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Re-use of partially purified iron color fixation solutions using electro-coagulation and ozonation in ripe table olive processing and packaging

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ABSTRACT

The present work investigates the feasibility of re-using partially purified iron fixation solutions by electro-coagulation followed by ozonation in another fixation stage of black ripe olive processing and/or as cover brines in packaging. Re-use after the addition of ferrous gluconate during the color fixation stage involves a slightly lower amount of iron penetrating into the olives than when tap water is used. As a result, the olives are slightly less dark before packing when a gluconate solution is re-used. However, it is possible to completely re-use the partially purified solution using 50% of it as a color fixing liquid and 50% to prepare the cover brine in the packaging or to fix the color using tap water to prepare the gluconate solution and 100% purified solution as cover brine, in which case this waste-water is completely eliminated from the industry. Iron concentration in the flesh and surface color are the same for these two working methods and ripe olives present the same flavor as olives produced following the traditional procedure using only tap water.

1. Introduction

The processing of ripe olives involves storage of the fruit for a variable period of time and a stage of darkening or oxidation in an alkaline medium. The darkening process consists of successive treatments of the fruits with a dilute solution of NaOH (lye); during the intervals between lye treatments the fruits are suspended in water and air is bubbled throughout the process (Sánchez-Gómez et al., 2006). During this operation the fruits darken progressively owing to the oxidation of orthodiphenols, hydroxytyrosol (3,4-dihydroxyphenyl ethanol) and caffeic acid (Brenes-Balbuena et al., 1992), but the color formed is not stable and fades progressively after oxidation. To prevent this deterioration, the fruits are immersed in ferrous lactate or gluconate for several hours (García et al., 2001). These efficiently fix the color as a result of the iron (Fe)-phenol complexes formed (Brenes et al., 1995). The product has a final pH above 4.6 and its preservation is only achieved by sterilization (Sánchez-Gómez et al., 2006).

During the process a large volume of heavily polluted solution is generated. The environmental impact has been decreased by the introduction of re-using technologies. Preservation solutions can be re-used in another preservation cycle after ozone treatment or acetic acid distillation and the quality of the final product is similar to the one persevered with a fresh acid solution (Medina et al., 2011). Also, this preservation solution can be added to tap water in washing during the oxidation stage (Brenes et al., 1998), although this use is limited by its high acidity and the presence of additives in some cases (Brenes et al., 2004).

Iron fixation solutions could be re-used if organic matters, mainly phenols, are removed. These compounds can be chemically bonded to the ferrous ions when additional ferrous gluconate is added, resulting in Fe-phenol complexes forming in the liquid (Brenes et al., 1995), thus preventing the cations from penetrating into the olives (García et al., 2001) and the color of olives not being fixed.

Electro-coagulation (EC) is an electrochemical method of treating polluted water whereby sacrificial anodes dissolve to produce active coagulant precursors (usually aluminum or iron cations) in the solution. This technology can be used for the removal of both color and colloidal particles in food industries

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(Şengil and Özacar, 2006; Yavuz, 2007).

The application of EC to waste-waters from the packaging of green table olives allows the industry to obtain a practically colorless solution of lactic and acetic salts which could be re-used in packing (García-García et al., 2011).

Ozone has been declared Generally Recognized as Safe (GRAS) and in 2001 it was admitted as a direct food additive for the treatment, storage and processing of food (EPA; Khadre et al., 2001). The green olive alkaline solutions treated with ozone may be re-used as fermentation brines after adding the appropriate amount of NaCl (Segovia-Bravo et al., 2007a and 2007b). Also, Spanish green olives may be packed with diluted (1:1) ozonated fermentation brines with similar organoleptic characteristics to those using fresh brine (Segovia-Bravo et al., 2008). In ripe olives, preservation solutions can be re-used in a new preservation cycle after ozone treatment and the quality of the final product is similar to the one persevered with fresh acid solutions (Medina et al., 2011).

The EC of ferrous gluconate solutions with aluminum in the anode and iron in the cathode removed most of the initial phenols in the solution, about 30% of the initial pollutant load and both lactic acid bacteria and yeast populations slightly decreased, while subsequent storage with bubbling ozonated air completely removed phenols and destroyed all micro-organisms (García-García et al., 2014a,b).

The present work investigates the feasibility of re-using partially purified iron fixation solutions using electro-coagulation followed by ozonation in another fixation stage of black ripe olive processing and/or as cover brines in packaging. Physico-chemical and sensorial analyses were performed to assess the quality of the final product.

2. Materials and methods

2.1. Olives

The experiments were carried out on olives (*Olea europaea* L.) of the Hojiblanca cultivar which had previously been preserved for a period of 8 months in acidic conditions (Castro et al., 2007). The physico-chemical characteristics of the liquid were: pH, 3.8 and free acidity, 11.3 g/L as acetic acid.

