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Technologies of winery wastewater treatment: a critical approach

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ABSTRACT

The production of wine is one of the important agricultural fields in Southern European countries and its importance to other parts of the world (e.g. Australia, Brazil, Chile, China, India, South Africa, and USA) is increasing and impacting on their economies. A high volume of winery effluents is produced everyday. Although the need for efficient treatment of winery wastewaters is important, using different technologies, other crucial factors also need to be taken into consideration—such as the geographic location of each country, etc. This review paper indicates that the composition of winery effluents located in many countries of world is different and the climate strongly influences the appropriate technology to be selected for wastewater treatment. Furthermore, the technologies used for winery wastewater treatment are investigated and briefly analyzed. The major concluding remark of this review is that: (i) the selection of the most appropriate treatment technology is based on the location of each industry (country); (ii) some future applied technologies (adsorption) enhance the possibility of selectively reusing some highly added value compounds (i.e. resveratrol) existed in winery wastewaters.

Keywords: Winery effluents; Treatment technologies; Biological technique; Economical aspects

1. Introduction

The production of wine is one of the most important agricultural fields in European countries (France, Italy, Spain, Germany, and Greece) and its importance to other parts of the world (e.g. Australia, Brazil, Chile, China, India, South Africa, and USA) is increasing and impacting on their economies [1–7]. In particular, the worldwide wine production is ~264 × 10^5 m^3 (data raised in 2010), of which 71% from Europe, 17% from America, 4% from Asia, 4% from Africa, and 4% from Oceania [8]. The worldwide wine consumption (data raised in 2010) is ~232 × 10^5 m^3, distributed by Europe (69%), America (19%), Asia (7%), Africa (3%), and Oceania (2%) [8].

Beginning from the strict definition of the term, “wine” is the product after the crushing and fermentation of grapes, followed by the straining of skins and seeds, storage, clarification, and maturation of the young wine. Wine industries produce large amounts of wastes during their annual vintage [9]. There are

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two major categories of winery wastes: (i) liquid (effluents) and (ii) solid wastes.

The majority of winery effluent is cleaning waste, as wineries must be kept meticulously clean to avoid contamination and spoilage. Effluent is produced mainly from (i) rinsewater, (ii) water used to wash outsides of equipment and floors, (iii) washwater containing alkali salts (i.e. caustic soda) to remove tartrate and other organic acids from insides of equipment, (iv) earth filtering, and (v) ion exchange processes. Winery solid waste contain (i) stalks, seeds, and skins (marc) produced during the crushing, draining, and pressing stages; (ii) sediments (lees) containing pulp, tartrates, and yeasts from the fermentation stage; and (iii) bentonite clay and diatomaceous earth from the clarification processes much of which is delivered to third party processors for producing cream of tartar and tartaric acid. Solid waste amounts depend on the extent of juice extraction, the number of fermentation and clarification stages used in the manufacture of each wine type, and the type of equipment used for these processes. A typical winery produces about one ton of marc per 9–13 tons of fresh grapes crushed, mostly of which is water (about 65%).

Furthermore, there is a strong factor that impacts the production of winery effluents and that is seasonal conditions. Winemaking is a seasonal process. At northern hemisphere, its highest activity takes place in autumn (it corresponds to vintages and fermentations), a notoriously less important activity in spring on the occasion of transfers (racking period) and filtrations, and its weakest activity during winter and summer. In particular, Bustamante et al. [10] report that the winery effluents production in Spain has been approximately 18×10^6 m^3/year, which is generated during only a few months of the year (August–October). The Spanish wine industry generates six times more wastewater than France or Italy, mainly due to the low cost of the disposal fee.

As it is obvious, a high volume of winery effluents is produced daily. Although the need for efficient treatment of winery wastewaters is important, using different technologies, other crucial factors need to be also taken into consideration—such as the geographic location of each country, etc. The novelty of this review is to critically comment on some questions as, is there any difference regarding the composition of winery effluents located in different countries of world? Does the climate of each country influence the appropriate technology to be selected for wastewater treatment? Do the economic conditions of each country allow the turn on novel (but usually more expensive) treatment technologies? All the above are some of the main topics which are discussed in the present study.

2. Composition of winery effluents

Wastewater volumes vary considerably between wineries and may reach 5,000 L per 1,000 tons of grapes crushed [9]. Some typical quantities of winery effluents are: (i) small wineries with up to 5,000 kg of grapes crushed per tons of vintage (gc/v) give about 1,000–9,000 L of effluent per year (effl/yr); (ii) medium wineries (5,000–20,000 gc/v) produce 5,000–100,000 L (effl/yr); and (iii) large wineries (over 20,000 gc/v) give 40,000–240,000 L (effl/yr) [11].

The composition of the winery wastewater varies daily and depends on activities within the winery throughout the year. In general, wastewater consists of organic matter and salts. It contains moderate nutrient loadings and has a low pH (below 5.5) [9]. The most micropollutants of the effluent are chemical fertilizers, pesticides, and herbicides used in producing grapes.

More specifically, winery effluents contain (i) simple dissolved compounds such as organic acids, sugars, and alcohols from grapes and wine, so the effluents have a high requirement for oxygen for biological decay; (ii) moderate salinity and high concentrations of sodium relative to calcium plus magnesium, and low concentrations of nitrogen and phosphorus relative to carbon; (iii) inorganic components from the water supply, alkali wash waters, and processing operations; and (iv) significant amounts of sulfur.

The characteristics of different winery wastewaters from all over the world contain the following parameters: pH, alkalinity, electrical conductivity (EC), soluble chemical oxygen demand (COD_S), total chemical oxygen demand (COD_T), five-day biochemical oxygen demand (BOD_5), total organic carbon (TOC), phenol, total nitrogen (TN), ammonia (NH_4^+), nitrates (NO_3^-), total phosphorus (TP) and phosphates (PO_4^{3-}), volatile solids (VS), volatile suspended solids (VSS), total solids (TS), total suspended solids (TSS), mixed solids (MS), mixed suspended solids (MSS), and volatile fatty acids (VFAs). Table 1 demonstrates the characteristics of the winery wastewater and compares the range of their values during the vintage and non-vintage period [12].

