

Effect of Electric Pulse Parameters on Releasing Metallic Particles from Stainless Steel Electrodes during Pulsed Electric Field Processing of Milk

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Abstract -- The acceptability of pulsed electric field (PEF) processing as an alternative method for liquid food preservation requires the elimination, or at least the reduction, of all the effects accompanying the flow of electric current. Metallic particles might be released from the electrode material as a result of electrically-driven electrochemical reactions. The presence of such metallic particles can affect the quality and the safety of PEF processed food. This study investigates the effect of varying the parameters of applied electric pulses on the amount of released metals aiming to reach the optimum conditions. It is expected that reducing the rate of releasing metals from the electrodes will extend their life time and reduce the running cost of PEF processing.

Index Terms— Metal Release, Milk Processing, Pulse Width, Pulsed Electric Fields

I. INTRODUCTION

The use of pulsed electric fields (PEFs) provides an alternative way to preserve liquid food instead of conventional thermal pasteurization. Upon the application of high-field pulses, electric charges accumulate across the membrane of any microbial cell present in the processing zone between the two electrodes. Within a few hundreds of nano-seconds, this charge accumulation results in an irreversible membrane breakdown which causes the cell to lose its viability. By this means, an extended shelf life could be obtained after PEF processing of beverages such as milk, juices, and beer [1]–[6]. The advantages of using pulsed electric fields over conventional thermal pasteurization include fresh-like taste, high nutrition value, retention of heat-sensitive enzymes, lower processing energy, and less contamination in processing equipment [2]–[6].

Sensory analyses are performed to evaluate the acceptance of PEF processed products against either thermally-pasteurized or fresh ones. In a study of combined heat/PEF processing of yogurt-based products, sensory evaluation by untrained students and technical panelists as well as physical measurements of color, °Brix, and pH indicated that there was no significant difference between the processed and control products [1]. The physical–chemical characteristics of blended orange and carrot juice after PEF processing have been investigated in comparison to thermal high-temperature

short-time (HTST) pasteurization [2]. Sensory analysis of odor and taste favored PEF processed products, and no significant difference was detected when comparing the effect of both techniques on pH, °Brix, and color. In a combination of moderate heat and PEF for the preservation of fruit smoothies, the accompanied sensory analysis showed no significant difference in the overall acceptance among untreated, moderately heated and PEF processed, and mildly pasteurized fruit smoothies [3]. The existence of sensitive fruits such as pineapple and banana was suggested by the authors as one possible reason for the overall sensory quality of the three products to be the same.

A hurdle treatment for orange juice by combining thermosonication (TS) and PEF has been compared to HTST pasteurization through shelf life and sensory evaluation [4]. All sensory attributes were rated equivalent for both techniques apart from the detection of a blander flavor in thermally pasteurized juice and a metallic flavor in TS/PFE-processed juice by few panelists. It was suggested that the combination of TS and PEF hurdles could explain the improved impact on the juice color observed experimentally. For investigating the effectiveness of PEF processing on beer, a comprehensive study was performed, including microbial, sensory, and quality analyses [5]. By comparing the concentration of 10 metallic elements in the beer samples before and after the PEF processing, a significant increase has been observed in the concentration of iron, chromium, manganese, and zinc ions. This increase caused an unfavorable degradation in the aspects of flavor/aroma and mouth feeling assessed through the sensory analysis. In addition, some of the panelists indicated a metallic mouth feeling in some samples. This comprehensive study shows that a potential challenge against PEF processed products may arise from the metallic electrodes.

In order to eliminate the electrode reactions occurring upon the application of PEF, an ion permeable polymer membrane can function as a physical barrier between each electrode and the liquid food [6]. On the other hand, only mono-polar pulses are permitted due to the selective nature of the membranes, membrane material is expensive and very sensitive to puncture by any electrical discharges, frequently maintenance is required, and the whole arrangement is complicated for industrial implementation. Due to these complexities, the reduction of electrode reactions, rather than a complete prevention, might be preferred as long as the

metal concentration remains within the limits dictated by food regulations. The rate of electrophoresis as well as electrochemical reactions has been suggested to be proportional to the net electric charge delivered to the PEF cell, and therefore a claim has been made that a “zero net charge delivery” substantially prevents fouling of electrode(s) and reduces electrochemical reactions in general [7], [8]. Authors explained that as long as no cumulative build-up of charge occurs, no electrochemical reactions will take place for any pulse of width shorter than a certain threshold. The charge build-up can be avoided by the same concept of zero net charge delivery. This claim is theoretically reasonable; however, no quantitative experimental results have been presented for justification.

