

# Effect of Washing with Acidified Water during Processing on the Quality of Spanish-Style Green Table Olive

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**Abstract:** Table olives are one of the most consumed appetizers in the world. Egypt is currently the largest producer of table olives in the world. Manzanilla is the most valued table olive variety of preparation for Spanish-style green olive, in this technique, the olive fruits are sorted, graded by size and finally treated with a dilute 1.5% (w/v) sodium hydroxide solution to remove bitterness (glucoside oleuropein). After this treatment, olives are washed with tap water several times at least 3 times to eliminate the excess of alkali. Washing waters of Spanish-style green olive processing are heavily contaminated waste streams that represent an important environmental problem that needs to be solved. The aim of this study was to evaluate the use of acidified water (HCl 1% or H<sub>2</sub>SO<sub>4</sub> 1%) in washing of olive fruits treated with alkaline as well as the efficacy of this technique on the resultant fruits quality and sustainability of water used. The obtained results demonstrated that the possibility of olive fruits were washed after lye- treatment to only one time, by using acidified water with HCl 1% (WAW<sub>HCl</sub>) or with 1% H<sub>2</sub>SO<sub>4</sub> (WAW<sub>H2SO4</sub>) compared with fresh water (3 times), and the re-use of resultant wastewater after neutralization with HCl 7% as a safe water for irrigation. Oleuropein is responsible for bitterness, its content decreased during processing and fermentation in all treatments. Regarding sensory properties of olive pickles (WAW<sub>H2SO4</sub>) gave the lowest score of defects 0.5% meanwhile high score of smell (8) and taste (9). The study concluded obviously that the possibility to use acidified water (H<sub>2</sub>SO<sub>4</sub> 1%) in olive fruits washing after lye-treatment without any changes in the olive pickles quality.

**Keywords:** Table olives, Manzanilla; *Olea europaea* L.; polyphenols, Spanish-style green olive; water saving

## INTRODUCTION

Olive trees (*Olea europaea* L.) are a millenarian crop that was extended by Romans, Phoenicians and Arabs through the countries in the Mediterranean basin (Sánchez-Rodríguez *et al.*, 2019). There are different olive varieties; some of them are used to extract olive oil and others for table olives because of their physical properties (volume, shape, firmness, etc.) (Cillidag, 2013). Table olives are one of the most consumed appetizers in the world; in fact, the global production of table olives for the 2019/20 crop year, showing a 13.9% increase to 2,925,500 tons compared with 2,569,000 tons produced in the 2018/19 season (IOC, 2020). Egypt is the biggest producer of table olives in the world. In 2019, Egypt is the world's second largest producer of table olives and produced around 450,000 tons in 2018/19 of which around 100,000 tons were exported. Egypt is expected to take the lead from Spain with a crop of 690,000 tons of olives compared with 497,000 last year (IOC, 2020).

Table olives composition is different from other fermented vegetables due to their high content of phenolic compounds and fatty acids, mainly oleic acid (monounsaturated), thus, it can be considered a functional food. Table olives' bioactivity can be influenced by many factors, such as cultivation technique and type of process to turn raw olives into table olives (Collado-González *et al.*, 2015).

Table olives are well known sources of phenolic compounds, the major of which are hydroxytyrosol, elenolic acid, tyrosol and caffeic acid; their concentration is depended upon the ripening degree and the treatment method olive drupe till they became edible (Blekas *et al.*, 2002; Charoenprasert and Michell, 2012). Bitterness in raw olives is usually attributed to the

presence of oleuropein, which is the most prevalent phenolics present at harvest. Ripe olives contained high levels of bitter phenolic compounds including oleuropein and ligstroside that make the fruit inedible (Soler-rivas *et al.*, 2000; Bianchi, 2003). However, oleuropein is not the only phenolic compound found in olives. Olive phenolics can be grouped into four broad categories: phenolic acids, phenolic alcohols, flavonoids, and secoiridoids (Charoenprasert and Mitchell, 2012). Also, the phenolic compounds contributed to sensory characteristics of olive products, further to their pharmaceutical and physiological benefits (Covas *et al.*, 2006).