A very useful comparative table is the following (Table 2), where it is obvious about the different compositions of effluents derived from various winery industries (i.e. distillery, wine distillery, molasses wastewaters, etc.) [1,2,7,10,13–22].

Table 1
General characteristics of winery wastewaters

Parameter	Vintage	Non-vintage
Suspended solids (mg/L)	100–1,300	100–1,000
pH	4–8	6–10
Total dissolved solids	<550–220	<550–850
Biochemical oxygen demand (mg/L)	1,000–8,000	<1,000–3,000
Total organic carbon (mg/L)	1,000–5,000	<1,000
Total Kjeldahl nitrogen (mg/L)	5–70	1–25
Sodium (mg/L)	110–310	250–460
Total phosphorus (mg/L)	1–20	1–10
Ratio of C:N:P	(30–100):4:1	(15–30):5:1
Calcium (mg/L)	13–40	20–45
Magnesium (mg/L)	6–50	10–20
Sodium absorption ratio (SAR)	4–8	7–9
Potassium (mg/L)	80–180	40–340

Table 2
Chemical characteristics of various distillery wastewaters

	Type of wastewater					
Parameter	Distillery	Wine distillery	Vinasse	Raw spent wash	Molasses	Lees stillage
pH	3.0–4.1	3.53–5.4	4.4	4.2	5.2	3.8
Alkalinity (meq/L)	–	30.8–62.4	–	2	6,000	9.86
EC (S/cm)	346	–	–	2,530	–	–
Phenol (mg/L)	–	29–474	477	–	450	–
VFAs (g/L)	1.6	1.01–6	–	–	8.5	0.248
COD_T (g/L)	100–120	3.1–48	–	37.5	80.5	–
COD_S (g/L)	–	7.6–16.0	97.5	–	–	–
BOD_5 (g/L)	30	0.2–8.0	42.23	–	–	20
TOC (mg/L)	–	2.5–6.0	36.28	–	–	–
VS (g/L)	50	7.3–25.4	–	–	79	–
VSS (g/L)	2.8	1.2–2.8	–	–	2.5	0.086
TS (g/L)	51.5–100	11.4–32	3.9	2.82	109	68
TSS (g/L)	–	2.4–5.0	–	–	–	–
MS (g/L)	–	6.6	–	–	30	–
MSS (mg/L)	–	900	100	–	1,100	–
TN (g/L)	–	0.1–64	–	2.02	1.8	1.53
NH_4^+ (mg/L)	0–45	55–900	–	1,200–12,540	–	10–50
NO_3^- (mg/L)	4,900	–	–	–	–	–
TP (g/L)	–	0.24–65.7	–	0.24	–	4.28
PO_4^{3-} (mg/L)	–	130–350	–	139	–	–

2.1. Phenols as high-added values components

The polyphenols of grapes are of great commercial–economic importance and high-added value, mainly due to their significant antioxidant, which slows atherogenesis by inhibiting the oxidation of low-density lipoprotein. As a result, polyphenols are widely used either as supplements or as raw materials for cosmetics, pharmaceuticals, and/or food. Especially, the presence of phenolics in the wine product has a definite impact on wine flavor and overall quality. Besides gas chromatography, high-pressure liquid column (HPLC) chromatography is used to measure monomeric and polymeric phenols including all major components in wine.

Polyphenols, exemplified by the hydroxylated stilbene resveratrol, have attracted considerable interest not only for their antioxidant but also for anti-aging, anticancer, anti-inflammatory, and cardioprotective effects. Resveratrol is a natural and low-molecular mass product emerged from the biosynthesis of phenylalanine. Moreover, it is thought to be an intermediate leading to some of the structurally more complicated polyphenols and flavonoids. This molecule has been adapted by nature as a phytoalexin in plants to protect against fungal attack (i.e. *Botrytis cinerea*) and injury such as exposure to Ultraviolet light, presence of metallic ions, and hydric stress. One primary dietary source of resveratrol is from grapes and wine as its processed derivative. Dry grape skins contain variable resveratrol concentrations that range between 21.5 and 174.0 μg/g due to factors as climate, exposure to infection, and cultivar strain. Typical concentrations of resveratrol in red wines vary from 0.6 to 8.0 mg/L and in white wines from 0.031 to 0.122 mg/L [23,24].

The determination of resveratrol in liquid samples contains many techniques such as gas chromatography, CG-MS, capillary electrophoresis, high-performance liquid chromatography HPLC, UV detection, electrochemical detection, fluorimetric detection, or mass spectrometry; resveratrol can be easily determined in wines by direct injection. Flavanols have similar chemical characteristics, so it has been difficult to separate and quantify them. HPLC is the most commonly used technique because it can provide different retention times and allow the identification of flavanols [23,25].

Although phenolics have (i.e. resveratrol) a positive impact on humans, there are many phenols which are very toxic and hazardous. Their existence in effluents made the life (human, environmental, etc.) very dangerous [26,27]. Phenolics exist in environment in various media (sewage sludge, wastewaters, river waters, and soil) [28–30]. There are results published in literature giving different levels for phenols. Some examples of nitrophenols concentrations (2-nitrophenol, 4-nitrophenol, and 2.4-dinitrophenol) were given for a river in Spain ranging from 0.1 to 5.0 μg/L [28]. Other works showed that over 40 mg/L was the concentration of phenol in river water (effluents originated from petrol industry). In general, the content of phenolic compounds in industrial wastewater (about 200–2,000 mg/L) is usually higher than the standard limits (mostly less than 0.5 mg/L) established for their release into aquatic environment. Phenols are also included in The List of Priority Pollutants by the US Environmental Protection Agency (EPA) [31]. Among the methods used to phenols removal, adsorption is one of the simplest and widely applied method. Examination of wastewater treatment containing phenolic compounds have shown that adsorption on activated carbon is considered as a most potential treatment technique [26, 27].

3. Technologies of treatment

Washing operations carried out during different winemaking steps, which are at the origin of the rejection of fully charged wastewaters, can be distributed as (i) during vintage preparation—washing and disinfection of materials; (ii) during grape reception—washing of reception materials (hoppers, destemmers, crushers, presses, dejuicers, conveyors, and transport pumps); cleaning the floors, with or without addition of cleaning products; (iii) during vinifications—rinsing of fermentation and clarification vats; cleaning the floors, with or without addition of cleaning products; (iv) during transfers—rinsing vats after transfers; cleaning the floors, with or without addition of cleaning products; and (v) during filtrations—rinsing kieselguhr and earth filters [32].

