

Review

# Chemical Coagulation/Flocculation Processes for Removal of Phenolic Compounds from Olive Mill Wastewater: A Comprehensive Review

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**Abstract:** Olive oil extraction processes generate three phases: Olive oil, solid residue (pomace) and aqueous liquor Olive Mill Wastewater (OMW). OMW causes serious environmental deteriorations such as coloring of natural waters, alteration of soil quality, phytotoxicity and odor nuisance. The direct discharge of this effluent into the soil bring various negative effects on the environment, due to its high load of organic matter and phenolic compounds. Coagulation, flocculation and their combination processes are among the most applied processes for wastewater treatment. The application of coagulation technique using mineral and inorganic polymeric coagulants and acid cracking is not always effective to reduce COD and phenolic compounds from OMW except lime. Although direct flocculation is a low treatment cost, use less chemical and produce less sludge, the efficiency of COD and phenolic compounds removal remain very low. Coagulation-flocculation process is developed in order to enhance the removal efficiency of organic matter from OMW by optimizing the operating conditions. However, many studies showed that the combination of various cationic organic coagulant and flocculant agents did not show any significant decrease of COD and phenolic compounds except for lime combination. In the present review, recent research studies dealing with the application of coagulation/flocculation for removal of phenolic compounds and COD from OMW are presented and compared. Furthermore, the main factors that influence the selection between coagulation, direct flocculation and coagulation-flocculation are presented and the principal removal mechanisms are discussed.

**Keywords:** Olive Mill Wastewater, Coagulation, Direct Flocculation, Coagulation-Flocculation, Mechanisms, Removal Efficiency

## Introduction

The production of olive oil is not restricted to the Mediterranean Basin. Lately, it is also increasing in other countries like France, Serbia, Montenegro, Macedonia, Cyprus, Turkey, Israel, Jordan, USA, Australia and the Middle East. According to the reports of International

Olive Council (IOC), 3.17 million tons of olive oil were produced in the season 2015/16 (IOC, 2016). In that year, the highest volume of olive oil was produced in Spain (1401600 t) followed by Italy (474600 t), Greece (320000 t), Turkey (150000 t), Tunisia (140000 t) and Morocco (130000 t). However, according to the latest reports, 2.53 million tons of olive oil were produced

globally in the year 2016/17 with 20% reduction as compared to the previous year (IOC, 2017). In 2016/17 year, the highest amount of olive oil was produced in Spain (1286600 t) followed by Greece (195000 t), Italy (182300 t), Turkey (177000 t) and Morocco (110000 t).

The IOC report for 2017 pretends an increase of olive oil world production in 2017/18 at 2.9 million tons. The production can reach 1.8 million tons in the European Union (EU), 287000 tons in Turkey, 220000 tons in Tunisia and 140000 tons in Morocco.

Since 2008, Morocco has almost doubled its olive production to 1.5 million tons and created over 300,000 new jobs. According to the Moroccan Center for Export Promotion, there are 784,000 hectares of olive groves, 120,000 tons of olive oil and 90,000 tons of table olives produced annually. The country is the second-largest global exporter of table olives, exporting 64,000 tons of olives, as well as 17,000 tons of olive oil. Morocco plans to increase olive cultivation to an area of 1,220,000 hectares, while production will increase to 2.5 million by 2020 according to the reports of Agriculture and Maritime Fisheries Moroccan Ministry (2015).

Although olive oil is a product of exceptional nutritional value, its production is associated with several adverse effects to the environment, mainly due to the formation a large amount of two by-products, a solid residue and an effluent known as Olive Mill Wastewater (OMW). Approximately 30 million m<sup>3</sup> of OMW are produced annually in the Mediterranean area, characterized by a high pollutant load (Chiavola *et al.*, 2014).

The straight discharge of OMW to the ground fields and superficial water bodies causes a various negative adverse effects on the environment, such as soil contamination, strong odor nuisance, hindrance of plants growth, underground leaks, water body pollution, as well as severe impacts to the aquatic fauna and to the ecological status. These negative effects are due to the presence of bio-refractory contaminants, including a wide variety of phenolic compounds, tannins, fatty acids and organohalogenated pollutants (Danellakis *et al.*, 2011; Karaouzas *et al.*, 2011; Martínez Nieto *et al.*, 2011; Hodaifa *et al.*, 2013; Ntougias *et al.*, 2013).

### *Processes for Olive Oil Extraction*

There are two main processes used by olive mill industry to produce olive oil: Discontinuous process (pressing) in traditional mills and continuous (centrifuging) process in modern units respectively (Fig. 1). The discontinuous process is the oldest and most widespread method for processing olive fruit to obtain olive oil. In this process, the olives are washed, crushed with stone rollers and kneaded with the addition of hot water. The resulting

paste is spread onto fiber disks that are stacked on top of each other and then placed in the press in order to drain the oil. These disks were traditionally made of hemp or coconut fibers but they are now made of synthetic fibers for easier cleaning and maintenance. The press extraction sub-process yields a liquid waste (OMW) and a solid fraction called olive pomace (olive cake) containing olive pulp, skin, stone and water. Finally, olive oil is separated from the water by vertical centrifugation or decanting. This process has many advantages such as cheap equipment, technical simplicity, minimum mixing time and small volume of OMW produced (40 to 60 L/100 kg olives) (Dermeche *et al.*, 2013). However, it also has many disadvantages, such as process discontinuity, contamination of the oil diaphragms, high manpower costs and high load of OMW (Ayoub, 2006).

During the last 20 years, a significant technological progress has been made in olive oil extraction industry. Manufacturers of processing equipment have developed the centrifuge systems (three-phase and two-phase) in order to improve processing efficiency and quality of olive oil. Currently, the majority of traditional olive mills have been replaced by integral centrifuge systems (Torres and Maestri, 2006).

In the centrifuge process, a horizontal centrifuge allows continuous operation. The olive oil production is based on the differences in the density of the olive paste components. The three-phase decanters requires the addition of water to the system, which dilutes out water-soluble compounds and separates the paste into three fractions: A solid residue (olive cake) and two liquid phases (oil and OMW). This process has numerous advantages including, increased production, minimized labor cost, smaller space requirement, better quality of oil, improved process control and ease in automation. But also comes with disadvantages such as higher levels of water and energy consumption, a higher OMW output (80-120 L/100 kg olives) (Albuquerque *et al.*, 2004) and more expensive installation (Roig *et al.*, 2006). In order to reduce the volume of OMW, the two-phase extraction process was developed since 1992. In this type of centrifuge, very small amounts of water are added to dilute the olive paste. Using this method, the olive paste is separated into two phases: Olive oil and wet pomace. The wet pomace generated is a semi-solid by-product (a combination of olive husk and OMW) known as two-phase olive mill wastewater (TPOMW). The main advantage of this process is minimizing the high cost of wastewater handling and disposal. However, the resulting TPOMW (10 L/100 kg olives) is difficult to manage because its pollutant load is more become too wet and concentrated (Di Giovacchino, 1996).

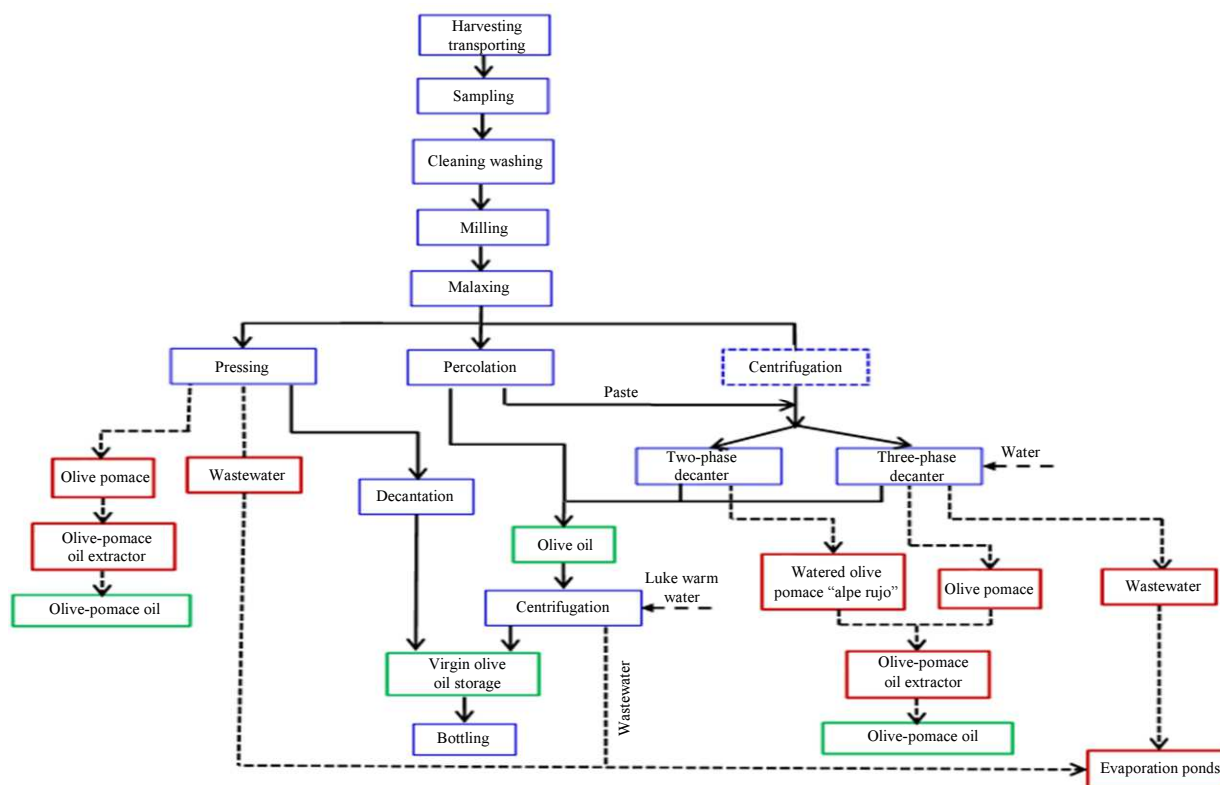


Fig. 1: Main processes of olive oil extraction

### OMW Characterization

#### Physico-Chemical Characteristics of OMW

The physico-chemical composition of OMW is extremely variable as it depends on several factors such as the extraction process, storage time, climatic conditions and cultivation parameters, as well as the type, quality and maturity of the processed olives. OMW typically exhibit intense violet-dark colour, strong odour, considerable saline toxicity reflected by high electric conductivity values and very heavy organic pollutants load. According to McElhatton and Do Amaral (2011), OMW is composed of (88-94%) water, (4-16%) organic compounds and (0.4-2.5%) mineral salts. In addition, OMW is known as recalcitrant effluent, which is characterized by an acidic pH (4-5.5). Table 1 presents a compilation of literature data on physico-chemical characteristics of different OMW according to its origin and olive oil extraction processes. As it can be seen, the pH of OMW is very acidic [3.50-6.00]. Assas *et al.* (2002) explains this high acidity by a self-oxidation reactions and polymerization of phenolic compounds. These compounds convert during the OMW storage before its acidity measured. These reactions result in a change in the initial color of OMW to a very dark black color. Nefzaoui (1991; Markus *et al.*, 2015) also recorded a high value of pH.

The use of this effluent for irrigation can damages soil, excepted calcareous soils where the equilibrium can be established (Nefzaoui, 1991). According to Table 1, it can be observed that the electrical conductivity of OMW varies from one system of trituration to another and it can take values ranging from 0.64 to 45.5 ms/cm and some cases can reach 50 ms/cm (Di Serio *et al.*, 2008). This highest concentration of salt is due to salting practices for the conservation of olive before milling, in addition to the natural wealth of OMW of dissolved minerals (Ouzounidou *et al.*, 2010). OMW is commonly composed of high concentration of Total Suspended Solids (TSS) (peel, pulp, ground, branches and leaves debris) derived from the washing procedure of the olive fruit. Alaoui Slimani *et al.* (2016) accorded this high concentration to the bad separation of OMW from the olive pomace. According to Guadalquivir Hydrographical Confederation 2006-2014, the standard limits of TSS for discharge on suitable soils should not exceed 500 mg/L. for this reason Zanjari and Nejmeddine (2001) indicated that the high TSS content (over 20 g/L), may affect the soil porosity by reducing large pores ( $r > 10 \mu\text{m}$ ) and increasing small pores ( $r < 0.1 \mu\text{m}$ ). On the other hand, Barbera *et al.* (2013) reported that the high quantity of TSS might cause plugging in irrigation systems that will lead to additional costs for farms. Concerning organic matter, OMW has high concentrations of recalcitrant

compounds such as lignins and tannins, phenolic compounds, lipids, protein, long-chain fatty acids and simple and complex sugars (Barbera *et al.*, 2013). The most commonly found sugars in decreasing quantities are fructose, mannose, glucose, sacharose, sucrose and some pentoses (Niaounakis and Halvadakis, 2004).

In addition, OMW presents a strong organic content BOD<sub>5</sub> [0.80-68.71 g/L] (in some cases up to 220 g/L) and COD [4.00-356.11 g/L], both are considered such as a global pollution parameters. On the other hand, these parameters give a good idea of OMW biodegradability. Actually, COD represents the total organic matter in OMW and BOD<sub>5</sub> represents only biodegradable fraction in it. If all the organic matter of OMW were biodegradable, BOD<sub>5</sub> = COD. Many organic molecules present in the OMW are not or very slowly biodegradable such as, the polyphenolic compounds (BOD<sub>5</sub><COD). BOD<sub>5</sub>/COD allows getting a realistic idea of the effluent biodegradability and choosing an efficient method of treatment (biological and/or physico-chemical treatment).

