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# A REVIEW ON OCCURRENCE, MEASUREMENT, TOXICITY AND TANNIN REMOVAL PROCESSES FROM WASTEWATERS

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## Abstract

A wide range and globally active agro-industries such as olive oil processing, winery, tannery, textile and food production discharge a large volume of wastewater containing tannins. Tannins are complex structured chemicals which cause high organic content, requiring high dissolved oxygen in wastewater treatment plants or producing oxygen depletion in the aquatic environment. Tannins are known to be hardly degraded in biological treatment. There has been evidence that the presence of natural tannins can, to some extent, form antioxidant potential in wastewater while their degradation products can interact with the oxidants used in the treatment or final disinfection, the final effluent can display toxicity to aquatic species as well. Therefore, there has been a progressive but still to a limited extent of search to remove these compounds effectively. Several processes including physico-chemical, adsorption biological treatment, membranes treatment and advanced oxidation processes (AOPs) such as ozone, electrocoagulation, UV/$H_2O_2$, Fenton processes, photocatalysis have been attempted to treat tannins in general as integrated to biological processes. This paper aims to present a critical review of the chemistry, as well as sources of tannins in industrial wastewater and gives informative data on their toxicity. It finally reviews treatment methods with their descriptive data on their efficacy to remove the tannins from different origin wastewater.

*Key words:* vegetable and synthetic tannins, toxicity, AOPs, removal of tannins, wastewater

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## 1. Introduction

Huge amounts of different kind of tannins namely vegetable (VT) and synthetic (ST) based tannins are being discharged to receiving waters originated from different kinds of industrial sectors (De Bruyne et al., 1999; Kalyanaraman et al., 2015; Lofrano et al., 2006; Mueller-Harvey, 2001; Schofiled et al., 2001). Most of these wastewaters are not adequately treated, since conventional treatments such as physico-chemical and biological processes are ineffective to degrade/remove and detoxify these recalcitrant compounds (He et al., 2007; Liu et al., 2010; Lofrano et al., 2007a, 2007b; Munz et al., 2009). Furthermore when huge amounts of metal agents are used to precipitate tannins, a secondary pollution is produced as a result of their release in treated effluents or concentrations in sludge.

The scientific literature on tannins has been for a long time focused on individual chemical species, e.g. tannic (Dentel et al., 1998; Vinod and Anirudhan, 2001) or gallic acid (Malini and Subhash, 2000; Tatsuo et al., 1989), thus providing only scanty information on tannin complex mixtures and their fate in the biological treatment being inhibitory to microbial growth, respiration and metabolism and aquatic environment (De Nicola et al., 2004, 2007). STs are potent inhibitors of nitrification process in wastewater treatment plants. The antimicrobial activities of tannins are well documented. They are

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able to inhibit the growth of many fungi, yeasts, bacteria, and viruses. Foodborne bacteria, aquatic bacteria, and off-flavor-producing microorganisms are inhibited by tannic acid and propyl gallate. Other physiological effects exerted by tannins are the acceleration of blood clotting, the reduction of blood pressure, the decreasing of the serum lipid level, the production of liver necrosis, and modulate immuno-responses (Chung et al., 2010).

Although any limit has not been established till now for the concentration of tannins in wastewater, these compounds are candidate to be considered as emerging pollutants and need to be properly managed for their implication on human health and ecosystems. To overcome the abovementioned problems, thus, several alternative treatment methods such as ozone oxidation (Babuna et al., 2007; Koyunluoglu et al., 2007), photocatalysis (Schrank et al., 2004), Fenton and Photo-Fenton oxidation (Lofrano et al., 2007a, 2007b), electrochemistry (Boye et al., 2005; Hanafi et al., 2010; Murugananthan et al., 2005) as well as hybrid processes (Benítez et al., 2008; Dias-Machado et al., 2006; Lafi et al., 2009; Saroj et al., 2005) have been investigated.

This paper aims to overview the sources, chemical and analytical issues, toxicity of VT and STs, their fate in the environment. A state-of-the art of treatment technologies applied to for their removal in industrial wastewater treatment plants is also discussed. As a need to control their discharge a special focus is given on the application of AOPs for their removal as a fist initiative according to our best knowledge.

## 2. Chemistry and analytical

### *2.1. Chemistry*

VTs are complex polyphenolic metabolites of plants and occur at high levels in a variety of foods, such as vegetables, fruits, seeds and plant-derived beverages (Bickley, 1992; Huang and Borthwick, 2005; Marin-Martinez et al., 2009).

VTs are known for their nutritional value or their astringency and taste, but they have gained considerable attention mainly due to their chemical properties such as their ability to bind proteins and metals (Haroun et al., 2013). The structure of some of them is shown in Fig. 1a.

VTs can be subdivided into condensed (CTs) and hydrolysable tannins (HTs), using the classification originally suggested by Freddenberg based upon two principal structural themes-oligomeric flavan-3-ols (proanthocyanidins) and poly-3,4,5-trihydroxyaroyl esters (gallotannins and ellagitannins) (Haslam, 1966). CTs have a flavonoid core as their basic structure, encompassing oligomers and polymers composed of favan-3-ol-nuclei (De Bruyne et al., 1999; Huang and Borthwick, 2005; Labieniec et al., 2003; Schofiled et al., 2001). The stereoisomeric compounds (+)/(-)-catechin and (+)/(-)-epicatechin differ in their stereochemistry in positions 2 and 3 and represent typical monomers (Fig. 1b).

