# Optimization of milk electroreduction: impact of low anode/cathode voltage difference application on its redox potential modulation during treatment and storage

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ORIGINAL PAPER

# Optimization of milk electroreduction: impact of low anode/cathode voltage difference application on its redox potential modulation during treatment and storage

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**Abstract** Milk degradation during processing and storage is mainly due to oxidation–reduction reactions. Electroreduction was proposed recently to modulate the redox potential of food such as milk. However, only one study was carried-out on milk with a hydrodynamic electroreduction cell, and this study concluded, according to its protocol, that 4 V was the best anode/cathode voltage difference. But, since electroreduction is an electromembrane process, energy consumption is a major concern. Optimization of milk electroreduction can be one of the ways for improving milk resistance to alteration. Our objectives in the present work were to (1) investigate the effect of low anode/cathode voltage differences on milk redox potential modulation during electroreduction, (2) optimize the process, and (3) compare storage of a low-voltage electroreduced milk with a non-electroreduced milk. It appeared from these results that electroreduction at anode/cathode voltage difference of 3 V was sufficient to ensure a significant decrease in redox potential and dissolved oxygen and allow an energy saving of 79% in comparison with a treatment at 4 V. It appeared also that oxygen is an important parameter to consider during storage of electroreduced milk. To our knowledge, this study is the first one to demonstrate that electroreduction process can be a technological and chemical free alternative to improve stability against oxidation with a low-energy consumption.

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乳电解还原过程的优化

**摘要:** 在乳的加工和贮藏期间，乳降解的主要原因是由氧化还原反应引起的。目前，人们认为电解还原可以调节诸如奶类食品的氧化还原电位　然而，仅有一项研究采用电解还原流体电池对乳进行过研究，研究结果得出最佳的阳极/阴极电压差是4v。但是，由于电解还原是一种电膜过程，能量消耗是主要考虑的因素之一。因此，乳的电解还原优化主要是改变乳的电阻。本文1)考察了电解还原过程中低电压差对乳的氧化还原电位的调节；2)优化电解还原过程；3)比较低电压差电解还原后的乳和非电解还原乳的贮藏稳定性。研究结果表明:当电解还原的电压差达到3V时，就可以显著降低乳的氧化还原电位和溶解氧浓度，与电压差为4V时相比可以节能79%。此外，氧的浓度是电解还原乳在贮藏过程中需要考虑的另一个重要参数。因此，电解还原技术是一种低能耗、无化学污染的保藏技术。

**Keywords** Milk · Redox potential modulation · Electrolysis with membrane · Energy consumption · Storage · Dissolved oxygen

**关键词** 乳·氧化还原电位调节·膜电解·能耗·贮藏·溶解氧

## 1 Introduction

Many modifications of milk composition appear during processing and storage. Milk degradation is mainly due to oxidation–reduction reactions. These reactions result in the alteration of sensitive compounds (unsaturated fat (Jensen et al. 1991), flavor substances (van Boekel 1998), change in microbiological flora (Brown and Emberger 1980), and thermal stability of milk (Moreton 1998)). Oxydation–reduction reactions have an important effect on the quality of dairy products, but manufacturers have few resources available to control them. Methods to control the redox potential were evaluated in food industries (addition of cystein or vitamin C) (Dave and Shah 1997), but they have the disadvantage of using chemical products.

Electrolysis which is an electrochemical process based on electrode redox reactions has already been used in milk to coagulate milk proteins (Janson and Lewis 1994), to reduce disulfide bonds in whey proteins (Bazinet et al. 1997), and recently to modulate the redox potential of milk (Bolduc et al. 2006). The electrolysis cell operates with only one membrane that separates two solutions circulating in each electrode compartment. In electrolysis, an external anode/cathode voltage difference is applied to the cell and chemical reactions occur at the electrode–solution interface. The anode induces oxidations, and reductions occur at the cathode (Gardais 1990). The electrode can act only as a source (for reduction) or a sink (for oxidation) of electrons transferred to or from species in solution, and this transfer always occurs at the electrode surface (Gardais 1990; Brett and Oliveira-Brett 1994).

Recently, Bolduc et al. (2006) applied electroreduction to modulate the redox potential of milk. They tested five anode/cathode voltage differences (2, 4, 6, 8, and 10 V) to electroreduce a pasteurized skim milk. These authors concluded, according to their protocol, that 4 V was the best anode/cathode voltage difference. Indeed, over 4 V foam appeared in milk during treatment due to water hydrolysis at the cathode and under 4 V not enough energy seems to be transferred to milk in order to reach the same redox potential as the other anode/cathode voltage differences applied in this work.

Optimization of milk electroreduction can be one of the ways for improving milk resistance to alteration. Since electroreduction is an electromembrane process, energy consumption is a major concern. However, no study was carried out on milk with a hydrodynamic electroreduction cell to determine the optimum anode/cathode voltage difference to be applied during the process in order to optimize its energy efficiency. Hence, in this present work, our objectives were to investigate the effect of low anode/cathode voltage differences on milk redox potential modulation during electroreduction, to optimize the process energy consumption, and to compare the storage of a low-voltage electroreduced milk with a non-electroreduced milk.