'Manzanilla' is the most valued table olive variety because of its high productivity and its good fruit quality. In Egypt, it is typical to harvest olives when they are green to process them following the Spain-style. 'Manzanilla' olives have medium aptitude for oil extraction whereas its oil has good quality and stability; therefore, this variety is perfect to be processed to table olives (ASEMESA, 2018). 'Manzanilla' olives have a thin peel and the flesh is delicate, hard, pulpy, tasty, and non-fibrous (Cano-Lamadrid *et al.*, 2015). Furthermore, the removal of the flesh from the pit is very easy (ASEMESA, 2018); this characteristic is important for the industry because it makes the pitting process easier (IOC, 2004).

Raw olives are firm and bitter, so some processes are necessary to make them edible. Each method of debittering produced a different style of table olives with a unique texture and chemical, microbial, and sensorial profiles, general, any processing method aims to remove the natural bitterness of this fruit, caused by the glucoside oleuropein and as a result, can alter the

health-promoting potential of various table olive products (Blekas *et al.*, 2002; Melliou *et al.*, 2015).

Table olives can be processed using different techniques, and the Spanish-style green table olive process is the most common in Egypt. It consists of: (i) treatment of debittering (lye treatment) to hydrolyze oleuropein, (ii) washing process, to remove alkali, and (iii) lactic acid fermentation (Cortés-Delgado *et al.*, 2016). During alkali treatment, some components, such as tocopherol and free fatty acids, diffuse from the olive peel to the surrounding liquid; this process increases the cellular membrane permeability and contributes to decreased peel firmness (Mojtaba *et al.*, 2015).

The Spanish processing method included lye treatment, for the total removal of the bitter compound oleuropein (generating hydroxytyrosol and elenolic acid glycoside), washing, brining and fermentation, sorting and packaging (Romero *et al.*, 2004). Additionally, current commercial table olive processing methods are some of the most water intensive methods used in commercial food processing and can require more than 7,571 liters of water per ton of olives (*e.g.*, Spanish method) and generate highly toxic wastewater. Throughout, in all stages of lye treatment, large quantities of clean water are used and wastewaters about 3.9-7.5 m<sup>3</sup>/t of olives (Abou-Zaid and Ibraheem, 2015). The washing solutions are heavily contaminated and contain a high content of sugars and phenolic compounds, particularly hydroxytyrosol (3,4-dihydroxyphenyl ethanol) (De Castro and Brenes, 2001).

Increased consumer demand for healthier food products that are produced in an environmentally sustainable manner, as well as industrial interest in decreasing processing time, water usage, and cost, demonstrates the need for innovation in olive processing technologies (Johnson and Mitchell, 2018). Spanish processing method of green olives produce about 3.5-liter wastewater per Kg olive (0.5 L for lye treatment, 2-2.5 L for washing 3 times and 0.5 L for fermentation, so the aim of this study was to reduce the quantity of washing water of Spanish-style processing from 3 times to only ones by using acidified water (HCl 1% or H<sub>2</sub>SO<sub>4</sub> 1%) in washing of olive fruits treated with alkaline as well as the efficacy this technique on the resultant fruits quality and sustainability of water used.

## MATERIALS AND METHODS

### Materials:

Manzanilla olives were obtained from a desert Road farm at Wadi El-Natron, Beheira Governorate, Egypt. Table (1) showed some characters of Manzanilla olive used in this study. Standard fatty acid and all chemicals used were of analytical grade and obtained from Sigma-Aldrich Chemical Co. England. Sodium hydroxide, NaCl, acetic acid and lactic acid were obtained from local market, Cairo Governorate, Egypt.

**Table (1):** Some characters of raw Manzanilla olive fruits used in Spanish-style process

Items	Manzanilla olive
Weight of 100 unit (g)	605
Flesh: stone	3.6: 1
Number of unit/Kg	180
Color	Green

### Methods:

#### Experimental design:

The experiment was carried out with Manzanilla olive fruits (*Olea europaea* Ponifarmis). The olive fruits must be fresh, firm to the touch, not shriveled and free of any marks due to insect bites or sting.

The experiment was carried out with Manzanilla fruit using Spanish-style process. It consisted of treating 30 Kg with 20 L lye solution (1.5 g NaOH/100 ml) until this reached 2/3 of the flesh (6h) followed by washing to remove the excess of alkali. The end of the washing process can be tested by using a few drops of the phenolphthalein indicator.

