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ENHANCEMENT OF MASS TRANSFER IN SOLID-LIQUID EXTRACTION BY PULSED ELECTRIC FIELD

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ABSTRACT

Laboratory-scale equipment was developed making the Pulsed Electric Field (PEF)-treatment possible during solid-liquid extraction. Preliminary experiments were performed for testing the effect of pulsed electric energy input on mass transfer kinetics. As example the kinetics of extraction of water-soluble polysaccharides fraction from linseeds (Linum usitatissimum L.) has been studied. Samples were submitted to PEF treatment at varying field strengths (0.5 to 5 kV cm^{-1}) applying a pulse numbers up to 900 with a pulse duration of 900 μs. Additional effect of moisture content of dried or wetted samples were also studied. The results indicated that recognizable increase in mass transfer rate started to occur at 0.5 kV cm^{-1} moderate field strength at short times of PEF treatment in the range of 2 min.

Keywords: pulsed electric fields, electropermeabilization, linseed, mucilage recovery, extraction kinetics.

INTRODUCTION

In the solid-liquid extraction processing a structurally dependent diffusion is characterized by the degree of solid matrix disintegration, which influences the amount of the compounds released into the solvent. Apart the traditional pre-processing methods of achieving a high level of cell wall's disruption such as mechanical, thermal or chemical treatment, a variety of new high electric field applications were successfully demonstrated. To date, high-voltage fields have been used mostly for degradation of organic compounds in water, inactivation of microorganisms in liquid products, and for intensification of mass transfer in reactive liquid-liquid extraction [1, 2].

In recent years, there has been an increasing interest in the application of pulsed electric field as a processing alternative for vegetable raw. Several combinations of PEF with other treatments such as pressing, osmotic dehydration and drying have shown advantages over individual processing [3]. In more recent research papers the impact of moderate electric pulses on the mass transfer during solid-liquid extraction of sugar and pigments from red beets, sugar beets, apples, carrots [4, 5], and of vegetable oils from maize kernels, olives and soybeans [6] has been investigated.

The effect can be attributed to the electrical damage of the cell walls (electropermeabilization) resulting in temporal or permanent pores formation and internal porosity increases. The unclear mechanisms of reduction in the mechanical integrity of the cell walls leads to the absence of criteria for choosing optimal parameters of PEF treatment for the wide spreading of vegetables.

The objective of the experimental work presented here is to develop an experimental set-up making the study of PEF-induced effect possible during solid-liquid extraction. Efficiency of this process was deduced by monitoring rates of mass transfer during mucilage recovery from linseed - water system.

THEORY

Some vegetables have an effective electrically conductivity σ_c over the range 0.01-0.1 S m^{-1} suggesting their suitability to be processed by PEF. Inside the heterogeneous plant tissues, the structure of the cell is maintained by the cell wall, and its selective permeability is provided by a thin membrane (5-8 nm) covering the cell just interior to the cell wall. The largest components building-up the membrane are electrically insulating lipids (mainly phospholipids connected by polar and non-polar interactions) and it may be considered as a dielectric interface between the conductive intracellular and extracellular tissues. As a result of a very low electrical conductivity of the membrane σ_m in the range of 10^{-4} – 10^{-6} S m^{-1}, the voltage applied inside the tissues drops exclusively across the cellular membrane and may provoke an electric breakdown at cellular level.

According to the theory proposed by Zimmerman [7] the transmembrane potential U_m induced on a cellular membrane in an external electric field is determined by the following equation:

$$U_m = \alpha f d_c E \quad (1)$$

with:

E - electric field strength, kV cm^{-1};

d_c – diameter of the cell, m;

α – geometry factor depending on the shape of the cell, equal to 0,75 for a spherical cell, and to 1 for a cell of cubic form;

f – factor, relating electrical and geometrical properties of the cell and of the cell membrane.