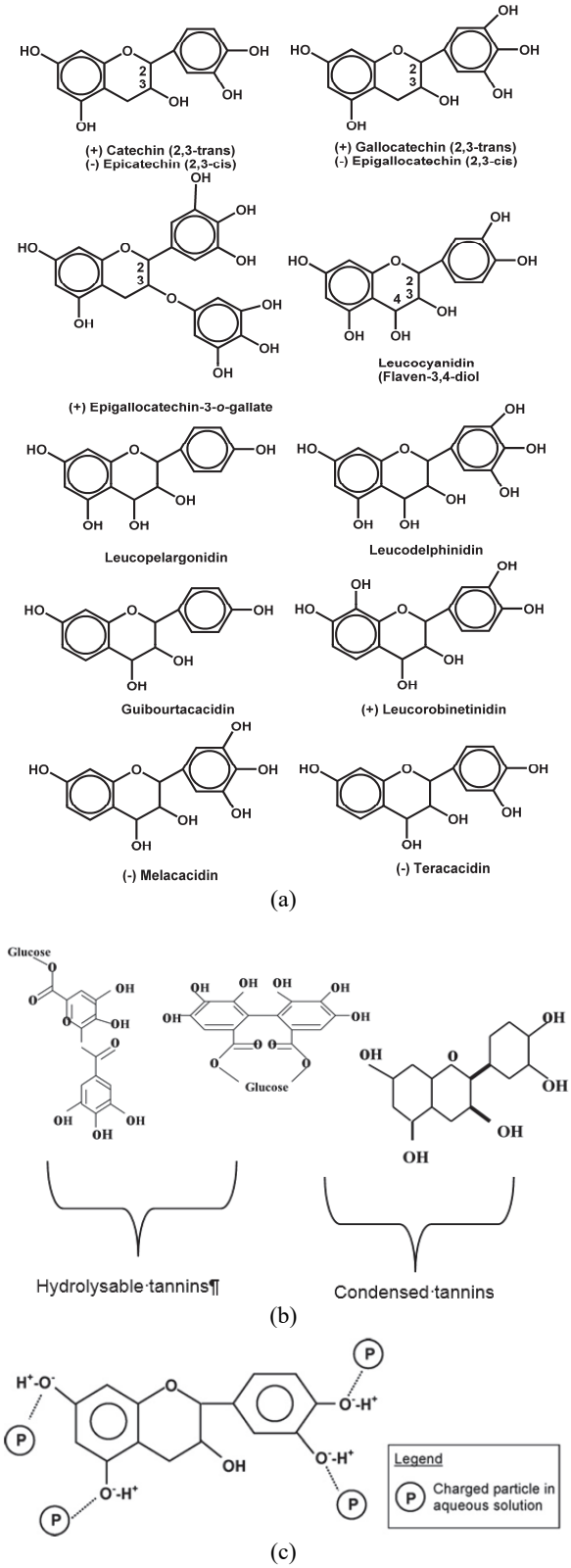


**Fig. 1.** (a) Chemical structures of some condensed vegetable tannins in different origin; (b) basic structures of hydrolysable and condensed tannins; (c) Schematic representation of basic tannin structure in aqueous solution and possible molecular interactions (modified from Yin, 2010)

Gallocatechin is another important monomer, bearing one additional hydroxy-group. Its stereoisomers are (+) /(-) gallocatechin and (+) /(-)-epigallocatechin. The linkage of monomeric units through C4–C8 interflavonoid bonds typically occur but they can be also linked through C4–C6 (Haroun et al., 2013). CTs are widely distributed in higher plants, particularly in conifers, HTs are of limited distribution in nature, only a limited number of plants contain sufficient amounts of these product to be of commercial value (De Bruyne et al., 1999; Svitelska et al., 2004).

In conventional activated sludge processes, natural tannins are not biodegraded. However some distinctions, occur: the CTs, such as Wattle and Quebracho have a very low biodegradability, whereas the HTs, such as Chestnut and Tara are moderately biodegradable (Munz et al., 2009).

HTs are derived from glucose esters of gallic acid and ellagic acid and are sub-classified into gallotannins and the ellagitannins (Huang and Borthwick, 2005; Mueller-Harvey, 2001). Gallic acid is commercially important in the food and pharmaceutical industries (Malini and Subhash, 2000). It is common presents in several agro-wastewaters, like olive oil factories, boiling cork and wine processing industries, and can be also considered as one of the simplest models of natural organic matter (Gernjak et al., 2003; Lucas et al., 2008; Svitelska et al., 2004). Synthetic tannins (STs) are a class of chemicals synthesized for industrial purposes (Koyunluoglu et al., 2007; Lofrano et al., 2007a). As their name implies, STs were first developed as alternatives to VTs tannins in the tanning of leather; subsequent developments lead to products that were specifically intended for use as an after treatment of dyed nylon (Burkinshaw, 1995).

The STs are useful to tannery to obtain special effects in processing or leather quality, including: clarification of VT solution; pre-tanning for faster vegetable tannage; lightening of colour in vegetable leather; lightening of colour in chrome tanned leather; producing fullness of feel; producing soft open tanning effect; mordanting leather for dyes; aiding in the penetration of dyes; aiding in shrunken grain effects (Lofrano et al., 2013). The first STs were prepared by Schiff (1875) by the condensation of two or more molecule of phenol-sulphonic acid in presence of oxychloride phosphorus (P-OCl). STs are composed of an extended set of chemicals such as phenol-, naphthalene-, -formaldehyde and melamine-based STs as well as acrylic resins. As consequence they present a complex chemical structures because they are composed of an extended set of chemicals such as phenol-, naphthalene-, -formaldehyde and melamine-based STs as well as acrylic resins (De Nicola et al., 2007). Formaldehyde, glutaraldehyde, phenols, uric acid derivatives and acrylates have a particularly effective tanning action. As a rule, STs are not used as the sole tanning agents, but produce very interesting results in conjunction with VTs or chrome tanning agents.

**Table 1.** Physicochemical and ecotoxicological properties of some STs

| *Source* | *Colour* | *pH* | *Density 20 $^0$C [kg/m3]* | *Solubility 20 $^0$C [g/l]* | *$COD_{equivalent}$ g·g* | *BOD/ COD* | *$UV_{254}$ [$cm^{-1}$]* | *$UV_{280}$ [$cm^{-1}$]* | *Daphnia magnaimmobility at non-diluted sample (%)*** | *Daphnia magna immobility at 50% diluted sample*** | *Fish toxicity (LC50- mgg-1)* | *References* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Leather tanning | White | 5.5-6 | 700 at 20 $^0$C | 100 | 1 | 0.1 | 1.32 | 1.48 | 100 | 50 | - | Lofrano et al. (2007) |
| Leather tanning | Yellow | - | - | - | 1 | 0.15 | 1.41 | 1.56 | 100 | 15 | - | Lofrano et al. (2007) |
| Leather tanning | White | - | - | - | 1.2 | 0.1 | 1.43 | 1.52 | 100 | 0 | - | Lofrano et al. (2007) |
| Leather tanning | Yellow | - | - | - | 1 | 0.11 | 0.55 | 0.78 | 100 | 20 | - | Lofrano et al. (2007) |
| Leather tanning | White | - | - | - | 0.8 | 0.04 | 1.8 | 1.39 | | | | Lofrano et al. (2008) |
| Leather tanning | White | - | - | - | 0.9 | 0.03 | 1.43 | 1.34 | | | | Lofrano et al. (2008) |
| Textile industry | Brownish liquid with a weak odor | 2.5-3.5 | 1.15 at 25$^0$C | Highly water | - | - | - | - | - | - | 1-10* | Koyunluoglu et al. (2007) |

* *Lethal concentration of pollutant (mg/L) causing 50% death of the studied test organism i.e. Leuciscus idus.* ** *Values for Daphnia magna calculated by PROBIT analys*

This is known as combination tanning process to produce more soften leather by applying a synthetic pre-tanning process (Lofrano et al., 2008). Among STs, the ones based on sulfonated naphthalenes and their formaldehyde condensates (SNFC) play a primary role, for volumes and quantity used in leather tanning industry (Munz et al., 2009). Technical SNFC mixtures result from the condensation products of 2-naphthalenesulfonic acid and formaldehyde and are characterized by a complex combinations of mono and disulfonated monomers and their condensed oligomers (up to n=11) (Song et al., 2003).

The salts of the sulphonic acids form valuable components of the commercial STs. As seen in Table 1, the ratio of $BOD_5$/COD, which indicates the biodegradability of the compounds, varies among the STs from 0.026 to 0.153. The absorbance values at 280 and 254 nm (indicating aromatic structure and double bound respectively) are high for all types of STs (Lofrano et al., 2007a).

On the basis of the studies conducted on naphthalene-sulfonic tanning agents, Song et al. (2005) proved that mono-sulfonated monomers (1-naphthalenesulfonate, 1-NSA and 2-naphthalenesulfonate, 2-NSA) is biodegradable with the use of cultured bacterial strains. Whereas di-sulfonates monomers (NDSA) show a more varied behaviour:1,5- and 2,7-naphthalene disulfonate are not biodegradable (Breithaupt et al., 2003), 1,6- and 2,6-naphthalene disulfonate are biodegradable and 1,7-naphthalene disulfonate seems to be minimally biodegradable (Reemtsma et al., 2002).

