Treatment of agro-industrial wastewaters by coagulation-flocculation-decantation and advanced oxidation processes – A literature review

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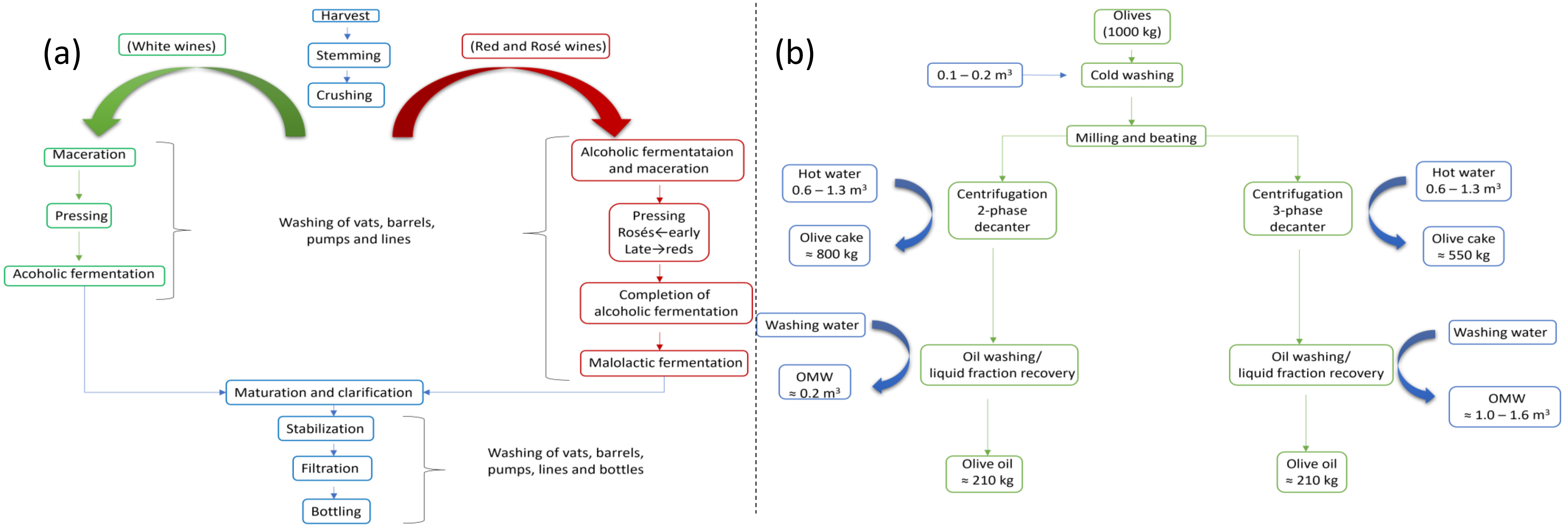
Introduction

- The agroindustry, is defined as a set of economic activities, including pro-duction, processing or industrialization and commercialization of agricultural and forestry products, either for food or non-food purposes
- In Mediterranean countries, most of the agroindustry in centered in the production of olive oil and wine, however, several other productions are of worthy mention: coffee, dairy, palm oil and pulp mill
- The wine, generate large volumes of wastewater with a high content of alcohols, organic acids, sugars and phenolic compounds
- The olive mill wastewater (OMW) contains water, organic constituents, mineral com-pounds, polyalcohols, polyphenols, volatile acids, nitrogen compounds, pectins, oil and tannins that gives the OMW its dark color



(a) Flow diagram of winemaking, (b) Two and three phase olive oil production scheme

Principles of coagulation-flocculation-decantation

(1) compression of the electrical double layer

- in which if ions are added into the solution or if the ions have greater charge (divalent or trivalent instead of monovalent), then the electroneutrality can be satisfied in a shorter distance