The total solids (TS) represent all mineral and organic particles in OMW. High TS concentrations [0.1-197.00 g/L] can be regarded as a form of pollution (Alba, 1994). According to Aktas *et al.* (2001), the TS content of centrifugation process is approximately two times more than the one in traditional process and it is in suspended form. This behavior is probably due to use of the cloth bags during the pressing process. OMW contains very significant amounts of mineral salts (Table 1), 80% is

soluble (phosphates, chlorides and sulfates) and 20% is insoluble (carbonates and silicates). The most representative elements are potassium (47%), carbonates (21%), phosphate (14%) and sodium (7%) (Tsagaraki *et al.*, 2007). In the wastewater as OMW, phosphorus can be in the form of inorganic salts (Orthophosphates, polyphosphates) and in the form of organic compounds dissolved or attached to suspended solids. The high levels of these elements can lead to eutrophication in storage ponds. As shown in Table 1, the metal charge of OMW is very important, especially of iron, copper, zinc and magnesium (Sellami *et al.*, 2008).

#### Phenolic Content of OMW

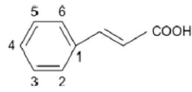
Phenolic compounds include many organic substances that all possess an aromatic ring with one or more substituted hydroxyl groups and a functional side-chain. Natural phenolic compounds include simple molecules, such as phenolic acids and highly polymerized compounds such as tannins. The phenolic compounds in olives are distributed between the olive oil, the solid phase pomace and the aqueous liquor wastewater (OMW). Only 2% of the total phenolic content of the olive fruit remains in the oil phase, while the rest is lost in the solid phase (approximately 45%) and the greatest percent in the OMW (approximately 53%) (Rodis *et al.*, 2002). In the same line, McNamara *et al.* (2008) reported that phenols present in olive stone and pulp tend to be more soluble in the water phase than in oil.

**Table 1:** Physico-chemical characteristics of OMW given by several authors

References	Vlyssides <i>et al.</i> (2004)	Achak <i>et al.</i> (2009b)	Hodaifa <i>et al.</i> (2013)	Belaqziz <i>et al.</i> (2016)	Agabo García and Hodaifa (2017)	Azzam (2018)
OMW origin	Greece	Morocco	Spain	Morocco	Spain	Jordon
Extraction process	Press	3-phase	2-phase	Press	3-phase	3-phase
pH	4.5	5.06	3.50-6.00	4.72	5.38	5.4
EC (ms/cm)	18	6.85	1.50-2.50	45.5	0.64	12.71
COD (g/L)	158.18	70.22	4.00-16.0	356.11	12.24	41.5
Na <sup>+</sup> (g/L)	0.4	0.46	n.d.	2.06	0.005	0.006
K <sup>+</sup> (g/L)	3.77	2.11	n.d.	2.45	0.02	0.02
Ca <sup>2+</sup> (g/L)	0.38	2.11	n.d.	0.24	0.005	0.002
Mg <sup>2+</sup> (g/L)	0.07	n.d.	n.d.	n.d.	n.d.	0.001
Fe (mg/L)	48	n.d.	n.d.	n.d.	23.8	Negligible
Cu (mg/L)	10.5	n.d.	n.d.	n.d.	n.d.	0.94
Mn (mg/L)	18.24	n.d.	n.d.	n.d.	n.d.	n.d.
Cl <sup>-</sup> (g/L)	0.21	1.42	n.d.	4.62	0.05	n.d.
TP (g/L)	17.15	13.45	0.10-1.00	9.37	0.13	0.35
PO <sub>4</sub> <sup>3-</sup> (g/L)	0.87	0.36	n.d.	2.77	n.d.	n.d.
TSS (g/L)	4.51	2.07	2.00-7.00	71	0.07	0.02
TS (g/L)	99.7	20.4	n.d.	197	0.1	n.d.
MM (g/L)	9.69	5.29	n.d.	88	0.04	n.d.
TNK (g/L)	1.15	1.96	n.d.	n.d.	0.04	n.d.
DBO <sub>5</sub> (g/L)	68.71	16.74	0.80-6.00	n.d.	0.35	n.d.
Sugar (g/L)	25.86	0.12	n.d.	n.d.	n.d.	n.d.
proteins (g/L)	28.3	n.d.	n.d.	n.d.	n.d.	n.d.
Density (g/L)	1.05	1.1	n.d.	n.d.	n.d.	n.d.

Chemical Oxygen Demand (COD), Total Phenols (TP), Total Suspended Solids (TSS), Total Solids (TS), Minerals Matters (MM), Total Nitrogen Kjeldahl (TNK), Biological Oxygen Demand (BOD<sub>5</sub>), not determined (n.d.)

**Table 2:** Most abundant phenolic compounds detected in OMW (DellaGreca *et al.*, 2004; Obeid *et al.*, 2007; Rodríguez *et al.*, 2009)

Compound name	MW (g/mol)	Substituent	Structure
<b>Cinnamic acid and derivatives</b>			
Cinnamic acid	148	-	
p-coumaric acid	164	4-OH	
Caffeic acid	180	3,4-OH	
Ferulic acid	194	3-OCH <sub>3</sub> , 4-OH	
Synaptic acid	224	3,5-OCH <sub>3</sub> , 4-OH	
<b>Benzoic acid and derivatives</b>			
Benzoic acid	122	-	
p-Hydroxybenzoic acid	138	4-OH	
Protocatechuic acid	154	3-OH, 4-OH	
Vanillic acid	168	3-OCH <sub>3</sub> , 4-OH	
Veratric acid	182	3-OCH <sub>3</sub> , 4-OCH <sub>3</sub>	
Gallic acid	170	3,4,5-OH	
Syringic acid	198	3,5-OCH <sub>3</sub> , 4-OH	
<b>Tyrosol and derivatives</b>			
Tyrosol	138	4-OH, R-H	
Hydroxytyrosol	154	3,4-OH, R-H	
3,4-Dihydroxyphenylglycol	170	3,4-OH, R-OH	
<b>Other phenol acids and derivatives</b>			
p-Hydroxyphenylacetic acid	152	4-OH	
3,4-Dihydroxyphenylacetic acid	168	3,4-OH	
<b>Flavonoids</b>			
Apigenin	270	R <sub>1</sub> -H, R <sub>2</sub> -H	
Luteolin	286	R <sub>1</sub> -H, R <sub>2</sub> -OH	
Quercetin	302	R <sub>1</sub> -OH, R <sub>2</sub> -OH	
Rutin	610	R <sub>1</sub> -OH, R <sub>2</sub> -O-rutinose	
<b>Ecoiridoids</b>			
Oleuropein	540	R-O-glucose	
Oleuropein aglycone	378	R-OH	

Phenolic compounds can be grouped into various classes according to the structural characteristics of their carbon skeletons. As shown in Table 2, the main classes are:

- *Derivatives of cinnamic acid* (p-coumaric acid, caffeic acid, ferulic acid and synaptic acid)
- *Derivatives of benzoic acid* (p-hydroxybenzoic acid, protocatechuic, vanillic acid, veratric acid, gallic acid and syringic acid)

Lesage-Meessen *et al.* (2001; Albuquerque *et al.*, 2004) showed that the phenolic profiles (caffeic acid, ferulic acid, p-coumaric acid, vanillic acid), identified by HPLC, are similar for two-phase or three-phase oil extraction processes, but the amounts of individual phenols, with the exception of vanillic acid, were higher for the two-phase system.

Derivatives of tyrosol (hydroxytyrosol and 3,4-dihydroxyphenylacetic acid).

Leouifoudi *et al.* (2014) reported that the tyrosol and hydroxytyrosol are the main phenolic compounds found

in OMW. Other phenolic compounds were also detected in OMW (Table 2), such as flavonoids (apigenin, luteolin, quercetin, rutin) and secoiridois (aglycone, oleuropein). Oleuropein is the most abundant phenolic compound in olive leaves and fruits and is responsible for the characteristic bitterness of olive fruit (Soler-Rivas *et al.*, 2000). It is degraded gradually into elenolic acid and hydroxytyrosol by an esterase during the mechanical olive oil extraction process (Visioli *et al.*, 2002). For this reason, hydroxytyrosol is considered as the most abundant phenol in OMW.

The phenolic content of the OMW is reported to fluctuate between 0.1-17.15 g/L, depending on various factors; olive cultivar, soil composition, ripeness of the fruit, storage condition prior to extraction and processing techniques. The climate and the geographical conditions have also been shown to alter phenolic content in OMW (Dermeche *et al.*, 2013; Obied *et al.*, 2005). Several authors (Quaratino *et al.*, 2007; Hanifi and El Hadrami, 2008; Doula *et al.*, 2012; Hanafi *et al.*, 2013; Papadaki *et al.*, 2018) reported that phenolics are responsible of the high toxicity of OMW and they are the

main compounds that suppress germination and may also lead to significant reductions in root growth. Moreover, the typical brownish-C color of this effluent has been explained by the presence of polymeric phenols that display a lignin-like structure and constitute its most resistant fraction (Hamdi, 1993).

From this analysis, it is clear that the wastewater streams produced during olive oil production have considerable different characteristics that, along with the final quality requirements, should be taken into account when selecting the most appropriate treatment strategy.

### *Important Strategies for OMW Treatment*

OMW is characterized by a strong offensive smell and a high degree of organic matter mainly comprising phenolic compounds, polysaccharides, sugars, proteins, nitrogenous organics, tannins and fats. Moreover, OMW has been found to be very phytotoxic and it also inhibits microbial activity because of the biocidal activity of the polyphenols contained (Roig *et al.*, 2006; Khoufi *et al.*, 2009; Yalılı Kılıç *et al.*, 2013; Amor *et al.*, 2015). For these reasons, the management and treatment of OMW have been considered as the main goal of the majority of research studies in this field.

The most common practice for the management of OMW includes the use of evaporation ponds and direct spreading in landfills and/or on soil. While evaporation ponds offer a good way of reducing the liquid portion of this effluent, they do not contribute to the reduction of its toxicity. They simultaneously impart an odor problem to the areas where such waste is stored and cause pollutant infiltration to groundwater and insect proliferation (Jarboui *et al.*, 2010; Michael *et al.*, 2014). Moreover, the direct spreading of raw OMW on agricultural lands has been thoroughly investigated during the last decades (Morisot, 1979; Rozzi and Malpeli, 1996; Marques, 2001; Di Bene *et al.*, 2013; Barbera *et al.*, 2014; Chaari *et al.*, 2015; Belaqqiz *et al.*, 2016; Keren *et al.*, 2017; Aharonov-Nadborny *et al.*, 2018) and it has been proved that it represents an alternative inexpensive technique compared to filtration-percolation (Achak *et al.*, 2009b) and coagulation-flocculation (Achak *et al.*, 2008). Many researchers have studied the result of the OMW application on soil and crops (Mekki *et al.*, 2006; Di Bene *et al.*, 2013; Belaqqiz *et al.*, 2016) and they found that it exerts beneficial and negative effects. Beneficial effects are related to its high nutrient concentration, especially potassium and its potential to mobilize soil ions (Roig *et al.*, 2006). Negative effects are associated with its high mineral salt content, low pH and the presence of phytotoxic compounds, especially polyphenols (Roig *et al.*, 2006). Therefore, excessive application into the soil may exceed the toxicity tolerance of soil microorganisms.

In recent years, many other management options have been employed to reduce OMW phytotoxicity in order to

reuse it for agricultural purposes (El-Abbassi *et al.*, 2011) and to make it suitable to be treated in conventional treatment facilities (Dhaouadi and Marrot, 2008). The main management options proposed can be classified as: (i) Physical processes (e.g., evaporation, distillation, combustion, centrifugation, filtration, pyrolysis, etc.), (ii) membrane filtration and separation processes (e.g., microfiltration-MF, ultrafiltration-UF, nanofiltration-NF, reverse osmosis-RO, etc.), (iii) oxidation and advanced oxidation processes (e.g., ozonation, photo-Fenton oxidation, TiO<sub>2</sub> photocatalysis, electrochemical oxidation, wet air oxidation, etc.), (iv) biological processes (e.g., aerobic active sludge, anaerobic digestion, etc.) and (vi) physic-chemical processes (e.g., adsorption, electrocoagulation, coagulation-flocculation, etc.).

Physical processes involve the concentration of organic and inorganic contents of OMW by evaporation of the water. The natural evaporation of OMW in ambient air with the use of solar energy in evaporation ponds or storage lakes (lagoons) has much lower energy costs and it is a simple technique (Jarboui *et al.*, 2009). In the hot period of the year, OMW is collected and stored in ponds where it undergoes natural evaporation until becoming completely dry. However, the large area needed, bad odor due to the anaerobic fermentation of the waste, infiltration and proliferation are the negative properties of evaporation (Roig *et al.*, 2006). Several distillation processes, which are already used in desalination and in the chemical and food industry, have been tested such as, vacuum, multiple effect and flash evaporation (Nitro-Atomizer, 1992; Leonzio, 2017). According to Niaounakis and Halvadakis (2004), although these processes are claimed to reduce significantly the volume of waste (70-75%) great differences exist in bibliography concerning their effectiveness, because it depends on many factors such as extraction process, olive ripening and especially storage time of the waste. The main drawback of distillation processes is related to the post-treatment and disposal of the produced emission. In addition, the distillate output and condensate produced contain a high level of volatile compounds such as alcohols, polyphenols and volatile acids. These compounds make the condensate too acidic (pH 4-4.5) and high values of COD (>3 g/L) and BOD (>4 g/L) (Niaounakis and Halvadakis, 2004). Combustion and pyrolysis processes have the advantages of reducing the volume of waste and providing the possibility of energy recovery, but they are radical and destructive techniques that eliminate any possibility of further use of OMW and they require expensive facilities and entail possible emission into the atmosphere of toxic substances. Centrifugation and filtration increase the pH and conductivity of the effluents and remove organic matter through phase separation and exclusion respectively. As shown, the simple physical processes are not able, if applied alone,

to reduce the organic matter and the toxicity of OMW to acceptable limits (Paraskeva and Diamadopoulos, 2006). Several researchers have proposed the combination of physical processes with other technologies. Usually a combination of physical processes or often a combination of physical processes coupled with coagulation/flocculation (Achak *et al.*, 2008) or adsorption technologies leads to more efficient organic matter removal. Application of sedimentation followed by centrifugation and then filtration showed that, after centrifugation, COD was reduced by 21% and BOD by 15% (Al-Malah *et al.*, 2000). Additional filtration did not remove any COD, but a further 16% reduction in BOD was observed. The combination of centrifugation and ultrafiltration provided the reduction of pollution caused by the wastes and the selective separation of some useful products that are present (fats, sugars, polyphenols, etc.). In contrast, approximately 90% COD reduction was achieved (Turano *et al.*, 2002). The combination of electrocoagulation and sedimentation proposed by Khoufi *et al.* (2007) allowed a COD reduction and decoloration of about 43 and 90% respectively.

