. By acquiring this information, further knowledge may be obtained regarding the parameters that influence grafting, such as grafting environment.

4. Conclusions

The results presented herein demonstrate the potential of EPR as a technique for monitoring membrane ageing and grafting procedures.

This study demonstrates that radicals formed in membrane polymers, due to membrane exposure to oxidation conditions (membrane ageing) and UV irradiation (UV grafting), can be identified and their dynamic formation, fading and reaction monitored. Also, the EPR technique showed to be sensitive to several parameters that influence membrane structural and molecular alterations.

Regarding membrane ageing, this work demonstrates the potential of using the EPR technique to detect radicals in both membrane and cleaning solutions, under different conditions. The knowledge that can be acquired with EPR may be very valuable since it can be applied for the development of new cleaning strategies which minimise their impact in membrane ageing.

Considering membrane grafting, this study demonstrates that EPR can evaluate radical formation under different UV grafting conditions (UV light intensity, irradiation time and presence or absence of monomer), allowing for a better understanding of the impact of different grafting parameters on the final membrane characteristics. The information provided by EPR may contribute significantly to the implementation of new and more efficient grafting procedures, allowing enhanced membrane grafting degrees and simultaneously avoiding membrane damaging caused by UV irradiation.

The combination of the EPR information, regarding radical concentration with membrane characterisation techniques such as, Fourier transform infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS), dielectric relaxation spectroscopy, scanning electron microscope (SEM) and atomic force microscopy (AFM), may allow for a molecular interpretation of the structural and morphological

changes occurred in membranes during ageing or after functionalisation, caused by the action of free radicals.

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Figure 1

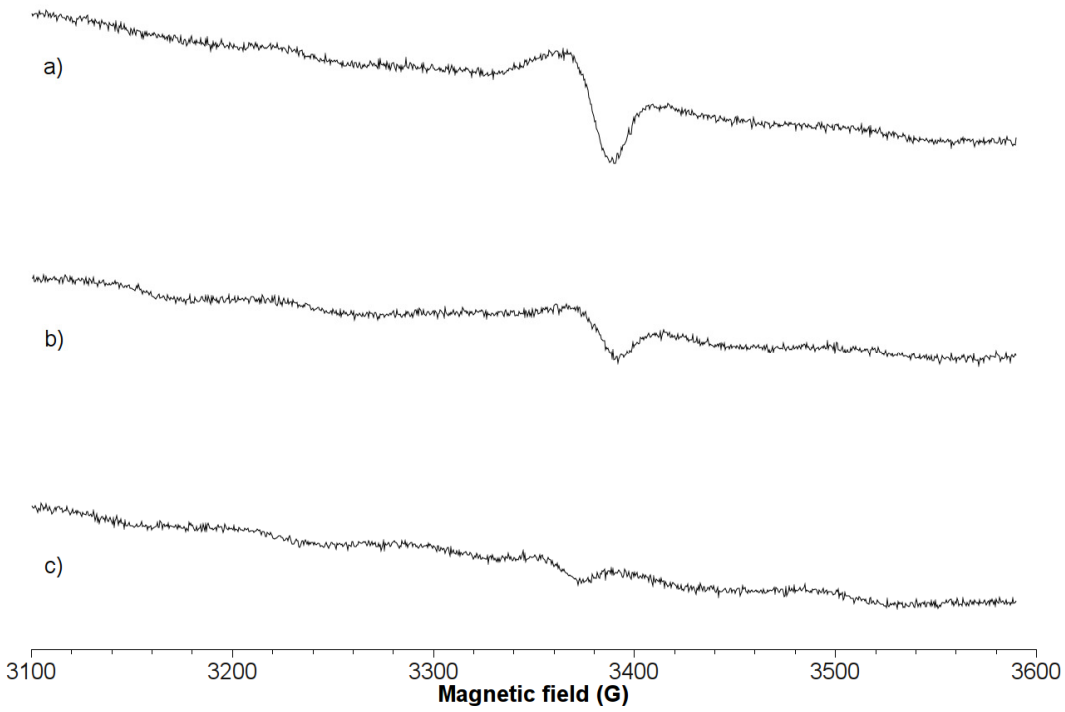

Figure 1. EPR spectra of membrane radicals formed after submerging pieces of membrane in water solutions of 80 % (v/v) a), 50 % (v/v) b) and 20 % (v/v) c) of bleach, at pH = 9. Blank tests were performed with deionised water and showed no radical signal (same yy scale).