(2) adsorption and charge neutralization

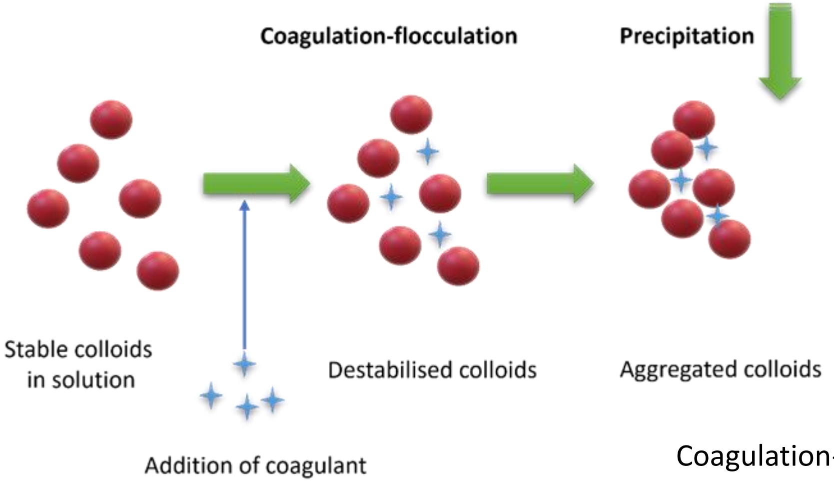
- in which particles can be destabilized by adsorption of oppositely charged ions or polymers

(3) adsorption and interparticle bridging

- in which the polymer may remain extended into the solution and adsorb on available surface sites of other particles, thus creating a ‘‘bridge’’ between particle surfaces that results in a larger particle that can settle more efficiently

(4) enmeshment in a precipitate, or “sweep floc”

- which occurs when high enough dosages of coagulant are used. The aluminum and iron forms insoluble precipitates and the particles become entrapped in the amorphous precipitates



Coagulation-flocculation-decantation scheme

Application of CFD process for agro-industrial wastewater treatment

Wastewater	Coagulant	Operational conditions	Results	References
Sanitary landfill leachates	Ferric chloride, aluminium sulphate and lime + polyelectrolytes	Fast mix = 5 min/ 200 rpm Slow mix = 55 min/ 60 rpm Sedimentation time = 1 h	COD rem = 80% Color rem = 100%	Tatsi *et al.*, [19]
Palm Oil Mill Effluent	Modified alum (Envifloc-40L) + industrial grade flocculant (Profloc 4190)	[Coagulant] = 15 g/L [Flocculant] = 300 mg/L pH = 6.0	Turbidity rem > 98% TSS rem = 30 – 95% Water recovery = 78%	Ahmad *et al.*, [20]
Winery wastewater	Potassium caseinate + bentonite	[Coagulant] = 1.0 g/L pH = 4.0 Fast mix = 150 rpm/ 20 min Slow mix = 20 rpm/ 20 min Sedimentation time = 12 h	Turbidity rem = 98.3% TSS rem = 97.6% Total polyphenols = 87.8%	Jorge *et al.*, [21]
Winery wastewater	Chitosan	[Chitisan] = 20 mg/L pH 4.0	Turbidity rem = 80% TSS rem = 94% COD rem = 73%	Rizzo *et al.*, [23]
Vegetable oil refinery wastewater	Opuntiaficus-indica (Cactus)	[Cactus] = 40 mL/L pH = 9.87	Turbidity rem = 99% Color rem = 95% COD rem = 76%	Dkhissi *et al.*, [22]

