Emission spectroscopy analysis during Nopal cladodes dethorning by laser ablation

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Abstract. Optical emission spectroscopy of the pulsed laser ablation of spines and glochids from Opuntia (Nopal) cladodes was performed. Nopal cladodes were irradiated with Nd:YAG free-running laser pulses on their body, glochids and spines. Emission spectroscopy analyses in the 350-1000 nm region of the laser induced plasma were made. Plasma plume evolution characterization, theoretical calculations of plasma plume temperature and experiments varying the processing atmosphere showed that the process is dominated by a thermally activated combustion reaction which increases the dethorning process efficiency. Therefore, appropriate laser pulse energy for minimal damage of cladodes body and in the area beneath glochids and spines can be obtained.

1. Introduction
Opuntia cactus succulent, young, soft and flattened stems known as cladodes or “nopalitos” are consumed as vegetable food. Good-quality nopalitos are thin, fresh-looking, turgid, bright-green colored and low in fiber content [1]. And at the present this product has a growing demand in the world market.

Laser ablation of glochids and spines was recently proposed as a novel solution. The laser radiation within a certain spectral region was found to be selectively absorbed by spines and glochids causing their removal while the fresh part of the vegetable remains without appreciable damage [5].

The laser beam heats and evaporates the glochids and spines material creating a plasma plume that expands depending on the laser pulse power density, surrounding atmosphere conditions, and target characteristics [6]. For example, we have found certain dependence of the moisture content within the areoles and the age of the cactus cladodes. These factors may induce certain fluctuations in the amount of ablated material affecting the dethorning process efficiency.

The laser ablation emission spectroscopy techniques (LIPS or LIBS) are well-known and commonly used for qualitative and quantitative elemental analyses of liquid, gaseous, and solid materials. This analytical method has several advantages because of its relative simplicity in sample preparation, little quantity of material requirements and the possibility of in situ and real time monitoring. Most of the laser induced plasma spectroscopy studies are made using Q-Switched pulsed laser radiation. In this work we analyze the optical emission spectra in the visible range of the plasma plume generated by free running regime fundamental harmonic Nd:YAG laser pulses.

The Opuntia cladodes dethorning process is shown to be dominated by a combustion reaction subsequent to thermally generated plasma. Experiments were carried out using a large quantity of samples of two different glochids and spines population kinds of areole. The processing atmosphere was also varied.
2. Experimental details
A fundamental harmonic (1064 nm) free running operated Nd:YAG pulsed laser with 1.2 Joules per pulse energy and 120 microseconds FWHM time duration was used during all the experiments. The multimode high divergence angle laser beam was focused into the samples through a single lens focal system like the one schematically represented in figure 1. The right angle interferential mirror and the focusing lens were set to fixed positions for vertical irradiation of the samples as well as the processing plane to obtain invariable irradiation spot size. Samples were placed using a manual micropositioning XY system and the radiation of the different stages of the plasma plume generated in the process was collected by moving the analysis point in the vertical direction over the center of the processing site. The analysis point dimensions were approximately 2 mm depth and 1 mm diameter. The collecting lenses-fiber array is composed of two suitable achromatic lenses and a 0.6 mm core diameter optical fiber. This radiation optical signal is transferred to an Ocean Optics USB 2000 VIS/NIR spectrometer with a 2048 pixels CCD detector and 350-1100 nm spectral range. Optical emission spectra are obtained by external synchronization with the laser pulse and automatically saved in an Ocean optics software; OOI:Base32 (see figure 1). The laser pulse repetition rate was set to 2 Hz allowing the software to properly save the data in the hard drive of the computer.
For sample preparation fresh young Opuntia cladodes were carefully cut in square shaped samples containing a single areole. Optical digital micrographs using 60x magnification were taken from the whole set of samples in different stages of the experiments. The samples were divided according their glochids and spines population into two different groups, “glochids areoles” and “glochids & spines areoles” (see figures 2 and 3). It must be pointed out that a large number of areole samples chose with similar dimension and shape were used in order to get as good as possible statistical results.

3. Results and discussion

The first group of experiments was directed to characterize the plasma plume evolution according to experimental observations in three main stages: plasma formation (near the areole), plasma evolution (from 2 to 7 mm from the areole) and plasma dissipation (more than 7 mm from the areole). In the first stage the obtained spectra are mainly due to continuous electronic emission, little appreciable presence of lines or molecular bands is observed. The second stage is dominated by high intensity molecular bands corresponding to some of the characteristic organic compounds present in the samples. The third stage spectra are characterized for a much less intensity of the characteristic emission bands and there is no electronic continuous emission. Figure 4 (a) shows the final appearance of a typical areole after the dethorning process is completed and figure 4 (b) presents a plot of the evolution of the optical emission spectra during the process.

The second group of experiments was directed to demonstrate the presence and the influence of a combustion process after the plasma formation. A suitable processing chamber with glass windows a gas conducts and manual valves was prepared to control the surrounding atmosphere during the dethorning process. Two different atmospheres were used, air and nitrogen, both at normal conditions of pressure and temperature. The plot in figure 5 shows the comparison of the obtained spectra. A completely different behavior is observed, the size of the visible plasma was considerable smaller in the nitrogen atmosphere, no emission bands are observed and at only 3 mm from the areole no optical emission is observed. Theoretical calculations for the estimated electronic temperature show that the first stage plasma is identical in both the atmospheres (approx. 4700 K), nevertheless in nitrogen the combustion process barely appears.
4. Conclusions
It can be concluded that the interaction of microsecond Nd:YAG pulsed laser radiation with Opuntia cladodes areoles is dominated by a thermally activated combustion mechanism considerably increasing the dethorning process efficiency. The glochids distribution in the areole increases the absorbed energy due to laser radiation dispersion creating plasma of high temperature (and pressure) which may complete the dethorning process with considerable lower efficiency in absence of oxygen. The optical emission spectroscopy technique is shown to be a suitable method for the dethorning process real-time monitoring and the possibility of the complex band emission pattern recognition (future work) may enable determining of contamination problems in such vegetable food.

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