Several semi-empirical models of phenomenological nature have been proposed for estimating the transmembrane potential and cell electropermeabilization probability. Taking into account the insulating properties of the cell membrane and simplifying the general phenomenological model, Bazhal et all. [3] proposed an approximate estimation for the coefficient f according to the following expressions:

$$f = (1 + \frac{\sigma_m}{2\sigma_c K}) / K \quad \text{where}$$

$$K = 1 + \frac{d_c \sigma_m}{d_m \sigma_c}(2 + \frac{\sigma_c}{\sigma_e}) / 4 \quad (2)$$

Considering usual conditions for vegetable tissues (cell size d_c of 10^{-4}-10^{-5} m, membrane thickness d_m about 10^{-8} m, and $\sigma_m << \sigma_c$) the expressions can be approximated as:

$K \cong 1$ and $f \cong 1$

and the potential U_m is proportional to the fields strength E and size of the cell d_c. This approximation confirms the fact that despite the large variety of morphological and electrical properties of the vegetables, similar values for charging of the insulated membrane up to a critical threshold U_{cr} on the order of 1V were reported. The corresponding electric field E_{cr} is

$$E_{cr} = \frac{U_{cr}}{d_c} \approx 10^2 - 10^3 V cm^{-1} \quad (3)$$

The most generally accepted mechanism of membrane electropermeabilization, based on a critical transmembrane potential concept consists of following steps (Fig. 1):

- Polarization of the membrane as a result of charge separation across the nonconductive membrane (the normal potential without external field U_o is considered approximately 10 mV);

• Temporal destabilization and reduction in the thickens of the membrane as a result of induced intra-cellular stress;

• Reversible breakdown of the membrane nearby the critical potential U_{cr} resulting in small conductive channels formation, which leads respectively to an immediate discharge at the membrane, re-sealing of pores, followed by a repeated charging process;

• Pores formation of an irreversible nature obtained by increasing the intensity of the electric field and pulse duration and number.

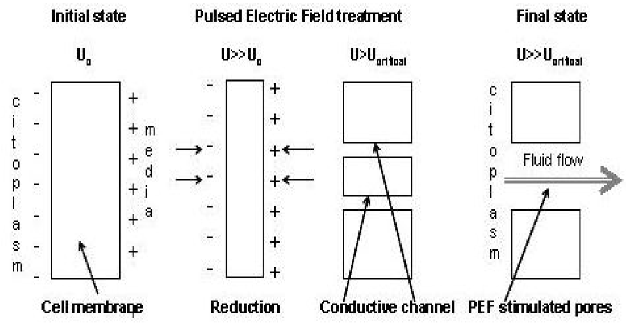

Fig. 1. Mechanism of dielectrical breakdown of the cell membrane.

The earlier experimental studies in the processing of vegetables [3-6] were conducted in static treatment chambers applying field strengths on the range 0.2–7.5 kV cm^{-1} with pulse duration of 10-1000 μs and up to 1000 pulse numbers, suggesting that the impact of both reversible and irreversible electropermeabilization had found applications.

EXPERIMENTAL

Sample Materials

Water-soluble non-starch polysaccharides fraction (principally mucilage) recovery from dry, ripe seeds of *Linum usitatissimum L.* was studied as example. Apart the fatty acids (30-40%) linseeds are rich sources of vegetable mucilage (about 5-6 % of the seed weight). The linseeds are flat, oval, with an average weight of 5.5 mg per seed, length being about 4-5 mm, and are approximately 2.5 mm wide and 1.5 mm thick. The mucilage is present on the surface of the seed, and can be easily extracted by water from the whole seeds.

Extraction procedure

The overall process of mucilage recovery from linseeds is presented in Fig. 2. The kinetic experiments were carried out in a batch-type stirred thermostated vessel. At specific intervals, the extraction was stopped and the solvent-dissolved mucilage bulk phase was then removed. The mucilage dissolved forms a viscous hydrogel surrounding the seed when it is wetted, the solution is extremely viscous and its removal required several separations. The seeds were separated by filtration using a hand sieve, brief washing with additional water, and centrifugation (at 3000-5000 rpm) of the collected seeds-solution filtrate to recover the residual solution retained by the seeds. The mucilage is recovered from the extracts

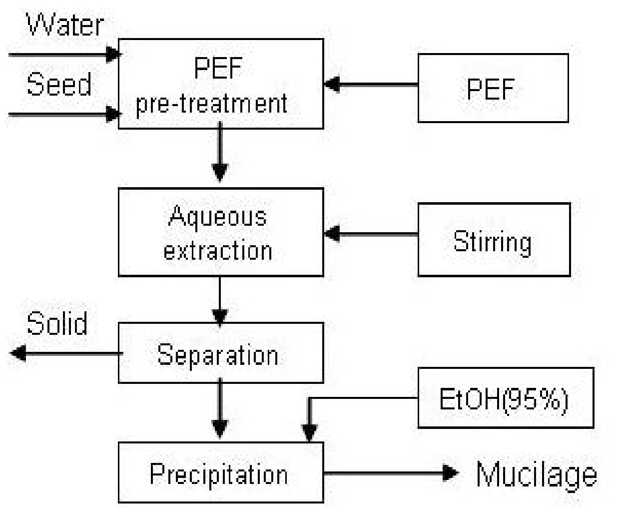

Fig. 2. Steps of mucilage recovery from Linseed.