The potential environmental impacts of winery wastewater include pollution of ground and surface water, soil degradation, and damage to vegetation and odors [9]. Due to the daily variability of effluents, in both quantity and quality, the evaluation of daily pollution is complex. In general, the production of 1 m^3 of wine generates a pollution load equivalent to 100 persons. The pH is usually acidic but, punctually, it may display basic values, on the occasion of the cleaning operations (with alkaline products and organochlorides) and on the occasion of chemical detartaration.

Therefore, an imperious need of monitoring wastewater volume throughout the year should be highly considered. This study will be very helpful in wastewater planning and management, as well as allowing measurement of water efficiency improvements in the winery. The difficulty of developing a wastewater management system without accurate knowledge of wastewater volumes is extremely high and results in either the development of a system that is not large enough and which will not work properly as planned or that is larger and more expensive than it needs to be [9].

There are two treatment options with a range of methods which can achieve effluent treatment objectives if they are used in an appropriate combination: (i) physical and chemical treatment and (ii) biological treatment [11].

In physical and chemical treatment, solids and suspended components can be separated from the effluent mass through the appropriate equipment such as coarse screening, sedimentation tanks, centrifugation, and microfiltration. The advantages of the physical treatment are: (i) reduction of the sludge amount build up in lagoons and wear on pumps, (ii) rapid reduction of the BOD concentration before disposal or reuse the effluent. Chemicals can be very helpful to enhance treatment characteristics (i.e. a pH correction can settle solids in a rapid way) and also to improve treatment suitability for land application [11].

Wastewater biological treatment consists of the following systems: aerobic, anaerobic, and combined anaerobic/aerobic [12].

A widely used form of biological treatment is anaerobic and aerobic lagoons. The design of lagoon systems should be done after extensive study of quantity, quality, and intermittent generation of the winery effluents, the potential odors affecting nearby landowners, and the finally adopted method of reuse or disposal [11].

Aerobic systems involve lagoons with installed large pumps in which the air is circulated through the water to support the natural aerobic bacteria. Some of the aerated technological systems that offer new advances in wastewater treatment systems are flat panel air lift bioreactor, bubble column bioreactors, and membrane aeration. Some of the above systems contain algae and bacteria either free or adsorbed onto an inert carrier that treat the water (i.e. polyethylene beads) [12].

Anaerobic systems and especially up-flow anaerobic sludge blanket (UASB) systems have been commonly used to treat effluents with a success of 80–98% removal of COD load of the winery wastewater [12]. A combination of anaerobic/aerobic lagoons was issued by many wineries for the treatment of their effluents. At first, a lagoon (anaerobic) favors the anaerobic digestion during the decomposition of high-strength wastewaters which excludes naturally the oxygen. Thereafter, there is a second lagoon (aerobic) with an oxygen-enriched aeration system and finally an oxidative lagoon which incorporates nutrient absorbing reeds and other aquatic plants and it is used for irrigation to vineyards [12].

Additionally, many wineries use sequence batch reactors (SBR) and artificial wetlands to deal with their effluents [12]. SBR systems are currently being adopted as the highest level of development in winery wastewater treatment. A system operation of SBR contains a mixture of the effluent with the biomass, and afterward an aeration of this mix is done on a constant basis by the use of a fine bubble membrane diffuser system that depreciates the consumption of the power. The aeration cycle lasts about 6 h. After that time, the contents of the basin are settled down and the clear effluent is extracted for storage or irrigation. An excess sludge is used to a sludge digester, in which it undergoes further aeration and finally it is used as a fertilizer on vines. The success of the SBR system reaches 98% removal of biological oxygen demand over a 5-d period or BOD_5 [12,15] (Figs. 1 and 2).

Artificial wetland systems are adopted by many wineries as a secondary treatment method for irrigation or reuse of the wastewater (Fig. 3). There is an excessive need of a non-variable composition and removal of large BOD amounts by aerobic or anaerobic systems of the wastewater before its application to the wetland plants in order for the plants to survive. The results of many studies carried out on constructed wetlands overseas have shown 92–98% BOD removal, 87–98% COD removal, 70–90% TSS removal, pH neutralization, 50–90% TN removal, and 20–60% TP removal [12].

A study of Andreottola et al. summarizes some more new biological treatments for winery effluents treatment reporting the major advantages and drawbacks [33]. In the case of aerobic/anoxic suspended biomass, the treatment with activated sludge has relatively low cost with easy management and the COD reduction is characterized as significant. On the other hand, drawbacks as temporary plant overloading during harvest

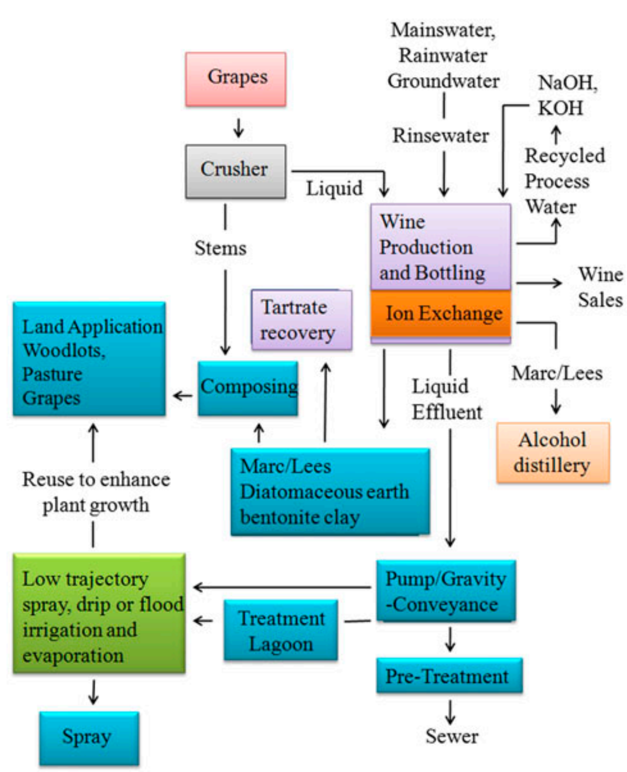

Fig. 1. Winery effluent management system.