## 2 Materials and methods

### 2.1 Materials

#### *2.1.1 Milk*

The electroreduction treatments were carried out on pasteurized skim milk of the brand Ultra Milk, commercially available and manufactured by Natrel (QC, Canada).

#### *2.1.2 Electroreduction system*

The system used was a MicroFlow type electrodialysis cell with a membrane electrolysis configuration (ElectroCell AB, Karlskoga, Sweden). The cell was separated in two different compartments by a cationic membrane (CMX-SB type, Tokuyama Soda Inc.,

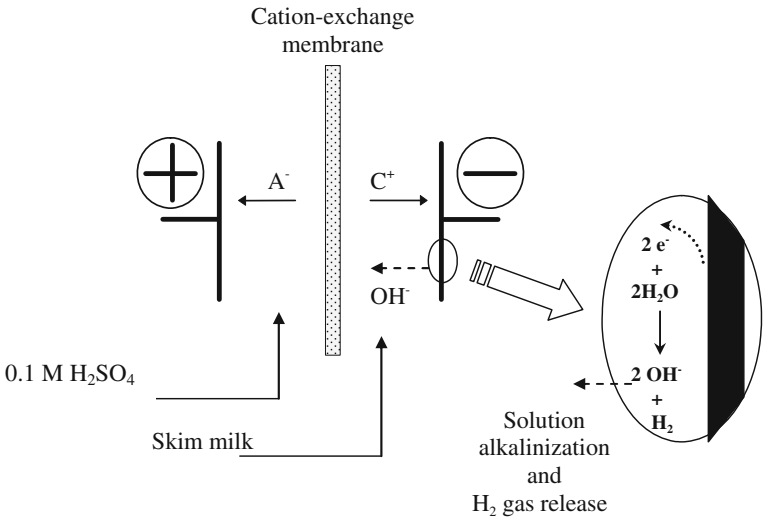


**Fig. 1** Electroreduction cell configuration and theoretical water electrolysis reduction reaction. $C^+$ cation, $A^-$ anion, $e^-$ electron, $H^+$ proton, $OH^-$ hydroxide

Japan) (Fig. 1). In each compartment, one polypropylene spacer (2.02 mm thick) was placed to allow the liquid to flow through and to have contact with a 10 $cm^2$ surface of both the membrane and the corresponding electrode. On one side of the membrane, the milk was in contact with a food-grade stainless steel cathode and on the other side of the membrane, the electrolyte (0.1 M $H_2SO_4$) was in contact with a dimensionally stable electrode (DSA-$O_2$) both supplied with the cell. The assembly was made watertight with rubber gaskets (1.23 mm thick) placed next to each of the electrodes, spacers, and membrane. Each cell compartment was connected to its own external tank (300 mL) to allow a continuous circulation during each treatment. Both electrolytes were circulated by two centrifugal pumps (Iwaki Magnet Pump, 10 $L.min^{-1}$ max, Iwaki Co, Ltd., Tokyo, Japan), and their flows were maintained at 300 $mL.min^{-1}$ by two flow meters (Aalborg Instruments and Controls, Inc., 500 $mL.min^{-1}$ max, Orangeburg, USA). The DC current between the two electrodes was supplied from an electrical power supply (Model HPD 30-10, Xantrex, Burnaby, Canada).

## 2.2 Protocols

### *2.2.1 Treatments*

Five anode/cathode voltage differences applied between the electrodes were tested: 1.5, 2, 2.5, 3, and 3.5 V. Each treatment was done in triplicate on 250 mL of skim milk and using an equal volume of 0.1 M sulphuric acid. During each treatment of 45 min, the oxidation–reduction potential (ORP), the dissolved oxygen (DO), the conductivity and the pH of milk were recorded as well as the current intensity at intervals of 30 s during the first 5 min of each treatment and at intervals of 1 min thereafter.

### *2.2.2 Storage*

After each treatment, a sample of electroreduced milk was rapidly poured in three 75-mL polypropylene jars, in parallel with a control non-electroreduced milk, and stored in a cold room maintained at 4 °C. The head-space in each jar was minimized by overfilling the containers. The first jar was opened each day during 8 days to compare with the results of Bolduc et al. (2006), while the second and the third jars were opened only at the fourth and ninth day of storage respectively. Redox potential, dissolved oxygen, and pH were recorded on each sample during storage.

## 2.3 Analysis methods

### *2.3.1 Redox potential measurement*

The ORP was measured using a VWR Symphony platinum electrode (Pt/Ag/AgCl, VWR Scientific, Mississauga, ON, Canada) filled with a solution of KCl 3 M. This electrode was connected to a VWR Symphony portable SP20 pH/ISE meter. The electrode was placed in the external reservoir containing the milk. The electrode reading was verified with a homemade solution of potassium ferrocyanide and potassium ferricyanide having a redox potential of +234 mV.