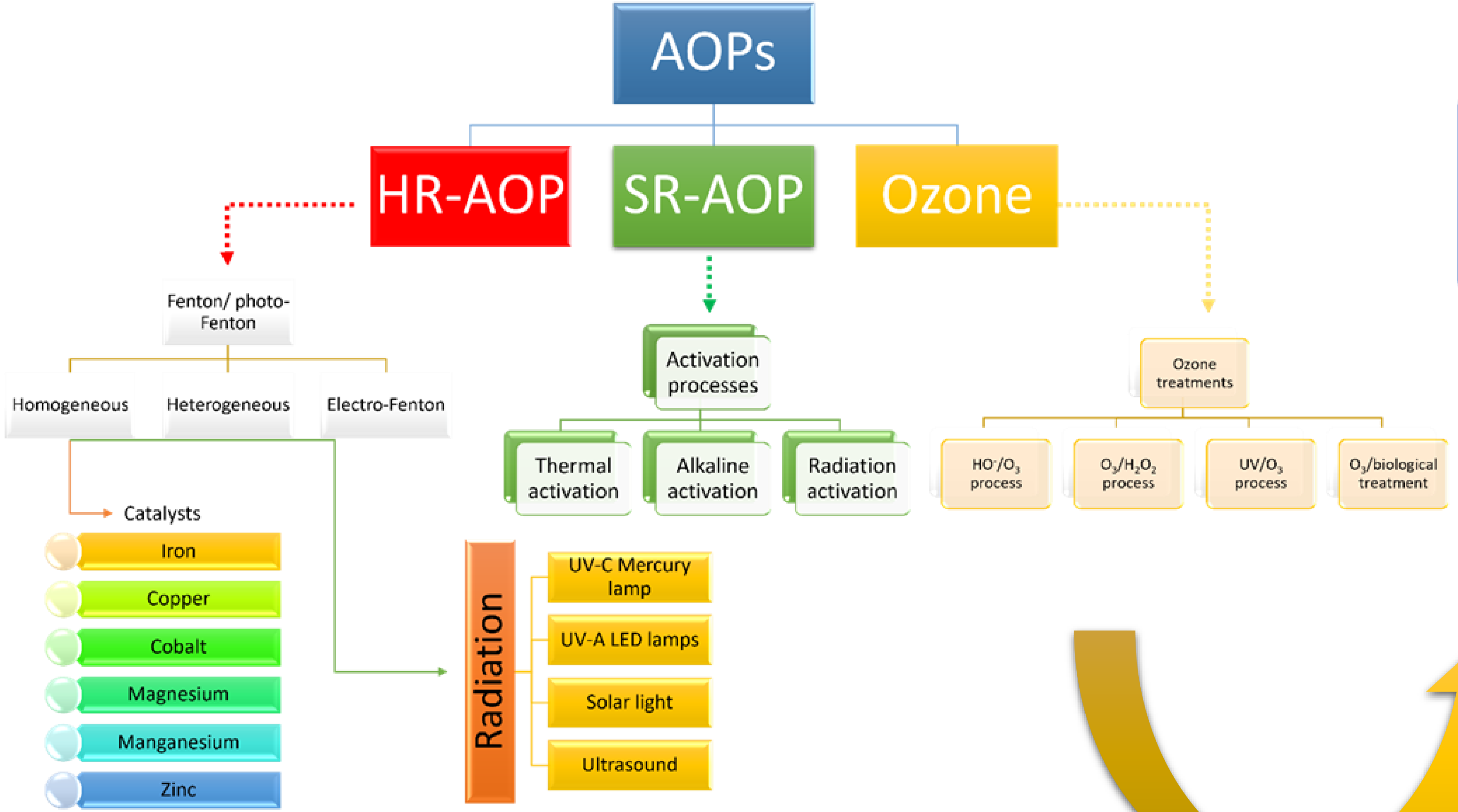


In the works of Tatsi *et al.*, and Ahmad *et al.*, it was observed that the mixture of metallic-based coagulants with a polyelectrolyte achieved an increase of the organic matter, turbidity and color removal

Jorge *et al.*, observed that the application of a mixture with potassium caseinate and bentonite achieved a high turbidity, total suspended solids (TSS) and total poly-phenols removal

In the work of Dkhissi *et al.*, a plant-based coagulant was applied for the treatment of vegetable oil refinery wastewater, achieving a high removal of turbidity, chemical oxygen demand (COD) and color

Advanced Oxidation Processes



Scheme of AOPs applied in wastewater treatment

Conventional treatment methods have been reported to be inefficient for agro-industrial wastewater treatment, considering that some contaminants are recal-citrant to some degree

Advanced oxidation processes (AOP) can be applied as an alternative or a complement treatment to degrade these recalcitrant compounds. The AOPs generate extremely reactive hydroxyl radicals (HO•) radicals that are responsible for the degradation of pollutants in the wastewater