Membrane processes, such as MF, UF, NF and RO, have been proposed to obtain effluent streams from OMW of acceptable quality for safe discharge in the environment, tree or land irrigation, or even for recycling and reuse in the olive mill facilities (Cassano *et al.*, 2011; Ochando-Pulido *et al.*, 2014; Zagklis *et al.*, 2015; Sanches *et al.*, 2016; Kontos *et al.*, 2016; 2018; Ioannou-Ttofa *et al.*, 2017). Most of these studies indicated that membrane processes exhibit high selectivity values required to achieve high water quality standards. They are more cost-effective than other conventional processes, require less area and can replace several unit treatment processes by a single one. However, the implementation of membrane technologies in OMW treatment suffer from various drawbacks, such as the membrane fouling, the energy cost and the membrane replacement (Miguel and Pulido, 2016; Ioannou-Ttofa *et al.*, 2017). In addition, the concentrate generated contains high levels of refractory organic pollutants and inorganic salts which needs further treatment before its disposal in the environment.

Advanced Oxidation Processes (AOPs) are based on the creation of very reactive species, such as hydroxyl radicals (HO<sup>•</sup>). According to previous studies, several organic pollutants can be decomposed partially or totally into other less toxic and more degradable substances by oxidation based on UV light or other processes. Generally, only a small fraction of the radiant energy is absorbed by the organic molecules, causing decomposition of small percentage of the pollutant molecules. AOPs have been extensively studied for the OMW treatment through ozonation, photo-Fenton oxidation, TiO<sub>2</sub> photocatalysis, electrochemical oxidation and wet air oxidation. Their efficiency was found to be significant (Gernjak *et al.*,

2004; Canizares *et al.*, 2007; 2009; Chatzisyneon *et al.*, 2009; Mert *et al.*, 2010; Belaid *et al.*, 2013; Michael *et al.*, 2014; Ioannou-Ttofa *et al.*, 2017; Davididou *et al.*, 2018). Although, AOPs manage a great COD reduction, but their operating costs are considerably high. It could be said that chemical oxidation emerges as a suitable alternative, when biological degradation is not applicable.

Biological processes use microorganisms to degrade the chemicals present in OMW. They are divided into aerobic and anaerobic processes according to the type of the microflora used (McElhatton and Do Amaral, 2011). Most aerobic biological processes, technologies and microorganisms have been tested for the treatment of OMW, aimed at reducing organic load, dark color and toxicity of the effluent (Beltrán-Heredia *et al.*, 2001; Roig *et al.*, 2006; Taccari and Ciani, 2011; Pelendridou *et al.*, 2014; Tekerlekopoulou *et al.*, 2017). In general, aerobic bacteria appeared to be very effective against some low-molecular-mass phenolic compounds due to their fast process kinetic and high removal rates, but they are relatively ineffective against the more complex polyphenolics responsible for the dark coloration of OMW (Ragazzi and Veronese, 1973; Olori *et al.*, 1990; Morillo *et al.*, 2009; Ioannou-Ttofa *et al.*, 2017). In addition, aerobic processes can operate efficiently only if the concentration of the feed is relatively low (1 g COD/L). High concentration can be tolerated only if the plant operates at a long hydraulic retention time and/or with high recycle ration (Rozzi and Malpeli, 1996; Tsagaraki *et al.*, 2007). Also, the aerobic treatment of concentrated wastewater yields huge volume of excess secondary aerobic processes to reach the required removal efficiency such as phenolic compounds and lipids. For all the above reasons, aerobic processes are unsuitable for direct and efficient treatment of OMW. Many researchers suggest that they can be used as pretreatment or posttreatment steps to increase the efficiency of the main treatment processes used (Azbar *et al.*, 2008; Justino *et al.*, 2009; Pelendridou *et al.*, 2014; González-González and Cuadros, 2015; Tekerlekopoulou *et al.*, 2017). Anaerobic treatment consists of a series of microbiological processes that convert organic compounds into biogas that can be used for energy production. However, OMW characteristics such as, the acidic pH, low alkalinity and low nitrogen content, as well the presence of lipidic and phenolic fractions, make this wastewater potentially toxic for anaerobic treatments (Boari *et al.*, 1984; Hamdi, 1991a; 1991b; Angelidaki and Ahring, 1992; Beccari *et al.*, 1998; Beltrán-Heredia *et al.*, 2001; Marques, 2001; Sampaio *et al.*, 2011). Therefore, some form of pretreatment and post treatment to eliminate phenolic compounds from OMW, apart from simple dilution, is usually necessary in order to reduce its toxicity and to permit the occurrence of microbial fermentation. In this regard, many authors directed their attention to a more promising alternative such as, co-

digestion of OMW with other substrate like agro-livestock (Gonçalves *et al.*, 2012a; 2012b; Sampaio *et al.*, 2011; Kougias *et al.*, 2014), physical chemical pretreatment (Filidei *et al.*, 2003; Ginos *et al.*, 2006; Ruggeri *et al.*, 2015) and Fenton's reagent process (Amor *et al.*, 2015; Maamir *et al.*, 2017).

Various physico-chemical processes such as adsorption, electrocoagulation and coagulation/flocculation have also been employed for the OMW treatment. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Al-Malah *et al.*, 2000; Zümriye and Jülide, 2001; Achak *et al.*, 2009a; Frascari *et al.*, 2016; Yangui and Abderrabba, 2018; Azzam, 2018). Adsorption also does not lead to the harmful substances and the organic sorbents can be used as fuel for power generation or as ferment substrate (Ahmad *et al.*, 2011). The most popular and widely used adsorbent material for treatment of OMW is activated carbon due to their excellent adsorption abilities for organic pollutants (Galiatsatou *et al.*, 2002; Azzam *et al.*, 2004; Aliakbarian *et al.*, 2015; Yangui and Abderrabba, 2018). In fact, many researchers have shown that activated carbon is an effective adsorbent for organic compounds removal, especially for phenolic compounds. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent (Babel and Kurniawan, 2003; Aktas and Cecen, 2007). Due to these facts, the search for a low cost and easily available adsorbent has led many investigators to search more economic and efficient techniques to use agricultural waste origin, along with industrial by-products as adsorbents (banana pith, orange peel, wheat straw, sawdust, powdered waste sludge, wheat shells, wheat bran and hen feathers). Many of these adsorbents have been tested and proposed for phenolic compounds removal (Sathishkumar *et al.*, 2008; Achak *et al.*, 2009a; 2014; Pathak *et al.*, 2015; Ali and Saeed, 2015; Kong *et al.*, 2016; Gupta and Gupta, 2016; Ingole *et al.*, 2017). Coagulation/flocculation processes have also been employed in OMW treatment due to its simplicity, effectiveness and low energy consumption (Kissi, 2002; Jaouani *et al.*, 2005; Achak *et al.*, 2008; Michael *et al.*, 2014; Enaime *et al.*, 2018). Additional agent coagulants are used in these processes in order to destabilize the suspended and colloidal matter of OMW and form an insoluble solid that can be removed easily from the waste. Destabilization of these colloids can be achieved either by reducing or increasing pH (neutralization) or by the addition of a precipitate-inducing agent (precipitation/occlusion). The effectiveness of coagulation process depends on the coagulating agent used, the dosage, the solution pH, the presence of divalent cations and destabilizing anions such as bicarbonate, chloride and sulfate ions (Duan and Gregory, 2003; Lin and Lee, 2013) and the nature of the

organic compound present in OMW (Dominguez *et al.*, 2007). In generally, coagulation process is effective in removing high molecular weight organics (complex phenolic compounds), but less so in removing smaller molecular weight fractions (Nissinen *et al.*, 2001). Flocculation process is usually more effective with higher molecular weight polymers. Adding excessive amount of polymer results in entire particle surface becoming coated with polymer, such that no sites are available to 'bridge' with other particles (Ebeling *et al.*, 2006; Sarika *et al.*, 2005). The flocs structure may differ as a function of physical-chemical conditions, as the flocs formed at the lower pH and dose are reported to be denser and less porous than those formed at higher pH and dose (Guigui *et al.*, 2002). In order to increase the effectiveness of elimination of suspended particles and insoluble substances from OMW, the combined coagulation and flocculation processes has also been studied (Ginos *et al.*, 2006; Chong, 2012; Iakovides *et al.*, 2014; Hattab and Bagane, 2016; Enaime *et al.*, 2018). Despite the simplicity, effectiveness, low energy consumption and efficiency of the coagulation, flocculation and their combination, these techniques still exhibit several disadvantages such as the need for pH adjustment before or after treatment, the sensitivity to temperature changes, the need for higher dosages, the sensitivity to OMW characteristics and composition, as well as the excessive sludge produced. To the best of our knowledge, there were few works in the literature concerning studies of phytotoxicity from sludge through the coagulation/flocculation process alone. From the above considerations, it can be concluded that the coagulation/flocculation treatment of OMW cannot be achieved without combination with another treatment process in which to further degrade the organic compounds to lower level. Sarika *et al.* (2005) studied the pretreatment of OMW by flocculation with cationic and anionic polyelectrolytes. The majority of the tested flocculants completely removed the TSS and reduced considerably the COD and the BOD<sub>5</sub>. In another study, combination of coagulation, acid cracking and Fenton-like process could result the phytotoxicity of final OMW to decrease (Yazdanbakhsh *et al.*, 2015). Stoller and Chianese (2006a) proposed a treatment process comprising an initial coagulation-flocculation with aluminium sulphate or aluminium hydroxide, followed by batch UF and NF in series with composite thin-film spiral-wound membranes. The two pretreatment processes yielded similar COD and BOD<sub>5</sub> rejection efficiencies. Alver *et al.* (2015) applied coagulation with FeSO<sub>4</sub> · 7H<sub>2</sub>O on three-phase OMW, observed a COD abatement equal to 51.4%, as well as 38.6% of Total Oxygen Carbon (TOC) and 52.1% of total nitrogen removal. According to Rizzo *et al.* (2008), the reclamation of OMW by coagulation with a natural organic coagulant, chitosan, followed by advanced oxidation processes including Photocatalysis (PC),



Fenton (F) or photo-Fenton (PF) has been studied. The optimum removal of TSS (81%) was achieved by chitosan coagulation at a pH value of 4.3 upon 400 mg/L coagulant dose. In a recent study, Enaime *et al.* (2018) investigated a new combined process, comprising filtration of raw OMW on two successive Olive Stone (OS) filters followed by a coagulation–flocculation. The results showed that the use of OS filter leads to a higher removal of TSS (82.5%) and fatty matter (73.8%) from the raw OMW and a depletion of total phenolic compounds (11.3%) and COD (23.2%).

### *Removal of Phenolic Compounds from OMW by Coagulation Process*

The coagulation process is a very important step in wastewater treatment, which is widely used, due to its simplicity and cost-effectiveness. Basically, coagulation is a physico-chemical process that facilitates the destabilization of fine particles (colloids) from wastewater to form a floc that can be easily filtered. This destabilization phenomenon includes various mechanisms such as charge neutralization, entrapment, adsorption and complexation with the coagulant's metal ions into insoluble aggregates (Henderson *et al.*, 2006). As far as phenolic compounds concerned and considering the olive oil extraction processes and origin of OMW, as well the structural characteristics of polyphenols carbon skeletons in term of number and position of acid functions (COOH and/or OH) on the aromatic cycle, the combined removal mechanisms will substantially differ (Duan and Gregory, 2003; Crittenden *et al.*, 2005). The result will therefore be a variable removal efficiency of coagulation and the formation of flocs with different sizes and structures (Jarvis *et al.*, 2006; Sharp *et al.*, 2006), which constitutes a serious challenge for the application of coagulation in the OMW treatment.

In addition, many researchers report that the efficiency of coagulation process to remove organic matter and phenolic compounds from OMW, depends mainly to coagulant's type and dosage, pH, mixing condition and temperature on the one hand and phenolic compounds properties including particle size, charge and hydrophobicity (Korshin *et al.*, 2009; Iakovides *et al.*, 2014) and the presence of anionic ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{3-}$ ,  $\text{Cl}^-$ ) and cationic ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{2+}$ ) minerals (Lin and Lee, 2013; Hecini and Achour, 2014), on the other hand.

### *Inorganic Metal Coagulant*

#### *Effect of Coagulant Dosage*

The conventional chemicals that are widely applied in OMW treatment, are mineral coagulants based on aluminum and iron. The aluminum coagulants include aluminum sulfate, aluminum chloride and sodium aluminate. The iron coagulants include ferric sulfate, ferrous sulfate and ferric chloride (Bahadori *et al.*, 2013). In

some cases, a combination of dual metal coagulants is also applied (Achak *et al.*, 2008). The addition of these cationic coagulants results in colloidal destabilization, as they specifically interact with and neutralize the negatively charged colloids. Recently, considerable interest and attention have been paid to preparing pre-hydrolysed metal-ion coagulants (inorganic polymers), based on either aluminum (poly-aluminum chloride) (Hu *et al.*, 2015; Wang *et al.*, 2017), or ferric iron (polyferric sulfate) (Zouboulis *et al.*, 2008) and/or, a mixed polymeric coagulant (polyaluminum-iron-sulfate) (Zhu *et al.*, 2005). These have been shown to perform better in some cases, in comparison with conventional coagulants such as aluminum sulfate or ferric sulfate (Jiang and Graham, 1996). Several studies of metal/polymer for removal of organic matter and phenolic compounds from OMW are reported in this review.