Figure 2

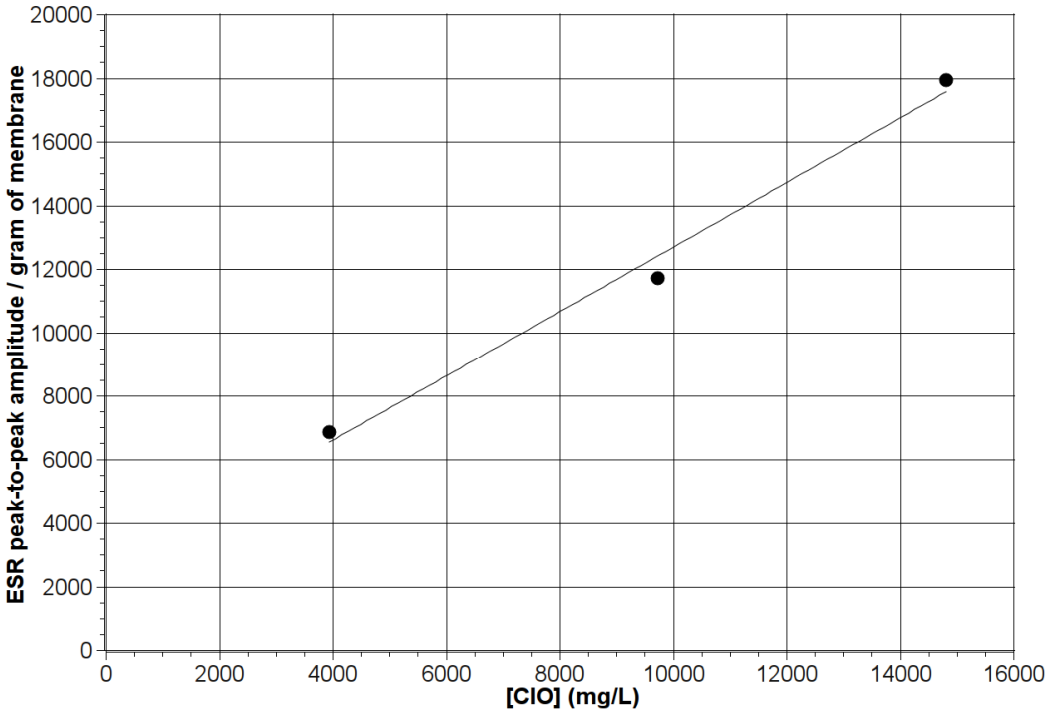

Figure 2. Influence of the hypochlorite solution concentration in the radical EPR signal in the membrane, determined by EPR.