*2.2. Analytical*

Due to their inherent properties (e.g. molar weight, Henry's constant etc), tannins are difficult to detect using gas chromatography. Among various methods attempted to detect VTs from plant extracts and in food and beverages, reversed-phase HPLC with UV-detection are the most frequently used (Benítez et al., 2009; López-Vélez et al., 2010; Romani et al., 2012). Mass spectrometry and NMR-spectroscopy allowed to achieve structural elucidations of these compounds, but only a few articles are reported in literature (Haroun et al., 2013; Zywicki et al., 2002). Table 2 presents some studies to determine tannin contents of different compositions.

To date no standard chromatographic methods have been developed for STs. Lofrano et al. (2007b, 2008) attempted to apply Liquid-Liquid Extraction (LLE), which is commonly used for phenolic analysis, followed by a derivatization procedure before a gas chromatograph-mass spectrometry (GC-MS) for screening two STs commonly used in leather tanning industry. Preliminary experiments conducted without derivatization resulted in poor resolution of chromatographic peaks with inadequate precision (Fig. 2a). After that a derivatization technique was adopted, and the obtained spectrum is shown in Fig. 2b. Accordingly a derivation procedure should be carried out as preliminary step for GC-MS analysis.

All fatty acids were determined as their respective methyl ester since the derivatization procedure caused their esterification (Table 3).

## 3. Industrial sources of tannins in wastewaters

Tannins have been recognized as a double-ended concern of global interest because they are also present in wastewater of several agro-industries as summarized in the Table 4.

**Table 2.** Detection of tannins in different compositions

| *Reference* | *Instrument* | *Compost* | *Tannin species* |
|---|---|---|---|
| Benítez et al. (2009) | HPLC | phenolic fraction of cork industry wastewater | gallic, protocatechuic, vanillic, syringic, ferulic and ellagic, the last one in a major extent |
| López-Vélez et al. (2010) | HPLC | 12 commercial Spanish red wines | gallic acid was the highest of the phenolic acids (mean value 81.11 mg/L) and (-)-epicatechin and (+)-catechin and were the next most abundant phenolics |
| Romani et al. (2012) | HPLC/DAD/ESI-MS | aqueous and hydro alcoholic myrtle and pomegranate | galloyl-glucosides, galloyl-quinic acids, ellagitannins and flavonoids |
| Hoong et al. (2010) | MALDI-TOF mass spectrometry (MS) and solid state CP-MAS$^{13}$C Nuclear Magnetic Resonance (NMR) spectroscopic technique | *Acacia mangium tannin* (condensed tannins) | oligomers of condensed tannins of up to 11 flavonoid units (3200 Da). |
| Haroun et al. (2013) | Hide powder method, combined method, Folin-Denis method, and Hagerman Butler method | *Acacia mangium tannin* (condensed tannins) of central and western Sudan | of the sixteen parts studied, nine had more than 10% tannin content |
| Chupin et al. (2013) | RP-HPLC | maritime pine (*Pinus pinaster*) bark condensed tannins | catechin was the main condensed tannin in the extracts while lower quantities of epicatechin and epicatechin gallate were also measured |

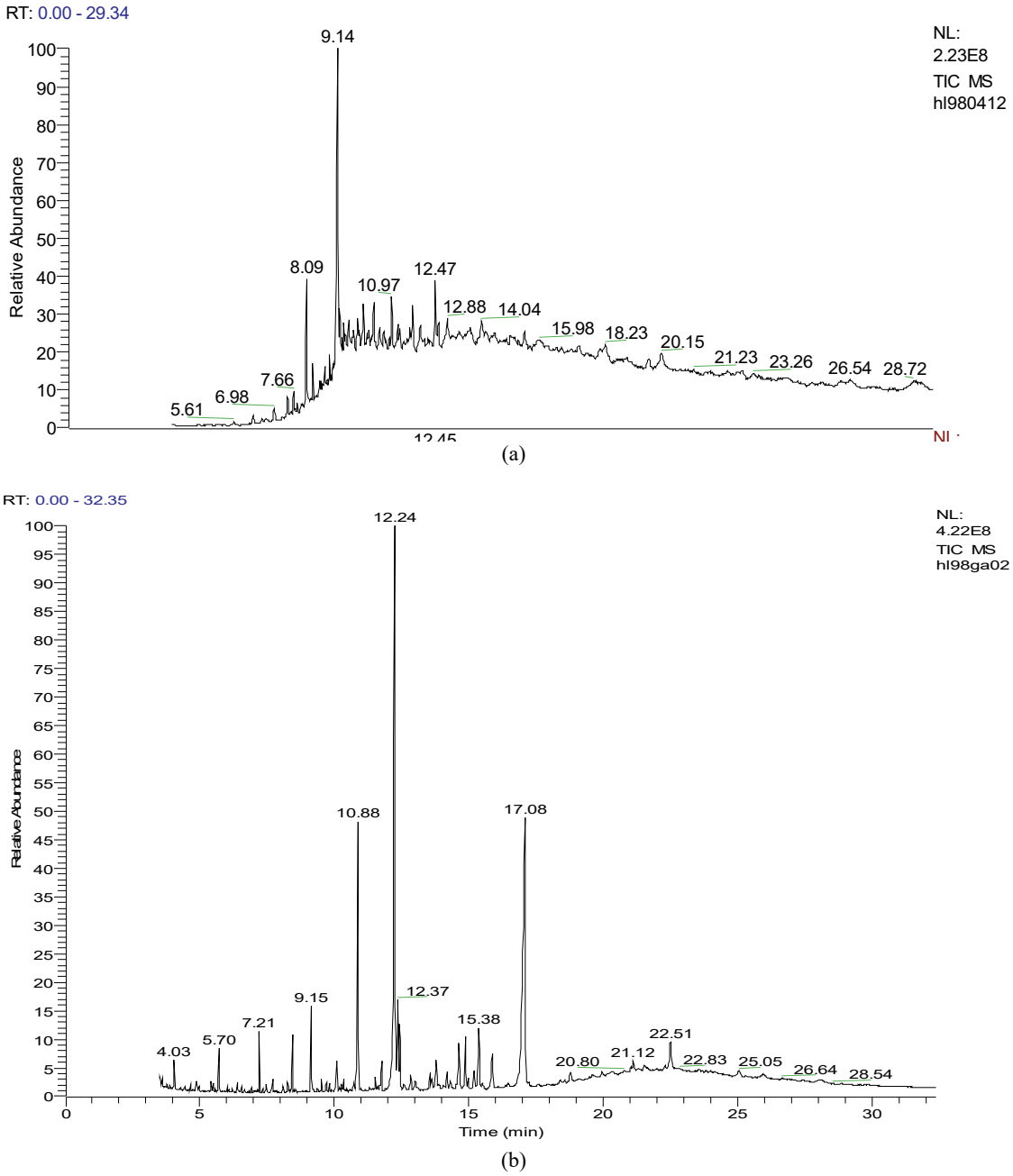


**Fig. 2.** GC-MS scan of a synthetic tannins investigated and after derivatization; inset GC-MS scan of a synthetic tannins investigated without (a) and after derivatization (b) (modified from Lofrano et al., 2008)