Achak *et al.* (2008) addressed the treatment of OMW with aluminum sulphate. The results showed a slight removal of phenolic compounds (32%) and Chemical Oxygen Demand (COD 33%) at optimum dosage (1.5 g/L) without correction of pH (pH = 4.55). These results were in agreement with Sbai and Loukili (2015) who concluded that at the same conditions of pH and dosage, the removal of phenolic compounds and COD from diluted OMW (10% v/v) did not exceed 32% and 42% respectively (Table 3). Kissi *et al.* (2001) also observed that the application of 1.9 g/L of aluminum sulphate and 2.72 g/L of ferric chloride at pH solution (4.20) allowed only 18% and 14% of phenolic compounds reduction and 35% and 30% of COD reduction respectively. In another study, the use of acid cracking (9.5 g/L) as coagulant at acidic pH2 showed a low removal of phenolic compounds (37%) and COD (46%) (Mert *et al.*, 2010). In a similar line, Ginos *et al.* (2006) tested the efficiency of various inorganic coagulants, involving magnesium sulphate, ferrous sulphate and ferric chloride applied to OMW, in term of organic matter and phenolic compounds reduction. Despite the variation of coagulants and their concentrations (1-4 g/L), the results showed an ineffectiveness removal of these compounds (Table 3). Ginos *et al.* (2006) showed that the application of 1 g/L of magnesium sulphate led to about only 8% and 38% of COD and phenolic compounds reduction respectively at the pH of original sample (pH 5.2). The authors observed that an increasing in the magnesium concentrations from 1 to 4 g/L had practically no effect on organic matter removal. In addition, ferric chloride at 1 g/L led to about 50% and 10% COD and phenolic compounds reduction, respectively; these values were reduced to 7% and 10%, when ferric chloride increases to 2g/L. while further increase to 3 g/L gave no removal of organic compounds. Jaouani *et al.* (2005) also observed that the application of ferric chloride (20 g/L) at solution pH 3.1 allowed only 44% and 34% of phenolic compounds and DCO reduction respectively. The results obtained by Iakovides *et al.* (2014) showed that the removal of phenolic compounds from OMW with

application of calcium chloride (5g/L) and magnesium chloride (7g/L) at solution pH 4.4 did not exceed 10% and 8% respectively. According to these results, at the pH of initial solution (acidic pH), the reduction of phenolic compounds and COD from OMW was very low regardless to the nature and dosage coagulants used.

Basically, the coagulation mechanism can be achieved with one, or a combination of the following mechanisms, after the addition of an inorganic coagulant agent (Duan and Gregory, 2003; Crittenden *et al.*, 2005):

- Electrostatic coagulation
- Adsorptive coagulation
- Precipitation coagulation

In electrostatic coagulation, the positively charged metal coagulants approach to the negatively charged colloids via electrostatic interaction. In the diffusive layer around the colloid, the positively charged ions accumulate and destabilizing the colloid. In adsorptive coagulation, particles are adsorbed to the positively charged hydrolyses products (i.e.,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})^{2+}$  or  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})^{2+}$ ). These products mainly occur at low pH 5.5. The optimal pH-range for adsorptive coagulation with iron salts is between 6 and 8, the optimal pH-range with aluminum salts is narrower and is about 7. Adsorptive coagulation is a rapid process. Within

one second, positively charged hydrolyses products are formed and are adsorbed to the negatively charged particles. Characteristics of adsorptive coagulation mechanism are that dosing is proportional to the removal of organic matter and that restabilization can occur after an overdose of coagulant. Indeed, the colloids will be positively charged and repulsion of the particles will take place. In precipitation coagulation or sweep coagulation, colloids are incorporated into neutral hydroxide ( $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$ ) flocs and precipitated. These metal hydroxide compounds are heavy, sticky and larger (Edwards and Amirtharajah, 1985; Lee *et al.*, 2014).

In our case, the most probable mechanism for the removal of organic matter and phenolic compounds from OMW is electrostatic and adsorptive coagulation. This explanation is in accordance with the studies of Zhang *et al.* (2003; Bacha and Achour, 2015), who reported that at acidic pH (pH 4), the coagulation mechanisms were ensured by mainly charge neutralization and complex reaction or chelate reaction between organic matter and dissolved aluminum species ( $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})^{2+}$ ) dominant at this pH. In line with this observation, Achak *et al.* (2008) noticed that at acidic pH, the low elimination of phenolic compounds from OMW could be attributed to the absence of the flocculating form of the coagulant such as  $\text{Al}(\text{OH})_3$ , which would confine the neutralized species.

**Table 3:** Selected research studies on the removal of COD and phenolic compounds from OMW by coagulation process using metal coagulants and lime

OMW origin	Phenols (g/L)	DCO (g/L)	Coagulant	Dose (g/L)	Phenols %	DCO %	pH	Ref
Morocco (3-phase)	1.42	71.56	$\text{Al}_2\text{SO}_4$	1.5	23	33	4.55	Achak <i>et al.</i> (2008)
			$\text{Al}_2\text{SO}_4$	1.5	41	40	7	
			$\text{Ca}(\text{OH})_2$	20	75	43	12	
			$\text{Al}_2\text{SO}_4 + \text{Ca}(\text{OH})_2$	1.5+20	54	38	12	
Morocco (3-phase diluted 10%)	0.89	27.16	$\text{Al}_2\text{SO}_4$	1.9	22	42	4.5	Sbai and Loukili (2015)
Morocco (3-phase)	4.2	122	$\text{Al}_2\text{SO}_4$	2.72	18	35	4.2	Kissi <i>et al.</i> (2001)
			$\text{FeCl}_3$	9.5	14	30	4.2	
			$\text{Ca}(\text{OH})_2$	4.12	37.5	53.6	7.5	
Greece (n.d.)	3.5	61.1	$\text{FeCl}_3$	9.58	10	50	4.5	Ginos <i>et al.</i> (2006)
			$\text{MgSO}_4$	7	38	8	5.2	
			$\text{FeSO}_4$	5	20	10	4.6	
			PAC	1	<10	<10	4.7	
			$\text{Ca}(\text{OH})_2$	60	67	<10	11.4	
Greece (3-phase)	1.9	40.9	$\text{FeCl}_3$	n.d.	10	43	1.5	Iakovides <i>et al.</i> (2014)
			$\text{MgCl}_2$		8	23	4.4	
			$\text{CaCl}_2$		10	25	4.4	
Turkey (3-phase)	3.8	150	$\text{FeCl}_3$	2.5	26	57	7	Gursoy-Haksevenler and Arslan-Alaton (2014)
			$\text{Ca}(\text{OH})_2$	6.7	30	56	11	
			$\text{Ca}(\text{OH})_2 + \text{Ac}$	6.7	47	63	11	Jaouani <i>et al.</i> (2005)
Iran (3-phase)	3.3	101	$\text{FeCl}_3$	20	44	34	3.1	Yazdanbakhsh <i>et al.</i> (2015)
			$\text{CaO}$	20	71	37	12	
Iran (3-phase)	n.d.	n.d.	$\text{FeCl}_3$	3	91.3	91.2	6	Aktas <i>et al.</i> (2001)
	n.d.	n.d.	A.c $\text{H}_2\text{SO}_4$	n.d.	30	46	2	
Turkey (traditional)	2.5	65.7	$\text{Ca}(\text{OH})_2$	25	73	41	12	Boukhoubza <i>et al.</i> (2009)
Morocco (3-phase)	2.08	120.3	$\text{Ca}(\text{OH})_2$	40	73	20	12	Lolos <i>et al.</i> (1994)
Greece (3-phase)	0.45	12.2	$\text{CaO}$	15	70	55	12	Alaoui Slimani <i>et al.</i> (2016)
Morocco (3-phase)	2.1	64	$\text{CaO}$	7.5	65	40	10	
			$\text{CaO} + \text{FeCl}_3$	7.5+1.5	75	58	n.d.	

determined; PAC: Poly-aluminium chloride; A.c: Acid cracking

### Effect of pH

The most important parameter affecting the effectiveness of organic matter removal is pH (Qin *et al.*, 2006). When the metal coagulant is added to the water, the hydrolysis reactions generate dissolved monomeric metal species and metal hydroxide precipitates and the distribution of those species depends on the pH of minimum solubility and total inorganic metal concentration. According to the bibliography, the hydrolyzing pH range for aluminum and iron (the most widely used) is between 5.5-7.7 and 4.5-7 respectively. If the pH is decreased below the optimal value, positively-charged dissolved Al or Fe species are generated ( $\text{Al/Fe(OH)}_2^+$  and  $\text{Al/Fe(OH)}^{2+}$ ). In case of a pH increase above the optimum, more negatively-charged Al/Fe species are formed ( $\text{Al/Fe(OH)}_4^-$  and  $\text{Al/Fe(OH)}_5^{2-}$ ) (Pernitsky and Edzwald, 2006). Noting that, away from the optimal range, especially at pH 3 and 11, the destabilization potential will be highly reduced and thus the small particles will not be able to aggregate into large flocs and the organic matter reduction will be very slight (Wang *et al.*, 2016). At optimum pH, the solubility is minimal and the main bulk of the coagulant is converted to solid floc particles, as shown below (Bratny, 2007):

*Stable colloid + Inorganic metal coagulant* → *Unstable colloid Flocs*  
(negatively – charged) (positively – charged) (optimum pH)

According to Greenland (1971), the solid floc formation can be obtained by two main types of mechanisms: Electrostatic adsorption and ligand exchange or complexation with the hydroxyl groups on the surface of  $\text{Al/Fe(OH)}_3(\text{s})$  (Lefebvre and Legube, 1993).

As far as phenolic compounds is concerned, Achak *et al.* (2008) reported on the one hand, that the coagulation-based removal process is more efficient when more positively charged Al species are generated, because the phenolic compounds are negatively-charged. On the other hand, the authors attributed the increase of abatement of polyphenols from 23% to 41% at pH range 6.31-7.08 (optimum pH) to the change of coagulation mechanism. It passed from charge neutralization-precipitation mechanism to adsorption mechanism. These results were in agreement with Yazdanbakhsh *et al.* (2015). In the same line, regarding the removal mechanisms of Al-based coagulants, Gregory and Duan (2001) reported that the positively-charged hydroxide precipitates act as destabilizing agents of organic compounds. The destabilization phenomenon occurs through the adsorptive deposition of the hydroxides on the surface of the negatively-charged particles, resulting in the charge neutralization of those particles. Besides, the positively charged metal-based precipitates could neutralize dissolved organic compounds, which lowers

their solubility and promotes their precipitation (Pourrezaei *et al.*, 2011). Rezeg and Achour (2005) studied the removal of gallic acid from water using sulphate aluminum at pH range (6-7). They concluded that the significant reduction of gallic acid can be explained by two mechanisms: Electrostatic charge neutralization by attraction of the partially dissociated organic compounds and mixture of the positively charged metal coagulant ( $\text{Al(OH)}_2^+$ ,  $\text{Al(OH)}^{2+}$ ) and amorphous  $\text{Al(OH)}_3$  and complexation with the hydroxyl groups on the surface of  $\text{Al(OH)}_3(\text{s})$ .

In another study, Gursoy-Haksevenler and Arslan-Alaton (2014) studied the removal of phenolic compounds from OMW using 2.5 g/L of  $\text{FeCl}_3$  at optimum pH (pH = 7). Contrary to previous results, authors showed that the removal of phenolic compounds was insignificant (26%). This behavior may be explained by the competitive complexation of the  $\text{OH}^-$  as ligand with metal (iron or aluminum). Therefore, the hydrolysis reaction to  $\text{Al(OH)}_3$  or  $\text{Fe(OH)}_3$  forms could be promoted at the expense of complexation reaction of organic matter. In the same way, Julien *et al.* (1994) reported that the reaction between  $\text{OH}^-$  and ferric pieces interferes with the formation of ferric-organism complexes and thus organic compounds removal efficiencies get lower.

Other research studies reported that the elimination of phenolic compounds by coagulation using inorganic coagulants depend on the number and the position of acid functions (COOH and/or OH) on the aromatic cycle. According to Lefebvre and Legube (1993), the type of acid group seems to play a significant role on the removal percentage. The results obtained with 17 aromatic compounds (acids and/or phenolic compounds) coagulated at pH 5.5 and at different doses (15, 30 or 40 mg/L) using iron-based coagulant allowed to define four classes of aromatic compounds regarding their behavior during iron coagulation. Aromatics bringing with only one acidic group (COOH or OH) or more (two or three) non-adjacent were not removed, such as benzoic acid, p-hydroxybenzoic acid, phenol, protocatechuic acid, vanillic acid, veratric acid, tyrosol and p-Hydroxyphenylacetic acid (Table 2). However, aromatics bringing at least two adjacent acidic groups (ortho position) were more removed such as hydroxytyrosol, 3,4-dihydroxyphenylglycol, acid gallic and salicylic acid (Table 2). This result is in accordance with the works of Rezeg and Achour (2005) who found that the application of aluminum sulphate allowed an important removal of gallic acid (72.58%) and pyrogallol (53.58%) compared with phloroglucinol (10%) (functions acid non-adjacent). Hecini and Achour (2014) also indicated that the efficiency of the coagulation using aluminum sulphate on the removal of organic compounds with phenolic functions (pyrogallo and phloroglucinol) depends on the number and position of phenolic groups on the molecules. The removal of some

phenolic compounds (benzoic acid, phenol, naphtol, salicylique acid, etc.) by coagulation and adsorption on performed floc at pH 5.4 using iron and at pH 6.8 using aluminum showed a perfect performance for compounds with at least two acidic functions (Julien *et al.*, 1994).

### Effect of Mineral Salts

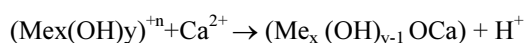
An important aspect to be taken into account when studying the removal efficiencies of phenolic compounds from olive mill effluent is the influence and effect of mineral salts. As shown in Table 2, OMW contains very considerable amount of mineral anions ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{3-}$ ,  $\text{Cl}^-$ ). These anions can affect the elimination efficiency of phenolic compounds from OMW. According to Clément *et al.* (1983), the removal of organic matter and widening of the optimum zone of the coagulation pH was mainly attributed to the affinity of the mineral anion towards the aluminum sulphate. Many studies (Afoufou *et al.*, 2007; Hecini and Achour, 2014) showed that the removal efficiency of organic compounds with phenolic functional groups (pyrogallol and phloroglucinol) from mineralized waters using aluminum sulphate depends mainly the presence of sulphate, phosphate and chloride, who are considered such concurrent ligands for hydroxyl ions. On the other hand, the inhibitory effect of mineral anions could be explained by the adsorption of these anions on the hydroxides by lowering the surface charge or even, to the limit, making it change its sign (Hecini and Achour, 2014), as shown below:



In another research studies, the mineral cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{2+}$  appear to improve the removal efficiencies of phenolic compounds and optimize the pH range for coagulation. Afoufou *et al.* (2007) addressed that the removal of organic compounds with phenolic functional groups from mineralized water seemed very significant compared with distilled water. This result was attributed to bridging effect of cationic metal and negatively charged colloids. This approach is in correlation with the studies done by Bernhardt *et al.* (1986; Wais-Mossa and Mazet, 1991).