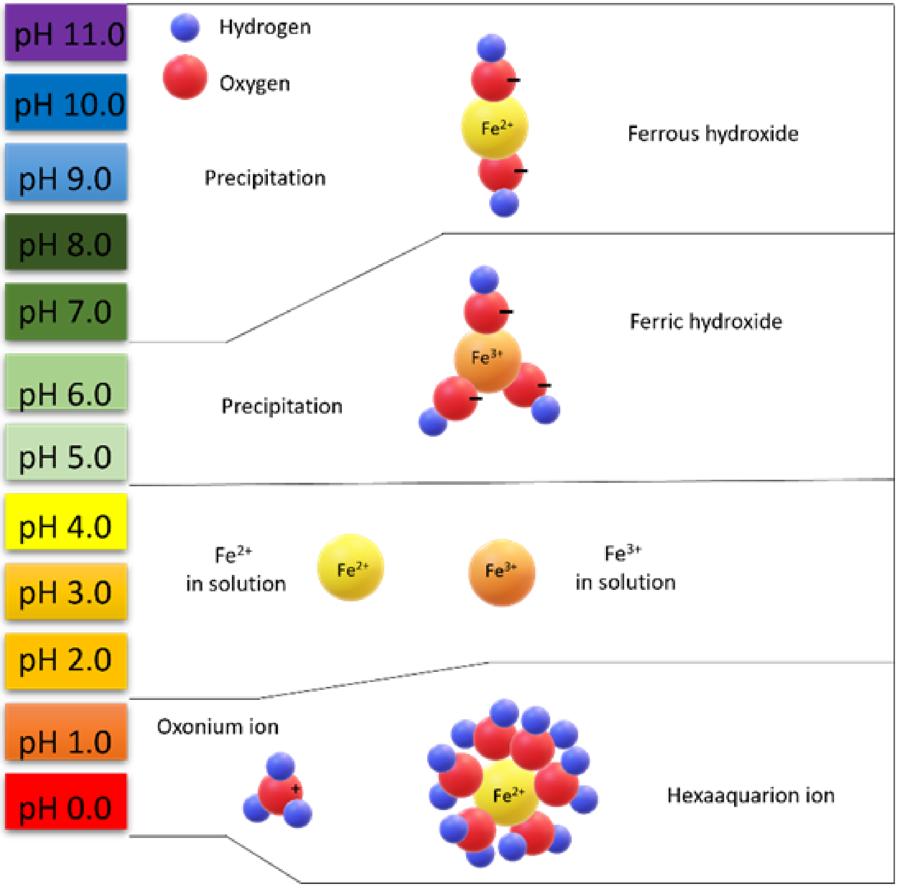
The AOPs can be divided in accordance to the oxidant used: hydroxyl radical based AOP (HR-AOP), sulfate radical based AOP (SR-AOP) and ozone based AOP

Oxidation potential against Standard Hydrogen Electrode of some relevant oxidants.

Oxidizing agent	Molecular structure	Oxidation potential (E^0) (V)
Fluorine	F_2	3.06
Hydroxyl radical	$HO^{\bullet}$	2.80
Atomic oxygen	O	2.42
Ozone	O_3	2.06
Hydrogen peroxide	H_2O_2	1.78
Hydroperoxyl radical	$HO_2^{\bullet}$	1.70
Manganate ion	MnO_4^-	1.67
Chlorine dioxide	ClO_2	1.50
Hypochlorite	ClO^-	1.49
Chlorine	Cl_2	1.36
Molecular oxygen	O_2	1.23

- The Fenton process was discovered in 1894 by H.J.H. Fenton for maleic acid oxidation. The Fenton reaction is based on the formation of HO• radicals, by the combination of hydrogen peroxide (oxidant agent) and iron ions (catalyst). In the Table above, it's observed that HO• is the second highest powerful oxidant after fluorine;

- One of the key parameters of the Fenton process is the solution pH, which is normally used between 2.0 and 4.0. At a pH < 2.0, the H^+ acts as a scavenger of HO• radicals, and it is produced oxonium ions $[H_3O_2]^+$ that causes the H_2O_2 to become electrophilic reducing its reactivity with iron. With the application of a pH > 3.5, the Fe^{3+} will precipitate as ferric hydroxide and at a pH > 7.0, the ferrous iron will precipitate as ferrous hydroxide.



Precipitation and form of iron catalyst at different pH.

Application of HR-AOPs in agro-industrial wastewater treatment.

Wastewater	Operational conditions	Radiation	Results	References
Winery effluents	pH = 3.0 $[H_2O_2]$ = 500 mg/L $[Fe^{2+}]$ = 5 mg/L DOC = 435 mg C/L	Solar radiation	DOC rem = 80%	Velegraki and Mantzavinos [39]
Crystallized-fruit wastewater	pH = 2.9 – 3.1 $[H_2O_2]$ = 5459 mg/L $[Fe^{3+}]$ = 286 mg/L COD = 20 – 35 g/L	UV LED photo-system (370 nm)	COD rem = 74%	Rodríguez-Chueca *et al.*, [40]
Winery wastewater	pH = 3.0 $[H_2O_2]$ = 0.5 M $[Fe^{3+}]$ = 5 mg/L COD = 10 g/L	Xenon emitting at 290 and 400 nm spectral range.	TOC rem = 95%	Ormad *et al.*, [42]
Agro-food industrial wastewater	pH = 3.0 $[H_2O_2]$ = 5000 mg/L COD = 3499 mg O_2/L	Mercury vapor lamp ((UV-C radiation, λ = 254 nm)	COD rem = 70%	Leifeld *et al.*, [43]
Olive mill wastewater	COD = 10 g O_2/L $[H_2O_2]$ = 10 mmol/L T = 45 ºC P = 525 W F = 20 kHz Time = 90 min	Ultrasonic Processor, VCX 750, with a frequency of 20 kHz	COD rem = 59%	Al-bsoul *et al.*, [41]