Figure 3

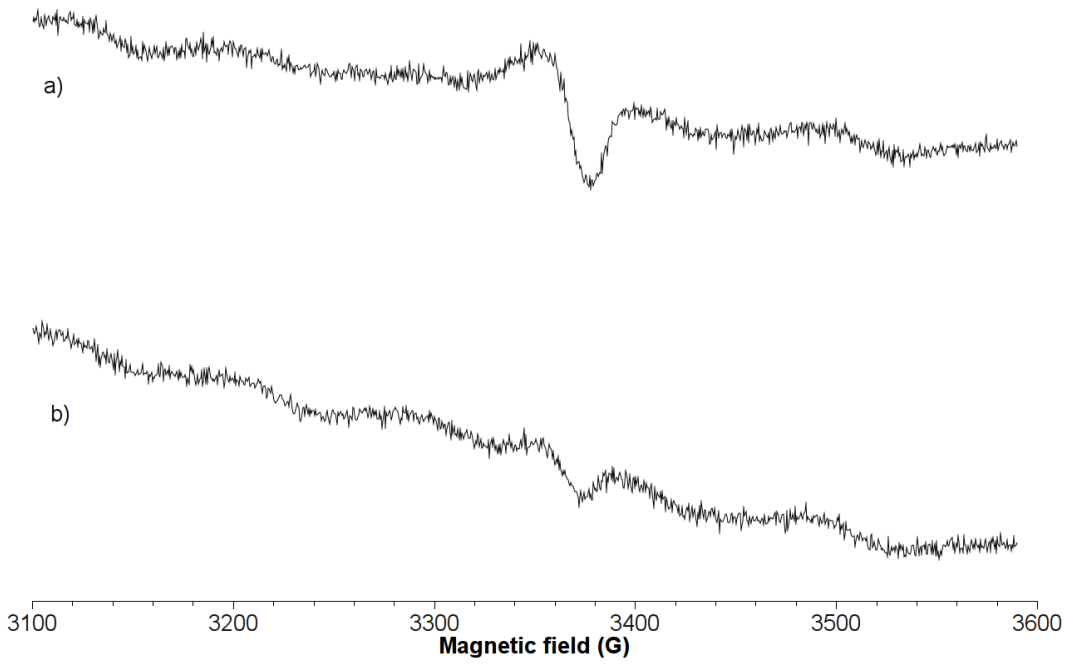

Figure 3. EPR spectra of membrane radicals formed after submerging pieces of membrane in bleach solutions of 20% and pHs of 8 a) and 9 b) (same yy scale).

Figure 4

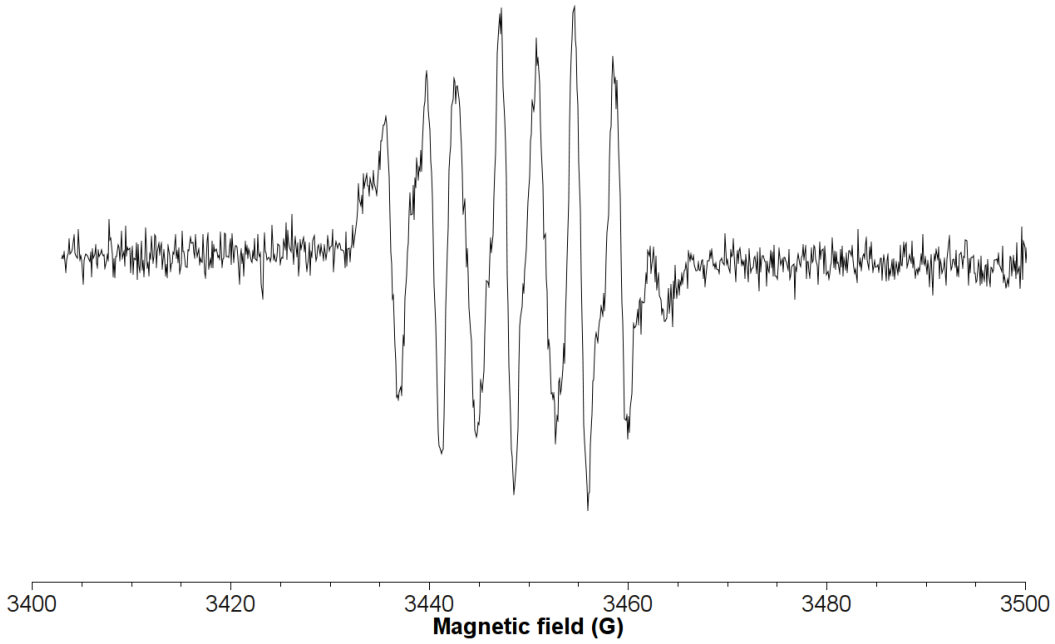

Figure 4. EPR spectra of DMPO in a cleaning solution of 10 % (v/v) of bleach.