*2.3.2 Dissolved oxygen*

The DO was measured using a VWR Symphony electrode (VWR Scientific) mounted with the specified membrane and filled with the supplied DO electrolyte solution. The electrode was connected to a VWR Symphony SP50D portable DO meter. The electrode was calibrated every 1 h as described in the supplier's manual.

*2.3.3 Conductivity*

The conductivity was measured with an immersible YSI probe (Model 3417, K= 1 $cm^{-1}$, Yellow Spring Instrument, OH, USA) connected to a YSI 3232 adaptor to allow readings on the YSI 3100 conductivity meter of the same fabricant. Since the conductivity varies proportionally with temperature and that the values were not automatically compensated by the conductivity meter, all readings were corrected to 25 °C using the method described by Bazinet et al. (2004).

*2.3.4 pH*

The pH was measured using a VWR Symphony pH electrode (VWR Scientific) equipped with an automatic temperature control and connected to a VWR Symphony SR60IC benchtop pH meter.

*2.3.5 Current density*

The current passing through the electrodes was read from a Mastercraft numerical multimeter (Mastercraft, Toronto, Canada) and divided by the electrode surface area (10 $cm^2$) to obtain the current density.

*2.3.6 Energy consumption*

The energy consumption was calculated according to the following equation (Bazinet et al. 1999):

$$E = UIt,$$

where $U$ is the voltage (volt), $I$ the current (ampere), $t$ the time of treatment (second), and $E$ the energy consumption (joule).

2.4 Statistical analyses

The data from the redox potential, dissolved oxygen, pH, conductivity of milk as a function of time were subjected to repeated measure analysis of variance using JMP IN software (Version 5.1, SAS Institute inc., Cary, NC). The data from the evolution of redox potential, dissolved oxygen, pH, and conductivity during storage with and without opening were also submitted to repeated measure analysis of variance. Polynomial regression curves were calculated for all the

data as a function of time using Sigmaplot (Version 3.0 for Windows, Jandel Scientific, Corte Madera, CA).

## 3 Results

### 3.1 Electroreduction treatments of skim milk

#### *3.1.1 Redox potential*

The repeated measure analysis of variance of the data showed that the anode/cathode voltage difference ($P<0.0001$), the time ($P<0.0037$), and the dual interaction time/voltage difference ($P<0.0001$) had a significant effect on the ORP value during electroreduction. The nonlinear regression hyperbola curves produced coefficients of determination ranging from 0.970 to 0.998.

All treatments performed on milk samples resulted in a significant exponential decrease of the ORP value as can be seen on Fig. 2. In this experiment, the mean initial ORP value for the pasteurized skim milk used was +130 mV. Generally speaking, raw milk has an ORP between +200 and +300 mV under aerobic conditions (Morris 2000), while recently Bolduc et al. (2006) observed an averaged value of +182 mV for the same brand of pasteurized skim milk. During electroreduction, the general trend was that the redox potential decreased drastically in the first minutes of the treatment, to then stabilize at a constant value corresponding to a plateau (Fig. 2). However, according to the anode/voltage difference the value of the final plateau was different; after 45 min of treatment, by applying an anode/cathode voltage difference of 1.5 V, it was possible to decrease the ORP value at 13 mV. Similarly, voltage differences of 2, 2.5, 3.0, and 3.5 V, decreased the ORP value to −137, −222, −331, and −350 mV, respectively. This decrease in the plateau value was in a quite linear fashion between 1.5 and 3 V to stabilize thereafter: the plateau value decreased of approximately 120 mV between 1.5 and 2 V, 87 mV between 2 and 2.5 V, and 110 mV between 2.5 and 3 V. Between 3 and 3.5 V, the final value of redox potential were similar at −331 and −350 mV, respectively.

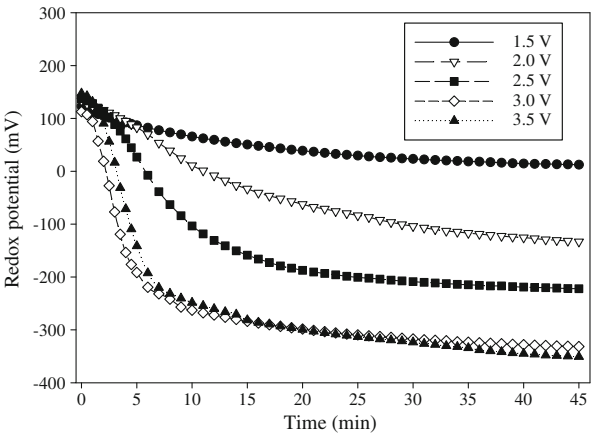


**Fig. 2** Evolution of redox potential during electroreduction treatments of milk at different low voltages

### 3.1.2 Dissolved oxygen

Based on the results of the repeated measure analysis of variance, the anode/cathode voltage difference ($P<0.0023$) and the dual interaction time/voltage difference ($P<0.0001$) had a significant effect on the evolution of the dissolved oxygen during the electroreduction treatment. The nonlinear regression hyperbola curves produced coefficients of determination ranging from 0.990 to 0.999.