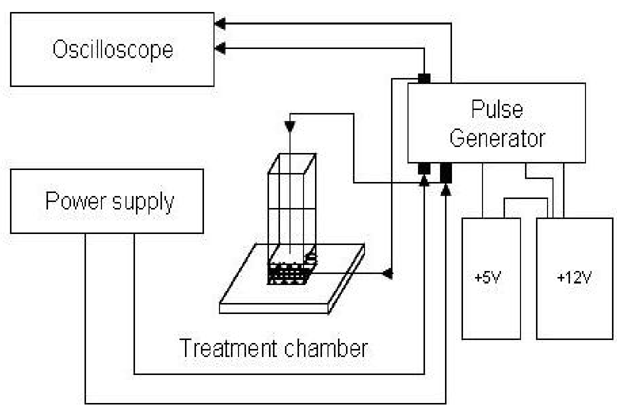

Fig. 3. Experimental set-up.

collected by precipitation (three part of alcohol to on part of extract) in 95,6 % ethanol–water azeotrope. The alcohol perceptible mucilage forms a stable bloc. The flocs were filtered and the weight of mucilage was measured gravimetrically after drying to a constant mass.

Pulsed Electric Field treatment

The simplified circuit of the experimental set-up developed for this purpose is represented in Fig. 3. Basically it consists of a generator that forms the pulses and of a treatment chamber with a discharging zone. The high field strengths are achieved through storing a large amount of energy in a charging circuit from a DC power supply, which is then discharged in the form of pulses through the solid samples in the treatment chamber. The pulses are monopolar rectangular of duration of 900 μs. The time between the pulses of 75 ms is significantly longer than the duration of the pulses. The chamber consists of 2 parallel stainless steel electrodes of area of 9 cm^2 placed in a polystyrene spacer. The upper one was positively charged while the other one was grounded for safety reasons. The external applied voltages may be extended up to 1800 V and field strengths can be varied gradually by the distance between the electrodes.

The experimental procedure has been divided in two groups. Samples of one group were to be used directly in solvent extraction in order to determine the kinetics of extraction at the following conditions: solid-liquid ratio 1:10, native pH of the suspension pH » 7, and rotation speed of 500 rpm that eliminates the external mass transfer resistance. Kinetics experiments were performed at temperature of 25, 35, and 45°C using samples with varying moisture content: dried seeds (3 %), seeds with initial moisture (7 %) and wetted seeds (12 %).

The second group investigates the effect of samples PEF pre-treatment prior to the conventional extraction. The PEF treatment time was about 2 min corresponding to 900 pulse numbers. Electrical field strengths ranging from 0.5 to 5 kV cm^{-1} were used which fell in two main categories. In one, the samples are treated with a mean power of up to 0.5 $kVcm^{-1}$. Higher power outputs ranging from 1 to 5 kV cm^{-1} were used in another group of experiments to study the effect of higher electric strengths.

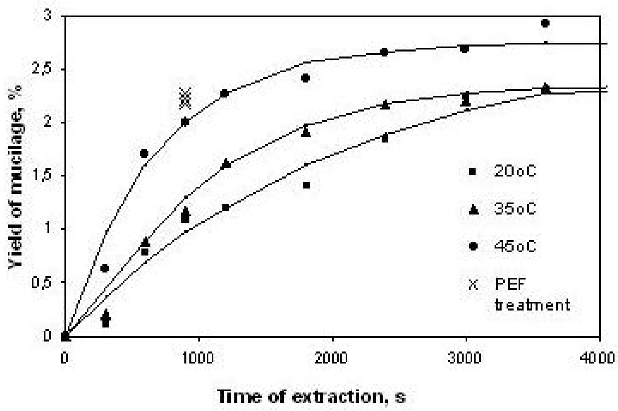

Fig. 4. Conventional versus PEF-assisted solid-liquid extraction.