In order to explain the removal efficiencies of organic compounds with phenolic functional in the presence of cationic metals three mechanisms were carried out by to Afoufou *et al.* (2007):

- Adsorption of cations (i.e.,  $\text{Ca}^{2+}$ ) on hydroxide flocs resulting in the creation of new adsorption sites:



- Formation of insoluble complex ( $\text{Ca}^{2+}$  - organic matter)

- The bridging effect of  $\text{Ca}^{+2}$  between the anionic forms of organic compounds and the negatively charged species of the coagulant at higher pH value

### Acid Cracking Coagulant

The reduction of phenolic compounds from OMW by coagulation process using acid cracking ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) has been investigated by numerous studies. Azbar *et al.* (2008) tested the treatment of OMW by coagulation with acid cracking at pH less than 2. The results showed no significant removal of COD (15%) and total phenol (4%). Kestioglu *et al.* (2005) found the same result, acid cracking resulted only in 38% COD and 23% total phenol removal at pH 2.0. In another study, the elimination of COD and phenolic compounds at acidic pH (pH 2) did not exceed 46% and 37% respectively (Mert *et al.*, 2010; Madani *et al.*, 2015). In another comparative study, the effect of acid cracking was investigated at pH 2.0 and allowed a low removal of COD (46%) and total phenol (37%) (Gursoy-Haksevenler and Arslan-Alaton, 2014; 2016). Recently, Gocer *et al.* (2017) also observed the same finding, a low removal of COD (46%) and total phenol (38%) with acid cracking  $\text{HCl}$  was detected.

From the above studies, it was find that removal of phenolic compounds and COD from OMW by coagulation with acid cracking was not efficient. For this reason, several studies showed that the usage of dual coagulants (acid cracking and inorganic metal coagulants) has benefits over the sole use of acid cracking and inorganic coagulants. These benefits are mostly related to the increase of effectiveness removal of phenolic compounds and organic matter and reduction of the inorganic coagulant dosage while producing larger, denser and stronger flocs (Lee *et al.*, 2014).

Mert *et al.* (2010) studied the treatment of OMW using various combinations (acid cracking+ $\text{FeCl}_3$ , acid cracking+ $\text{FeSO}_4$  and acid cracking+ $\text{Al}_2(\text{SO}_4)_3$ ) with varying dosage under varying pH conditions. They concluded that  $\text{FeCl}_3$  dosage of 4 g/L at pH 9 resulted in best COD and phenol removal for OMW. Removal efficiencies increased from 46 to 67% for COD and from 37 to 72% for phenol when the OMW was first subjected to acid cracking.  $\text{FeSO}_4$  at pH 10 and 4 g/L dosage, the removal increase from 37 to 69% for phenol and from 46 to 66% for COD. While COD removal at a  $\text{Al}_2(\text{SO}_4)_3$  dosage of 5 g/L increase from 37 to 63% for phenol and from 46 to 64% for COD at pH 8. Application of acid cracking at pH 2 alone and combined with  $\text{Al}_2(\text{SO}_4)_3$  (6 g/L) and  $\text{FeCl}_3$  (3 g/L) at optimum pH 8 was suggested by Kestioglu *et al.* (2005). The results showed a very important reduction of COD and phenolic compounds for combined treatments.  $\text{FeCl}_3$  resulted in a 95% of COD and 90% of total phenol. On the other hand, 94%

of COD and 91% of total phenol were observed in experiments using  $Al_2(SO_4)_3$ ,  $FeSO_4$ ,  $Al_2(SO_4)_3$  and  $FeCl_3$  were tested by Azbar *et al.* (2008), under predetermined optimum pH conditions after acid cracking with varying dosages (from 0.5 to 6 g/L) to compare the results and to choose the best for further biological treatment. The results reported that  $FeSO_4$  was the best chemical agent in terms of removing total phenol (53%).

From the above considerations, it can be concluded that acid cracking alone is an inefficient way of removing COD and total phenol from OMW. However, the usage of dual coagulants (acid cracking + inorganic metal coagulants) removal more effectively organic matter. On the other hand, it was reported that during the coagulation process with acid cracking + iron-based coagulants is more effective in removing COD and phenolic compounds in comparison with acid cracking + aluminum based coagulants. Similarly, the results from other studies showed that iron-based coagulants are more effective in removing organic matter, due to the higher charge density of iron coagulants, compared to the aluminum-based counterparts (Hahn *et al.*, 2002). According to Fitzpatrick *et al.* (2004; Xiao *et al.*, 2010), the main reason for such difference is the formation of more and larger flocs during coagulation process involving iron coagulants, than those formed during aluminum-based coagulation.

### *Inorganic Polymeric Coagulants*

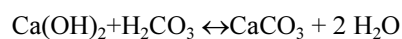
As previously reviewed, the mineral coagulants based on aluminum and iron are one of the most widely used coagulants in conventional wastewater treatments. These coagulants reported a significant removal of COD and phenolic compounds from OMW at optimum pH, in addition of their low cost, ease of use and availability. However, the application of these mineral substances is quite limited nowadays and has been reduced due to numerous disadvantages. As reported by many studies, its usage would cause two important environmental consequences (i) an increase in metal concentration in the treated water (which may have human health implications); (ii) production of large (toxic) sludge that is difficult to dehydrate (Ward *et al.*, 2006; Alaoui Slimani *et al.*, 2016; Zahrma *et al.*, 2017). In order to minimize the drawbacks of inorganic coagulants, many factors have been taken into consideration to find the alternative and reduce the dosage of the harmful inorganic coagulants. Therefore, new types of reagents based on pre-hydrolysed forms of aluminium and iron have been developed (Ginos *et al.*, 2006; Bratby, 2007). In this regard, the most studied and applied pre-hydrolyzed metal-ion coagulants are Poly-Aluminum Chloride (PAC) (Ginos *et al.*, 2006; Wang *et al.*, 2017; Hu *et al.*, 2015), Poly-Ferric Chloride (PFC) (Cao *et al.*, 2011), Poly-Ferric Sulfate (PFS) (Zouboulis *et al.*,

2008), as well as various composite inorganic coagulants such as Polymeric Aluminum Ferric Sulfate (PAFS) (Zhu *et al.*, 2005), Polymeric Ferric Zinc Sulfate (PFZS) (Wei *et al.*, 2016) and Polymeric Phosphate Aluminum Chloride (PPAC) (Zheng *et al.*, 2011). In comparison with inorganic coagulants, some of the advantages of these polymers are: Lower coagulant dose requirements, increase in the rate of separating the solid and water phases arising from larger agglomerate sizes, efficiency at low temperatures (hydrolysing metal coagulants perform less well at low temperatures), a smaller volume of sludge, a smaller increase in the ionic load of the treated water, a less pH-dependent process and a reduced level of aluminium in the treated water. Polymer-based products also improve settleability and increase the floc toughness (Renault *et al.*, 2009). According to Cheng and Chi (2002) and Wei *et al.* (2016), the main organic matter removal mechanisms using inorganic polymeric coagulants were generally attributed to adsorption, entrapment, complexation, charge neutralization and to a lesser extent.

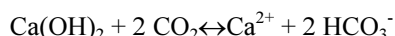
In previous studies, Jiang and Graham (1996; Jiang *et al.*, 2016) reported that these inorganic polymeric coagulants showed better removal capacities toward organic matter from wastewaters at neutral pH, in comparison with coagulants such as aluminum sulfate or ferric sulfate (Nandy *et al.*, 2003). These results are in accordance with the studies of Ginos *et al.* (2006; BaiChuan *et al.*, 2010). Ginos *et al.* (2006) revealed that the application of PAC (1 g/L) at pH 4.7 did not show any significant reduction of COD and phenolic compounds (<10%). According to Nandy *et al.* (2003), this behavior may be due to the low solution pH since PAC is particularly effective for pH values above neutral. In the same line, BaiChuan *et al.* (2010) found that when the coagulation condition is acidic (pH 4), the coagulants (poly-ferric silicate sulphate, poly-ferric sulphate) tested did not perform well in organic compounds removal. This behavior may be explained by the fact that the carboxyl groups of organic compounds are difficult to be hydrolyzed due to the high concentration of  $H^+$ . Furthermore,  $H^+$  could react with organic molecules, which competed with the complex reaction between ferric pieces and organic compounds (Tipping *et al.*, 1990).

### *Potential of Lime based Coagulant*

The two forms of lime mostly used in wastewater treatment as coagulant are quicklime (CaO) and hydrated lime ( $Ca(OH)_2$ ), although its action and behavior are different from that of mineral coagulants and inorganic polymeric coagulants. When lime is added to the water, the pH increases, resulting in the formation of carbonate calcium from the natural alkalinity in the water:



The increase in carbonic acid concentration and calcium added of the lime results in the precipitation of calcium carbonate (CaCO<sub>3</sub>). The calcium carbonate crystals enmesh colloidal particles in the same way as aluminum or iron flocs. When lime is used as a coagulant, the pH has to be lowered in order to stabilize the water chemically. Carbon dioxide is normally used for this purpose, wherein the following reaction is involved:



Moreover, apart from its positive economic impact in terms of chemical cost and energy requirement, lime was effectively considered by several studies to remove the suspended, colloidal material and mainly phenolic compounds.

Ginos *et al.* (2006) investigated the effectiveness of using lime as coagulant agent in removing of phenolic compounds from OMW. The results demonstrated that phenolic compounds content decrease considerably (67%) at solution pH 11.4 and at 60 g/L of Ca(OH)<sub>2</sub>. The comparison of effectiveness phenolic compounds removal using Ca(OH)<sub>2</sub> and mineral coagulants (FeCl<sub>3</sub>, MgSO<sub>4</sub> and FeSO<sub>4</sub>) showed in addition to a higher removal efficiency of lime, these materials may be advantageous over lime because (i) the concentration needed is considerably lower than that with lime to achieve comparable removals, (ii) the change of solution pH following lime addition is far greater than that with other materials and (ii) lime generates greater volume of sludge.

In another work, Achak *et al.* (2008) studied the removal of organic matter from OMW using a range of lime between 5 and 30 g/L. At optimum conditions, i.e., 20 g/L of lime and solution pH 12, the phenolic compounds and COD removal were about 75% and

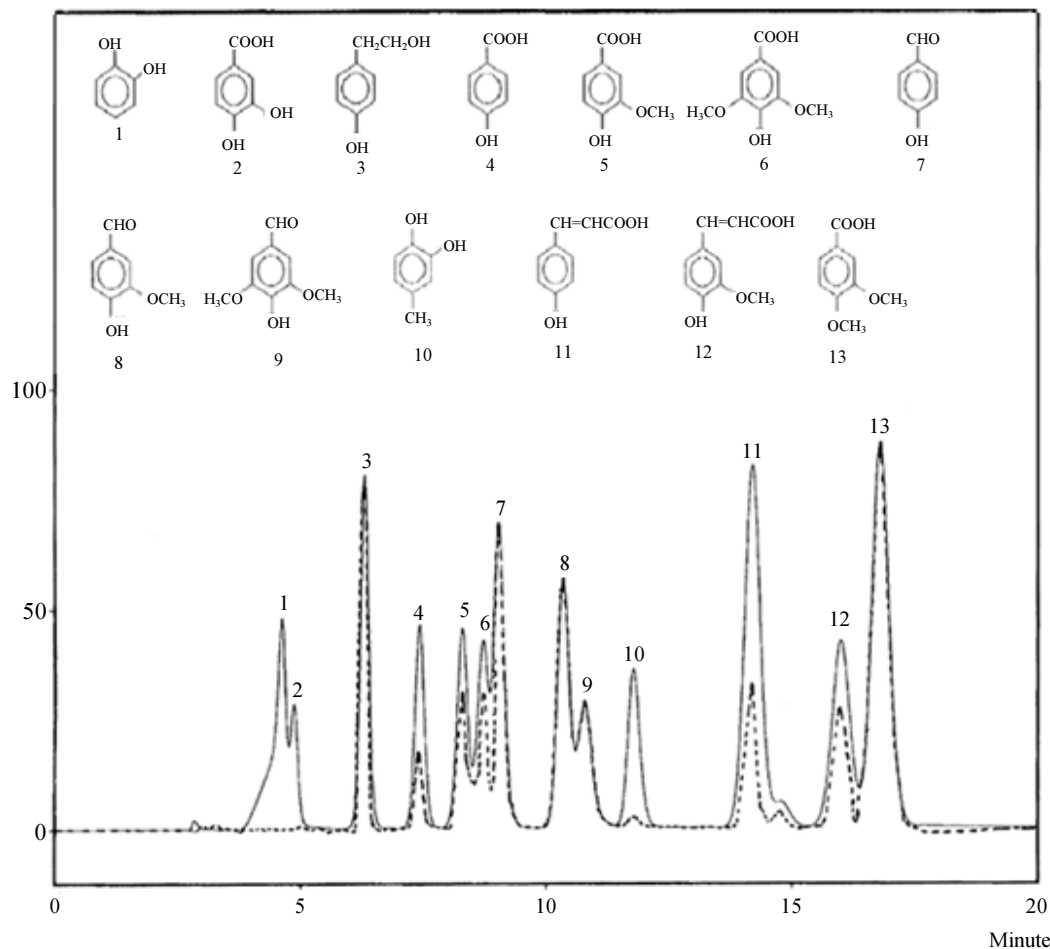
43% respectively. The authors concluded that the entrapment of suspended and colloidal particles by lime is carried out through the sweep coagulation mechanism. On the other hand, the calcium carbonate formed at basic pH acts as a weighting agent by increasing the density of the settle able particles, thereby enhancing their settlement.