The DO decreased during the treatment as shown in Fig. 3. This decrease in dissolved oxygen was proportional to the increase in voltage difference applied between the working electrodes. The DO concentration was brought down from an average initial value of 9.5 $mg.L^{-1}$ to 6, 6.8, 6, 4.2, and 3.2 $mg.L^{-1}$ during the course of the electroreduction treatments at 1.5, 2, 2.5, 3, and 3.5 V, respectively. The final level of DO observed for anode/cathode voltage differences of 1.5, 2, and 2.5 V were quite similar, while the levels for 3 and 3.5 V where different from one another and from the levels observed at lower voltage differences.

### 3.1.3 pH

The repeated measure analysis of variance of the data showed that the anode/cathode voltage difference has no effect on the pH ($P>0.1084$) while the time ($P<0.0001$) and the dual interaction time/voltage difference ($P<0.00221$) had a significant effect on the pH evolution during electroreduction treatment. The quadratic linear regression curve calculated for all the anode/cathode voltage difference averaged has a coefficient of determination of 0.860.

Whatever the voltage difference applied, the pH of milk decreased during electroreduction in a similar way (Fig. 4). The mean initial pH value of the pasteurized milk used in this study was 6.77, ranging between 6.74 and 6.81, which is in agreement with pH 6.6–6.8 reported in the literature (Amiot et al. 2002). The evolution, whatever the anode/cathode voltage difference was the same as confirmed by the linear regression calculated for all data. However, the final pH presented an average value of 6.56, corresponding to a pH decrease of 0.2 unit.

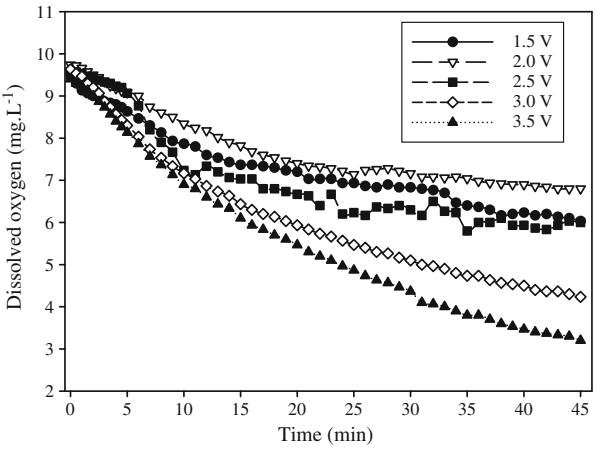


**Fig. 3** Evolution of DO during electroreduction treatments of milk at different low voltages

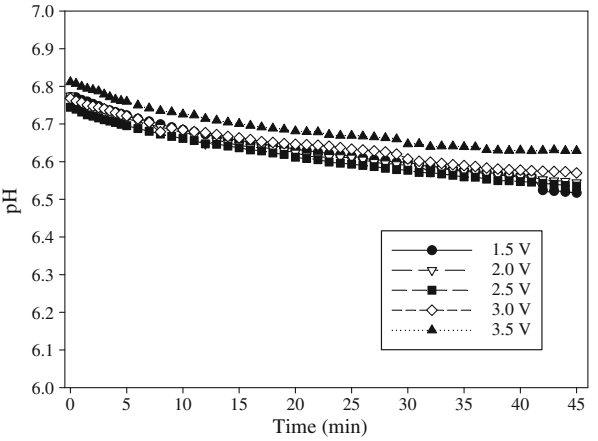


**Fig. 4** Evolution of pH during electroreduction treatments of milk at different low voltages

### *3.1.4 Conductivity*

According to the repeated measure analysis of variance, there was no significant differences between the evolution of conductivity measurements in all treatments (no effect of voltage difference, $P>0.2058$; no effect of time, $P>0.4741$; and no effect of time/voltage difference interaction, $P>0.1456$). Figure 5 shows the evolution of conductivity measurements during each electroreduction. The mean initial value of conductivity of the pasteurized milk used in this study was 4,493 $\mu S.cm^{-1}$ and was quite constant at an average value of 4,484±53 $\mu S.cm^{-1}$ all along the treatment.