Experimental results verified that electrochemical reactions are proportional to the width of applied pulses after a critical width [9]. It should be noted that in [9], experiments applied sinusoidal waveforms of only 15V and 150V peak-to-peak voltages resulting in a maximum electric field of 0.15 kV/cm and a maximum current of 480 mA which are far below typical PEF conditions. By comparing the metallic particles released with three different mono-polar pulse shapes, it was observed that pulse shapes featuring a combination of positive and negative currents are preferred to those featuring only positive currents [10]. Authors explained this observation by considering that the negative part of the current may reverse some of the electrochemical reactions. By reviewing the European legislations for fruit juices and drinking water, the measured values of dissolved metals after PEF processing of orange juice are found to be far below the legislation limits; on the contrary, the life time of the electrodes is estimated to treat only 276,000 liters of orange juice before being discarded [11].

This paper focuses on the electrode reactions associated with PEF processing and how to minimize these reactions by optimizing the electric pulse parameters.

II. PROBLEM FORMULATION

The acceptability of PEF processing as an alternative method for liquid food preservation requires a deep understanding of all undesirable electrochemical reactions accompanying the flow of high current through the liquid, especially those involving the electrode material. These

electrode reactions lead to an electrode material migration into the liquid food under processing which may affect PEF commercialization through safety, quality, and cost aspects. First, the type and amount of electrode material which may exist in PEF processed food must be within health safety regulations before introducing it as a processed food to the market. Second, the “taste” quality of PEF processed food should be capable of competing with other conventional preservation methods. The presence of any metallic mouth feeling may stand against consumers’ acceptance to this technology. Third, the price and life time of electrodes should be included in the economical assessment studies of PEF systems. Electrodes featuring lower price and/or longer life time will enhance the feasibility of PEF technology, and consequently, attract more investment.

A pulse generator and an electrode pair are the two main components comprising any PEF system operating either in batch-mode or continuous-mode. The function of such electrode pair is to introduce the generated pulses into the liquid food under processing. Electrochemistry defines this system as an electrolytic cell where an external source of electrical energy is responsible for driving an electrical current through the cell. This electrical current has an electronic nature (electrons) in the conductive solid electrodes and an ionic nature (ions) in the conductive liquid electrolyte. And as a result, electrochemical reactions will take place at the electrode/electrolyte interfaces to satisfy the condition of electric current continuity.

The occurrence of electrode reactions might be avoided by maintaining the potential of the double layer capacitors, which represent each electrode/electrolyte interface, below the reaction potential of electrode material through controlling the shape (amplitude/width) of the applied pulses. Table I lists some PEF conditions required for achieving microbial inactivation. It can be seen that the range of electric pulse parameters is 25–40 kV/cm and 1–4 μ s. These ranges account for various microorganisms which differ in their sensitivity to PEF processing as well as various treatment media. Unfortunately, these typical conditions for pulse amplitude and width will cause some unavoidable electrode reactions.

TABLE I
SAMPLES OF TIMES ROMAN TYPE SIZES AND STYLES

Food data			Process data		Electric pulse data						Pulse density	Energy density	Ref
Name	Cond mS/cm	pH	Flow mL/min	Temp °C	Shape	Polarity	Peak kV/cm	Width μ s	Rate Hz	Energy J	mL ⁻¹	J/mL	
Yogurt	5.6	4.2	1666.7	30	square	mono	30	1.4	500	(2.24)	(72)	(161)	1
Orange – carrot	4.5	3.8	60	-	square	bi	25	2.5	767	(0.086)	(9204)	(788)	2
Fruit smoothie	4.62	4.3	-	15	square	(bi)	34	1	<25	(9.48)	(68.6)	650	3
Orange	4.17	3.8	(15.75)	55	square	mono	40	1	15	(11.68)	(57.1)	(667)	4
Beer	1.58	-	60	4	square	bi	41	4	(300)	(0.164)	(3600)	(589)	5
Orange	3	3.8	6000	40	square	bi	30	1	(335)	(7.46)	6.7	50	11