In other studies, the impact of lime pre-treatment on phenols removal for seventeen different olive mill effluent was evaluated. The precipitation with lime (15 g/L) allows the elimination of 65% of polyphenols and only 28% of volatile phenols (Aktas *et al.*, 2001). The phenolic compounds could be removed totally or partially and some of them were not affected as shown in Fig. 2. According to Aktas *et al.* (2001), this behavior was accorded to the structures and number of acid functions (COOH and/or OH) on the aromatic cycle, it was observed that the substances with two phenolic groups in the molecule (catechin) which are highly phytotoxic were totally removed, the substances which contain both phenolic and carboxyl groups (vanillic acid, syringic acid) were adsorbed partially and the substances which have only one phenolic or carboxyl group (tyrosol, veratric acid) were not affected by lime. This finding was in accordance with results obtained by Jaouani *et al.* (2005; Boukhoubza *et al.*, 2009).

Once again, the treatment of the effluent with increasing concentrations of CaO showed that the minimal amount of lime was sufficient for effective removal of the phenols (71%) in the range pH of 12-12.4 (Jaouani *et al.*, 2005). The comparison of the results obtained with lime and FeCl<sub>3</sub>, allowed authors to conclude that lime was more effective to eliminate phenols from the OMW (71% against 44% for FeCl<sub>3</sub>), particularly for high molecular weight fraction.

**Table 4:** Selected research studies on the removal of COD and phenolic compounds from OMW by coagulation process using acid cracking alone and combined with metal coagulants

OMW origin	Phenols (g/L)	DCO (g/L)	Acid cracking+coagulant concentration (g/L)	Phenols %	DCO %	pH	Ref.
Extraction process							
Turkey (3-phase)	3.7	128.1	Acid cracking H <sub>2</sub> SO <sub>4</sub>	31	53	1.3	Kiliç <i>et al.</i> (2009)
Turkey (3-phase)	0.2	38.07	Acid cracking HCl	46	38	1.5	Gocer <i>et al.</i> (2017)
			Acid cracking H <sub>2</sub> SO <sub>4</sub>	66	17	2	
Turkey (3-phase)	5.58	115	Acid cracking H <sub>2</sub> SO <sub>4</sub>	37	46	2	Mert <i>et al.</i> (2010)
			Acid cracking+FeCl <sub>3</sub> (4.0)	72	67	9	
			Acid cracking+FeSO <sub>4</sub> (4.0)	69	66	10	
			Acid cracking+Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (5.0)	63	64	8	
Turkey (3-phase)	3.8	150	Acid cracking H <sub>2</sub> SO <sub>4</sub>	39	58	2	Gursoy-Haksevenler and Arslan-Alaton (2014)
			Acid cracking+FeCl <sub>3</sub> (2.5)	45	61	7	
			Acid cracking+ FeCl <sub>3</sub> (2.5)	47	62	3	
			Acid cracking+ Ca(OH) <sub>2</sub> (6.7)	47	63	11	
Turkey (3-phase)	9.68	185.6	Acid cracking H <sub>2</sub> SO <sub>4</sub>	23	38	2	Kestioglu <i>et al.</i> (2005)
			Acid cracking+Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (6.0)	91	94	8	
			Acid cracking+FeCl <sub>3</sub> (3.0)	90	95	8	
Turkey (3-phase)	4.03	97.6	Acid cracking H <sub>2</sub> SO <sub>4</sub>	4	15	2.2	Azbar <i>et al.</i> (2008)
			Acid cracking+FeCl <sub>3</sub> (6.0)	19	27	7	
			Acid cracking+ Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (6.0)	27	47	7	
			Acid cracking+ Fe <sub>2</sub> SO <sub>4</sub> (6.0)	53	30	7	



**Fig. 2:** The HPLC chromatograms of artificial phenolic mixture before (—) and after (-) lime treatment. (1) catechin, (2) protocatechuic acid, (3) tyrosol, (4) p-hydroxybenzoic, (5) vanillic acid, (6) syringic acid, (7) p-hydroxybenzaldehyde, (8) vanillin, (9) syringaldehyde, (10) 4-methylcatechol, (11) p-coumaric acid, (12) ferulic acid and (13) veratric acid (Aktas *et al.*, 2001)

In the same way, Kissi *et al.* (2001) showed that the utilization of lime could be considered as a very effective, economical and high performance depurative mean of OMW pre-treatment, mainly if it takes into account its important role in the odor's elimination and its availability at low prices in countries like Morocco.

Alaoui Slimani *et al.* (2016) reported that the addition of CaO (7.5 g/L) allowed the adjustment of the acidic pH 4.6 to a basic pH 10. The neutralization by lime leads the transformation of phenols to phenates with the formation of  $C_6H_5O^-$  ions (Macheix *et al.*, 1990). The authors indicated a significant elimination of polyphenols (68%) and COD (40%). Similar results were reported by Aktas *et al.* (2001).

In addition, to the simplicity and effectiveness of lime application in reduction of phenolic compounds in the OMW, a large amount of the fatty components, which prevent the evaporation of water by forming an impermeable film on the surface of the wastewater in the ponds, can be removed. After lime application, the pH

was brought to 12, some toxic or hard-to-degrade constituents of the OMW were eliminated and the remaining pollutants could be treated biologically after neutralization. It is also known that application of lime shortens the required retention time in settling lagoons and sludge resulting from storage could be either composed or mixed with olive mill solids wastes before disposal or other operations and uses. In the same line, many authors indicated that the recycle of sludge could be a viable alternative. In this regard, the innovative use of sludge for example as a fuel (Van der Bruggen *et al.*, 2003), a soil conditioner (Nigam *et al.*, 2000; Pearson *et al.*, 2004), a combustion matter (Alaoui Slimani *et al.*, 2016) or a building material (Balasubramanian *et al.*, 2006) has been studied by several researchers.

In order to reduce the large amount of sludge produced and enhance the removal efficiency of organic matter from OMW by lime, the combination of lime and inorganic coagulants have been developed by many studies. The effects of coagulation process using acid

cracking combined with  $\text{Ca}(\text{OH})_2$  were examined by Gursoy-Haksevenler and Arslan-Alaton (2014). For this purpose, 6.7 g/L  $\text{Ca}(\text{OH})_2$  was added to OMW at pH 11.0.  $\text{Ca}(\text{OH})_2$  precipitation carried out without acid cracking resulted in 56% COD, 30% phenols removals, whereas for combined treatment, removal efficiencies were 63% COD and 47% phenols (Table 4). Alaoui Slimani *et al.* (2016) evaluated the evolution of removal of COD and phenolic compounds from OMW after treatment with CaO and  $\text{FeCl}_3$ . According to their results, the addition of  $\text{FeCl}_3$  as an inorganic coagulant allowed an important removal of organic matter. The reduction of COD and polyphenols is respectively 58 and 75%.  $\text{FeCl}_3$  allowed the passage of the dissolved form of pollutants to an insoluble particulate form that can be easily retained by simple decantation and gives settleable floc (Yaakoubi *et al.*, 2010). In another study, Achak *et al.* (2008) revealed that the successive addition of  $\text{Ca}(\text{OH})_2$  to 1.5 g/L of  $\text{Al}_2\text{SO}_4$  raised the pH at 10 g/L of  $\text{Ca}(\text{OH})_2$  and induced a removal of COD (38%) and polyphenols (54%) at a dose of 20 g/L of  $\text{Ca}(\text{OH})_2$ . The successive addition of aluminium sulphate to 15 g/L of  $\text{Ca}(\text{OH})_2$  involved only a slight variation of the pH and allowed the elimination of COD (36%) and polyphenols (35%) at a dose of 3 g/L of  $\text{Al}_2\text{SO}_4$ . Contrary to previous studies, the comparison between the two coagulant combinations indicated that  $\text{Al}_2\text{SO}_4$  combined with  $\text{Ca}(\text{OH})_2$  did not show any significant enhance in removing of COD and phenolic compounds, the best coagulation was obtained by application of 20 g/L of lime used alone.

#### *Removal of Phenolic Compounds from OMW by Direct Flocculation Process*

As previously reported, the coagulation process using inorganic coagulants and acid cracking is not always perfect in removing COD and phenolic compounds from OMW, due generally to the formation of small flocs when coagulation takes place or generation of fragile flocs which break up when subjected to physical forces. It is not only necessary to overcome these problems but also to improve the process in order to obtain good quality effluent and rapid sedimentation of the flocs formed. To do so, direct flocculation process was proposed and investigated by several studies (Sarika *et al.*, 2005; Ginos *et al.*, 2006; Iakovides *et al.*, 2014; Hodaifa *et al.*, 2015; Lourenço *et al.*, 2017). Recently, many synthetic organic polymers have been used as the main flocculants such as polyacrylamide, polyacrylic acid, poly (diallyl dimethyl ammonium chloride) (poly DADMAC), cyanoguanidine, polyamine etc. and they are classified into four forms: Positively charged (cationic), negatively charged (anionic), amphoteric (contains both cationic and anionic groups) and neutral (non-ionic). Ionic polymers or “polyelectrolytes” of

various structures are usually used as coagulant aids to enhance the formation of larger floc in order to improve the rate of sedimentation (Bratby, 2007; Iakovides *et al.*, 2014). The effect on the efficiency of flocculation process depends mainly on polymer weight, structure (linear versus branched), amount of charge, charge type and composition. Table 5 shows the main characteristic of several polyelectrolytes used. The nature of the charges is the main parameter that will have significant effect followed by molecular mass and charge density (Lee *et al.*, 2014). In addition, according to Bohuslav Dobias (2005), the parameters that are measured to justify flocculation efficiency include settling rate of flocs, sludge volume produce, amount of pollutants removal and turbidity or supernatant clarity.

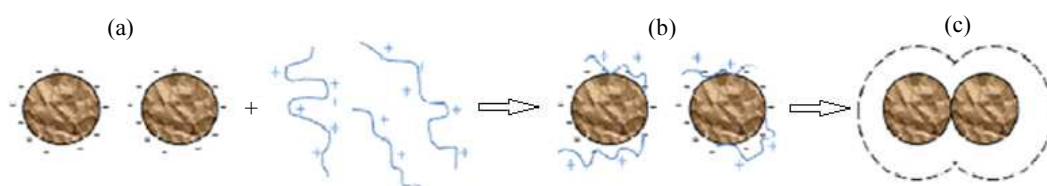
In practice, many studies are promoting the application of synthetic organic polymers, as primary coagulants in water and wastewater treatment system, more than metal-based coagulants (Bolto *et al.*, 1998; Bolto and Gregory, 2007; Matilainen *et al.*, 2011; Iakovides *et al.*, 2014; Hodaifa *et al.*, 2015), because they offer significant advantages in flocculation process. Polymeric flocculants are easy to handle and immediately soluble in aqueous systems, do not affect the pH of the medium and it is possible to synthesize them with various functions (positive, negative or neutral charge) with various molecular mass and charge density where it can be used to produce a good settling performance at relatively low cost (Ahmad *et al.*, 2008). The concentration of polymers used for direct flocculation is workable at any pH condition: Acidic, neutral and basic medium (for example polyamines are effective over a wide range of pH). This behavior is in contrast with the coagulation process where the effective treatment was obtained by precipitation of metal hydroxides at adjusting pH. In addition, the concentrations needed of flocculants are only a few milligrams per liter and generate less volume of nonhazardous sludge because the flocs formed are dense, large, compact and closely packed. Concerning the treatment cost, Lee *et al.* (2014) noted that direct flocculation cost is at least 3.6 times lower than coagulation-flocculation treatment due to larger volumes of phyto-toxic sludge produced from coagulation-flocculation process.

For the case of phenolic compounds and COD removal from OMW, various polyelectrolytes were mostly applied (Table 6). Ginos *et al.* (2006) studied six polymers of polyacrylamide, which have all a high molecular mass, for treatment of OMW. Four cationic polymers allowed a considerably removal of phenolic compounds (54-58%) and COD (10-30%) at a common concentration of 287 mg/L. However, two anionic polymers did not show any significant remove of these compounds. According to Lee *et al.* (2014), the main coagulation mechanism for organic matter and phenolic



compounds (negatively charged) removal using cationic polymers is charge neutralization. In general, neutralization charge takes place when the flocculants and the adsorption site are of opposite charge. The flocculation results of the reduced surface charge of the particles and hence a decreased electrical repulsion force between colloidal particles (mainly phenolic compounds), which allows the formation of Van Der Waals force of attraction to encourage initial aggregation of colloidal and fine suspended materials to form micro flocs (Fig. 3).

In research of Hodaifa *et al.* (2015), five organic polymers (three cationic and two anionic) have been used to achieve the separation of phases (liquid treated-sludge) at different concentrations (1-1000 mg/L). The results showed a slight reduction of total phenols (11.3-25.1%) and COD (5.6-20.4%). In this study, authors concluded that the elimination of the total phenolic compounds by flocculants was instantaneous in the case of all cationic flocculants. However, the removal of total phenols was proportional to the dose of flocculants used.