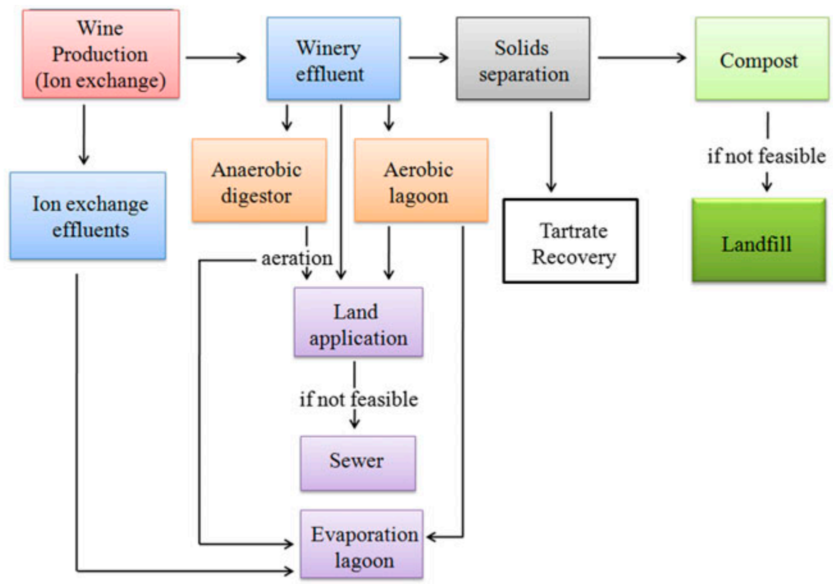

Fig. 2. Biological treatment of winery wastewater.

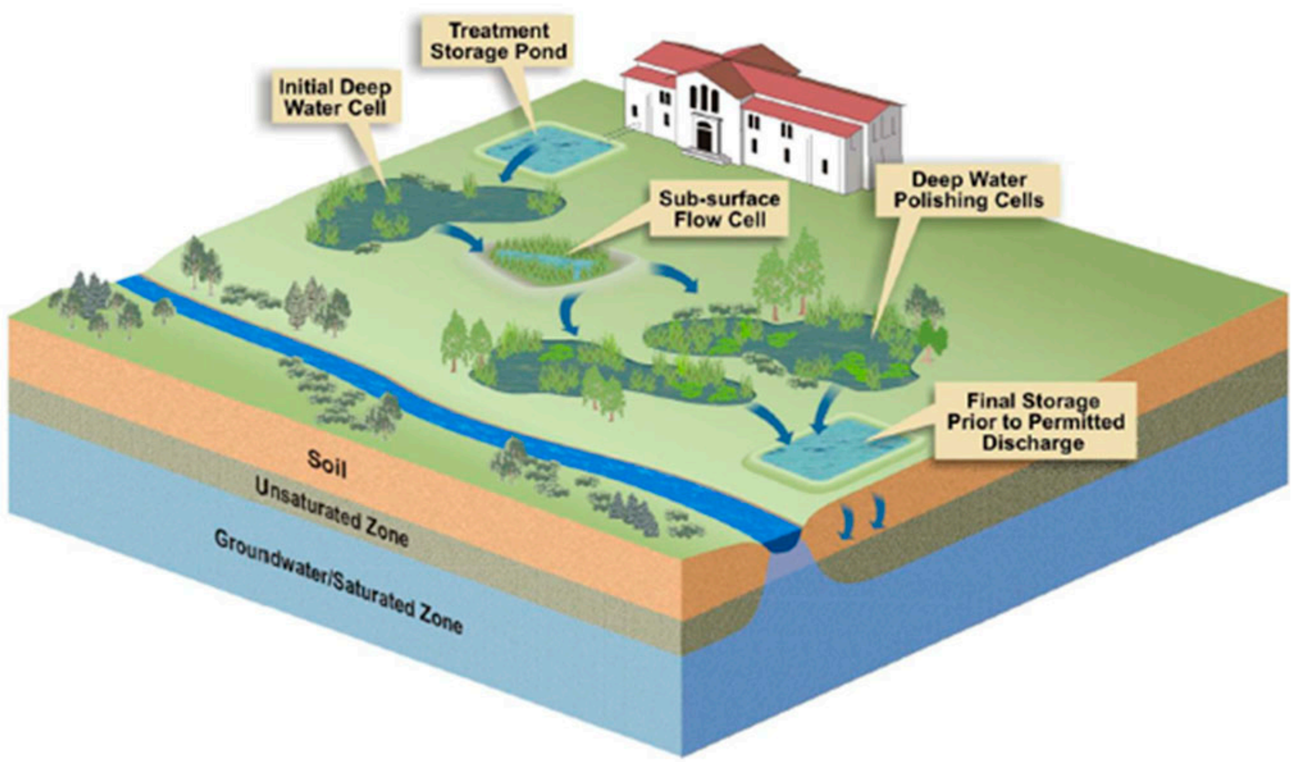

Fig. 3. Wetlands for winery wastewaters [49].

period, occasional bulk phenomena, and decrease of sludge settleability can be noted; in general, this process can be considered as energy intensive. Furthermore, MBR (membrane bioreactors) process presents positive points as: (i) great improvement in treated water quality, (ii) effluent free of SST and bacteria with UF (ultrafiltration) membrane; (iii) possibility of direct reuse on-site; (iv) lower sludge production; (v) rapid start up; (vi) low footprint area; and (vii) absence of voluminous secondary settler; and (viii) operations not affected by settling properties of sludge. On the contrary, additional costs for membrane modules, increase in energy consumption compared with activated sludge, and decrease in filterability caused by membrane fouling are some of the major drawbacks. SBR has other crucial advantages as (i) widespread solution for small wineries; (ii) Optimal configuration is a SBR fed once a day; (iii) simplified automation; (iv) low capital cost; and (v) moderate operating costs. The need of a daily storage (aimed to reduce the shock loading) is the main drawback.