Figure 5

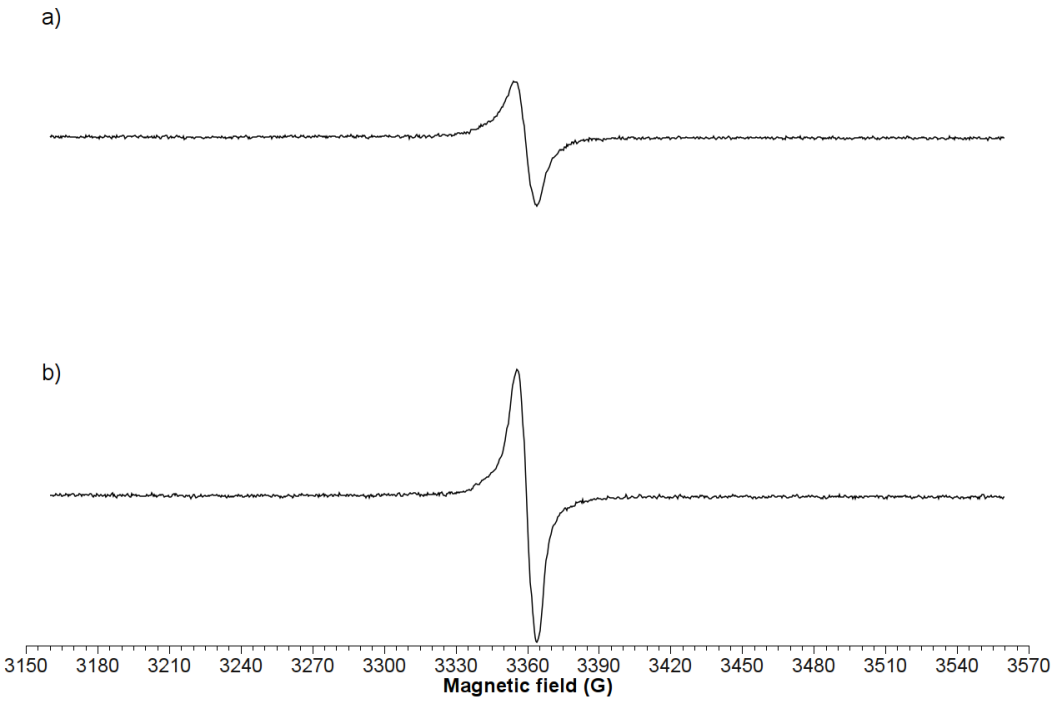

Figure 5. EPR spectra of PES membranes irradiated in pure hexane solutions using different light intensities (same yy scale): a) Membrane irradiated with a light intensity of 30 mW/cm^2, b) membrane irradiated with a light intensity of 60 mW/cm^2.