**Fig. 3:** Flocculation mechanism by charge neutralization (a) particles negatively charged and cationic polymers (b) adsorption of polymers onto the surface of particles (c) flocculation

**Table 5:** Characteristics of several polyelectrolytes

Polyelectrolytes	Chemical formula	Charge	Molecular mass	Solubility in water	Biodegradability
Polyacrylamide	$\left[ \text{CH}_2 - \underset{\substack{  \\ \text{C}=\text{O} \\   \\ \text{NH}_2}}{\text{HC}} \right]_n$	Cationic	Medium	Complete	Not
Polyacrylic acid	$\left[ \text{CH}_2 - \underset{\substack{  \\ \text{C}=\text{O} \\   \\ \text{O}^- \text{Na}^+}}{\text{HC}} \right]_n$	Anionic	Medium	Complete	Not
poly(DADMAC)	$\left[ \text{CH}_2 - \underset{\substack{  \\ \text{N}^+ \\   \\ \text{H}_3\text{C} \quad \text{CH}_3}}{\text{C}} \right]_n \text{Cl}^-$	Cationic	High	Complete	No data
Guanidine	$\text{H}_2\text{N} - \text{C}(\text{NH}) = \text{NH} - \text{C} \equiv \text{N}$	Cationic	Low	Complete	No data
Polyamine	$\left[ \text{N}^+ (\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_2 \right]_n \text{Cl}^-$	Cationic	Medium	Complete	Not
Polyethylenimine	$\left[ \text{N}^+ (\text{H})_2 - \text{CH}_2 - \text{CH}_2 - \text{N}^+ (\text{H})_2 \right]_n \text{Cl}^-$	Cationic	Medium	Complete	Not
Polyallylamine	$\left[ \text{CH}_2 - \underset{\substack{  \\ \text{NH}_2}}{\text{CH}} \right]_n$	Cationic	High	Complete	Not

**Table 6:** Direct flocculation process with polyelectrolyte for the COD and phenolic compounds removal

OMW origin	Phenols (g/L)	DCO (g/L)	Flocculant	Charge	Dose (g/L)	Phenols %	DCO %	Ref.
Extraction process								
Greece (3-phase)	n.d	89.2	FLOCAN 23	Anionic	3	n.d	38	Sarika <i>et al.</i> (2005)
			FO-4700	Cationic	3	n.d	32	
			FO-4490	Cationic	3	n.d	28	
			FO- 43.50	Cationic	3	n.d	28	
Greece (3-phase)	n.d	57.1	FLOCAN 23	Anionic	3	n.d	20	
			FO-4700	Cationic	3	n.d	40	
			FO-4490	Cationic	3	n.d	22	
			FO- 43.50	Cationic	3	n.d	55	
Greece (2-phase)	n.d	4.5	FLOCAN 23	Anionic	0.033	n.d	33	
			FO-4700	Cationic	0.066	n.d	70	
			FO-4490	Cationic	0.033	n.d	62	
			FO- 43.50	Cationic	0.17	n.d	18	
Greece (3-phase)	3.5	61	FO-4700	Cationic	0.28	56	20	Ginos <i>et al.</i> (2006)
			FO-4490	Cationic	0.28	58	30	
			FO- 43.50	Cationic	0.28	56	30	
			FO- 4190	Cationic	0.28	54	10	
Greece (3-phase)	3.5	61	AN 934	Anionic	0.28	30	20	
			FLOCAN 23	Anionic	0.28	50	28	
Spain (2-phase)	0.17	24.3	Floc CS49	Cationic	1	17	16	Hodaifa <i>et al.</i> (2015)
			Floc CS45	Cationic	1	24	17	
			Floc CS51	Cationic	0.3	12	5.6	
			QG2001	Anionic	0.1	17	20.4	
Greece (3-phase)	1.98	40.93	Nalco 9913	Anionic	0.4	11	13	
			PDADMAC	Cationic	2	35	46	
Greece (3-phase)	2.99	82.45	PEI	Cationic	5	15	35	Iakovides <i>et al.</i> (2014)
			PAA	Cationic	1.5	40	36	
Portugal (3-phase)	n.d	11.8	PAH	Cationic	3	21	32	Lourenço <i>et al.</i> (2017)
			60MC	Cationic	0.05	n.d	46	
			60MP	Cationic	0.05	n.d	44	
			60M1SC	Cationic	0.05	n.d	47	
			60M2SC	Cationic	0.05	n.d	34	

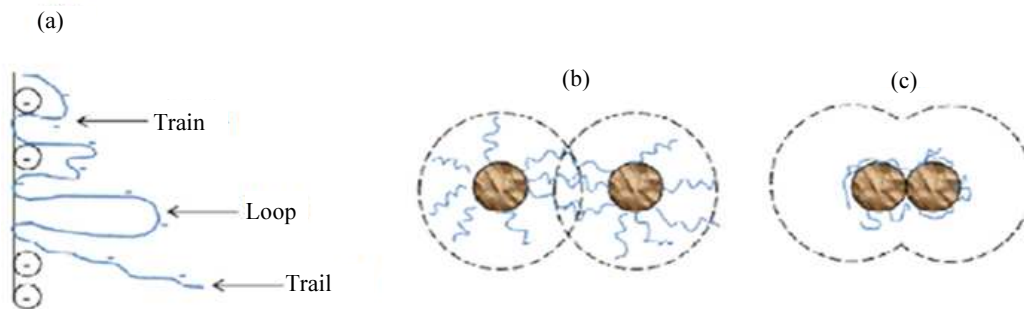
PDADMAC: Polydiallyl Dimethyl Ammonium Chloride; PEI: Polyethylenimine; PAH: Polyallylamine Hydrochloride; PAA: Polyallylamine

In another study, the application of various polyelectrolytes (PDADMAC, polyethylenimine (PEI), polyallylamine hydrochloride (PAH) and polyallylamine (PAA)) in removing of organic load of olive oil industry wastewater gave encouraging results (Iakovides *et al.*, 2014). The polyelectrolytes used were chosen according to their high molecular mass and their positive charge. The results showed that the utilization of PDADMAC (2000 mg/L), PAH (3000 mg/L), PEI (5000 mg/L) and PAA (1500 mg/L) allowed 46%, 32%, 35% and 36% COD and 35%, 21%, 15% and 40% phenolic compounds removal respectively. Iakovides *et al.* (2014) concluded that PDADMAC is suitable for phenolic compounds removal, whereas PAA is suitable for COD removal. The removal mechanism of phenolic compounds from OMW using PDADMAC and PAA may be due to polymer bridging. In general, polymer bridging with longer chains (high molecular weight) is more effective than a one with shorter chains (low molecular weight) according to Razali *et al.* (2011). Indeed, when the polyelectrolytes is in contact with a colloidal particle (mainly phenolic compounds), some of its functional groups are adsorbed on the surface of the particle while other surfaces of the polymer remains unoccupied (Fig. 4). This behavior allows polyelectrolytes to be extended into

solution and produce loops and tails to promote bridging of flocs (Fig. 4).

Sarika *et al.* (2005) studied the treatment of three different olive oil processing effluents by means of direct flocculation using four cationic and two anionic polyelectrolytes. Although most of them were found capable of removing considerably the concentration of COD, without altering solution pH, One of the cationic polyelectrolyte appears to be the most promising flocculant concerning the treatment of olive mill effluent from three-phase by about 55% COD reduction.

Recently, Lourenço *et al.* (2017) studied the development of new, hydrophobically modified, flocculants directed to oily effluents application. Four cationic polyelectrolytes (60 Mc, 60 MP, 60 M1SC and 60 M2SC) were synthesized using two different health-friendly formulations and applied as low dosage flocculation agents in the pre-treatment step for OMW. This study revealed that the hydrophobic modification improves noticeably the flocculation performance of cationic polyelectrolytes in the treatment of OMW. In the best conditions, it was possible to achieve 47% COD removal with only 53 mg/L of flocculant. Contrary to previous studies, encouraging results were obtained after addition of only 13 mg/L of modified flocculants.



**Fig. 4:** Flocculation mechanism by bridge formation (a) adsorption of polymer onto the surface of particles (b) polymer bridging between particles (aggregation) (c) flocculation

#### *Removal of Phenolic Compounds from OMW by Coagulation-Flocculation Process*

Coagulation-flocculation is a chemical water treatment process where the cation inorganic salts are commonly used as coagulants and synthetic organic polymers are usually employed as flocculants (Michael *et al.*, 2014; Lourenço *et al.*, 2017; Sillanpää *et al.*, 2018). Coagulation tends to overcome the factors that promote particles stability and form agglomerates or flocs. Flocculation is the process of whereby destabilized particles, or particles formed as a consequence of destabilization, are induced to come together, make contact and thereby form large(r) agglomerates.

As previously reported, the coagulation process is not always perfect as it may result in small flocs when coagulation takes place or produce fragile flocs, which break up when subjected to physical forces. Also, in direct flocculation process, the majority of synthetic organic polymers used are resistant to biodegradation, which is usually extremely slow (Bolto and Gregory, 2007; Brostow *et al.*, 2009) and their application is mostly limited to organic-based wastewater with high concentration of suspended and colloidal solids (Lee *et al.*, 2014). For these reasons, there is an increasing demand to reduce dosage of the harmful inorganic coagulants and organic flocculants and to improve the process to removal organic load from OMW. In this respect, many studies tried to investigate the combination of coagulation and direct flocculation processes in removing COD and phenolic compounds from OMW. According to Radoiu *et al.* (2004), the use of flocculants not only can increase the density and the solidity of the flocs formed, it also can reduce the consumption of coagulants and increases the reliability of the work and the throughput capacity of the treatment plant.

As presented in Table 7, many studies have proved that the addition of a polymeric flocculants to an inorganic coagulants showed better removal where it was effective in the reduction of environmental concerned parameters (COD and phenolic compounds), reduce the amount of coagulant used and thus reduced the cost of the coagulation/flocculation process (Sarika *et al.*, 2005;

Ginos *et al.*, 2006; Pelendridou *et al.*, 2014; Michael *et al.*, 2014; Iakovides *et al.*, 2014; Papaphilippou *et al.*, 2013; Ioannou-Ttofa *et al.*, 2017).

Iakovides *et al.* 2014 reported that the combination of calcium hydroxide (20 g/L) as coagulant and PDADMAC (1.25 g/L) as flocculant exhibited the best results, up to 76% and 56% in terms of phenolic compounds and COD reduction respectively. According to the authors, the explanation of this behavior might be the high pH value (pH 13) of solution, which leads to their destruction.

The treatment of two different OMW units (W1, W2) by means of coagulation-flocculation using Polyaluminum Chloride (PAC)/FLOCAN 23-20 and Aluminum Sulphate (ASM)/Praestol 2240 was investigated by Pelendridou *et al.* (2014). The results demonstrated that the use of combination of PAC/FLOCAN 23-20 is advantageous over ASM coagulation with anionic polyelectrolyte Praestol 2240. The maximum removal of COD and phenolic compounds corresponded to a concentration of 4 g/L of PAC and 0.01 g/L of FLOCAN 23-20 was 36% and 45% respectively. While the addition of ASM at various concentrations had practically no effect on COD and phenolic compounds removal. Pelendridou *et al.* (2014) reported that the one possible reason for the non-stable behavior of ASM is its chemical structure. Specifically, the presence of sulfate ions ( $\text{SO}_4^{2-}$ ) in the solution can lead to the partial sorption of the some sulfate ions in the Stern layer. On the other hand, the different coagulant concentration demand for W1 (4 g/L) and W2 (2g/L) using PAC/ FLOCAN 23-20 combination lies primarily in the wastewater composition as W1 has a high organic content than W2 (Pelendridou *et al.*, 2014).

Papaphilippou *et al.* (2013) investigated the combination of  $\text{FeSO}_4$  (6.67 g/L) as coagulant and FLOCAN 23 (0.28 g/L) as flocculant. They stated that the COD and phenolic compounds removal was 72% and 40% respectively, as reported in a study by Ioannou-Ttofa *et al.* (2017; Michael *et al.*, 2014). Decreasing coagulant dosage at 5 g/L (while keeping the flocculant concentration unchanged) resulted in COD and phenolic compounds removal slightly dropped to 68% and 30% respectively.

Ginos *et al.* (2006) who studied OMW treatment by coagulation–flocculation using 5 g/L of FeSO<sub>4</sub> and 0.287 g/L of FLOCAN 23, reported a low COD (21.8%) and phenolic compounds (33.2%) reduction. Discrepancies between the two studies may be attributed to different operating conditions such as (i.e., longer stirring times were employed in Papaphilippou *et al.* (2013) study), as well as different OMW samples tested.

In another study, Ginos *et al.* (2006) studied the effect of coupling 5 g/L FeSO<sub>4</sub> or 30 g/L Ca(OH)<sub>2</sub> with four cationic flocculants (FO-4700, FO-4490, FO- 43.50, FO- 4190 referred to as K1-K4 respectively) and Two anionic flocculants (AN 934 and FLOCAN 23 referred to as A1 and A2 respectively). In all cases, a common flocculation concentration of 0.28 mg/L was employed. The majority of the tested flocculants led the moderate removal of COD (10-30%) and significant removal of phenolic compounds (12.5-60%). Ginos *et al.* (2006) also reported that the coagulation-flocculation with Ca(OH)<sub>2</sub> always resulted in greater total phenols removal than treatment with FeSO<sub>4</sub> with reduce the dosage of Ca(OH)<sub>2</sub> used (Table 3 and 7).

Synthetic study of phenolic compounds removal from OMW by coagulation, direct flocculation and coagulation-flocculation processes.

The chemical composition of OMW is highly variable depending on various factors, such as the olive type, the geographical and climatic conditions, the tree age, the cultivation system, the degree of maturity of the fruit, the type of oil extraction process applied, the use of pesticides and fertilizers, etc. (Kallel *et al.*, 2009; Yay *et al.*, 2012). More specifically, OMW contain significant amounts of suspended, dissolved and colloidal matter were also relatively high as compared with most industrial effluents. Through the years, researchers

have tested a variety of technologies for OMW treatment. Among of theme, coagulation/flocculation is one of the most widely used solid-liquid separation process for the removal of suspended and dissolved matter, colloid and organic matter present in OMW (Gursoy-Haksevenler and Arslan-Alaton, 2014).

Coagulation process is the conventional treatment method where the cationic inorganic metal salts are commonly used as coagulants. Generally, phenolic compounds are in form of colloidal suspensions and dissolved organic matters consisting of negatively charged particles. When particles are similarly charged, the resulting repulsive forces tend to stabilize the suspension and prevent particle agglomeration. In order to achieve destabilization of particles and enhance the removal percentage of phenolic compounds, several mechanisms were proposed such as charge neutralization, Adsorption-precipitation, electrostatic patch coagulation and complexation with coagulant’s metal ions into insoluble aggregates (Duan and Gregory, 2003; Crittenden *et al.*, 2005; Henderson *et al.*, 2006). The most commonly used coagulants in OMW treatment are the trivalent salts of iron and aluminum, ferrous sulfate and calcium hydroxide. According to the related literature, the efficiency of coagulation process to remove organic matter and phenolic compounds from OMW mainly depends on the coagulant’s type and dosage, pH, mixing conditions, organic load of solution and the presence of divalent cations and destabilizing anions such as bicarbonate, chloride, calcium and sulfate ions (Afoufou *et al.*, 2007; Hecini and Achour, 2014). According to many studies, coagulation process is one of the most economical and environmentally friendly methods suitable for the treatment of OMW.