In the case of anaerobic processes, Andreotolla et al. give also important points (either positive or negative) for the applied biological treatments [33]. For anaerobic digestion with suspended biomass, the enhanced methane production in the case of co-digestion with waste activated sludge in line with the low cost is the major advantages. A SBR presents other positive points as: (i) biogas production and energy recovery; (ii) optimization of cycle length by automation; and (iii) low-excess sludge production. The negative point is that on-line monitoring and modeling are needed for optimization. UASB (upflow anaerobic sludge blanket) presents high activity of granular sludge, good settleability, and low-sludge production. On the other hand, hybrid USBF combines the main advantages of the anaerobic filter and UASB reactors (no clogging problems and low-sludge production).

4. Selection of technology (criteria)

There are some criteria (common in wineries) for the selection of proper biological treatment (anaerobic or aerobic) for winery effluents. Due to the high content on organic biodegradable compounds of winery wastewaters, anaerobic technology systems are the simplest and most inexpensive processes due to their lower operation costs for aeration and sludge processing. Although there are some disadvantages of anaerobic systems, those can be overcome through inoculation techniques, such as (i) slow turn-on time to the process which favors the development of the methanogenic microbial community; (ii) efficiency of the treatment which can be reduced on account of the composition of the effluent and its variable substances; and (iii) production of malodors [12,32].

However, the anaerobic treatment is not enough to degrade the effluent quality and make it suitable for discharge in surface waters. As a result, if there is no choice of co-treatment of the winery effluent in an aerobic wastewater treatment plant, an aerobic system should follow the anaerobic. The downside of aerobic systems is their high-energy requirements and therefore, high costs which can be reduced in case of a low-wastewater flow. In small wine industries where the low investment cost is the determinative factor for their survival, the one-way option should be an aerobic process if there is a need for high-quality effluent [12,32].

A brief example can be derived from a small winery located in North Greece (Simeonidis Winery, Kavala city). At first, it is substantial to say that the total number of wineries in Greece is estimated as 682 [34]. This number is very large compared to the total population of Greece (~11 million persons). The largest proportion of them is located in Peloponnese (182 wineries), followed by Macedonia (143 wineries), and Central Greece (139 wineries). Crete is classified in the middle (54 wineries) and, Thrace and Epirus gather the lowest percentage (13 and 10 wineries, respectively). The remaining wineries are located on many Greek islands (at least one in each island).

Some basic hypothetical questions can be posed in wastewater treatment as "what is the most efficient way of treating wastewater", "how does the implementation of these methods affect profitability", etc. Attempting to give replies in the above, a major point should be taken into account: the amount of wastewater produced is directly correlated with financial losses, and therefore profitability of wineries today.

In general, wineries spend a large amount of water which gets bigger when the wineries' production is only national. The estimated wasted water can be reached about three times the amount of the produced wine. Therefore, the high cost of wastewater can be a significant financial problem for a winery. The fact that makes small wineries more profitable in economical issues than larger ones is that they acquire a smaller capital for their operation. Despite the fact that many micro wineries do not use anaerobic treatment for their effluents (not only because they thing it is useless for their waste amounts, but also for its high price), there is a need to find a way of their wastewater disposal. There are opinions about the latter; Kleban and Nickerson [35] report that the success of small beverage (wine or beer) industries owes to their product uniqueness and its environmental friendliness to some extent. O'Neil [36] suggests that a winery should consider the installation of an anaerobic system only when the wastewater charges exceed the sum of $250,000. In case that the annually production of wastewater charges costs around $19,000–$22,000, a winery should turn to an outside company to treat their wastewater than to install their own wastewater treatment system.

It is estimated that between the processes of cleaning and bottling the ready for sale product, the ratio of effluent and wine production can even reach 1:2. The differential production rates of the wineries can make effluent amounts low or extremely high. Among the methods of the wastewater treatment, there are some which are used more than others. According to a significant approach of Speece [37], the two commonly used methods of aerobic and anaerobic treatment have some significant differences. Despite their technical similarities, the two methods differ in some points of their treatment way such as their electrical power usage and the produced byproducts (methane gas, and excess microbial cell). However, in order to export a credential conclusion all expenses should be taken into consideration. So, the final cost difference between the two methods can reach \$250–\$300 per metric ton of waste. In that cost, the excess microbial cell production is considered as an additional disposal charge which varies in different wineries. Malina and Pohland [38] declare the dominance of anaerobic treatment in wineries (or other drinking company) due to the high amounts of COD in industrial wastewater. If COD exceeds 20,000 mg/L, only anaerobic methods can reduce it. Nowadays, some of the industries which use a full-scale anaerobic treatment are pharmaceuticals, alcohol distilling, fruit processing, landfills leachate, and paper industry.

Some production of wineries is smaller and that fact makes them unable to finance the cost for an anaerobic wastewater treatment. Usually, these wineries choose to dispose their wastewaters into sewage and they pay a fee or treat wastewaters to the point it is allowed for them to be disposed in the sewer systems of their community. A relatively recent method of wastewater treatment utilizes some existing wetlands. For many years, wetlands have been used for these purposes in small industries although many professionals are aloof in a wetland's ability to treat large quantities of effluent. Because of their lack of technology, their suitability for proper treating of the effluent is questionable. Verhoeven and Meuleman [39] compare the two main methods of wetlands treatment; surface-flow and infiltration wetlands. According to achieved studies on a wetland in Netherlands, it is assumed that they both are effective to some degree. The first wetland method, called surface-flow, lasts 10 d and consists of a variety of plants which have a kind of bacteria that are able to suspend contents of the wastewater. The process steps are the following: (i) sedimentation of the suspended solids; (ii) expansion of the dissolved nutrients into this sediment; (iii) mineralization of the organic stuff; (iv) nutrients auction by micro-organisms and vegetation; (v) microbial transformations into gaseous components, and (vi) physiochemical adsorption and subsidence in the sediment.