**Table 3.** Tentative chemicals determined with derivatization in some STs (>90% probability) (adapted from Lofrano et al., 2007b)

| ***Synthetic tannins and >90% probabilistic chemicals identified*** | |
|---|---|
| ST1 | ST2 |
| Trimethyl(2,6 ditert.-butylphenoxy)silane | Trimethyl(2,6 ditert.-butylphenoxy)silane |
| Octanedioic acid | Octanedioic acid |
| Azelaic acid | Azelaic acid |
| Dibutyl phthalate | Dibutyl phthalate |
| Hexadecanoic acid | Hexadecanoic acid |
| Octadecanoic acid | Octadecanoic acid |
| Oleic acid | Oleic Acid |
| Trimethyl(4-(4-[(trimethylsilyl)oxy]benzyl)phenoxy)silane | Trimethyl(4-(4-[(trimethylsilyl)oxy]benzyl)phenoxy)silane |
| Hexadecanoic acid | Hexadecanoic acid |
| 2,2-Bis[(4-trimethylsiloxy)phenyl]propane | 4-Trimethylsiloxyphenylphenoxysulfone |
| Tetradecanoic acid | Trimethyl(4-tert.-butylphenoxy)silane |
| | 4-Trimethylsiloxyphenyl-2'-trimethylsiloxyphenylsulfone |

**Table 4.** Tannin concentrations in different agro industrial wastewaters

| *Reference* | *Industry* | *Location* | *Concentration* |
|---|---|---|---|
| Marin-Martinez et al. (2009) | Tannery industry | Mexico | 450 kg/m$^3$ of *Quebracho* extracts; 150 kg/m$^3$ remains in wastewaters |
| Babuna et al. (2007) | Textile dyehouse | Turkey | 150 mg/L of estimated typical final concentration of VTs and STs |
| Koyunluoglu et al. (2007) | Textile dyehouse | Turkey | 120 mg/L of estimated typical final concentration of VTs and STs |
| Mohan and Karthikeyan (1997) | Effluents from pulp and paper mills | India | 50-55 mg/L |
| Benítez et al. (2008) | Cork process industry wastewater | south west of Spain | 897 mg/L of tannic acid |
| Benítez et al. (2009) | Cork processing plant wastewater | San Vicente de Alcántara (Extremadura Community, Spain) | 761 mg/L of tannic acid; ellagic acid was also measured ($3.0\times10^{-5}$ M) |
| Dias-Machado et al. (2006) | Exhausted cork boiling wastewaters | North of Portugal | estimated 660–780 mg/L of tannic acid |
| Lafi et al. (2009) | Olive mill wastewater | Jordan | measured a content of 270 mg/L of total polyphenols |
| Hanafi et al. (2010) | OMW (olive extraction plant) | Morocco (Marrakech) | 260 mg/L |
| Dhaouadi et al. (2008) | OMW | | measured a concentration of 5410 mg/L of phenols |
| Lucas et al. (2009a, 2009b) | Winery wastewater | Portugal | measured concentration as equivalent gallic acid of 103 mg/L |
| Mosteo et al. (2006) | Winery wastewater | Spain | 29 -39 mg/L) of gallic acid |
| Beltrân et al. (2001) | Effluent of a commercial winery factory | Badajoz and Villafranca de los Barros (Badajoz province, Spain) | measured 735 mg/L of gallic acid |
| Zhang et al. (2010) | Exhausted coffee | China | a low tannin content as compared to other plants such as leaves of *Kandelia candel* and *Rhizophora mangle* (106 mg/g and 219 mg/g, respectively) |

*3.1. Leather tannery*

Among many agro-industries releasing tannins, leather tanning industry is one of the most important discharging both VTs and STs (Bienkiewicz, 1983; Lofrano et al., 2007a; Meric et al., 2005). The VTs (*Quebracho*, *Mimosa*, *Chestnut*, *Myrabolams*, *Valonia*) and STs are both used in the tannage in order to convert hides and skins to leather and as retanning agents (Cassano et al., 2003; Lofrano et al., 2007a, 2007b, 2010; Marin-Martinez et al., 2009; Munz et al., 2009). Possessing lower molecular weight STs diffuse into the hide more rapidly than VTs. Both VTs the STs are not completely fixed by skins and remain in the effluent creating environmental problems owing to the high content of organic matter discharged in the wastewaters (Cassano et al., 2003; Lofrano et al., 2007a, 2007b, 2013; Munz et al., 2009; Scholz and Lucas, 2003).

*3.2. Textile industry*

The STs and tannic acids are frequently used also during polyamide dyeing with acid, metalcomplex or direct dyes at the after-rinsing stage to increase the fixation rates and wet fastness onto the dyed fabric (e.g. nylon) in textile industry (Babuna et al., 2007; Burkinshaw, 1995; Dentel et al., 1998; Koyunluoglu et al., 2007). STs for nylon fabric are typically water soluble, anionic formaldehyde polycondensed of arylsulphonates and sulphonates of dihydroxydiaryl sulphones (Burkinshaw, 1995). Aqueous discharge of acid dyebath containing acid dyestuffs along with either STs or VTs has a typical pH of around 3.5-4.0 and a temperature of approximately 80-85 $^{o}$C (Babuna et al., 2007).

*3.3. Paper mill*

Papermaking involves five basic phases and each one can be carried out by a variety of methods: debarking, pulping, bleaching, washing and pulp or paper production (Ali and Sreekrishnan, 2001). Wastewater derived from the debarking process in paper mills has been found to contain large amounts of tannins that contribute as much as up to 50% of the COD of these wastewaters (Ali et al., 2001). Moreover, since the tannins tint these wastewaters, they tend to absorb more light and heat and retain less oxygen than unprocessed water, thereby negatively affecting the aquatic flora and fauna.

*3.4. Cork industry*

The processing of the raw cork from *Quercus suber* to obtain the final material in its first step produces a dark liquor which contains some corkwood extracts, such as phenolic acids, tannic fraction, 2,4,6-

trichloroanisol and pentachlorophenol (Benítez et al., 2009; Mazzoleni, 1998). As consequence a high content of phenols (360-410 mg tannic acid/L) and tannins (250-270 mg tannic acid/L) has been detected in cork wastewater (Bernardo et al., 2011).

### *3.5. Olive mill*

Olive mills produce effluents containing the highest load of phenolic compounds including HTs and CTs (Hanafi et al., 2010; Lafi et al., 2009; Pepi et al., 2010). However it has not been found a model compound for measuring the phenolic content of OMW. The high-molecular-weight phenolic compounds similar in structure to lignin give olive mill wastewater (OMW) its characteristics recalcitrant brownish black colour. It has been found that the concentration of phenols can be as high as 10 g/L (Amat et al., 2003; Khoufi et al., 2007).

### *3.6. Winery*

Gallic acid is considered one of the most representative phenolic compounds present in the winery wastewaters (Lucas et al., 2008; Mosteo et al., 2006). The total polyphenol content of winery wastewater can vary in a wide range (100-1000 mg/L gallic acid) (Lofrano and Meric, 2016).