Fenton process

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2)$$

Photo-Fenton process

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \quad (3)$$

$$Fe(HO)^{2+} + hv \rightarrow Fe^{2+}\ HO^{\bullet};\ \lambda < 580\ nm \quad (4)$$

$$H_2O_2 + hv \rightarrow 2HO^{\bullet};\ \lambda < 310\ nm \quad (5)$$

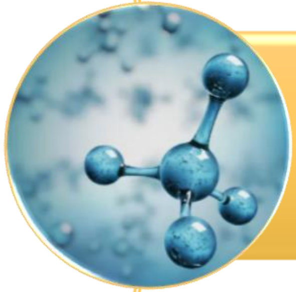
Sono-Fenton process

$$H_2O +))) \rightarrow HO^{\bullet} + HO^{-} \quad (6)$$

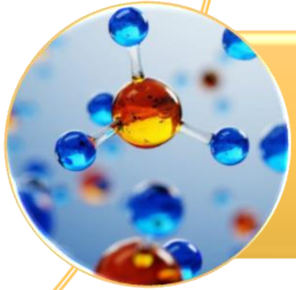
$$H_2O_2 +))) \rightarrow 2HO^{\bullet} \quad (7)$$

$$FeHO_2^{2+} +))) \rightarrow Fe^{2+} + HO_2^{\bullet} \quad (8)$$

In the work of Velegraki and Mantzavinos, a pilot-scale solar Fenton process was applied for the treatment of winery wastewater in a CPC photocatalytic reactor under natural solar irradiation. The results showed that the photo-Fenton process utilizing solar energy is highly efficient in the mineralization and detoxification of real winery wastewater