A highly important data is the amount of produced wastewater during the production of one barrel of wine. Unofficially, many wineries claim that wastewater is almost five times the amount of produced wine. This requires a further investigation such as going to a real winery and asking the amount of the produced wastewater per barrel of wine. That information will be very useful to estimate the total amount of produced wastewater monthly or annually. A local small winery of North Greece (Simeonidis Winery, Kavala city, Greece) also confirms the above after personal contact with the owner. After the collection of all that information, it will be easier to identify the most commonly used method of treating wastewater. To figure out all the above, there should be a comparison of the profit configuration before and after each technology's application to conclude whether it leads to benefit or damage to the winery. The main objective is the determination of the most efficient way of coping with wastewater and this will be accomplished through the estimation of the winery's profits against expenses.

A cost-benefit analysis will be used to ascertain the costs and the money saved from the new applied technologies and eventually their effect in profitability. Moreover, an investment in a wastewater treatment system will help the concepts of net present values which can be used to examine the changing rate of future cash flows. For the net present value it is required: (i) the initial capital for the implement of a wastewater treatment system, and (ii) to pay for the equipment to be compiled. Once this is done, the winemaker will estimate the years of revenues it will take to fully pay back the money borrowed on financing the wastewater treatment system. After the above cost information, the winemaker should take into account the partial budgeting which includes the cost of one technology in comparison with the cost of a newer technology to see their benefits and detriments.

The above cost information (energy and wastewater treatment costs) needs to be collected from different sources such as secondary companies that wineries co-operate for this work, or directly from the wineries. It is impossible to collect all this information from a large number of wineries for different reasons, so it will be assumed that the energy and wastewater costs are the same throughout the wine industry. The last necessary assumption is that a winery would consider installing an anaerobic system instead of another, although its installation costs can be very high.

Apart from some assumption, some limitations already exists. The wastewater treatment costs informations are values already estimated as a result of actually running the method of treatment, although estimated numbers can be used to get a general image of what the figure would be like. Just like the assumptions, a limitation that may develop is that energy costs vary throughout different regions. Therefore, the numbers used to illustrate the costs would be from a few wastewater companies. Another serious issue is that some wineries may consider unnecessary to install a treatment system, so, they may just decide to pay a fee for the disposal of their effluent rather than to treat it. At last, the biggest limitation is the denial of many wineries to broadcast their financial statements. As a result, wineries that are not publicly traded refuse to release any information about their profitability. Nevertheless, many wineries were reluctant to release such information as they consider them private or they didn't have an accomplished answer useful for this investigation. Another common problem was the determination of the water costs in every winery, which would help the estimation of treatment cost.

4.1. Qualitative approach

A good way to control the quality of wastewater is to control what gets into the waste streams in the first place. Many wastes can readily become useful resources. With the right management, they can be assets rather than risks to the environment. Some factors to watch for in winery wastewater are: (i) chemical (or biochemical) oxygen demand (COD and BOD); (ii) suspended solids (SS); salts such as sodium (Na), calcium (Ca), magnesium (Mg), and potassium (K); salinity (electrical conductivity—EC units); nutrients such as nitrogen (N) and phosphorus (P); acidity or alkalinity (pH); dissolved oxygen levels (DO). One of the most important factors is the winery effluent volume.

The volume of winery effluent to be treated, and the timing of its generation, will be governed by the volume of grapes crushed and/or the amount of wine made, and the length of vintage. Therefore, two points can be considered: (i) the bigger the crush or the more wine made, the bigger the volume of effluent; (ii) the longer vintage lasts, the greater the period over which large amounts of effluent are generated. The design of wastewater treatment plants must also allow for peak volumes and loads. Water use in the winery drives the volume of wastewater to be treated. Its main use is for cleaning; washing down floors, equipments, tanks, barrels, and transfer lines. As it can be clearly understood, the volume of effluent is a crucial factor designing the appropriate winery wastewater treatment method. Table 3 presents the water volumes used for different sized wineries [11,40].

The main goal is to approach a draft description of some economical factors regarding the designing of winery wastewater treatment. Some under-estimation parameters are high-SS, nutrients, COD, salts, extreme pH conditions, and pathogens. Especially when there is high concentration of SS, the solid organic matter should be removed as soon as possible. Effluent that is high in suspended solids will benefit from screening and settling to remove the solids as byproducts or sediments, making the waste stream easier to treat. This also helps to reduce the potential for odor problems. Keeping as many solids as possible out of the waste stream to begin with, through cleaner production practices, is a first step (Fig. 4). Another key to winery wastewater treatment is to reduce organic loads. Remove solids early and deal with high-strength wastes at their source. So, when solids are in the waste stream, management options include: (i) screens, skimmers, and sumps—for large particles, greater than 500 μm (0.5 mm); (ii) filters—for smaller particles (10–500 μm); (iii) chemically assisted settling (e.g. flocculation)—for fine particles (<10 μm); (iv) air or chemically assisted flotation for particles with high-surface area to volume ratios; and (v) sedimentation or settling for heavy particles. Recovered solid wastes may be composted.

Going to an economical business case for winery wastewater management, some requirements are: (i) assessment of the change in operating costs, from a whole of winery and vineyard perspective; (ii) consideration of capital costs, in context against the value of existing infrastructure; and (iii) determination of non-cash costs and benefits, including implications for ease of management. The terms introduced are the holistic appraisal, operating and capital costs, finance and accounting, and non-cash costs and benefits.

Beginning from the holistic appraisal, the key to a wastewater business plan is to consider the matter holistically. Operations within the winery, the treatment plant, and the end use of treated water (including the sale or use of byproducts and the value of any recycled water in the vineyard) should all be factored into the business case. Consider capital expenses and operating costs along with the impacts of changes in operations and the adoption of new practices. Considering these

Table 3
Volumes of water use for different sized wineries

Equivalent crush (ton/year)	Water use (kL/year)		Water use (kL/ton of crush)	
	Average	Range	Average	Range
<1,000	1,000	300–2,500	2.4	0.4–8.0
1,000–2,500	5,600	850–19,000	3.7	0.6–11.6
2,500–5,000	10,000	5,000–20,000	2.4	1.1–5.1
5,000–10,000	14,000	4,400–30,000	2.3	0.5–4.9
10,000–50,000	41,000	17,000–60,000	2.0	0.9–3.6
>50,000	160,000	45,000–290,000	1.5	0.6–1.8
Overall			1.94	0.4–11.6