### *3.7. Coffee production*

Coffee industry discharges caffeine, fat, and peptic substances, as well as many different macromolecules including lignins, humic acid and tannins (Zayas et al., 2007). Total polyphenols and tannins represent <6% and <4% of the exhausted coffee wastes, respectively (Pujol et al., 2013).

## 4. Fate of tannins in wastewaters and its toxicity

Tannins are known to exhibit methanogenic toxicity to an extent that depends on the degree of polymerization (Field et al., 1988). The hydrogen-bonding reactions with proteins are postulated to cause toxicity to bacteria, because such interactions interfere with the functioning of enzymes (Haslam, 1974; Gupta and Haslam, 1980; Liu et al., 2010; Schofiled et al., 2001).

Several studies have been carried out to evaluate the toxicity of tannins to microorganisms, especially to anaerobes (Ali and Sreekrishnan, 2001; Chen et al., 2008; Field and Lettinga, 1987; Temmink et al., 1989). The study performed by Field and Lettinga (1987) showed that gallotannic acid is a potent inhibitor of methanogenesis and the toxicity persisted despite the rapid degradation of gallotannic acid to volatile fatty acids and methane. Concentrations representing 30% inhibition approximated to 700 mg/L of gallotannic acid. Field and Lettinga (1987) hypothesized that the toxicity might have involved the 'tanning' of proteins such as enzymes located at accessible sites in the methanogenic bacteria.

Comparing toxicity of CTs and HTs, HTs tannins are more toxic than that of condensed tannins (Liao et al., 2003). It is attributed that hydrolysable tannins are apt to decompose into gallic acid by hydrolyzation, which is easy to impair human health (Liu et al., 2010).

Rao and Mariappan (1972) reported that 320 mg/L of tannin was toxic to *Catla catla,* a fresh water fish. The bark of Norway spruce (*Picea abies*) was added to aquaria containing carp (*Cyprus carpio* L.*)* under semi-static (sub-acute toxicity) and flow-through (acute toxicity) conditions and it was demonstrated that CTs from spruce bark are toxic, not only to methanogens, at concentrations present in the paper mill wastewaters but also to aquatic organisms, like fish (Temmink et al., 1989).

A comparative study of the toxicity of mimosa tannin and phenol-based ST was carried out by monitoring sea urchin (*Paracentrotus lividus* and *Sphaerechinus granularis*) early development and marine algal growth (*Dunaliella tertiolecta*). 1 mg/L of both VT and ST water extracts affected sea urchin embryogenesis. (De Nicola et al., 2007). Fertilization success of sea urchin sperm was increased up to 0.3 mg/L ST or VT, then was inhibited by increasing tannin levels (1-30 mg/L). Cell growth bioassays in *Dunaliella. tertiolecta* exposed to VT and ST water extracts showed non-linear concentration-related toxicity.

A battery of tests (*Daphnia magna*, *Artemia salina*, *Selenastrum capricornutum* and *Lepidium sativum*) was carried out in our previous study Lofrano et al. (2008) to assess the toxicity of different syntans. The bioassays used resulted in different sensitivity and end-points. *D. magna* and *S. capricornutum* were found to be the most sensitive species, whereas all syntans investigated did not display any toxic effect on *A. salina* even at the highest concentrations tested. Poly-condensed phenols with formaldehyde (ST2) displayed more sever toxicity than sulphonated based tannin (ST1) on *Daphnia magna*. ST2 corresponded to the highest COD and the lowest $BOD_5$ /COD ratio.

More recently Libralato et al. (2011) provided the ecotoxicological characterisation of lignin (0.2–440 mg/L) and tannin (0.1-500 mg/L) considering the marine alga *Phaeodactylum tricornutum* (Bohlin) as testing species. NOEC and LOEC values for both compounds were determined as <0.1 mg/L and 0.1 mg/L, respectively while $EC_{50}$ values were set at 113.84 (100.90–128.45) mg/L for lignin and at 26.04 (20.10–33.95) mg/L for tannin.

The toxicity tests are useful analytical tools for screening of chemical analysis and as an early warning system to monitor the behaviours of WWTPs. The use of different end points is the best approach to evaluate the risk because they are reliable indices of the toxic impact of effluents in the aquatic environment.

## 5. Removal processes of tannins from wastewater

Several methods have been attempted to treat wastewater containing tannins. Among them the

recent advances have been recorded from basic processes through advanced oxidation processes and hybrid treatments. Since during the oxidation process some by-products (intermediates) are formed and the effluent may become more toxic than the untreated solutions or the parent compounds, respectively, the overall efficiency of the treatment process for this class of chemical pollutants strictly depends on the toxicity of treated effluents. Therefore, the use of bioassays to optimize AOPs when applied to treat toxic effluents or compounds is considered crucial to assess the applicability of these processes. However only few studies investigated the toxicity after treatment (Lofrano et al., 2007a, 2007b, 2008; Koyunluoglu et al., 2007; Schrank et al., 2004) the missing of these date does make not possible a complete assessment of the treatment technologies.

### *5.1. Physicochemical treatment*

#### *5.1.1. Adsorption*

Mahesh et al. (1999) reported the study of tannin removal from coffee curing industrial effluents using adsorbent materials. Maximum adsorption was registered between pH 3.0-4.5 for activated coconut shell (ACS) and 5.5 to neutral pH for industrial grade granular activated carbon (IGGAC) respectively. The removal of tannin from aqueous media by cationic surfactant-modified bentonite clay was studied in a batch system at pH 3.0 using different initial tannin concentrations of 10, 25, 50, and 75 μmol/L (Anirudhan and Ramachandran, 2006). The adsorbent exhibited higher tannin removal efficiency (>99.0%) at the concentration of 10.0 μmol/L at pH 3.0 and $30^0$C after 6h. The maximum adsorption at the pH range 3.0–4.0 was due to the external hydrogen bonds formed between phenolic⁻OH groups of tannin and the hydrogen-bonding sites on the clay. The un-dissociated tannin molecules dominating at low pH were hydrophobic and more adsorbable than the ionized forms as the hydrophobic bonding became the driving force for adsorption. Increase in pH increased the solubility of tannin; this means decreased uptake, as there is a nearly inverse relationship between sorbate solubility and adsorption potential.

Similar findings were observed more recently by Liu et al. (2010) who established that Konjac glucomannan (KGM), a low-cost neutral polysaccharide derived from the tubers of *Amorphophallus konjac*, modified by deacetylation in alkali solution to make it insoluble (DKGM), would have good potential to adsorb tannins. Varying amounts (0-80 g/L) of DKGM were used in 50 mL tannin solution at concentration of tannin 1 or 5mmol/L while pH and temperature of tannin solutions were kept at 3.3 and 20ºC, respectively. After adsorbent dosage increases to approximate 20 g/L, the removal efficiency increased smaller. The adsorption kinetics of tannin onto DKGM better fits into the pseudo-second-order kinetics model (Liu et al., 2010) rather than pseudo-first-order kinetics model (Anirudhan and Ramachandran, 2006).