Values between brackets are not reported by authors

In this paper, a solution to such problem is introduced by optimizing the parameters of applied high-field electric pulses, namely the peak voltage, pulse width, and number of pulses. The first two parameters will affect the charging process of the double layer capacitors representing the electrode/liquid interface; hence, the rate of releasing metallic particles can be minimized. Since the pulse energy could vary in a wide range, the energy density is the factor to be considered for any comparison. The number of pulses is to be adjusted so that the same amount of energy is supplied to the liquid under various combinations of peak voltages and pulse widths.

III. MATERIALS AND METHODS

A. Experimental Setup

The PEF setup, shown in Fig. 1, is capable of processing various liquid foods by adjusting its operating parameters as per requirements. The setup is operated in a continuous mode where the liquid food is subjected to the high-field pulses while flowing through the treatment chamber. Due to the repetition rate limitation on applied pulses, this system is usually operated with very low flow rate to achieve a certain energy level per unit volume of the liquid under processing. Equivalently, the liquid could be circulated several times in a closed loop cycle at a high flow rate to achieve the same energy level per unit volume. This high flow rate will significantly enhance the cooling of the treatment chamber by convection. This closed loop operation should be fine while studying the electrode material reactions as long as no biological test is to be carried out. However, in real operation for liquid food preservation, the open loop operation with low flow rate ensures that every part of the liquid is subjected to the sufficient processing.

1) Treated Liquid Food:

The use of real liquid foods in metal detection experiments gives accurate results compared to those obtained with adjustable aqueous solutions [10], [11]. Each experimental run requires a volume of 1000 mL liquid food.

Beatrice® pasteurized 2% partially skimmed milk (Parmalat Canada) was purchased from local grocery stores. The average electrical conductivity and pH are measured to be 5.23 mS/cm and 7.0, respectively.

2) Treatment Chamber:

The treatment chamber comprises a housing and an electrode assembly. The housing comprises an inlet for receiving liquid to be treated and an outlet for allowing the treated liquid to be retrieved. The electrode assembly comprises two electrodes having opposing convex electrode surface sections defining there between a biconcave processing zone [12]. Electrode assembly is made of stainless steel (type 316) alloy with a gap spacing of 1 mm. Scanning

Electron Microscope (ESM) is utilized to analyze the composition of the electrode material. The main elements and their percentage weights are iron (66%), chromium (17%), nickel (12%), molybdenum (3%), and manganese (2%).

After each experimental run, the chamber is opened and entirely washed by tap water and liquid soap; then, sandpaper is used to remove any adherent films formed on the surface of both electrodes; and finally, a piece of medical cotton soaked with ethanol removes any fine particles and keeps the electrode surface clean.

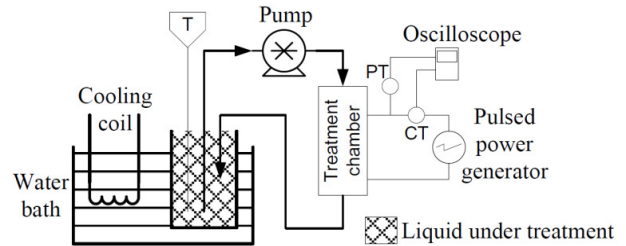


Fig. 1. Experimental setup for PEF processing

3) Pulsed Power Generator:

Electrical pulses are generated through a simple capacitor discharge circuit which produces a repetitive RC exponential decay voltage waveform across the treatment chamber load. Fig. 2 shows the schematic diagram of the pulsed power generator. Two identical parallel capacitors (0.3 μ F each) are initially charged through the treatment chamber load by a constant-current capacitor-charging supply. Once the thyatron switch receives a trigger pulse, the capacitors are rapidly discharged through the treatment chamber load generating the desired high voltage pulse. This circuit topology is meant to reduce the electrophoretic and electrochemical effects within the liquid food under processing [7], [8].