2.2. Darkening process

Assays were carried out on 2 kg of olives suspended in 2 L of liquid (lye, water or iron solution) placed in eight 0.15 m diameter 0.3 m high, PVC cylindrical containers with conical bases. The darkening process consisted of a treatment with 23 g/L NaOH solution (lye) for 4.5 h, sufficient time for the lye to reach the pit. The olives were then covered with tap water for 20 h. After draining, the olives were put in a new washing solution (tap water/preservation olive solution, 3/1) for 24 h (Brenes et al., 1998) and air was bubbled throughout the oxidation process (0.3 m^3/h). Finally, the liquid was poured off and the fruits passed to the color fixation phase where they were covered with a 0.1% ferrous gluconate solution with the pH adjusted to 4.5 by the addition of HCl (3 M), no aeration was applied during the first 2 h and then the olives were aerated for another 8 h (0.3 m^3/h).

Plain olives (175 g) were bottled (A-314 jars) with 145 mL of cover liquid with 32 g/L NaCl and 0.15 g/L ferrous gluconate. The jars were closed and sterilized at 121 °C for 15 min in a computer-controlled Steriflow retort (Madinox, Barcelona, Spain). The jars were kept at ambient temperature and the olive quality was measured at 3 months from packing.

2.3. Partially purified iron solutions by EC and ozonation

Ferrous gluconate solution samples were collected for eight darkening processes similar to those commented above at the Instituto de la Grasa pilot plant. The liquids were pooled and stored in a cold room (6–7 °C) for 1–4 days until EC.

The EC was carried out in a plexiglass parallelepiped reactor (2.0 L). Two pairs of Al/Fe (anode/cathode) electrodes connected in a bipolar mode were placed in the electrochemical reactor, the total effective surface area of the electrodes was 91 cm^2, the distance between the lowest part of the electrode and the cell was 0.8 cm and between electrodes was 1 cm. The volume of liquid treated each time was 1.6 L and to allow for an adequate homogenization of the waste-water, the liquid was magnetically stirred by 2 bars. A direct current was imposed by a stabilized power supply (Quasar 500, CRS Industrial Power Equipment, Calco, Lecco, Italy) for 50 min at 25 mA/cm^2 current density (García-García et al., 2014a). After filtration through Filter-Lab Ref 1305 (Barcelona, Spain) to remove the flocks, the liquid was pooled and stored for 2–3 days in a cold room (6–7 °C).

For preparing solutions for color fixation and cover brine, 6 L and 3 L respectively of partially purified liquid by EC was then treated by bubbling ozonated air (0.7 g O_3/h) through a synthetic glass diffuser introduced at the bottom of the vessel until 2.1 g O_3/L of liquid was supplied. The ozone was produced by TODOZONO1, Mod TD ZN equipment (Colmenar Viejo, Madrid, Spain).

To further conduct electricity in the electrolytic solution during the electro-coagulation 10 g NaCl/L was added to ferrous gluconate solutions. Other physico-chemical characteristics of ferrous gluconate solution used in experiments and once treated by EC and later ozonation (ready to re-use) are shown in Table 1.

2.4. Experimental design

All experiments were performed once the fruits had been darkened, ie during the color fixation stage and packaging of ripe olive processing.

The effects of type of color-fixing solution (tap water or partially purified solution) were studied using a gluconate solution prepared with tap water as the control and two solutions with 50% and 100% of partially purified solution. In all cases the fixation solutions were prepared with a concentration of 1 g/L ferrous gluconate with the pH adjusted to 4.5 by the addition of HCl (3 M). Hourly, the iron concentration in the liquids and the surface color of the olives were analyzed. The experiments were run in duplicate at ambient temperature (25–26 °C).

In addition, the possible use of the partially purified color fixing solutions in packaging was studied. The maximum volume of solution to re-use (fixation and packaging) was limited by the ferrous gluconate solution used and generated in the process on the experiments and in industries, 1 L fixing solution/kg olives.

Thus, if all the purified liquid was used in the fixation, only tap water can be used to prepare the cover brine in packaging. If only half of the purified liquid was used in the fixation stage, water or the other 50% purified liquid could be used for packaging. And finally, if water was used to prepare the ferrous gluconate in the fixation process, cover brine can be composed of 50% or 100% of the purified solution or just tap water. Packed ripe olives in which tap water was used to prepare ferrous gluconate solution and the cover brine were used as the control.

2.5. Chemical analysis

Titratable acidity and pH of solutions were measured using a Metrohm 670 Titroprocessor (Herisau, Switzerland). Titratable