Thirty Kg were divided into three portions:

1. 10 Kg were washed with fresh water 3 times (control).
2. 10 Kg were washed with acidified water with HCl 1%. (WAW<sub>HCl</sub>)
3. 10 Kg were washed with acidified water with H<sub>2</sub>SO<sub>4</sub> 1.0%. (WAW<sub>H2SO4</sub>)

The debittered olives were then brined with 10% NaCl solution. The total acid expressed as lactic acid content of the brine should be 0.3% for fermentation. Olive samples were taken after 3 months of fermentation for analyses.

### Analyses

#### Physical and chemical analyses:

The average weights of samples were determined by measuring the weights of 30 olive fruits and their pits were removed and weighted. Some of the chemical and physical properties (moisture, color, fruit and pit weight) of the olives were analyzed according to AOAC (2005). Proximate composition (moisture, crude protein, crude oil, crude fiber, total sugars and ash) were determined for the prepared Manzanilla table olive fruits according to Official Methods (AOAC, 2005). Also, pH of olives fruits was determined according to AOAC (2005).

#### Phenolic compounds

##### Preparation of extracts

For polyphenols measurement, all samples were previously treated in order to extract them according to the method described by McDonald *et al.* (2001) with slight modifications. Five grams of dried olives were mixed with 25 ml of methanol and centrifuged at 3000 rpm/5 min (Sigma 2-16 K, Germany). The residue was extracted again in the same conditions, and the extracts were combined then filtered.

### Total polyphenols compounds and its profile

The total polyphenols content of the methanolic extracts was determined with Folin-Ciocalteu reagent as described by Malik and Bradford (2006). Total polyphenols values were expressed as gallic acid equivalents (GAE, mg/100g dry weight) from a calibration curve ( $y=0,0036x$ ;  $R^2=0.99$ ). Qualitative analysis of phenols and phenolic acids was performed with gas chromatography/mass spectrometry according to Boskou *et al.* (2006).

### Oil extraction

Dried Manzanilla olive fruits were ground in a laboratory mill and soaked in n-hexane for 24 h twice. Solvent was collected and evaporated under vacuum. The produced oils were filtered and kept in dark bottles in the refrigerator until used.

### Gas chromatography analysis for fatty acids

#### Methylation of fatty acids

An aliquot of oils, about 10mg, was dissolved in hexane and then 0.4ml 2N KOH in anhydrous methanol was added (Cossignani *et al.*, 2005), after 3 min, 3 ml water was added. The organic layer was separated, dried over anhydrous sodium sulfate, and then concentrated with a N<sub>2</sub> stream to around 0.5ml for GC analysis of fatty acids methyl esters (FAMF) as described below.

#### Identification of fatty acids methyl esters by GC

Agilent 6890 series GC apparatus provided with a DB-23 column (30 m x 0.32 mm x 0.25  $\mu$ m). Fatty acids methyl esters directly injected into the GC. Carrier gas was N<sub>2</sub> with a flow rate of 2 ml/min, splitting ratio of 1:100. The injector temperature was 250°C and that of FID detector was 270°C. The temperature settings were as follows: 150 to 225°C at 5°C/min, and then held at 225°C for 20 min. peak identification was performed by comparison of the retention time (RT) for each peak with those of standard fatty acids. The peaks areas were measured using the Chemstation Program, and relative areas of the identified fatty acids were recorded.

### Sensory evaluation

The consumer test was based on the gustatory (acid, salty and bitter) and kinesthetic sensations (hardness, fibrousness and crispness) of the evaluation sheet for the Methods of sensory analysis of table olives (IOC, 2010). The panelists were 8 experienced judges of Oil and Fat Research Dept., Food Technology Research Institute, Agricultural Research Center, habitual consumers of olives with a high level of training due to their participation for decades in the development of the method for the sensory analysis of table olives.

## RESULTS AND DISCUSSIONS

### Chemical evaluation of olives

The chemical composition of fresh olive fruit of Manzanilla and the changes in the chemical composition of Spanish-style green table olive (control, WAW<sub>HCl</sub> and H<sub>2</sub>SO<sub>4</sub>) during processing are presented in Table (2). The proximate composition of fresh Manzanilla olive fruit were 63.32, 15.73, 7.87, 5.35, 3.98 and 3.75% for moisture, lipid, fiber, sugar, ash and protein, respectively.

The moisture content of pickled Manzanilla olives recorded the highest moisture content compared to fresh olive fruits. The moisture content of the final product considered an important parameter related to firmness and other sensory properties. The increase in moisture contents could be attributed to the decrease in total soluble solids during the fermentation period (Abou-Zaid and Ibraheem, 2015).