#### *5.1.2. Membrane technologies*

Pressure-driven membrane separation processes (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)) constitute attractive alternative candidates to conventional wastewater treatments for purification of tannin wastewater because of their high removal efficiencies and also because they allow reuse of the treated water or some of the valuable waste constituents as the same tannins (Benítez et al., 2009; Cassano et al., 2003; Romero-Dondiz et al., 2015; Scholz and Lucas, 2003). Benítez et al. (2009) obtained a very high removals of ellagic acid and color (>90%), high removals of absorbance at 254 nm and tannic content (>70%) by using UF and NF membranes for the purification of cork processing wastewater. A NF process was carried out by Cassano et al. (2003) for recovering tannins and water from exhausted baths of leather tanning industry and reusing them as tanning agents and washings. NF resulted to be a technically viable method for recovering tannins from spent tannin liquors and pollution control in vegetable tanning factories.

The recovery of VTs was obtained in an on-site pilot membrane filtration plant by Scholz and Lucas (2003). Their experiments proved that the implementation of a recycling plant for VTs can offer significant savings on chemicals with a 15% reduction in vegetable tanning agent and 90% process liquor recovery.

Over the last years, the recovery of polyphenols from OMW has been also achieved in the laboratory using membranes (El-Abbassi et al., 2009), for the purpose of application in the pharmaceutical industry. Although the above utilization is technically feasible, it is too early to achieve large-scale application (Hanafi et al., 2010).

### *5.2. Biological treatment*

The degradation of gallotannins by an anaerobic bacterium, *Achromobacter* sp. was reported for the first time by Lewis and Starkey (1969). Deschamps et al. (1980) carried out a detailed study on this phenomenon and by enrichment culture technique using tannic acid as the sole source of carbon, isolated fifteen bacterial strains belonging to the genera *Bacillus*, *Staphylococcus*, and *Klebsiella*. Bacteria able to grow in the presence of tannins are commonly considered tannin-resistant and resistance is not limited by species or geographical barriers (Pell et al., 2000).

Tannase enzyme catalyses the breakdown of HTs such as tannic acid, methyl gallate, ethyl gallate, n-propylgallate, and isoamyl gallate. Tannic acid is completely hydrolysed to gallic acid and glucose through 2,3,4,6,-tetragalloyl glucose and two kinds of monogalloyl glucose (Aguilar et al., 2007).

Li et al. (2009) carried out biological treatment of simulated tannic acid (TA)-containing wastewater by activated sludge in order to find the optimal biodegradation conditions and to investigate the

aerobic biodegradation kinetics. Firstly batch experiments under different pH (5-8), temperature (15-35$^0$C), and aeration rates (12 -30 L/h) were carried out to find the optimal degradation conditions of tannic acid solutions in SBR reactors/flasks by Li et al. (2009). The initial concentration of the tannic acid was controlled at around 800 mg/L. However the highest degradation rate of tannic acid occurred at pH within the range 5 - 8, indicating the high adaptation of microorganisms to a wide pH range. In stable operation stage, the average removal percent of tannic acid reached 85.2%.

Membrane bioreactors (MBR) have been applied in recent times to wastewater containing phyto-toxic and antibacterial polyphenolic components such as in olive mill effluents (Dhaouadi and Marrot, 2008; El-Abbassi et al., 2009), cork (Benítez et al., 2008, 2009), leather tanning wastewater (Munz et al., 2009). According to the study of Dhaouadi and Marrot (2008) the concentration of phenolic compounds (5410 mg/L), which can be associated with the presence of tannins, was significantly reduced (92% of removal) treating OMW by MBR. However it has been reported that phenolic compounds were mostly retained on cell surfaces. By comparing Conventional Activated Sludge (CAS) Process and (MBR) in regards to biodegradability of tannins, it did not appear to be significant. Since in nature the most important degraders of tannins are fungi in the next future more investigations should be performed about this group of organisms.

### *5.3. Advanced oxidation processes*

Advanced oxidation processes (AOPs) involve the generation of highly reactive radical species, predominantly hydroxyl radicals ($HO^{\cdot}$) which react non-selectively with a wide range of organic compounds (Beltrân et al., 2001; Beltran de Heredia et al., 2005; Lofrano et al., 2007, 2013; Lucas et al., 2009a, 2009b, 2010).

#### *5.3.1. Fenton and photo-Fenton oxidation*

Fenton oxidation (FO) process is one of the oldest advanced oxidation processes which is being increasingly used in the treatment of contaminated wastewater where can lead to the complete mineralization of some organic compounds, converting them to $CO_2$, $H_2O$ and inorganic ions (Meric et al., 2004). The rate of FO process essentially depends on pH, temperature, doses of $H_2O_2$ and $Fe^{2+}$ and chemical structure of the organic compounds (Lofrano et al., 2007b). The Fenton like process consists of a mixture of ferric ion $Fe^{3+}$and hydrogen peroxide. During this process, $Fe^{2+}$ is produced in situ from the reaction between $Fe^{3+}$ and $H_2O_2$, which in turn reacts with $H_2O_2$ to produce more $OH^{\cdot}$ radicals. The $Fe^{2+}/Fe^{3+}/H_2O_2$ system has its maximum catalytic activity at pH = 2.8–3.0. At elevated pH, the ferric ion precipitates as ferric hydroxide and at lower pH, the complexation of $Fe^{3+}$ with $H_2O_2$ is inhibited.

The study by Lofrano et al. (2007a) showed that independently from their chemical structure (containing different compounds) STs were rapidly oxidized (in 10-15 min) in the presence of 600 mg/L of $H_2O_2$ and 500 mg/L of $FeSO_4$ at pH 3.0, 40–45°C and 30 rpm conditions, achieving a 80–90% of COD removal (Fig. 3).

As the continuation of the previous work, the $[H_2O_2]/[Fe^{2+}]$ ratio was varied to optimize Photo-Fenton processes by using different light sources (UV-A and UV-C). A combination of $H_2O_2$ and UV radiation with ferrous ion $Fe^{2+}$ or ferric ion $Fe^{3+}$, the so-called photo-Fenton process, involves irradiation with light, which increases the rate of contaminant degradation by stimulating the reduction of $Fe^{3+}$ to $Fe^{2+}$.

A 300/750 (w/w) ratio of $[H_2O_2]/[FeSO_4]$ increased degradation of ST1 and mineralisation efficiency was observed as shown in Fig. 4. As seen in Fig. 4, after 15 minutes of Fenton oxidation and photo-Fenton oxidation using both UV-A and UV-C the COD removal efficiency of initial 300 mg/L equivalent of ST was 62%, 78% and 76% respectively. Toxicity tests showed an increase in toxicity after 10 min due to treatment schedules by Fenton oxidation and photo-Fenton (UV-A). The increase in toxicity was associated with the higher amounts of by-products formed at that time.

Lucas et al. (2008) reported a 90.8% of removal of an initial concentration of $5.3 \times 10^{-4}$ mol/L gallic acid by Fenton's process ($[Fe^{2+}] = 5.3 \times 10^{-5}$ mol/L; $[H_2O_2] = 2.7 \times 10^{-3}$ mol/L) after 7.5 minutes of reaction, at pH 4. In the same study the gallic acid oxidation by the ferrioxalate process ($[H_2O_2] = 2.7 \times 10^{-3}$ mol/L; $[Fe^{3+}] = 5.3 \times 10^{-5}$ mol/L; [Oxalic Acid] = $1.7 \times 10^{-5}$ mol/L), considered as a Fenton-like process, was also evaluated.