**Table 7:** Removal efficiencies of OMW treatment using coagulation-flocculation process

OMW origin	Phenols (g/L)	DCO (g/L)	Coagulant/flocculant	Dose (g/L)	Phenols %	DCO %	Ref.
Extraction process Greece (3-phase)	1.9	40.9	Ca(OH) <sub>2</sub> /PDADMAC	20/1.25	76	56	Iakovides <i>et al.</i> (2014)
Greece (W1) (3-phase)	12.08	87.5	PAC/ FLOCAN 23-20	4/0.01	45	36	Pelendridou <i>et al.</i> (2014)
			ASM/ Praestol 2240	4/0.01	15	10	
Greece (W2) (3-phase)	4.11	42.5	PAC/ FLOCAN 23-20	2/0.01	34	41	Papaphilippou <i>et al.</i> (2013)
			ASM/ Praestol 2240	2/0.01	22	30	
Greece (3-phase)	1.67	43.3	FeSO <sub>4</sub> / FLOCAN 23	6.67/0.28	40	72	Ginos <i>et al.</i> (2006)
			FeSO <sub>4</sub> /FLOCAN 23	5/0.28	30	68	
Greece (n.d.)	3.5	61.1	FeSO <sub>4</sub> /A1	5/0.28	12.5	22.5	Ginos <i>et al.</i> (2006)
			FeSO <sub>4</sub> /A2	5/0.28	12.5	32.5	
			FeSO <sub>4</sub> /K1	5/0.28	32.5	22.5	
			FeSO <sub>4</sub> /K2	5/0.28	32.5	27.5	
			FeSO <sub>4</sub> /K3	5/0.28	25	22.5	
			FeSO <sub>4</sub> /K4	5/0.28	25	25	
			Ca(OH) <sub>2</sub> /A1	30/0.28	55	12.5	
			Ca(OH) <sub>2</sub> /A2	30/0.28	55	15	
			Ca(OH) <sub>2</sub> /K1	30/0.28	47.5	10	
			Ca(OH) <sub>2</sub> /K2	30/0.28	50	10	
			Ca(OH) <sub>2</sub> /K3	30/0.28	50	10	
			Ca(OH) <sub>2</sub> /K4	30/0.28	60	30	

PAC: polyaluminum chloride; ASM: aluminum sulphate; A1: AN 934; A2: FLOCAN 23; K1: FO-4700; K2: FO-4490; K3: FO- 43.50; K4: FO- 4190

**Table 8:** Market prices for bulk sales of chemical materials (Sarika *et al.*, 2005; Ginos *et al.*, 2006)

Chemical materials	Price €/tonne
<b>Coagulants</b>	
Lime	130
FeCl <sub>3</sub>	350
FeSO <sub>4</sub>	150
<b>Polyelectrolyte</b>	
Polyaluminum chloride (PAC)	300
<b>Cationic flocculants</b>	
FO-4700	2980
FO-4490	2800
FO-4350	2800
FO-4190	2800
<b>Anionic flocculants</b>	
FLOCAN 23	2500
AN-934	2550
Praestol-2240	3100

The main advantages of this process over others is its simplicity, low energy consumption, low CO<sub>2</sub> emission (0.4 g of CO<sub>2</sub> per kg of COD removed from waste) (Pelendridou *et al.*, 2014) and low capital cost. As presented in Table 8, the market price of coagulants is very much lower compared to other chemical materials.

Coagulation process has been used for many years as main treatment due to its beneficial. As shown in Table 3, the lime application allowed a significant removal of phenolic compounds at basic pH (up to 60-70% reduction of the initial phenolic compound values) and part of the COD (40-50%). However, the major limitation of lime is the increase of solution pH and hardness, the low COD removal capacity typically between 20-50% and the generation of excessive volumes of sludge. In addition, from Table 4 and several report it is observed that the usage of dual coagulants (acid cracking + inorganic metal coagulants) can give very attractive results in removing COD and phenolic compounds. However, inorganic coagulants application has been reported not worthy in reducing organic matter (up to 10-40% reduction of the initial COD values). Also, their usage is quite limited nowadays and has been reduced due to several disadvantages. As reported in many studies (Jaouani *et al.*, 2005; Tzoupanos and Zouboulis, 2008; Mert *et al.*, 2010; Otlea and Seleka, 2012; Alaoui *et al.*, 2016), their usage would cause many important environmental consequences, which are; pH adjustment before or after treatment, sensitivity to temperature changes, production of large volumes of sludge which will create disposal problem and an increase in metal (e.g., aluminium) concentration in the treated water which may have human health implications (Flaten, 2001; Ward *et al.*, 2006). According to Polizzi *et al.* (2002; Banks *et al.*, 2006), recent epidemiological, neuropathological and biochemical studies suggest a possible link between the neurotoxicity of aluminium and the pathogenesis of Alzheimer's disease. Other disadvantage include the need for high doses of coagulants because the charge neutralization is not usually

sufficient and the inefficient of process towards very fine particles. For these reasons, various studies noticed that coagulation process is only a partial solution and must be used in combination with others treatments as pretreatment or posttreatment because the treated wastewater still has a high load of phenolic compounds and COD.

In this context, many research studies have proved that the real treatment of OMW by coagulation cannot be achieved without combinations of existing technologies such as, advanced oxidation processes (Ginos *et al.*, 2006; Rizzo *et al.*, 2008; Amaral-Silva *et al.*, 2016), aerobic biological treatment (Jaouani *et al.*, 2005; Pelendridou *et al.*, 2014; Chiavola *et al.*, 2010), Fenton processes (Rizzo *et al.*, 2008; Lucas and Peres, 2009; Yazdanbakhsh *et al.*, 2015; Madani *et al.*, 2015; Gursoy-Haksevenler, Arslan-Alaton, 2014; Michael *et al.*, 2014; Alver *et al.*, 2015; Ioannou-Ttota *et al.*, 2017), catalytic ozonation (Eren *et al.*, 2015) and membrane processes (Stoller and Chianese, 2006b; 2007; Stoller, 2009).

In order to minimize the drawbacks of coagulation process and enhance the elimination of phenolic compounds and COD from OMW, two processes have been taken into consideration; direct flocculation and coagulation-flocculation processes. Direct flocculation is the physical process of bringing the destabilized particles in contact to form larger flocs that can be more easily removed from suspension. Flocculation is usually used in conjunction with and preceded by coagulation. The process is generally accomplished by slow mixing of the destabilized suspension to provide an opportunity for the particles to come into contact with one another and bridge together. In direct flocculation, the mechanism is attributed to (1) neutralization of the negative charge of colloidal particles and (2) bridging the aggregated destabilized particles together to form flocs (Chong, 2012). An important aspect to be taken into account and reported by Chong (2012) is the use of flocculants at any range of pH values including acidic, neutral and base medium. The use of high molecular weight polymers could bridge the colloidal particles with loops and tails at any pH condition. This phenomenon is in contrast with the coagulation process where the complex precipitates of metal hydroxides are only obtained at the desired pH after addition of coagulant and pH alteration.

In practice, many studies are promoting the utilization of polyelectrolyte, as flocculants in OMW, more than metal-based coagulants, because they produce large, dense, compact and stronger flocs with good settling characteristic compared to those obtained by coagulation process (Renault *et al.*, 2009; Lee *et al.*, 2014). They can also involve the application of lesser dosage of flocculants, less pH dependent and reduce the residual fraction of unbound metallic compounds (Chang *et al.*, 2005; Gao *et al.*, 2008). In addition, direct flocculation generates less volume of sludge (Hodaifa *et al.*, 2015) because the flocs formed with strong bridging

mechanism are denser and closely packed. In addition, as the polymers are organic in nature, thus some of the sludge generated is readily for disposal after simple treatment. For this reason, various reports are predicting that the use of polymeric flocculants can reduce the overall treatment cost by 25-30%, in comparison with metallic coagulants treatment (Nozaic *et al.*, 2001). However, although polyelectrolytes find a wide range of applications as flocculants in removing organic matter from industrial wastewater, the potential associated with their use presents numerous disadvantages such as ineffectiveness removal of phenolic compounds and COD (Table 6), high cost (Table 8), less biodegradability and toxicity (Ginos *et al.*, 2006). According to Bolto and Gregory (2007) the normally used anionic and non-ionic polymers are generally of low toxicity, but cationic polyelectrolytes are more toxic, especially to aquatic organisms. In order to improve the efficiency of direct flocculation process, many researchers have studied the development of natural low-cost (bio-flocculants) alternatives to synthetic polyelectrolytes (Rizzo *et al.*, 2008; Renault *et al.*, 2009; Fragoso and Duarte, 2012; Speltini *et al.*, 2016; El Moussaoui *et al.*, 2018). The major advantage of natural polymer is its non-toxicity to the environment and biodegradability. Compared with conventional chemical flocculants, bio-flocculants are safe, fairly shear stable, easily available from reproducible agricultural resources and produce no secondary pollution (Bolto and Gregory, 2007). Not only this, as biopolymers are biodegradable, the sludge can be efficiently degraded by biologic process (Renault *et al.*, 2009). Thus, they have high potential to be applied not only in food and fermentation processes, pharmaceutical, cosmetic, downstream processing but also in water and wastewater treatment as OMW.

On the other hand, the addition of inorganic metal compounds as coagulants and polyelectrolytes as flocculants stimulates the destabilization of colloidal materials and promotes the agglomeration of small particles in large flocs that are able to quickly settle. Regarding treatment mechanism, coagulation-flocculation is based on charge neutralization (coagulation), followed by bridging (flocculation), while in direct flocculation, the charge neutralization and bridging occur concurrently.

Radoiu *et al.* (2004) studied the combined use of coagulants and flocculants. They reported that the use of flocculants not only can increase the density and the solidity of the flocs formed, it can also reduce the consumption of coagulants and increases the reliability of the work and the throughput capacity of the treatment plan. Other authors found that coagulation-flocculation process could reduce the cost of treatment. However, many studies reported that the combination of various cationic organic coagulants and flocculant agents did not show any significant decrease of COD and phenolic compounds except for lime combination ( $\text{Ca}(\text{OH})_2$ )

(Table 7). As presented above, the chemical treatment by coagulation-flocculation is not efficient for the reduction of organic materials in OMW. However, this process may be applied to wastewater as posttreatment or pretreatment to remove the suspended solids.

## Discussion

According to this literature study, the chemical materials (coagulants, polyelectrolytes, cationic and anionic flocculants) showed interesting results for removal of the organic matter from OMW. However, despite the number of published research papers, the treatment of OMW by coagulation/flocculation processes still limited on laboratory scale and have not been applied on industrial scale, mainly due to the complex nature of the effluent.

There are several strategies and combination techniques concerned by the removal of phenolic compounds and organic charge from OMW that can be proposed and can be summarized as follows:

The treatment of OMW by coagulation and coagulation-flocculation depends mainly to coagulant and flocculants type and dosage, pH, mixing condition, the presence of anionic and cationic minerals and phenolic compounds properties. In most of the article, the reduction of COD and polyphenols at acidic pH of OMW is very low regardless to the type and dosage coagulants used. In order to increase the removal efficiency, the optimization of pH parameter is recommended. However, direct flocculation process is workable at any pH condition.

The important removal of suspended and colloidal matter and mainly phenolic compounds is obtained by lime. Many studies reported that the reduction of phenolic compounds could exceeds 60%. However, the basic pH of treated effluent and large volume of sludge produced could limit this technique. For this reason, several alternative solutions could be tested. (i) innovative use of sludge as a fuel, a soil conditioner or a building material. (ii) neutralization of basic pH allows the application of a biologic treatment.

In the case where the aim is to decrease the sludge volume produced, the suitable process to use is coagulation-flocculation. However, the combination of coagulants and flocculants agents not show any significant decrease of the organic matter. Indeed, this process can be applied as pre-treatment to remove the suspended solids.

The applicability of chemical coagulants for OMW treatment can be more efficient if it is preceded by a pre-treatment process such as natural evaporation in ambient air with the use of solar energy in evaporation ponds or storage lakes (lagoons).

The coagulation/flocculation treatment of OMW cannot be achieved without combination with another treatment process in which to further degrade the organic

compounds to lower level. The best combination can be realized by comprising filtration of raw OMW on two successive Olive Stone (OS) filters. The results show that the use of OS filter leads to a higher removal of total suspended solids (82.5%) and fatty matter (73.8%) from the raw OMW (Enaime *et al.*, 2018).

## Conclusion

OMW is produced in a limited period and in large quantities and their chemical and physical characteristics vary according to cultivars, harvesting time, type of olives and the extraction technology (pressing or centrifuging). For all above-mentioned reasons, flexible and efficient treatment plants are necessary.

In this review, a focus on the relevant state-of-the art on physico-chemical processes for the treatment of OMW is presented, including coagulation, direct flocculation and coagulation-flocculation. Each treatment process has its advantages as well as drawbacks. In terms of effectiveness, all research studies reported that coagulation process using mineral and inorganic polymeric coagulants and acid cracking, direct flocculation with synthetic organic polymers and coagulation-flocculation did not show any significant removal of COD and phenolic compounds from OMW.

In this sense, it is evident from the consideration above that a single process cannot offer an efficient in removing of phenolic compounds and COD and viable solution to the problem. For these reasons, the combination of coagulation, direct flocculation and coagulation-flocculation with existing technologies (advanced oxidation processes, aerobic and anaerobic biological, Fenton processes, adsorption, infiltration-percolation and membrane processes) are recommended as pre-treatment or post-treatment by various authors.

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## Author's Contributions

**Mounia Achak:** Contributed to analyzing, discussing and interpreting the data; Writing the paper and checking the final review.

**Fatima Elayadi:** Contributed to studying literature research of coagulation process, revising paper and addressing the corrections.

**Wafaa Boumya:** Contributed to studying literature research of coagulation and flocculation processes and checking the final review.

## Ethics

This article is original and contains unpublished study. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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