Data in Table (2) revealed that the chemical composition of Spanish-style Manzanilla olive, all studied treatments led to a decrease in total fat. From the same table, it could be noticed that, the highest loss of crude fat was recorded for lye treatment followed by washing acidified water with HCl or H<sub>2</sub>SO<sub>4</sub>, this may be due to the effect of these treatment on the permeability of cell wall of olive fruits leading that to lipids loss in soaking and brine solutions. These results agreed with the results previously reported by Abou-Zaid and Ibraheem(2015).

**Table (2):** Effect of different treatments on chemical composition of Manzanilla olive fruits (%)

Proximate composition	Fresh olive	Treatments		
		Control	WAW <sub>HCl</sub>	WAW <sub>H2SO4</sub>
Moisture (%)	63.32	64.25	65.32	67.14
Crude oil (%)	15.73	14.84	14.79	14.22
Crude protein (%)	3.75	5.21	5.03	3.93
Total sugar (%)	5.35	ND *	ND	ND
Ash (%)	3.98	6.06	5.99	4.89
Crude fiber (%)	7.87	9.64	8.87	9.82
Total polyphenols content (mg/100)	604	375	240	235

Fresh olives: fresh Manzanilla olives; ND: not detected

Control: Final product of Spanish-style Manzanilla olives, after 3 months' fermentation washed 3 times with fresh water

WAW<sub>HCl</sub>: Final product of Spanish-style Manzanilla olives, after 3 months' fermentation washed one time with acidified water HCl 1.0%

WAW<sub>H2SO4</sub>: Final product of Spanish-style Manzanilla olives, after 3 months' fermentation washed one time with acidified water H<sub>2</sub>SO<sub>4</sub> 1.0%

Total sugar of fresh olive was 5.35%, however when the olives are washed or lye treated and fermented, sugars are also completely lost or consumed along with other soluble compounds or by microorganisms. These results are in agreement with that reported by Hurtado *et al.* (2008) and Cardoso *et al.* (2010). The mentioned data in Table (2) indicated obviously that, all studied treatments had a positive effect on polyphenol removing comparing to the traditional treatment (control) either for olive fruits after treatments (WAW<sub>HCl</sub> or H<sub>2</sub>SO<sub>4</sub>), where the maximum removing rate was recorded for WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> (235 g/100g), while the minimum removing rate was recorded for traditional treatment (control) (375 mg/100g). These results are in harmony with those of Abou-Zaid and Ibraheem(2015).

### Changes of fatty acids during processing

Fatty acid composition of olive oil extracted from Manzanilla olive, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> compared with control after 3 months of fermentation and fresh olive are represented in Table (3). There are some variations in the fatty acid composition of WAW<sub>HCl</sub>, WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> and control compared with fresh olive were observed.

As shown in Table (3), palmitic, oleic acid and linoleic acid in all samples were found as major fatty acids. The levels of oleic acid were 76.60, 74.47, 71.98 and 71.66 and linoleic acid were 10.34, 9.12, 11.17 and 10.33 and palmitic acid were 8.82, 9.93, 10.97 and 11.05 for fresh olive, control, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> respectively. Oleic acid content decreases during processing and fermentation of WAW<sub>HCl</sub> (6.03%) and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> (6.44%) compared with control (2.78%). The results also showed that total saturated fatty acids content tend to increase (29-44%), while total unsaturated fatty acids tends to decrease of WAW<sub>HCl</sub> (4.48%) and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> (5.73%) compared with control (3.85%), may be due to that unsaturated fatty acids high affected with NaOH during processing and saturated fatty acids more stable. The level of saturated fatty acids of control (29.63%), WAW<sub>HCl</sub> (34.4%) and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> (44.05%) olive samples increased during processing and fermentation compared with fresh olive. Also, the ratio between saturated and unsaturated fatty acids in all samples was increased (30-72%) during processing and fermentation. The results are in agreement with that reported by Salas *et al.* (2000).