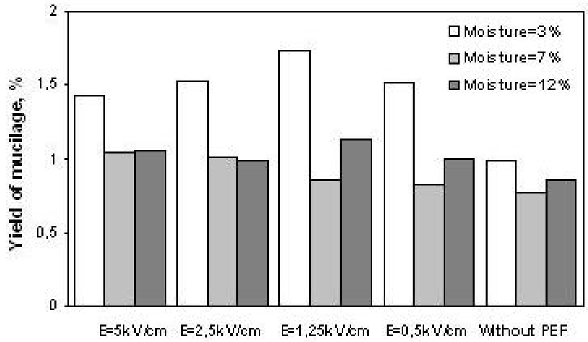

Fig. 5. Effect of PEF treatment at different moisture contents.

RESULTS AND DISCUSSION

Results of comparative extraction tests with or without PEF pretreatment are reported in Fig. 4. The yields were reported in terms of mass of dried precipitate to the mass of the solid phase. An extraction time of at least 3000 s at room temperature was required for near equilibrium conditions under conventional extraction, giving about 50 % separation efficiency for one stage extraction. The increase in temperature yielded fairly similar equilibrium concentrations and sensible increase in the rate of extraction, the effect was more pronounced at 45°C. This effect is due mainly to the strong temperature dependence of the high mucilage viscosity which decreased at increased temperatures, or more complex effect of solubility of polysaccharides, again dependent on the temperature used.

Three different voltages giving the same field strength E of 1 kV cm^{-1} were used to compare the effec-

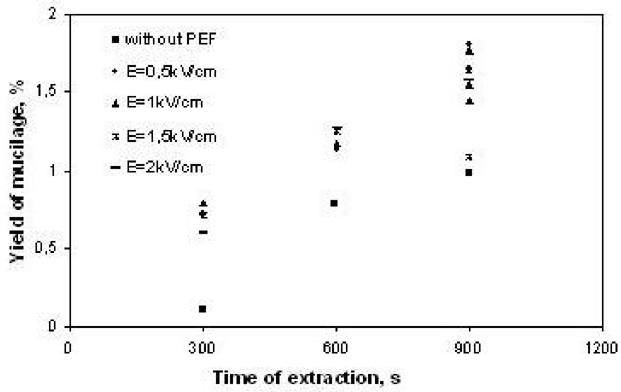

Fig. 6. Comparison of effectiveness of PEF treatment at different field strengths.

tiveness of the PEF treatment. It is apparent that the PEF pre-processing accelerated extraction in a similar manner as that exhibited by an increasing of temperature up to 45°C, or at room temperature within the first 15 minutes produced yields similar to those following 1h extractions without PEF treatment.

The yields of extraction without and with PEF were compared together at different moisture contents in Fig. 5. The results presented concern the first 15 minutes of extraction after PEF treatment (applied in this case at voltage of 1.25 kV). Experiments carried out indicated that partially removing moisture from the material seemed to enhance the PEF-induced effect. This dependence has not been cleared yet and it may be correlated with changes in electrical conductivity and the influence of excess quantities of air and extraparticle liquid in the pores of untreated samples [3].

Several trials were carried out to locate a suitable level of PEF treatment. Fig. 6 presents some examples of mucilage yields versus time at different times of extraction after the PEF application, and different values of field strength, *E*. It was observed from the results that practically reliable experimental data were recorded at 0.5 kV cm^{-1} field strength beyond the generally accepted electrical breakdown level. However, an increase from 1 to 5 kV cm^{-1} did no result in further increase in the mucilage yield confirming earlier studies [4, 6].

The main problem consisted in the poor reproduction and inconsistency of certain experimental data that may be attributed to some unfavorable factors: great affinity of jelly-like mucilage for the seeds and the difficulty of its removal; possible PEF-induced fast kinetics of electrical conductivity increase, which in turn decreased the resistance of the chamber and reduced the pulse width. Additional effects are the heterogeneous structure of the solid and the presence of conductive debris in the samples, which may provoke non-uniform treatment as well as operational problems.

CONCLUSIONS

PFE treatment was shown to be effective for mass transfer enhancement during aqueous extraction of polysaccharide compounds from linseeds, increasing the rate of extraction by 50 – 80 % under certain processing conditions.

Further work will be needed to determine preconditions of an effective PEF treatment: mechanic and thermal pretreatment of the solid phase (dehulling, milling and fractionating of the linseeds, optimal moisture content) in a larger range of process parameters (field strength and pulse number) resulting in both reversible and irreversible structural changes. The major problem arising is the determination of conditions of steady PEF-treatment regime without any disruption of electrical treatment caused by overflow of acceptable maximum current value. For this purpose accurate measurements of sample electrical conductivity and possible structural changes before and after PEF treatment would prevent inconsistent results due to applicability of the PEF systems.

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