Figure 6

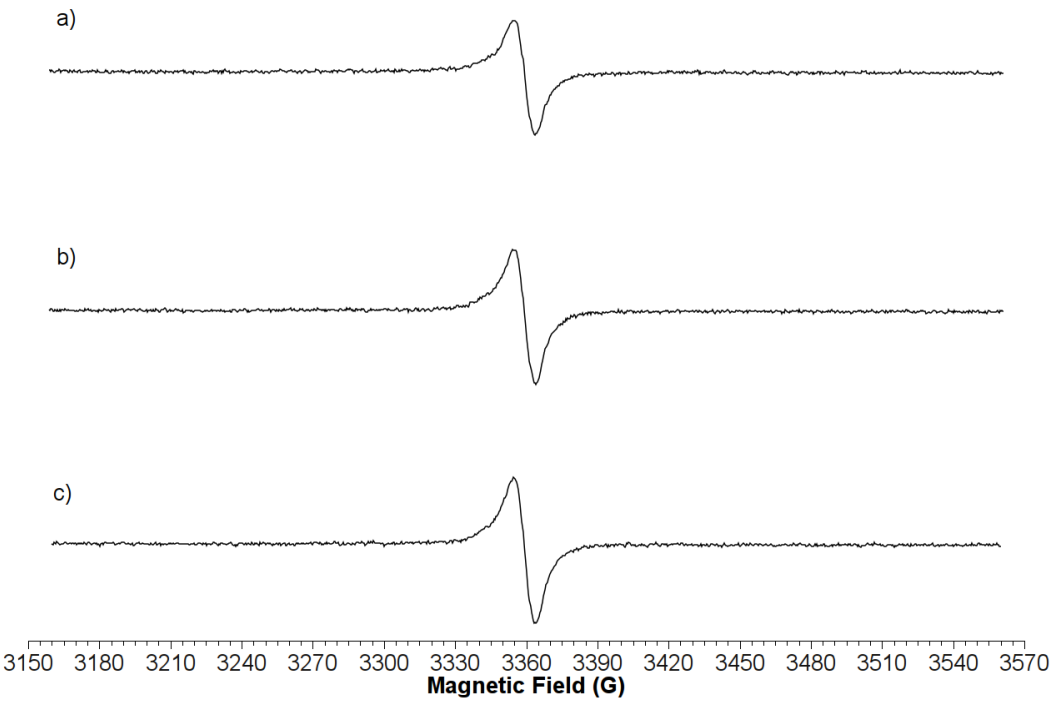

Figure 6. EPR spectra of PES membranes in pure hexane, obtained after different times of irradiation (same yy scale): a) After 180 sec of irradiation, b) After 300 sec of irradiation, c) After 600 sec of irradiation.

Figure 7

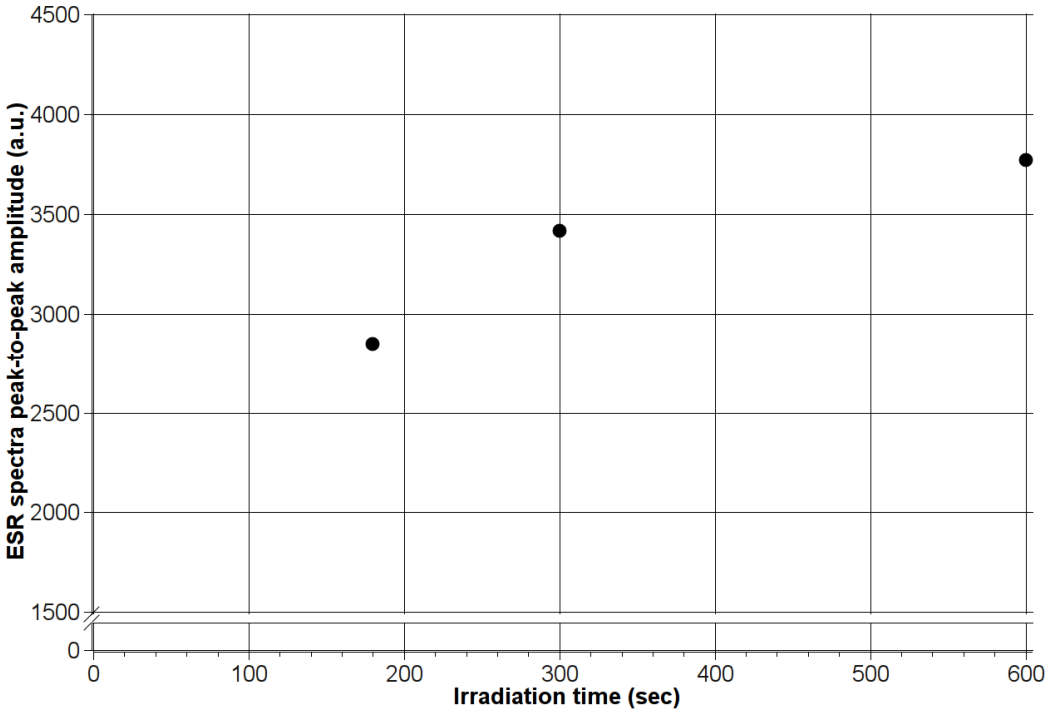

Figure 7. Variation of EPR spectra maximum peak-to-peak amplitudes obtained for PES membranes at different irradiation time.