**Table (3):** Fatty acid profile (%)

Fatty acid	Fresh olive	Treatments		
		Control	WAW <sub>HCl</sub>	WAW <sub>H<sub>2</sub>SO<sub>4</sub></sub>
Palmitic C <sub>16:0</sub>	8.82	9.93	10.97	11.05
Palmitoleic C <sub>16:1</sub>	0.73	0.71	0.69	0.67
Stearic C <sub>18:0</sub>	2.64	4.99	4.48	5.53
Oleic C <sub>18:1</sub>	76.60	74.47	71.98	71.66
Linoleic C <sub>18:2</sub>	10.34	9.12	11.17	10.33
Linolenic C <sub>18:3</sub>	0.82	0.78	0.69	0.76
Arachidic C <sub>20:0</sub>	0.05	ND *	0.02	ND
<b>Total saturated fatty acid</b>	11.51	14.92	15.47	16.58
<b>Total unsaturated fatty acid</b>	88.49	85.08	84.53	83.42
<b>Monounsaturated fatty acid</b>	77.33	75.18	72.67	72.33
<b>Polyunsaturated fatty acid</b>	11.16	9.9	11.86	11.09
<b>Total saturated/total unsaturated fatty acid</b>	0.13	0.17	0.18	0.19

Fresh olives: fresh Manzanilla olives; ND: not detected

Control: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed 3 times with fresh water

WAW<sub>HCl</sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water HCl 1.0%

WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water H<sub>2</sub>SO<sub>4</sub> 1.0%

### Changes of phenolic compounds

Oleuropein and related bitter phenolics can be reduced in table olives through several different mechanisms. Strong acids or bases can penetrate the olive flesh directly, where free H<sup>+</sup> and OH<sup>-</sup> ions catalyze the hydrolysis of oleuropein at the ester group that connects the hydroxytyrosol/tyrosol to the elenolic acid moiety. This hydrolysis reaction produced the non-

bitter hydrolysis products oleoside methyl ester and hydroxytyrosol/tyrosol (Soler-rivas *et al.*, 2000).

During brine-based processing, bitter phenolics are removed from the olive by diffusing from the fruit into surrounding brine. Once these compounds have diffused into the brine, the acid and/or the enzymatic action of exogenous enzymes,  $\beta$ -glucosidase, and esterase from the microbiota present in the brine or surface of the

olive can hydrolyze the phenolic compounds (Medina *et al.*, 2017). While phenolic compounds diffuse out of the olive, salt and acid from the brine diffuse in, changing the chemical and sensory profile of the product (Maldonado *et al.*, 2008). If the cellular structure of the olive is compromised, either by chemical (*e.g.*, lye), physical (*e.g.*, cracking, slitting, or destoning), or the natural biochemical softening, diffusion can occur more rapidly.

The polyphenols profile and content of resultant Manzanillo olive fruits were tabulated in Table (4). The obtained results demonstrated obviously that, all washing with acidified water treatments had noticeable effects on polyphenol removal than control. The main phenolic components found in fresh Manzanillo olive were oleuropein, hydroxytyrosol, hydroxyphenyl acetic acid and tyrosol (Table 4).

**Table (4):** Polyphenols profile and content (mg/kg) in fresh Manzanilla olive, control, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub> (mg/kg)

Phenolic compounds	Fresh olive	Treatments		
		Control	WAW <sub>HCl</sub>	WAW <sub>H<sub>2</sub>SO<sub>4</sub></sub>
<b>Phenolic acids</b>				
Cinnamic acid	0.35	0.18	0.14	0.16
Hydroxyphenyl acetic acid	24.72	19.93	20.42	19.06
Hydroxybenzoic acid	5.64	3.25	4.33	3.80
Caffeic acid	0.47	0.41	0.38	0.33
Coumaric acid	2.16	1.48	0.95	1.82
Vanillic acid	3.87	1.90	1.85	2.03
Syringic acid	0.49	0.22	0.41	0.28
<b>Phenolic alcohol</b>				
Hydroxytyrosol	46.88	41.30	42.11	43.39
Tyrosol	18.23	14.68	14.96	15.23
<b>Flavonoids</b>				
Taxifolin	0.51	0.47	0.33	0.47
Apigenin	2.14	1.96	2.00	1.79
<b>Secoiridoids</b>				
Oleuropein	72.55	13.15	10.22	13.41
Verbascoside	1.28	0.85	1.16	0.78

Fresh olives: fresh Manzanilla olives

Control: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed 3 times with fresh water

WAW<sub>HCl</sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water HCl 1.0%

WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water H<sub>2</sub>SO<sub>4</sub> 1.0%