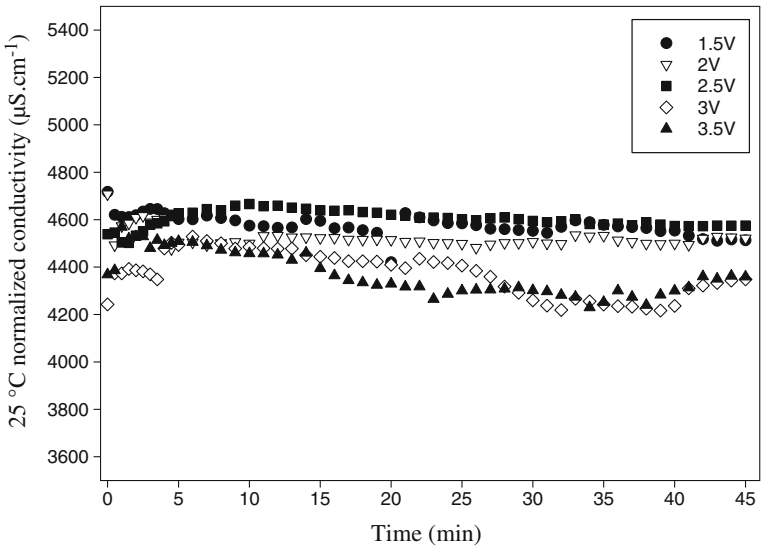


**Fig. 5** Evolution of normalized conductivity during electroreduction treatments of milk at different low voltages

### *3.1.5 Current density*

The repeated measure analysis of variance of the current density data, without values at time 0, showed that only the anode/cathode voltage difference ($P<0.0001$) has a significant effect on the current density evolution during electroreduction. The linear regression curves produced coefficients of determination ranging from 0.650 to 0.997.

The current density was quite constant all along the electroreduction treatment, and the plateau value increase with an increase in anode/cathode voltage difference (data not shown). The flow of electrons transferred to the milk increased as a function of the anode/cathode voltage differences applied between the working electrodes. For an increase in anode/cathode voltage difference from 1.5 to 3.5 V, the current density increase of approximately 6.5 $mA.cm^{-2}$. The current density values for low voltages (1.5, 2, and 2.5 V) were very low but different one from another (data not shown). The increase in current density was in a linear fashion between 1.5 and 2.5 V (0.38 $mA.cm^{-2}.V$) and in an exponential way thereafter between 2.5 and 3.5 V since the reduction potential of electrochemically active species was reached; the current density increased of 4.4 $mA.cm^{-2}$ from 2.5 to 3.0 V and of 7.6 $mA.cm^{-2}$ from 3.0 to 3.5 V.

### *3.1.6 Energy consumption*

It appeared from these results that electroreduction at anode/cathode voltage difference of 3 V was sufficient to ensure a significant decrease in ORP and DO. Furthermore, based on a 35 min-treatment calculation, and with the data obtained for the averaged current at 3 V (27 mA in the present work, with an average initial conductivity of 4,484 $\mu S.cm^{-1}$) and at 4 V (100 mA, according to Bolduc et al (2006) with an average initial conductivity of 4,438 $\mu S.cm^{-1}$ and the same electrolysis cell), the respective energy consumption calculated were 170 and 840 J. For 3.5 V, the energy consumption calculated was 478 J.

## 3.2 Storage of electroreduced milk

After treating the milk by electroreduction, the objectives were to verify if the ORP value, the dissolved oxygen values and the pH remained stable during the storage of milk at refrigerated temperature and to compare their evolution with a non-electroreduced milk. Furthermore, these three parameters where measured in two conditions, with a daily measurement of the same jar (with opening) during 8 days and with one jar for one measurement (without opening) at days 1, 4, and 9, in order to limit the incorporation of oxygen and to study its impact.

### *3.2.1 Redox potential*

According to the repeated measure analysis of variance, with and without opening there was a significant effect of anode/cathode voltage difference ($P<0.0001$ for both conditions) and of the double interaction time/voltage ($P<0.0001$ for both conditions) on the ORP evolution during storage of modulated milk. The evolution in time of the redox potential was significantly different ($P<0.0421$) only without opening.

With and without a daily opening, the non-electroreduced control milk presented the same evolution of ORP during its storage, with a quite linear increase of redox potential from 124 to 225 mV (Fig. 6a, b). Milk electroreduced at 1.5, 2.0, and 2.5 V showed also similar evolution of their ORP with and without opening during all the storage with increase of their respective ORP of approximately 135, 367, and 358 mV, but with some difference in their evolution. Samples that were treated at 1.5 V had always a positive ORP value, with a starting value lower than the one of control milk (42 vs 124 mV), but after only 1 day of storage, they reached the values of control milk. Milk treated at 2.0 and 2.5 V, with initial ORP values of −131 and −203 mV reached a positive ORP after 2 days of storage, and thereafter presented similar values as control milk. Milk treated at an anode/cathode voltage differences of 3.0 and 3.5 V showed similar evolution but this ORP evolution was different with and without daily opening of the jar. With opening, these samples started with similar negative values of −317 and −315 mV, respectively, at 3.0 and 3.5 V, and after 3 days of storage presented positive values of 48 and 8 mV, respectively, and thereafter reached a plateau at approximately 63 and 116 mV. Without opening, they presented negative values for a