Figure 8

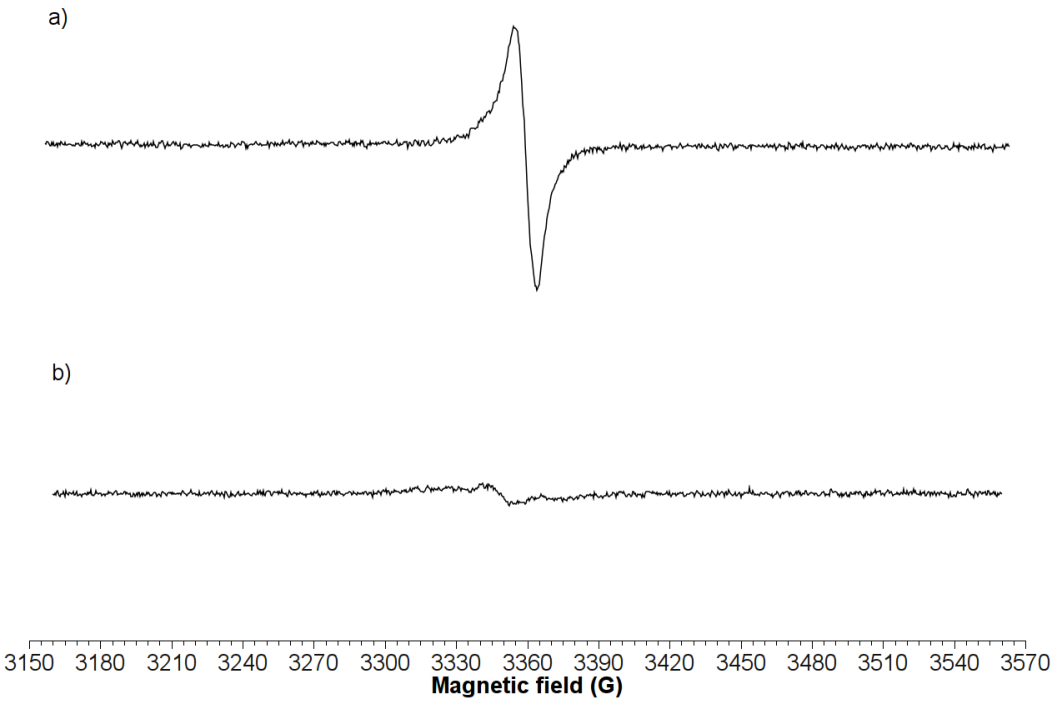

Figure 8. EPR spectra obtained for PES membranes irradiated in different solutions (same yy scale): a) pure hexane, b) 1% v/v NVP.