This circuit is capable of generating negative pulses with an adjustable peak voltage through controlling the capacitor charging voltage. However, the pulse shape and width are dependent on the ohmic resistance of the treatment chamber load, and hence on the electrical conductivity of the liquid food under processing. Connecting only one capacitor in the circuit allows the generation of voltage pulses with relatively shorter pulse width. The operating frequency is kept at 21 Hz.

4) Electrical measurements:

Voltage across as well as current through the treatment chamber load are continuously monitored by a Tektronix 3044B oscilloscope through a high voltage probe and a current transformer for pulse applications, respectively. The oscilloscope is

capable of storing the waveforms on all channels with a record length of 10,000 points which are utilized to compute the energy and charge per pulse through simple discrete integration.

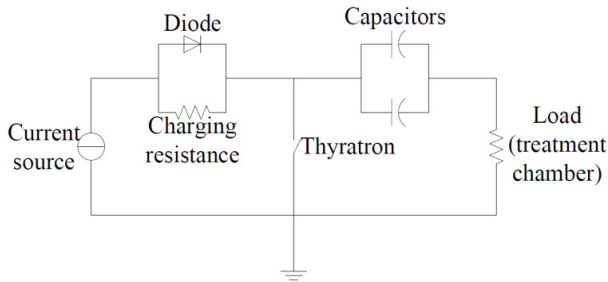


Fig. 2. Schematic diagram of the pulsed power generator

5) *Tubing and pump:*

A peristaltic pump is utilized with 9.5 mm tubing to circulate the liquid food through the treatment chamber at a flow rate of 500 mL/min.

6) *Cooling system:*

To avoid the heating effects of the high-field pulses, the temperature of the liquid food is continuously monitored by a digital-probe thermometer and controlled within a range of 20 to 25°C through a controllable cooling water bath. The liquid itself with its high flow rate will enhance the cooling process of the treatment chamber through convection.

B. Metal Concentration

To assess the metal concentration in the liquid food under processing, a 25 mL sample is pipetted out at certain time spans which correspond to the required number of pulses. Blank samples are pipetted out before turning on the pulse generator. Since the analytical equipment is capable of measuring the metal concentration accurately in simple inorganic solutions, liquid food samples are to be subjected to a preparation stage [5], [11] in order to digest all the organic components.

1) *Sample preparation:*

Collected samples are digested through a wet digestion [13], [14] procedure as follows:

- Accurately pipette 10 mL out of each sample into a 50 mL polypropylene digestion vessel
- Add 10 mL of concentrated nitric acid
- Cover the vessel with a reflux cap
- Use a hot block of 110°C for 4 hours
- Remove the vessel from the hot block
- After reaching the room temperature, add ultra pure water (18.2 MΩ.cm) to make up the volume of liquid inside the vessel to 20 mL

The above procedure leaves the samples completely digested and in an acidic medium which perfectly suits the operation of the analytical

equipment. It should be noted that a dilution factor of 2 exists implicitly in this procedure, and hence all quantitative measurements will be multiplied by 2. Samples are collected with 25 mL size with the intention of dividing each of them into two independent digestion vessels so as to reduce any experimental error introduced through the digestion procedure itself.

2) *Analytical equipment:*

The analytical equipment used for measuring trace metal concentration is an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with a radial configuration. Yttrium (Y) as an internal standard is used to eliminate any matrix effects, especially those introduced due to high calcium concentration [15].

In the beginning of each session, ICP is calibrated with certified standards and the best calibration curve is chosen. Prepared samples are fed automatically to the ICP with a radial exposure time of 10 sec repeated for 3 times. A quality control check is carried out every 5 samples to compensate for any drifting. This calibration and quality control procedure improves the reproducibility of results through different sessions. The ICP has a limit of detection of 4.3, 2.7, 8.2 ppb for chromium, iron, and nickel, respectively.

C. Statistical Analysis

Factorial experiments are designed with 5 full replications. Since each sample is divided into two parts during the preparation procedure as mentioned above, it is expected to get 10 replicates for each point. For the statistical analysis and plotting of data, SPSS Statistics v19 software is utilized. The significance of any parameter under study is determined through the Analysis of Variance (ANOVA) tool with a Fisher significance test at $P \leq 0.05$. Plotted data include error bars representing two-sided 90% confidence intervals.