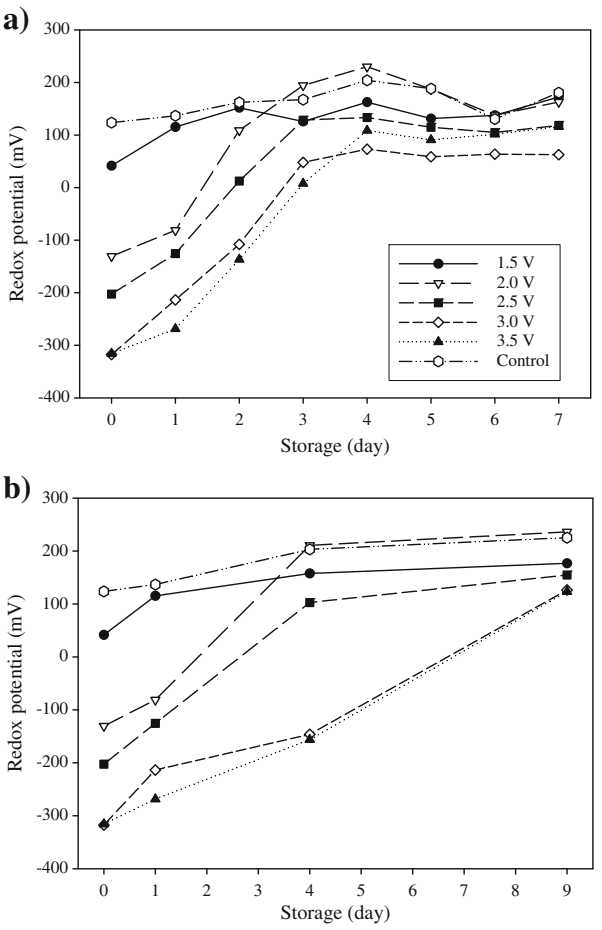


**Fig. 6** Changes in oxidoreduction potential of pasteurized milk treated at different low voltages during its refrigerated storage **a**) with daily opening and **b**) without opening

longer period since after 4 days of storage they presented negative values of −146 and −156 mV, respectively, for 3.0 and 3.5 V treatments. However, at the end of the 9-day storage their values were positive at 126 and 124 mV.

### *3.2.2 Dissolved oxygen*

The repeated measure analysis of variance showed, with and without opening, a significant effect of anode/cathode voltage difference ($P<0.0001$ for both conditions), of time ($P<0.0001$ for both conditions) and of the double interaction time/voltage ($P<0.0061$ and $P<0.0261$ respectively with and without opening) on the dissolved oxygen evolution during storage.

Control milk presented a different evolution of its DO values during its storage with and without opening (Fig. 7a, b). During storage with daily measurement in the same jar, the level of DO was maintained constant during the first 4 days of storage and then decreased drastically at a value close to 0 after day 6. During storage without contact with ambient air, the DO concentration decreased in a linear fashion during the 9-day storage from 8.5 to 3.3 $mg.L^{-1}$. Electroreduced milks presented similar evolution as control milk but reached a DO values close to 0 faster than control milk (Fig. 7a, b). Furthermore, the higher was the anode/cathode voltage difference applied, the faster was the decrease in DO. Hence, during storage with opening, the DO concentration of samples treated by electroreduction was quite constant during 4 days at 1.5 V, 3 days at 2.0, 2.5, and 3.0 V, and only 2 days at 3.5 V. Thereafter the samples reached a concentration close to 0. During storage without opening, the DO concentration for samples treated at 2.5, 3.0, and 3.5 V reached values close to 0, after 4 days, while at 1.5 and 2.0 V, the DO concentrations were 2.2 and 0.5 $mg.L^{-1}$ for the same laps of time. However, the DO concentrations for samples electroreduced at 1.5 and 2.0 V were lower than those observed with opening of the jar: 5.0 vs 2.2 $mg.L^{-1}$ and 2.0 vs 0.5 $mg.L^{-1}$, respectively.

### *3.2.3 pH*

The repeated measure analysis of variance showed, with and without opening, a significant effect of time ($P<0.0001$ for both conditions) on the pH evolution of electroreduced milk during storage. The anode/cathode voltage difference applied during electroreduction of milk has no significant effect ($P>0.0934$ and $P>0.4652$ with and without opening respectively) on milk pH evolution during storage. However, the control milk present a different pH evolution with ($P<0.0075$) and without ($P<0.0454$) opening in comparison with electroreduced milk.

Figure 8 shows the evolution of the pH of modulated milk during storage at refrigerated temperature. Whatever the anode cathode voltage difference applied during electroreduction of milk, the pH value was the same. However, pH value of the electroreduced milk changed in time. When the milk was opened daily, pH increased from an averaged starting value of 6.58 to a maximum value of 6.73 after 2 days of storage, and then began to decrease slightly and linearly to 6.63 after 7 days of storage. In the same condition of storage, control milk presented a higher initial value of 6.82, which was constant during the first 4 days of storage and then decreased similarly to pH 6.73 ; Both control and electroreduced milks presented a