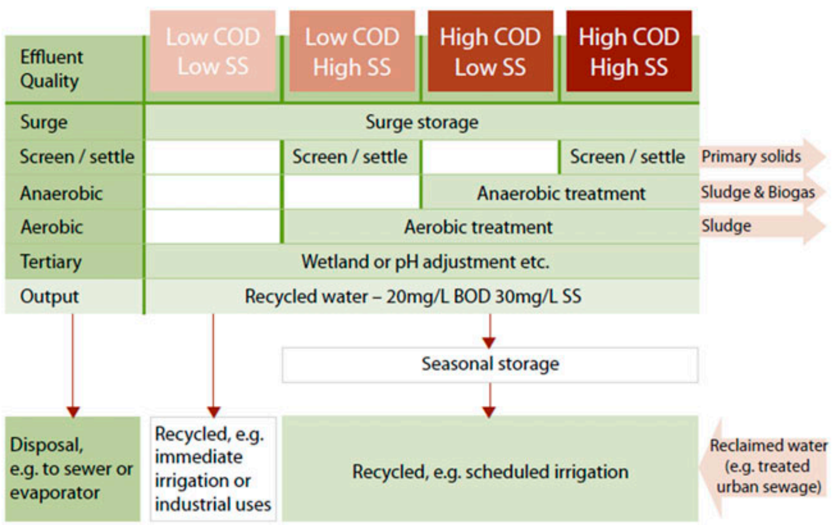

Fig. 4. Treatment options for different effluent characteristics [11].

issues will permit the ready development of standard accounting measures (such as Net Present Value, Internal Rate of Return, and Payback Period) as well as providing information for qualitative assessments. Key information may be presented in a summary table, along with the accounting measures, for a balanced assessment.

The other parameter of operating costs and benefits imply some changes in those type of costs and the impact on cash flows in the winery, treatment plant, and vineyard: (i) direct costs (and incomes)—changes in expenses for chemicals, energy, labor, consultants, chemical analysis, byproduct disposal (or sale), regulatory fees, and miscellaneous expenses; (ii) changes in labor requirements and management input for operation, maintenance, monitoring, and reporting; (iii) operational benefits—increased efficiency in converting grapes to wine, increased water use efficiency, fewer blockages or breakdowns, benefits from automation and reduced treatment costs as a result of cleaner production initiatives, reduced regulatory costs; (iv) ancillary costs, e.g. additional training to implement cleaner production initiatives or to operate new equipment; and (v) discharge costs and benefits—any benefits from byproducts (e.g. their value as fertiliser or recycled water in the vineyard), changes in discharge fees or license requirements, or impacts on vineyard operations and maintenance.

Due to the worldwide economic crisis, the capital costs influence the selection of treatment method (Table 4) [11,41]. It must be considered any changes to the company balance sheet and ancillary matters: (i) total capital cost (additional land, installed plant and equipment, plus new infrastructure such as power and water), and the depreciation allowance for any new treatment facility; also the capital value and

Table 4
Combined operating and capital costs for wastewater treatment

Equivalent crush (ton/year)	Sampling size (Capital cost/Operating cost)	Combined cost ($/kL)		Combined cost ($/ton)	
		Average	Range	Average	Range
<1,000	4/5	36	8.8–55	33	8.6–56
1,000–2,500	6/6	19	8.3–35	40	14–66
2,500–5,000	6/3	7.2	5.7–10	18	12–29
5,000–10,000	3/3	6.1	1.8–8.8	23	3.9–44
10,000–50,000	7/7	5.6	0.7–11	11	1.7–21
>50,000	2/2	7.1	4.6–9.5	6.8	5.2–8.4
Overall	28/26	8.8 ± 1.9	–	14 ± 3	–

Note: Assumes an overall conversion of capital to yearly cost of 15%.

depreciation allowance for any plant to be replaced; (ii) any revenue from the sale of plant, equipment or water rights that are no longer needed, or any reserves to cover replacement costs; and (iii) any possibility of access to government grants for environmental improvement.

Another point of consideration is the funding options and their accounting implications: (i) potential sources of funds, e.g. operating revenue or borrowings; (ii) availability of funds and any impacts on other projects; (investment options, e.g. contracting out services or leasing new plant from a third party instead of purchasing, avoiding a capital outlay, and replacing post tax depreciation with a pre-tax operating expense; and (iii) consequences for the Balance Sheet and the Profit and Loss Statement. All the above can be represented in Table 5 [42].

However, after extensive screening of literature there is no any techno-economical analysis given for winery effluents. For this reason, it is impossible to quantitatively predict some economical data, but only this can be done qualitatively as presented in Table 5 [42].

5. Aspects—reuse suggestions

One of the most crucial factors of each industry is the reuse potential of the produced wastes, chemical reagents, or used water. In particular, water is used in many parts of the winery for a variety of purposes, many of which do not require high-quality water. Used water may be suitable for reuse for the same or other purposes. Examples include: (i) bottle cleaning water is usually still of relatively good quality and may, with some treatment, be reused for the same purpose, for tank washing or for truck washing; (ii) cellar cleaning water may contain organics but is still quite suitable for reuse to clean floors; (iii) water used to test for barrel leaks may be reused for the same purpose; (iv) push-through transfer water is highly variable in quality, but may be reused for the same purpose; (v) water from liquid-ring vacuum pumps is generally fairly good quality and can be recirculated through the pumps; and (vi) relatively low-quality water can be used for hardstand and truck washing.

Chemical reagents which are difficult to treat have special treatment needs or are costly to remediate are prime targets for reuse. Examples include: (i) caustic cleaning agents (i.e. KOH and NaOH can be re-circulated if the pH is monitored and the agent is replaced when necessary); (ii) recovery of used diatomaceous earth for use as body-feed on pre-coat filtration (with savings of up to 85% feasible).

In some cases, it may be feasible to discharge treated winery effluent as a trade waste to a sewer system, or to truck it off-site to another treatment plant. Treatment will need to conform to the acceptance protocols of the sewer or off-site manager (i.e. differences in treatment capacity between urban and country treatment plants may result in differing acceptance criteria). Stormwater is generally precluded from tradewaste, as it is from normal sewers.

Leachfields and constructed wetlands may be used as a treatment process, and especially for leachfields, may incorporate ultimate disposal as part of the treatment process.