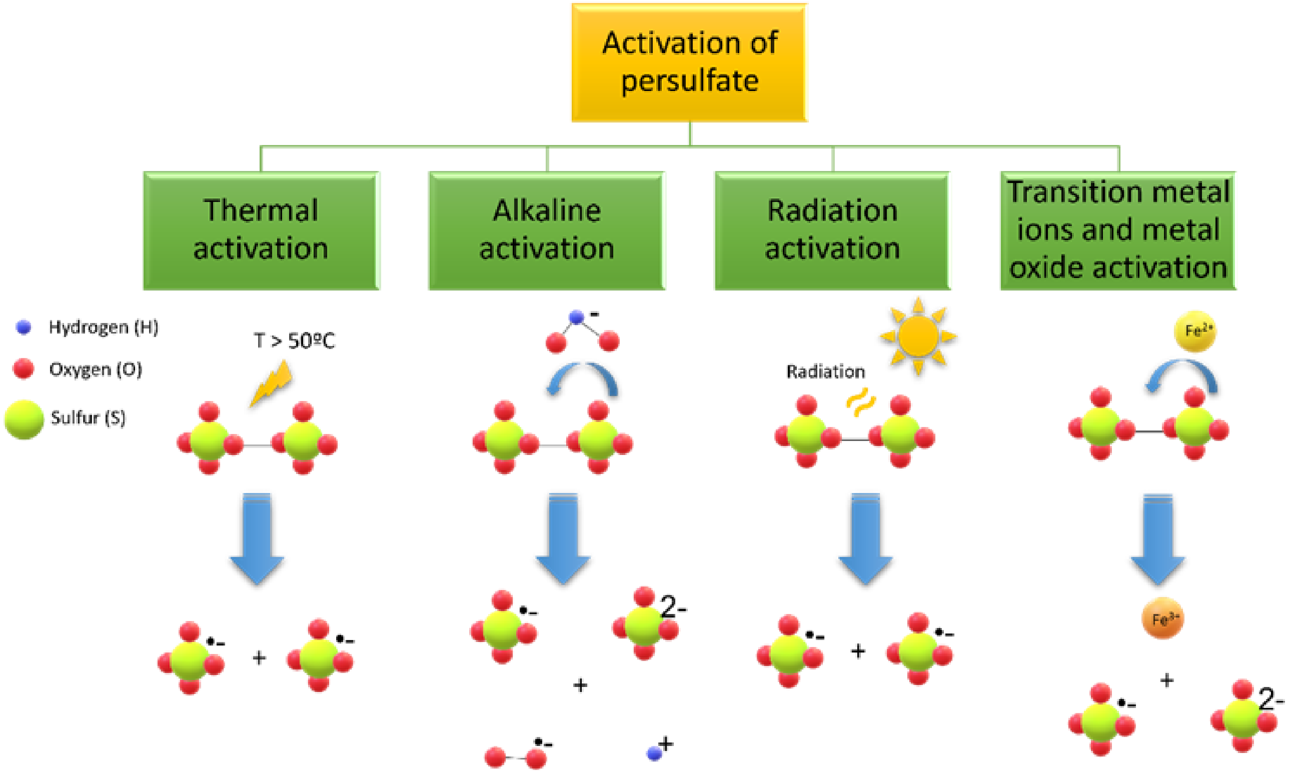


Rodríguez-Chueca et al., used a UV-A LED light system to treat crystallized-fruit effluents, characterized by a very low biodegradability (BOD5/COD <0.19). The photo-Fenton process was coupled with the CFD process and results showed an increase of the COD removal and biodegradability



In the work of Al-Bsoul et al., a Sonicator (Ultrasonic Processor, VCX 750, Ger-many) with a frequency of 20 kHz was applied through a horn (40 mm diameter) into a cylindrical double-jacketed Reactor for the treatment of OMW. The COD removal achieved a high removal rate (k = 0.0309 min^{-1}) under the best operational conditions

SR-AOPs



Schematic representation of the activation mechanism of persulfate.

- The interest in persulfate began in earnest around 2000–2002, when work on persulfate began to appear regularly in conference proceedings and in presentations at major remediation meetings.
- There are two types of sources to obtain the sulfate radical (SO_4•-):
- (1) peroxymonosulphate (HSO_5-; PMS), which is the active ingredient of a triple potassium salt, 2KHSO5•KHSO4•K2SO4;
- (2) persulfate (PS), which is a colorless or white crystal and has high stability.

Heat activation

$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$	(9)
$HSO_5^- \rightarrow SO_4^{\bullet-} + HO^\bullet$	(10)

Base activation

$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + HO_2^- + H^+$	(11)
$S_2O_8^{2-} + HO_2^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} + O_2^{\bullet-} + H^+$	(12)

UV activation

$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet-}$	(14)
$HSO_5^- + hv \rightarrow SO_4^{\bullet-} + HO^\bullet$	(15)
$H_2O + hv \rightarrow H^\bullet + HO^\bullet$	(16)
$S_2O_8^{2-} + H^\bullet \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+$	(17)
$HSO_5^- + H^\bullet \rightarrow SO_4^{\bullet-} + H_2O$	(18)

Transition metal activation

$S_2O_8^{2-} + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + SO_4^{2-}$	(19)
$HSO_5^- + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + HO^-$	(20)

SR-AOPs

Application of SR-AOPs in agro-industrial wastewater treatment.

Wastewater	Operational conditions	Results	References
Winery wastewater	COD = 5000 mg O_2/L UV-A LED 70 W/m^2 PMS/Co^{2+} = 3.33/1.33 mM pH = 6.5 T = 323 K Time = 180 min	COD rem = 86%	Rodríguez-Chueca *et al.*, [49]
Olive mil wastewater	COD = 800 mg O2/L TOC = 284 mg C/L Total polyphenols = 300 mg/L pH = 5.0 [Fe^{2+}] = 300 mg/L [PS] = 600 mg/L	COD rem = 39% Total phenols rem = 63% TOC = 37%	Domingues *et al.*, [51]
Winery wastewater	TOC = 1700 mg C/L Solar radiation pH = 4.5 [PMS] = 10 mM [Fe^{2+}] = 10 mM	TOC rem = 51%	Rodríguez-Chueca *et al.*, [52]
Winery wastewater	COD = 9870 mg O_2/L $S_2O_8^{2-}$/H_2O_2 ratio = 0.1:0.025 (g/g) pH = 7.0 T = 343 K Time = 2 h	COD rem = 81.4%	Jorge *et al.*, [50]

In the work of Rodríguez-Chueca *et al.*,, a high COD removal was obtained with activation of PMS by transition metal (Co^{2+}) and high temperatures (T = 323 K)

In the work of Jorge *et al.*, the sulfate radicals were activated by high temperatures, achieving 81.4% COD removal

In the work of Domingues *et al.*, the application of PS/Fe^{2+} in the treatment of OMW achieved a total polyphenols removal of 63%