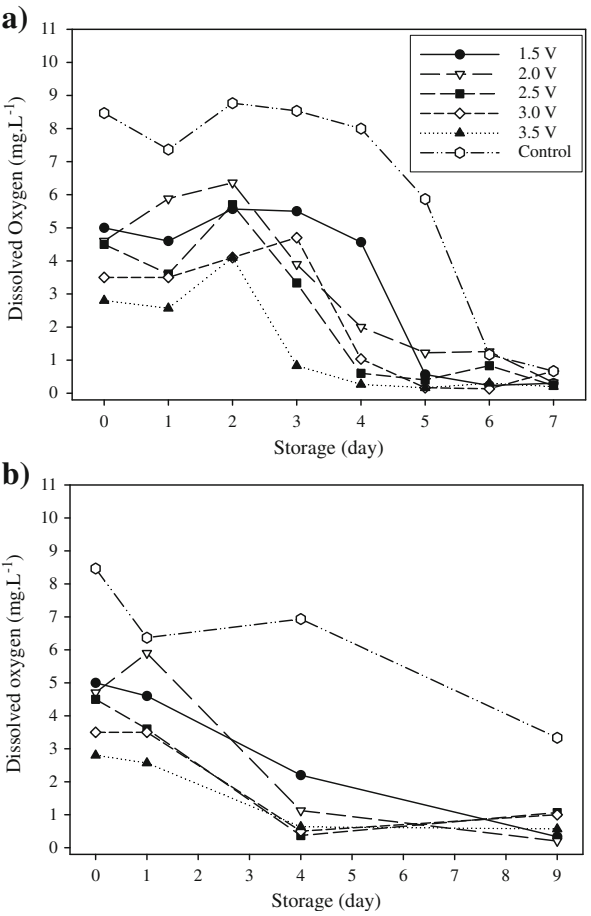


**Fig. 7** Changes in DO of milk treated at different voltages during its refrigerated storage **a**) with daily opening and **b**) without opening

similar 0.1 pH unit decrease between days 4 and 7. Without opening, after 1 day of storage the pH value was increased from 6.58 to 6.72 and then remained constant until the end of the storage. Control milk presented a quite stable pH value during the 9-day storage without opening with an averaged pH value of 6.81.

## 4 Discussion

### 4.1 Electroreduction treatments of skim milk

It appeared from these results that a 3.0-V treatment is sufficient to reduce the redox potential of milk to negative values, and that treatments with anode/cathode voltage difference under 3.0 V do not provide enough energy to reduce all reducible species present in the milk. The different values of plateau for the redox potential would be explained by the different working electrode potential; the greater the electrode potential, the faster the electron transfer rate (Tallec 1985). From 3.0 V and over, the maximum reduction seems to be reached, and no more species would be reduced.

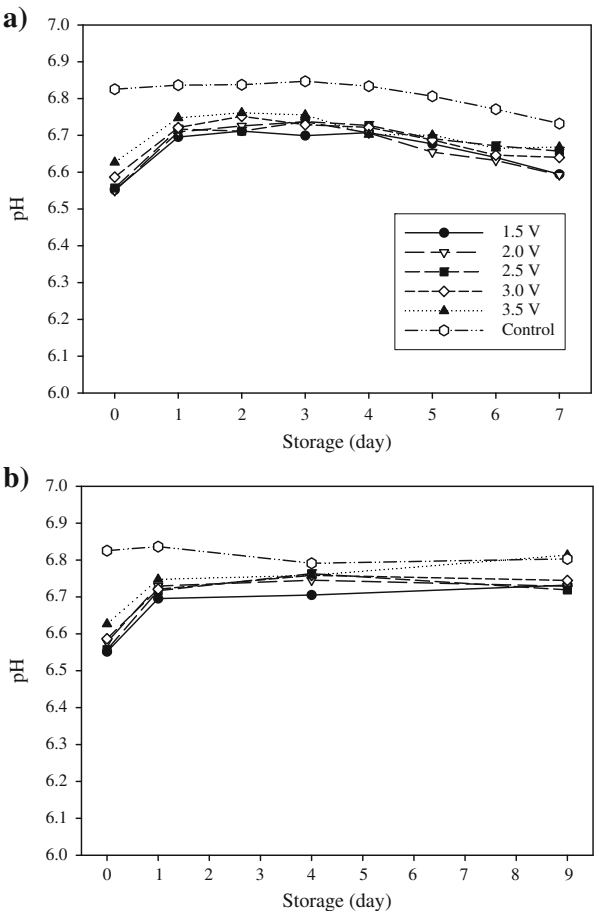


**Fig. 8** Changes in pH of milk treated at different voltages during its refrigerated storage **a**) with daily opening and **b**) without opening

The decrease in the concentration of oxygen observed is directly related to the reduction reactions taking place at the cathode; $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (Tallec 1985). Electrons are transferred from the electric circuit to the cathode and then to milk in which they are accepted by active species, one of them being oxygen. The protons necessary to this reaction would be provided by sulphuric acid from the anodic compartment. The protons of the dissociated acid would migrate through the cationic membrane to the milk cathodic compartment. These migrated protons would be consumed by dissolved oxygen to form water or they would simply be reduced in dihydrogen according to the following equation, $2H_2O+2e^- \rightarrow H_2+2OH^-$ (Tallec 1985). As demonstrated by Schreyer (2007) during electroreduction, in a static electrolysis cell, of different milk fractions, oxygen is an electrochemically active compounds, and its reduction contributes to the decrease in the redox potential value. In addition it appeared , that during electroreduction, the milk was slightly acidified. This decrease would be due to the transfer of protons from the anodic compartment to the cathodic compartment (Bazinet et al. 2009). Furthermore, in the range of anode/cathode voltage difference used in this study, the migration of $H^+$ ions would compensate for the decrease in pH generated by the formation of