IV. RESULTS AND DISCUSSION

Upon the application of high-field pulses, the voltage across and the current through the treatment chamber are recorded as in Fig. 3. Cases (a) and (b) have relatively shorter pulse width since only one capacitor has been utilized; whereas in cases (c) and (d), two capacitors are connected in parallel. The charging voltage has been set for a peak voltage of 30 kV/cm in (a) and (c) and of 40 kV/cm in (b) and (d). These four cases differ in their input energy per pulse; hence, the number of applied pulses in each case is to be adjusted so that the total energy per unit volume (energy density) is the same. At this point, it will be assumed that within these four cases, the energy density can reflect the resulting microbial inactivation of the PEF processing and should be fixed when comparing the metals released in different cases.

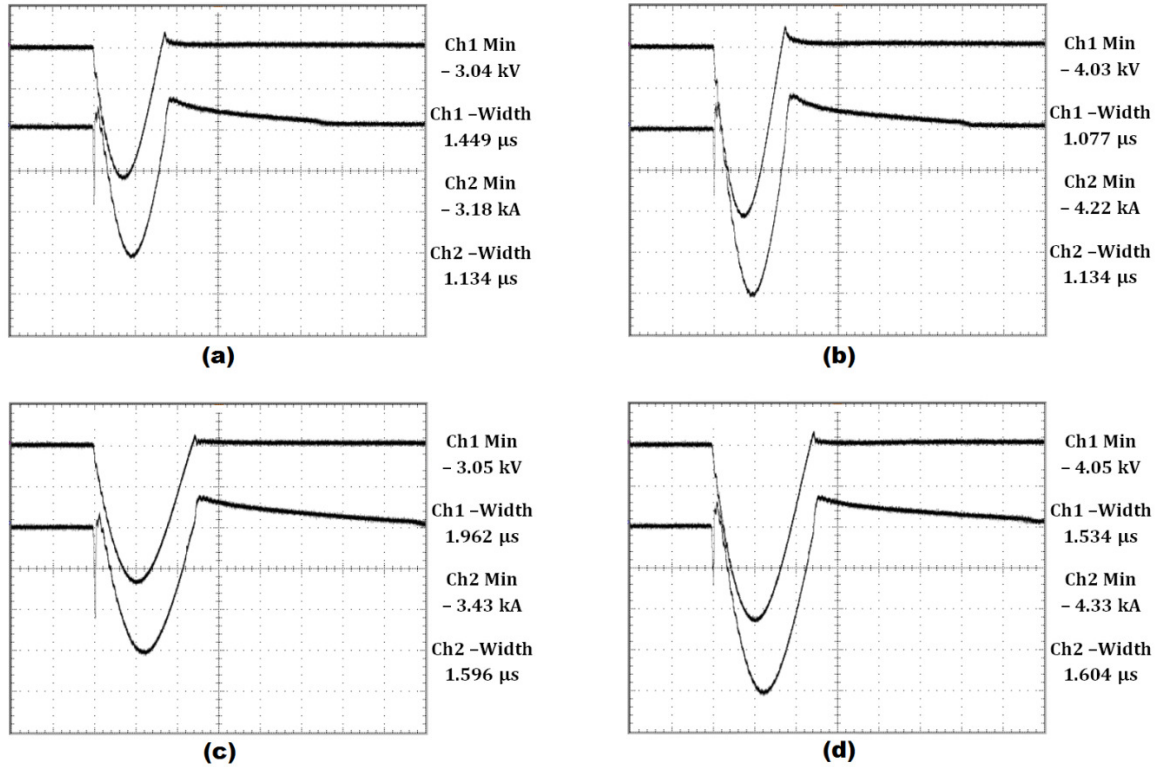


Fig. 3. Typical voltage (lower) and current (upper) waveforms when utilizing one (a,b) or two (c,d) capacitors. Horizontal scale: 1 $\mu\text{s}/\text{div}$; vertical scale: 1 kV/div and 1 kA/div for voltage and current waveforms, respectively