Ozone-based AOPs

- In 1840, Schönbein discovered ozone and by 1872 the chemical structure of ozone (O_3) was finally confirmed as a triatomic oxygen molecule;
- In 1886, de Meritens found that ozone could be used as a germicide for sterilization of polluted water and after a few years of pilot tests at water treatment plants in Paris, ozone was firstly used in water treatment (and used continuously) in Nice, France in 1906 for drinking water disinfection;
- Ozone is a powerful oxidant with a redox potential of 2.07 V in an alkaline solution

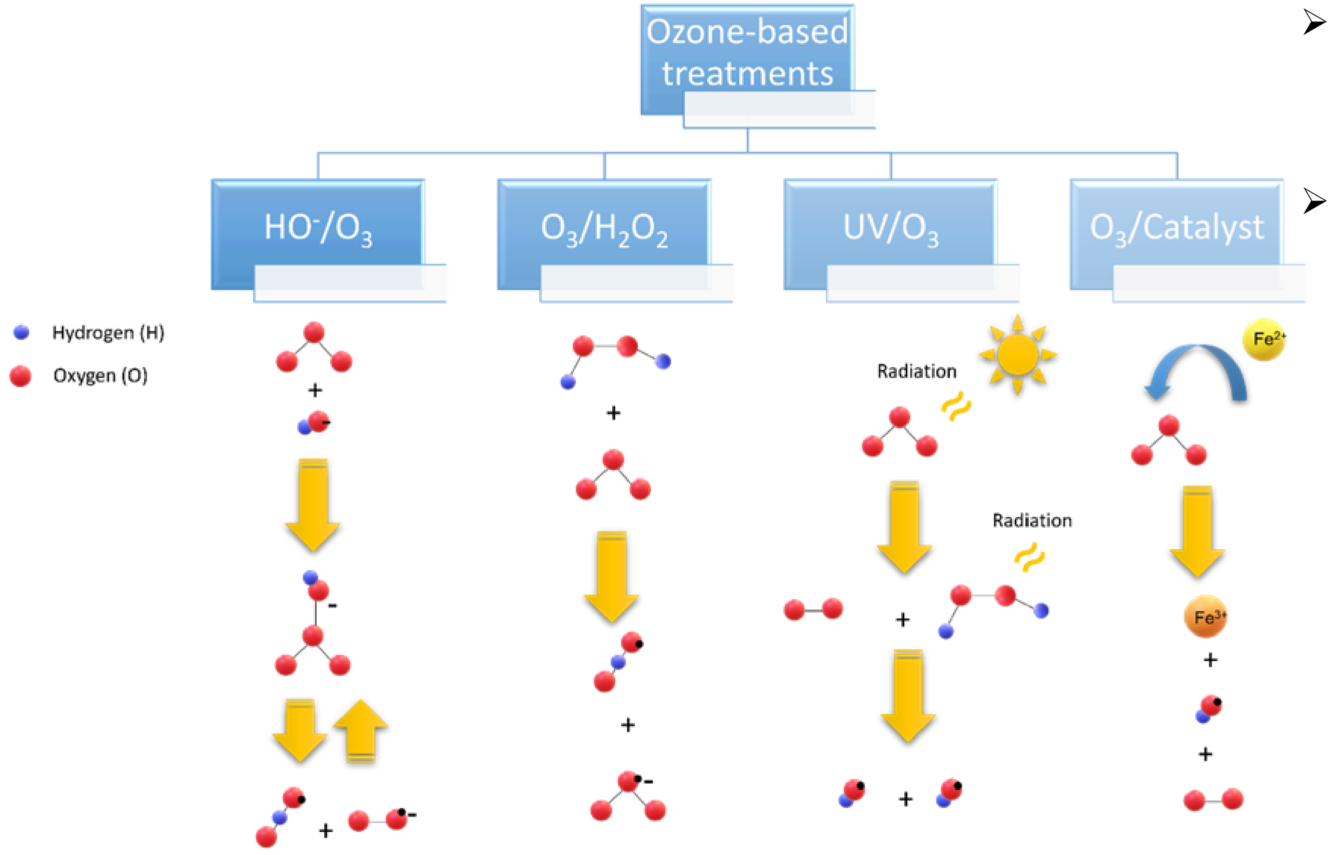


Illustration of different ozone-based treatments

Ozone in alkaline conditions

$O_3 + HO^- \rightarrow HO_4^-$	(21)
$HO_4^- \leftrightarrow HO_2^\bullet + O_2^{\bullet-}$	(22)
$O_2^{\bullet-} + O_3 \rightarrow O_2 + O_3^{\bullet-}$	(23)
$O_3^{\bullet-} \rightarrow O_2 + O^{\bullet-}$	(24)
$O^{\bullet-} + H_2O \rightarrow HO^\bullet + HO^-$	(25)