Figure 9

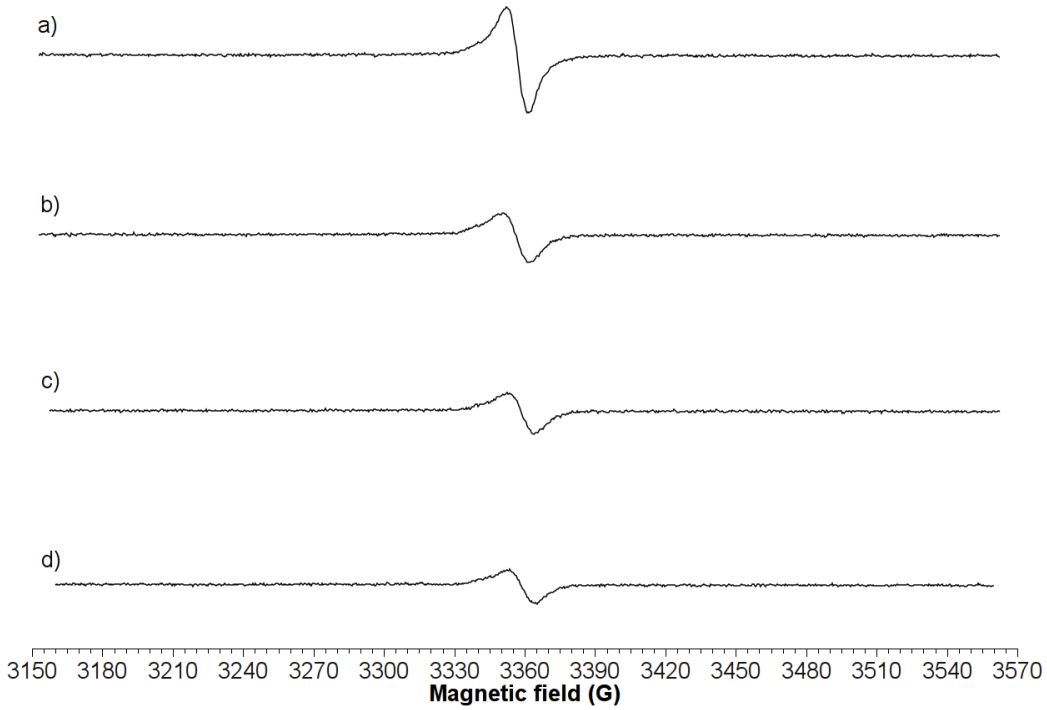

Figure 9. EPR spectra of irradiated PES membranes obtained after different times upon ceasing the irradiation: a) at the moment irradiation is stopped, i.e. 0s, b) 60 seconds after irradiation, c) 180 seconds after irradiation and d) 300 seconds after irradiation.

Figure 10

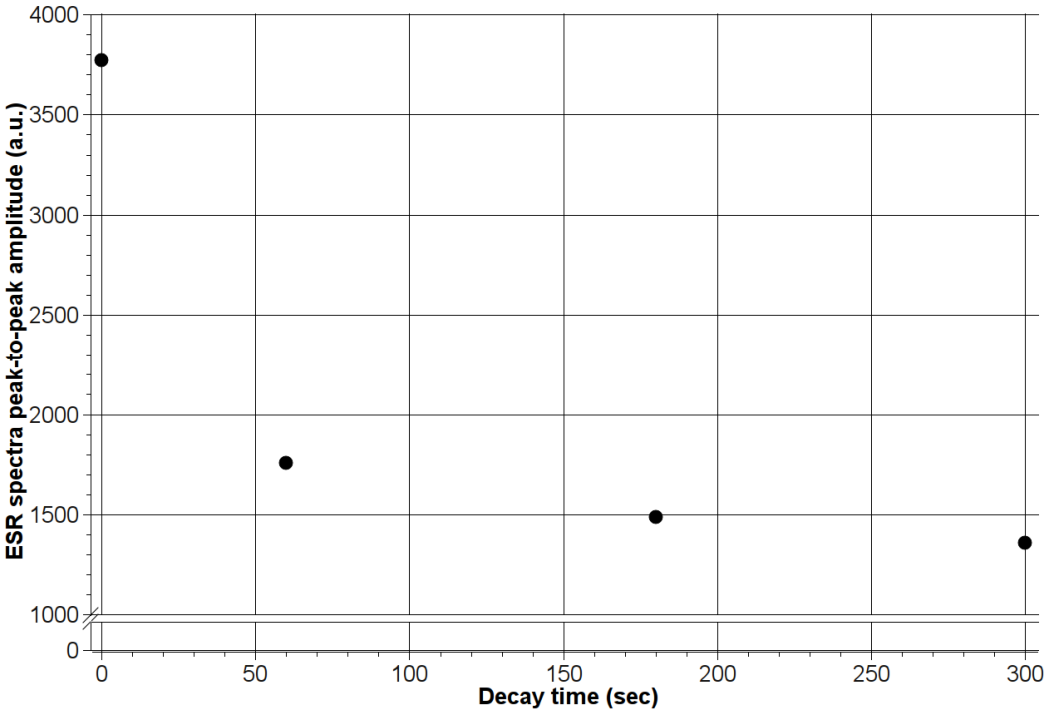

Figure 10. Variation of EPR spectra maximum peak-to-peak amplitudes obtained for irradiated PES membranes at different times after ceasing irradiation.

Table 1. EPR spectra signals achieved in different conditions of chemical cleaning: influence of pH and concentration of cleaning agent

Percentage of bleach in cleaning solution	pH of the cleaning solution	EPR Spectra peak-to-peak amplitude /g of membrane $\cdot 10^4$
20%	8	1.19 ± 0.13
20%	9	0.69 ± 0.03
50%	9	1.17 ± 0.16
80%	9	1.79 ± 0.20