Also, the results in Table 4 showed that amount of all phenolic compounds decreased during processing and after fermentation in control, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>, concurred with the results obtained by Gomez-Rico *et al.* (2008) reported that oleuropein showed the highest level among the others phenolics and decreased during processing but the content of oleuropein was high affected during processing and fermentation in all samples. These results in harmony with those of Servilli *et al.* (2006), the phenolic compounds undergo during olive processing mainly, the alkaline hydrolysis and/or the microbial degradation of oleuropein into hydroxytyrosol and elenolic acid glucoside during debittering and brining process. Meanwhile, the content of hydroxyphenyl acetic acid, tyrosol and hydroxytyrosol were less affected during processing and fermentation (Abou-Zaid and Ibraheem, 2015).

#### Organoleptic characteristic

The sensory profile technique was used to study the sensory attributes which best characterize the three processing styles of Manzanilla olive. Sensory

evaluation of Spanish-style green Manzanilla olives (control, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>) was investigated after processing and 3 months of fermentation process. The obtained results are tabulated in Table (5). The results showed that treated (WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>) gave the lowest score of defects 0.5% meanwhile exhibited a high score of smell and taste 8 and 9. But, control gave high score of defect 2% and high score of smell and taste 8 and 9 followed by WAW<sub>HCl</sub> gave 1.5% defect and 8 and 7 score of smell and taste. These results in harmony with those of Maria *et al.* (2010) reported that sensory evaluation led to the conclusion that a revision of technological procedures may improve the final quality of product. The results of three treated samples showed that good quality of hardness, texture and crispness while salty and acid tastes give medium score. The best debittering conditions was the olives washed with acidified water with H<sub>2</sub>SO<sub>4</sub> gave the lowest score of bitterness and defect 2 and 0.5% and a high score of smell and taste. The results are in agreement with that reported by Maria *et al.* (2010).

**Table (5):** Sensory evaluation of the resultant Spanish-style Manzanilla olives

Sensory attributes	Treatments		
	Control	WAW <sub>HCl</sub>	WAW <sub>H<sub>2</sub>SO<sub>4</sub></sub>
Acid	4.5	5	3.5
Salty	5.0	6	5
Bitter	3	2.5	2
Hardness	7	6.5	7
Crispness	7	6.5	7.5
Fibrousness	6.50	7.5	8.5
Smell	9	8	9
Taste	8	7	8
Color	Yellowish green	Yellowish green	Yellowish green
Defect (%)	2	1.5	0.5

Control: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed 3 times with fresh water

WAW<sub>HCl</sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water HCl 1.0%

WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water H<sub>2</sub>SO<sub>4</sub> 1.0%

#### Changes in pH value during fermentation of treated Manzanilla olive

After washing with fresh water and acidified water to eliminate the residual alkali (lye), olives are covered with sodium chloride solution 10% (brine) and left to develop lactic fermentation. Initial brine concentration is 10% NaCl but rapidly declines to 6% due to the high content of interchangeable water in the olive. Fermentation starts as soon as the olives are placed in brine. After alkaline treatment, the pH values of olives were 12.1, 11.5 and 11.2 for control, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>, respectively, down to the value of 8.2, 7.8 and 7.5 after washing. After 10 days' fermentation, the pH values of olives were 6.3, 5.5 and 5.2, it continued to decline the value of 4.8, 4.5 and 4.5. This low pH promoted the growth of lactic acid bacteria. At the end of lactic fermentation, the pH reached 3.6, 3.6 and 3.5 for control, WAW<sub>HCl</sub> and WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>, respectively.

The results are in agreement with that reported by Sanchez *et al.* (2001) which mentioned that lactic acid bacteria started fermentation immediately after washing at pH 9. In this case obviously, the strain used as starter is not necessarily eleuropeinolytic because lye has just demolished the bitter glucoside. The importance of this type of starter is to reduce the log phase and spoilage.

Spanish processing method of green olives produce about 3.5-liter wastewater per Kg olive (0.5 L for lye treatment, 2-2.5 L for washing 3 times and 0.5 L for fermentation, so the aim of this study was to reduce the quantity of washing water of Spanish style processing from 3 times to only ones by using acidified washing water. Also, neutralizing the alkalinity of wastewater tends to produce safe water which can be utilized.