By plotting the concentration of iron in the processed milk as a function of the input energy density from the PEF system, Fig. 4 shows that milk has an initial iron content of slightly below 300 ppb. This iron content rises to the range of 400-450 ppb at about 300 J/mL input energy and reaches a maximum of 550 ppb at about 900 J/mL input energy. All cases show a non-linear relationship between the increase in the iron content and the input energy, or the number of pulses. Although energy in the range of 300-600 J/mL may be sufficient for microbial inactivation, a higher range is included in this study for the sake of comparison between cases. It can be seen from Fig. 4 that relatively shorter pulses (utilizing one capacitor) releases less iron from the electrodes when the voltage peak is kept the same. This observation agrees with the concept of charging the double layer capacitors discussed in [7]–[11]. When comparing the two voltage levels at a certain number of capacitors, one can observe that increasing the voltage level slightly increases the iron content. The ANOVA test shows significance only for the number of capacitors. To conclude, the optimum pulse should feature relatively short pulse width with a peak voltage satisfying the minimum field required for microbial inactivation.

Same conclusions can be reached from the nickel content but at a lower range of concentration as shown in Fig. 5. Although chromium is the second main element in the electrode material, Fig. 6 shows a slight increase in its content after the PEF processing which is found to be

statistically insignificant. Because of being relatively small, the differences in chromium content between the four cases are almost masked by the estimated experimental error. This observation with chromium can be attributed to its higher resistance to electrochemical reactions with respect to iron and nickel. For long operation of the electrodes, another problem may appear on their surface when the various composing elements are not reacting at the same rate. The ANOVA test for nickel and chromium also showed significance only for the number of capacitors.