Ozone + H_2O_2

$H_2O_2 \leftrightarrow H^+ + HO_2^-$	(26)
$HO_2^- + O_3 \leftrightarrow HO_5^-$	(27)
$HO_5^- \rightarrow HO_2^\bullet + O_3^{\bullet-}$	(28)

Ozone + UV

$O_3 + H_2O_2 + h\nu \rightarrow HO^\bullet + O_2 + HO_2^\bullet$	(29)

Ozone + catalyst

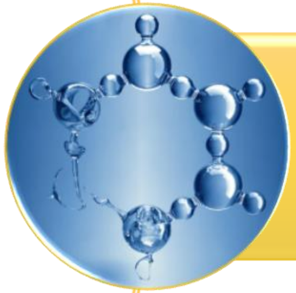
$M^{n+} + O_3 + H^+ \rightarrow M^{(n+1)+} + HO^\bullet + O_2$	(30)
$O_3 + HO^\bullet \rightarrow O_2 + HO_2^\bullet$	(31)
$M^{(n+1)+} + HO_2^\bullet + HO^- \rightarrow M^{n+} + H_2O + O_2$	(32)

Ozone-based AOPs

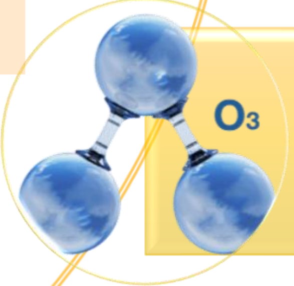
Application of ozone-based AOPs for agro-industrial wastewater treatment.

Wastewater	Operational conditions	Results	References
Winery wastewater	COD = 9432 mg O_2/L pH = 4.0 $[Fe^{2+}]$ = 1.0 mM Ozone flow rate = 5 mg/min Air flow = 1.0 L/min	COD rem = 66.4%	Jorge *et al.*, [21]
Industrial wastewater	COD = 12 g O_2/L O_3/Solar radiation/TiFeAC Ozone dose = 4 g/L/h pH = 7.0 Time = 5 – 8 h	TOC rem = 70% COD rem = 80%	Chávez *et al.*, [57]
Tequila Industry Vinasses wastewater	COD = 37 g O_2/L Ozone dose = 30 mg/L Flow rate = 0.1 L/min	Color rem = 91% COD rem = 50%	Ferral-Pérez *et al.*, [59]
Olive mill wastewater	COD = 13160 mg O_2/L Ozone dose = 765 mg/L	COD rem = 56% Total phenol rem = 61%	Oz *et al.*, [60]
Olive mill wastewater	$O_3/BiFeO_3/S_2O_8^{2-}$ O_3 dose = 600 mg/h $[S_2O_8^{2-}]$ = 0.05 M m_{BiFO3} = 0.6 g pH = 12 T = 30 ºC	Total polyphenols rem = 82.9% COD rem = 98.0%	Iboukhoulef *et al.*, [58]

In the work of Jorge *et al.*, a winery wastewater was previously treated by CFD process achieving a COD removal of 48.0%. With application of ozonation, the COD removal increase to 60.7%



In the work of Chávez *et al.,* it was observed that application of ozonation process as a complement of biologic process could achieve higher organic matter removal



In the work of Iboukhoulef *et al.*, a $BiFeO_3$ nanocatalyst was developed and applied in a $O_3/BiFeO_3/S_2O_8^{2-}$ system with a COD removal of 98.0%

Conclusions

The agro-industry has shown to be very important for the development of the populations, been capable to respond to the need to provide food and to develop the economy of the countries, generating large volumes of wastewater. Therefore, it is necessary to perform treatments of coagulation-flocculation-decantation and advanced oxidation processes before releasing these wastewaters. Based in literature review, it is concluded:

1. Several reviews show that application of plant-based coagulants have similar efficiency than metallic coagulants, with lower costs and reduced environmental contamination

2. The literature review shows that HR-AOPs are effective in the removal of organic matter from agro-industrial wastewater, reducing the toxicity to lower levels

3. The literature review shows that PMS and PS have similar effect in the removal of or-ganic matter from agro-industrial wastewater. The results also show a high efficiency of SR-AOPs, for the removal of total polyphenols

4. The literature review shows that application of ozonation process have a high effi-ciency in the removal of organic carbon and total polyphenols from agro-industrial wastewater

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Thank you for your attention