hydroxide ion by water hydrolysis reaction at the cathode (Tallec 1985). The electroreduction treatment changed only the redox state of the milk species which explains the stability of conductivity data during the treatments (Bolduc et al. 2006). The application of a 3 V treatment instead of the 4 V value suggested by a previous study (Bolduc et al. 2006) would allow an energy saving of 79% and the energy saving for a 0.5 V decrease in the anode/cathode voltage difference applied would be of 43%. In addition, the energy consumption requested for the process of milk electroreduction is very low in comparison with the energy consumption of the pumps used for the recirculation of milk.

### 4.2 Storage of electroreduced milk

These experiments confirm the fact that the ORP modulation by electroreduction treatment has a major impact on the starting ORP value during storage, and that reincrease in ORP would be dependent on the oxygen exposition. This exposition certainly had an impact on the stability of the ORP values measured during storage since oxygen could diffuse in the milk medium easily (Moyssiadi et al. 2004). In the present study, the rise of the concentration of oxygen during the first 2 days was not observed or was not as clear as the one reported (Bolduc et al. 2006). Furthermore, the fact that the DO concentration decreased all along storage without opening while it was constant during 4–5 days confirmed the hypothesis of Bolduc et al. (2006) concerning the fact that the initial rise in the concentration of oxygen can be mainly attributed to the contact of milk samples with ambient air during measurements. However, concerning the hypothesis of Bolduc et al. (2006) on DO concentration decrease observed after or not the DO concentration plateau which would involve growth of aerobic microorganisms from the pasteurized milk, *Pseudomonas* spp., would be in contradiction with the present results. It appeared that the contamination of the control milk was very low, and no change in DO concentration was observed during 4 days of storage at 4 °C; the critical biomass of aerobic microorganisms would be reached only after 4 days of storage. Consequently, the decrease in DO concentration observed during the first 4 days for electroreduced milk would not be due to the initial microflora of milk. Two hypotheses could be postulated: (1) either the contamination was due to the growth of aerobic microorganisms from the interior surface of the electroreduction system and electrodes surfaces or (2) other milk components were involved in this DO concentration drop in the first 4 days of storage. This other specie could not be lipids, which by the way of auto-oxidation could have consumed oxygen, since in skim milk, residual lipids were at low concentration of about 0.1%. In fact, although the main residual fat molecules in skim milk are phospholipids, which are very sensitive to oxidation by oxygen (Amiot et al. 2002), their low concentration could not explain the decrease in DO up to 5 ppm. The DO concentration decrease could be due to whey proteins. In fact, Fukuzawa et al. (2005) demonstrated the antioxidant effect of bovine serum albumin which is due amongst others to the trapping of active oxygen molecules. Consequently, proteins probably also interfere on the modulation and stability of DO concentration as well as on the ORP during storage. Furthermore, the values of redox potential reached by treatment of 3 V and over are effective to maintain negative or reductive conditions in milk during its storage and up to 7 days. It appeared also that oxygen is an important

parameter to consider during storage of electroreduced milk. In fact, during electroreduction up to 70% of the dissolved oxygen was consumed. However, according to the conditions of storage and the presence or not of oxygen, its concentration can decrease constantly or stay stable during part of the storage before decreasing. Hence, with opening daily during storage, samples started with negative values and presented positive values after only 3 days of storage, while without opening, they presented negative values for a longer period. After 4 days of storage samples without opening presented negative values close to −150 mV, respectively, for 3.0 and 3.5 V treatments. Milk samples opening daily for taking measurements simulate the habit of the majority of consumers. This practice allowed oxygen to be incorporated to the milk and this could be responsible for the re-oxidation of the milk electroreduced species. This demonstrated the importance of controlling the oxygen concentration during storage to keep the solution in reductive or protective conditions. The rise in ORP during storage confirms that the changes in redox state of some milk species (mainly proteins) caused by the electroreduction treatments would be reversible and that the storage container material would be an important factor to consider when storing electroreduced milk to diminish or limit reincorporation of oxygen due to a potential diffusion through the wall of the container (Rysstad et al. 1998).

## 5 Conclusions

Due to the sensitivity of milk to oxidoreduction reactions, electroreduction process could be a technological and chemical free alternative to improve its stability against oxydation. It appeared from these results that electroreduction at 3 V was sufficient to ensure a significant decrease in ORP and DO and to allow an energy saving of 79% in comparison with a treatment at 4 V. Furthermore, at our knowledge this study is the first one to demonstrate the energy consumption efficiency of milk electroreduction. This technology could be used to increase considerably the quality of enriched milks during storage. Consequently, further works are currently under way to characterize and monitor the evolution of lipids in electroreduced milk, and to study the effect of the container wall material on the diffusion of oxygen and evolution of redox potential in electroreduced milk during storage.

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