However less than 5% of gallic acid removal could be achieved. Lucas et al. (2008) observed a similar degradation capacity in all photo-Fenton processes by using UV-C and UV-A, adding Fenton reagents ($[Fe^{2+}] = 5.3 \times 10^{-5}$ mol/L, $[H_2O_2] = 2.7 \times 10^{-3}$ mol/L) to the same solution of gallic acid, independently from the light source.

#### *5.3.2. Electrochemical treatment*

In electrocoagulation (EC) process, aluminum or iron hydroxide flocs, which destabilize and aggregate the suspended particles or precipitates and absorb dissolved contaminants, are produced by anodic dissolution followed by hydrolysis (Hanafi et al., 2010). Application of different anodic materials with different electrocatalytic properties can affect reactor treatment efficiencies (Szpyrkowicz et al., 2001). Szpyrkowicz et al. (2001) applied EC to wastewater collected at the common effluent treatment plant of Ranipet (India), in which about 400 small tanneries (both chrome and VT), discharging their raw effluent.

The wastewater used was sampled after the anaerobic lagoon and presented a content of tannins ranging from 23.9 to 83.7 mg/L. For a current density

of 4 A $dm^{-2}$ and operation without any mechanical or hydraulic mixing, a 60% depletion of tannins occurred in the first 10 min.

EC treatment of olive mill wastewater (OMW) was attempted by Hanafi et al. (2010) using an aluminum electrode under the conditions of electrolysis time of 15 min, NaCl concentration of 2 g/L, initial pH value of 4.2 and current density of 250A $m^{-2}$ a large amount of polyphenols from OMW (70%). Accordingly the authors reported that toxicity performed on *Bacillus cereus* decreased within 15 min of the EC treatment up to 70%.

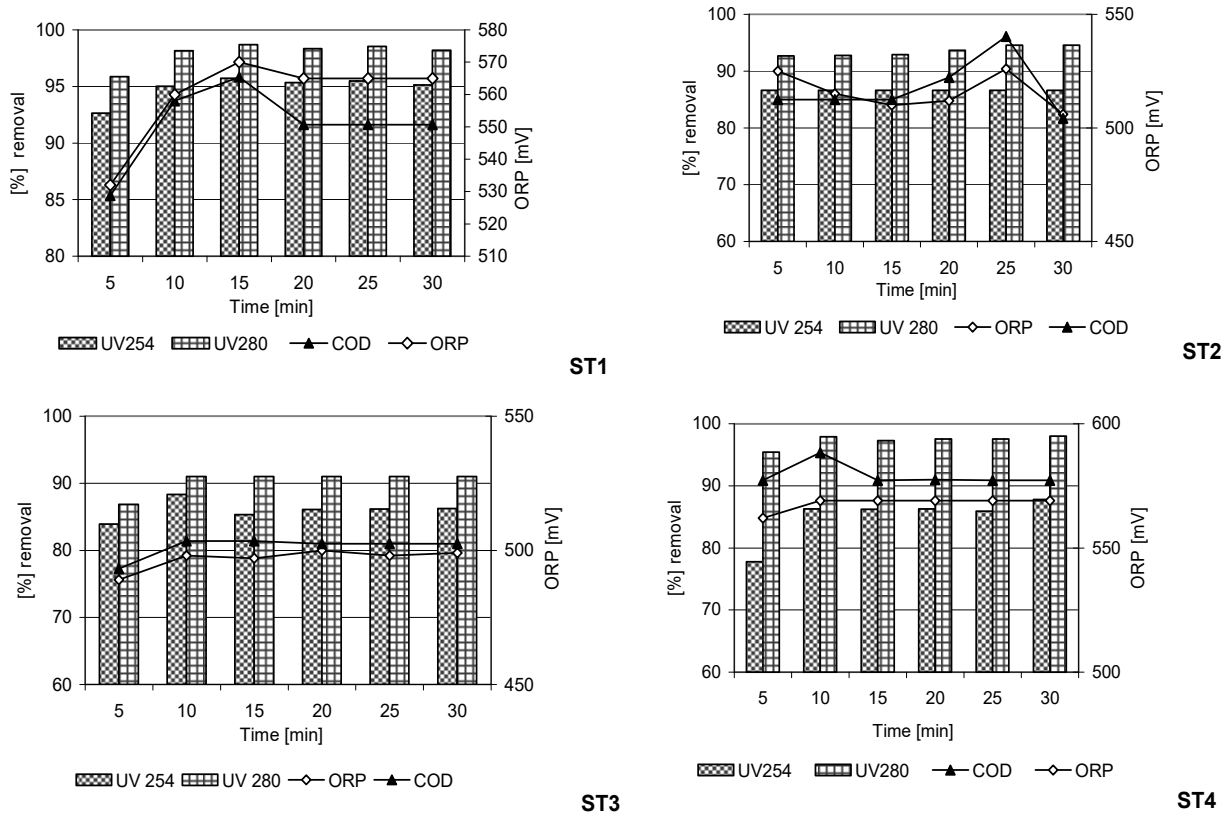


**Fig. 3.** COD and UV removal for some synthetic tannins ST1 cresol-based (a), ST2 poly-condensed formaldehyde and disulphane with sulfonic aromatic acids (b), ST3 phenol-based (c), ST4 condensed phenol- based (d) versus time using 600/500 w/w ratio of $H_2O_2/FeSO_4$ at 30 rpm, 43 $^0$C and 3.0 pH. (Lofrano et al., 2007a with kind permission of Elsevier)

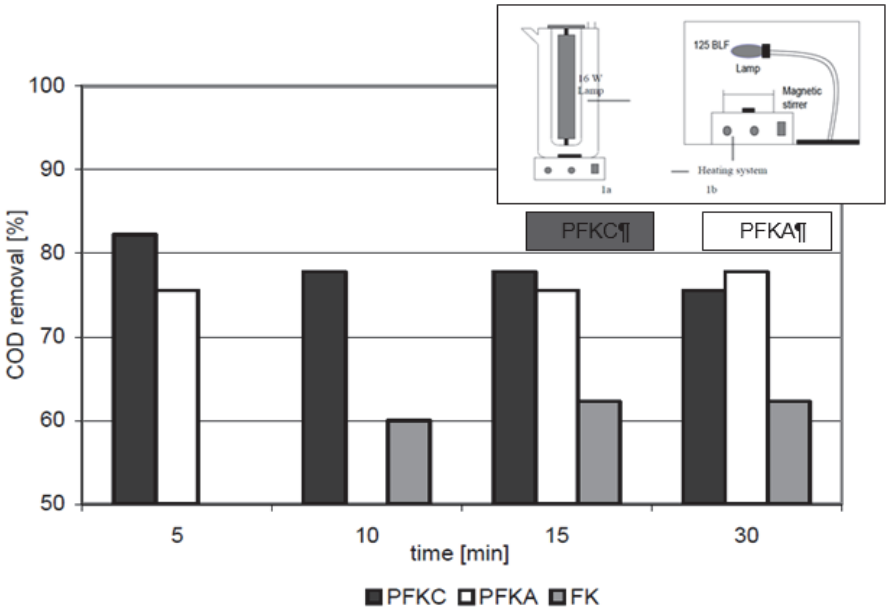


**Fig. 4.** Time interval removal for 300 mg/L of synthetic tannin using 300/750 (w/w) of $H_2O_2/FeSO_4$ at pH 3.0 and temperature 45$^o$C Inset: Photo-Fenton process experimental set-up (modified from Lofrano et al., 2007b)