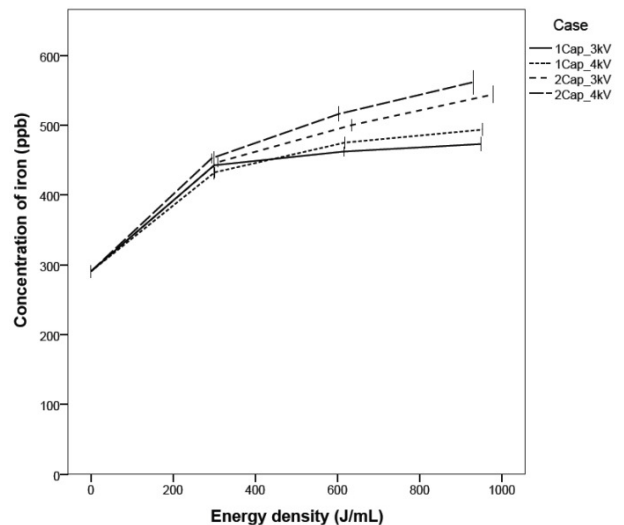


Fig. 4. Mean concentration of iron

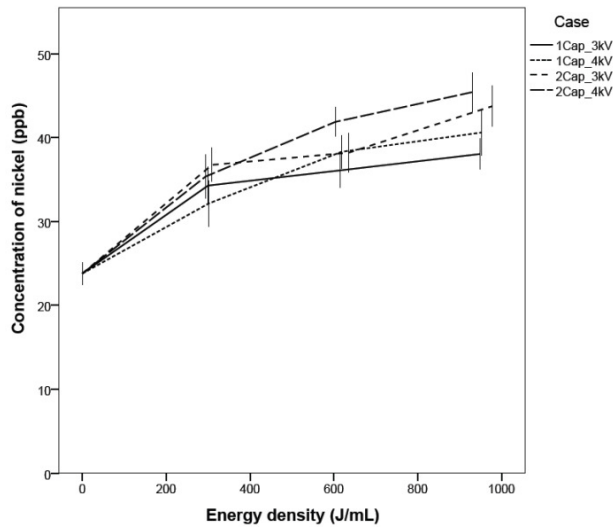


Fig. 5. Mean concentration of nickel

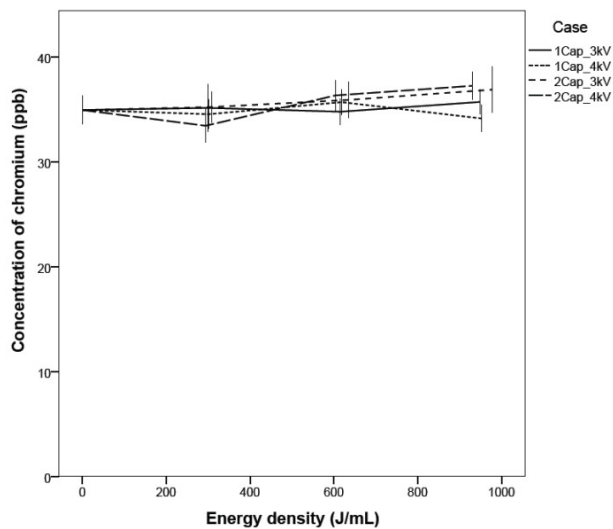


Fig. 6. Mean concentration of chromium

In a separate experiment, the effect of just the physical interaction between the milk and the electrode material is tested by circulating the milk through the PEF system without applying any electric pulses. In this experiment, the residence time of milk between the two electrodes exceeded 1.5 the maximum residence time for any experimental run in the main experiment. Only iron in Fig. 7 shows a significant increase in its content. For nickel and chromium, their content remains unchanged. Even the observed increase in iron content is much less than that observed in the main experiment when electric pulses are applied. This difference confirms that the release of metallic particles during PEF processing is due to electrochemical reactions at the electrodes and not due to just the physical contact between the milk and the electrodes.

Experimental results with orange juice in [11] give the contribution of solely the PEF electric pulses to 14.98, 0 and 0.69 ppb for iron, chromium, and nickel respectively. One

can interpret these low values by checking the utilized energy density in the corresponding row in Table I. An increase from 258 to 2859 ppb and from 0 to 526 has been reported in [5] for iron and chromium after PEF processing of beer. Nickel content was not measured in [5]. Even though the energy density was within the range used here, the reported values of the increase in the iron and chromium contents are much higher. The acidity of beer may account for this difference with respect to neutral milk; further investigation should consider the effect of food composition and pH.

By reviewing the regulations for food industries dictated by governments in North America, limitations were mainly concerned with the presence of heavy/toxic metals (cadmium, lead, and mercury). None of the metals which could be used as electrodes is mentioned in the American regulations [16] while only aluminum and copper are mentioned in the Canadian ones [17].

V. CONCLUSIONS

Releasing metallic particles from the electrode material is found to be unavoidable when typical conditions for PEF processing are applied. Electrochemical reactions are the main contributor in releasing metals. These reactions are dependent on the parameters of the generated electric pulses, namely peak voltage and pulse width. Experimental results showed that relatively shorter pulses are preferred to longer ones. Varying the peak voltage has a lower impact on the amount of released metals; hence, peak voltage is to be chosen as the minimum value required for generating the sufficient electric field for microbial inactivation. It should be noted that the optimization process of the electric pulse parameters considered the comparison of released metals at the same energy input per unit volume. Further investigation should consider the comparison of released metals at the same microbial inactivation levels.

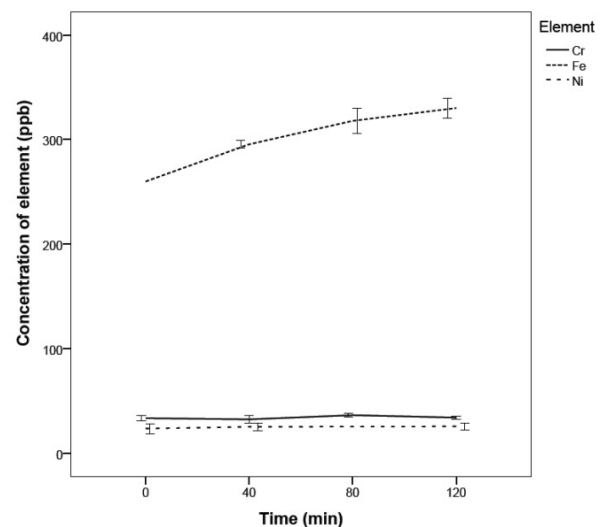


Fig. 7. Mean concentration iron, chromium, and nickel during circulation

Although the released amounts of each element are less than the original content in the unprocessed milk, the reported metallic mouth feeling in literature should be taken into account. Therefore, in addition to optimizing the electric pulse parameters, future work may consider the use of chemically resistive elements (chromium, titanium, or platinum) as coating for the electrodes.

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