**Table (6):** Changes in pH value during fermentation of treated Manzanilla olive

Time of determination	Control	WAW <sub>HCl</sub>	WAW <sub>H<sub>2</sub>SO<sub>4</sub></sub>
After alkali treatment	12.1	11.5	11.2
After washing	8.1	7.8	7.5
After 10 day of fermentation	6.3	5.5	5.2
After 30 day of fermentation	4.8	4.5	4.5
After 45 day of fermentation	4.1	3.8	3.9
After 60 day of fermentation	3.8	3.6	3.6
At the end of lactic fermentation	3.6	3.6	3.5

Control: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed 3 times with fresh water

WAW<sub>HCl</sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water HCl 1.0%

WAW<sub>H<sub>2</sub>SO<sub>4</sub></sub>: Final product of Spanish-style Manzanilla olive after 3 months of fermentation washed one time with acidified water H<sub>2</sub>SO<sub>4</sub> 1.0%

## CONCLUSION

Increased consumer demand for healthier food products as well as high quality products that are produced in an environmentally sustainable manner, as well as industrial interest in decreasing processing time, water usage, and cost, demonstrates the need for innovation in olive processing technologies. Regarding, the effect of washing of Spanish-style green table olive by acidified water was not affected on the quality of olive during processing and after fermentation. The washing acidified water with acids (HCl, H<sub>2</sub>SO<sub>4</sub>) decreasing processing time, decreasing water usage, improving sustainability, increasing the health properties of processed fruit, and decreasing production cost. The quantity of washing water of Spanish-style processing reduced from 3 times to only ones by using acidified washing water. Also, neutralizing the alkalinity of wastewater tends to produce safe water which can be utilized.

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## تأثير عملية الغسيل بالماء المحمض أثناء التصنيع على جودة زيتون المائدة الأخضر المصنع بالطريقة الأسبانية

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تم دراسة تأثير استخدام الماء المحمض بحمض الكبريتيك 1% أو حمض الهيدروكلوريك 1% في غسل ثمار الزيتون صنف مانزانيلو المصنع بالطريقة الأسبانية (باستخدام قلوي هيدروكسيد الصوديوم 1,5%) على جودة وخصائص الزيتون الناتج. وقد شملت هذه الطريقة نقع ثمار الزيتون صنف مانزانيلو في هيدروكسيد صوديوم 1,5% لمدة 6 ساعات حتى وصل اختراق محلول هيدروكسيد الصوديوم 3/2 الثمرة. ثمار الزيتون الناتج من معاملة القلوي السابقة تم تقسيمه إلى ثلاث أجزاء: الجزء الأول تم غسله بالماء 3 مرات وفي كل مرة يتم نقع الزيتون من 4-6 ساعات على الأقل وفي المرة الأخيرة يتم النقع لمدة 12 ساعة (عينة المقارنة). الجزء الثاني تم غسله بالماء المحمض بحمض الهيدروكلوريك 1% مرة واحدة فقط حيث تم نقع الزيتون به لمدة 6 ساعات ومقارنتها بعينة المقارنة. الجزء الثالث تم غسله بالماء المحمض بحمض الكبريتيك 1% مرة واحدة فقط حيث تم نقع الزيتون به لمدة 6 ساعات ومقارنتها بعينة المقارنة. تم تجميع الماء المتخلف عن المعاملات السابقة ومعالته بمحلول 7% حمض هيدروكلوريك قبل التخلص منه. وكانت أهم النتائج المتحصل عليها: إن غسل الزيتون بماء محمض بحمض كبريتيك 1% أو هيدروكلوريك 1% أنت إلى توفير كمية كبيرة من ماء الغسيل (حوالي 60% من كمية الماء المستخدم في الغسيل بالماء غير المحمض (عينة المقارنة). الماء المستخدم في المعاملة بالقلوي والماء المستخدم في الغسيل تم معادلته بمحلول 7% حمض هيدروكلوريك وبالتالي أمكن استخدام هذا الماء مرة أخرى في الري. المعاملة الثالثة وهي غسل الزيتون بماء محمض بحمض كبريتيك 1% كانت أكثر تأثيراً في إزالة المرارة، كما كان لها تأثير إيجابي ملحوظ على نسبة العيوب بالثمار الناتجة التي وصلت إلى 0,5% مقارنة بنسبة العيوب في عينة المقارنة والتي وصلت إلى 2% والمعاملة الثانية (الغسيل بماء محمض بحمض هيدروكلوريك 1%) والتي وصلت نسبة العيوب بها إلى 1,5%.