*5.3.3. Ozone*

It is hypothesized that polyphenolic macromolecules like tannins are prone to attack by electrophilic agents such as ozone (Koyunluoglu et al., 2007; Saroj et al., 2005). A huge literature is available regarding the ozonation of tannin-like polyphenols such as debittering table olive wastewaters or winery wastewater (Beltrân et al., 1999; Lucas et al., 2009a). Upon their exposure to ozone significant biodegradability improvement as a consequence of de-polimerization of aldehydes and carboxylic acids was reported by Amat et al. (2003). Only few studies deal with the ozonation of STs (Babuna et al., 2007; Koyunluoglu et al., 2007). The effect of ozonation on the COD distribution and toxicity of raw and ozonated natural and STs in textile dyebath discharges samples, according to their molecular weight cut-offs was assessed by Koyunluoglu et al. (2007). Ozone experiments were carried out on solutions of VTs and STs with an initial COD of 1195 mg/L and 465 mg/L respectively, at two different pHs (3.5 and 7) and varying ozone doses (0-2000 $mgO_3$). Toxicity tests revealed no significant changes in the acute toxicity of ozonated VT samples. Therefore ozonation cannot be considered an appropriate method for VT degradation.

Studies carried out by Beltrân et al. (2001) on winery wastewater confirmed this mechanism for ozone treatment: pH sequential cycles (acidic and alkaline periods) were required to obtain a high rate of mineralization of organics. Further studies carried out by Lucas et al. (2009a) established that the degradation rate of polyphenol by ozonation is faster at acidic pH than at alkaline pH. Therefore, it may be concluded that the ozonation at natural pH (acidic pH) should be favored over the same reaction at alkaline pH.

*5.3.4. Photocatalysis*

The photocatalytic oxidation of a phenolic mixture (167-1886 mg/L sum of concentrations of the three phenols) including gallic acid, tyrosol and syringic acid was carried out by Gimeno et al. (2003) in the presence of titanium dioxide and inorganic peroxides. The results obtained in UV-An irradiated solutions revealed that hydrogen peroxide at the concentration of 5.5 mM was the most effective option to degrade phenolic compounds. A high concentration of organic molecules may compete with the electron acceptors (oxygen or $H_2O_2$) for adsorption onto active sites so that electron trapping can be partially inhibited (assuming that organics do not directly react with holes).

Gallic acid degradation by heterogeneous and homogeneous photocatalysis using different radiation sources: solar and ultraviolet radiation was carried out by Lucas et al. (2008). After 60 minutes of irradiation under a low-pressure mercury vapor lamp and at pH 4, 34.7% of removal of an initial concentration of 5.3 × 10−4 mol/L of gallic acid was achieved, a superior value compared to the removal obtained with a UV lamp with a medium-pressure mercury lamp (20.2%) and highly superior one to the solar radiation (2.3%).

The gallic acid degradation by $TiO_2$ was also evaluated in the study of Lucas et al. (2008). It was observed that the $TiO_2$ (Degussa P25) itself cannot remove the phenolic compound studied, and that after 60 min of contact time no adsorption process occurred. The combination of $H_2O_2$ [$2.7\times10^{-3}$ mol/L] with $TiO_2$ [0.5 g/L] and solar radiation showed a degradation of 52.1%.

*5.3.5. Sono-chemical treatment*

Experiments were conducted by Svitelska et al. (2004) for the degradation of CT by using ultrasonic irradiation (US) at different pH values (4-12), with or without $H_2O_2$ (0.05 M) and temperature around $50^0$C; also at various $H_2O_2$ concentrations (0.01-0.05), pH 10.5 and temperature around $50^0$C; and finally at different temperatures (22, 34 and $50^0$C), pH 10.5 and 0.05 M $H_2O_2$. Initial CT concentration was 1 g/L, corresponding to 70 mg/L of TOC. In the absence of $H_2O_2$ at alkaline conditions the authors observed an intensive coloration of solutions noticing the same extensive coloration of procyanidin (condensed) tannins during their autoxidation; changes in aromatic structure of some tannins (detannification) were also detected. According to their studies, the removal of CT 20–30% higher in the presence of sonication than in silence. The best result, 94% of CT removal and 77% of TOC reduction, were obtained under US at pH 11.4, with $H_2O_2$ concentration 0.05 M and temperature around $50^0$C.

*5.4. Hybrid processes*

Considering the difficulties encountered during the biological treatment of wastewater containing tannins, advanced oxidation processes (AOPs) and combinations thereof with biological treatment appears to be a feasible and better option. The presence of this kind of compounds for the microorganisms frequently makes impossible the complete biological treatment of winery wastewater. On the other hand biological treatment mineralizes a large biodegradable portion reducing number and concentrations of compounds that may compete for consumption of hydroxyl radicals thus increasing overall efficiency of Fenton reaction and lowering costs.

Beltran de Heredia et al. (2005) proved that aromatic and total polyphenolic concentration of wine distillery wastewaters aerobically treated was significantly reduced (removal >90%) in the early 5 min. of Fenton oxidation. A combined treatment consisting of an aerobic biological process followed by a chemical oxidation using Fenton's reagent in winery wastewater was also carried out by Lucas et al. (2009b).

More recently Justino et al. (2009) evaluated the efficiency of two treatments involving fungi (especially Pleurotus sajor caju) and photo-Fenton oxidation, sequentially applied to olive mill

wastewater for organic compounds degradation and toxicity mitigation. According to their studies the photo-Fenton oxidation followed by biological treatment was more efficient (reduction of total phenolic content 81-92%) than the inverse sequence (biological treatment followed by photo-Fenton oxidation). On the other hand Kalyanaraman et al. (2015) demonstrated as Fenton's reagent pre-treatment resulted in 51% and 85% reduction of COD and phenol removal due to mineralization, with subsequent improvement in BOD5/COD ratio of tannins from 0.196 to 0.443. As consequence wastewater pre-treated with Fenton's reagent resulted in BOD5 and COD of 26 and 210 mg/L in the aerobic treated final effluent.

## 6. Conclusions and future outlooks

Vegetable and synthetic tannins (VT and STs) are used for many industrial and human consumption purposes. VTs have become sustainable and ecofriendly solution for environmental engineering problems while their large consumption needs to be optimized by the use of synthetic tannins at industrial applications.

Recent analytical methods for the detection of hydrolyzable tannins (HTs) are less thoroughly developed. There are still few studies available. on the determination of HTs by mass spectrometry.

Toxicity studies have indicated that tannins are hardly biodegraded thus after certain environmental concentrations they become toxic. Thus the need of integration of strong oxidation processes namely called advanced oxidation processes (AOPs) has become obvious. Hybrid processes coupling physico-chemical, chemical or photo advanced oxidation processes with biological treatments can solve the problem of degrading these important organo pollutants. Although there are still difficulties to overcome with the use of AOPs, lying in the high cost of reagents such as ozone, hydrogen peroxide or energy light sources like ultraviolet light, the use of solar radiation as an energy source, has been the most popular green alternative to reduce treatment costs. There have been many aspects of tannins evaluated. This review paper is to mention the need of research advances which should continue to evaluate optimum control of tannins for considering safeguard of environment and human health.

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