Highly saline water may be best managed by evaporation, providing the climate and site are suitable and there are adequate provisions for the long-term management of salt residues. Odor, generally caused by volatile fatty acids from the breakdown of organic material, will be a problem if COD levels are too high. With expert advice, nitrate may be added to promote the formation of odorless carbon dioxide rather than volatile fatty acids, or commercial enzymes may be used. Maintaining a shallow depth also assists in avoiding anaerobic conditions and the formation of malodours.

Table 5
Comparison of aerobic and anaerobic treatment options

Feature	Aerobic				Anaerobic	
	Trickling filtration	Activated sludge	Sequencing batch reactor	TF/AS hybrid	Anaerobic (lagoon/digester)	High-rate anaerobic treatment
Operable BOD range, mg/L[a]	Up to 7,500	Up to 5,000	Up to 7,000	Up to 8,000	Typically >50,000	Up to 25,000
Typical BOD range, mg/L[a]	<3,000	<1,000	<2,000	<3,000	>5,000	2,500–10,000
BOD removal	90–97%	90–99%	90–98%	90–99%	85–95%	70–90%
Reliability/robustness	Very good	Fair	Good	Very good	Fair	Poor
Resistance to shock loads	Very good	Fair	Good	Good	Fair	Poor
Power usage efficiency	Good	Fair	Poor	Good/fair	Excellent[d]	Very good[d]
Potential for odor control	Fair–poor[c]	Fair	Fair	Fair/poor	Good[b]	Good[b]
Operational simplicity	Excellent	Poor	Fair	Very good	Good	Fair
Minimization of sludge	Good	Poor	Fair	Good/fair	Excellent	Very good
Plant size	Very good	Very good	Excellent	Very good	Fair/poor	Good
Capital cost	Good	Very good	Excellent	Fair	Fair	Poor
Annual costs	Good	Poor	Poor	Fair	Excellent	Very good

[a]Operable BOD category refers to the upper range for BOD that this option can efficiently handle (treatment processes can be designed to handle greater BOD loads, but typically this will not be effective).
[b]Good odor minimization provided the unit is covered.
[c]Although the potential for odors is relatively high for trickling filters, emissions may be readily managed.
[d]The energy efficiency of anaerobic processes is rated highly, because of the potential for producing an energy rich gas. Equipment for mixing and transferring would still be required and without the benefit of the gas, these options would be rated as "good" only.

Water from wineries may be irrigated as a direct discharge to land or treated, stored, and used for scheduled irrigation (as may recycled urban effluent).

A variety of crops, pastures, woodlots, and amenity plantings may be irrigated immediately with treated winery effluent—including vines. The vegetation may be selected due to its requirements for (or ability to accommodate) specific quality water at the time when treated winery effluent is produced. Remnant native vegetation will not usually tolerate irrigation. There is long experience in irrigating pastures and woodlots with recycled water and rapidly growing expertise with vines as well. Annual fodder crops (i.e. cereals for hay) are also proving valuable as they are robust, cope with variable rates of irrigation (in tune with supplies), and result in the export of large amounts of salt and nutrients.

If treated effluent is stored it may be used as required by selected crops—including as supplementary irrigation water for vines. Scheduled irrigation may generate better returns from the treated winery effluent. Vineyards may also be irrigated with water that is recycled from urban sewage treatment plants either on its own, in conjunction with treated winery effluent, or with water from other sources. For more information on irrigation, see Irrigation essentials. If water intended for irrigation is high in COD, it will soon (within 48 h) become anaerobic as aerobic microbes use up the available oxygen. Anaerobic digestion can release unfavorable odors (e.g. hydrogen sulfide—rotten egg gas) and leads to a reduction in pH. Stored water may also increase in salinity through evaporation.

In some cases, treated winery effluent may be of value back in the winery (e.g. for wash-down), for other agricultural activities, or to neighbors as a source of water for industrial use. Industries that may be thirsty for recycled water include: (i) intensive livestock facilities—e.g. feedlots and poultry; (ii) industrial sites (timber processing, concrete); (iii) batching or cement mixing, and quarries; and (iv) irrigation (amenity plantings, parks, golf courses, hay fields, or woodlots).

5.1. Molecular imprinting in winery wastewater treatment

Apart from the conventional processes used in industry for the removal of pollutants from wastewaters (flotation, degradation, etc.), an adsorption/binding recent process is used from researchers to selectively recognize and adsorb/bind target molecules (pollutants) from effluents. It is a great of interest to prepare/design materials, which only selectively remove pollutants from wastewaters, as ions, dyes, phenols, and other typical and potential target molecules. This can be achieved with some special polymers via the technique of molecular imprinting [43,44] (Fig. 5). The polymers produced for this purpose are Molecular Imprinted Polymers (MIPs).

The ability to selectively recognize a target molecule in a vast pool of similar molecules is essential to biological and chemical processes. This process is called molecular recognition and it is an event that occurs everywhere in nature. It occurs when two molecules are both geometrically and chemically complementary; that is, when they can both "fit together" spatially as well as bind to each other using non-covalent forces, including hydrogen bonds, electrostatic interactions, hydrophobic interactions, and weak metal coordination [45]. Examples of this process include the binding of an enzyme to a substrate, a drug to a biological target [46], antigen/antibody recognition in the immune system, and the formation of messenger RNA from DNA templates [47]. The molecular recognition is central to how biological systems work, especially at the cellular level. The observation of the various systems where processes of recognition occur (enzyme substrate complexes, antibody–antigen systems, DNA replication, membrane receptors, etc.) has indicated a certain number of directions for the preparation of synthetic systems capable of molecular recognition.

Based on the above description of MIPs, in line with the valuable properties of resveratrol (existed in high concentrations in winery effluents), it will be a very good idea to incorporate a preliminary stage of treatment before proceeding to aerobic or anaerobic stage. In particular, Chen et al. [48] prepared magnetic MIPs using surface molecular imprinting technique with a super paramagnetic core-shell nanoparticle as a supporter. These MIPs were tested for resveratrol binding from winery effluents. However, in that study, the process was done with lab-scale experiments and not in columns as usually done in industry. The adsorption capacity was good (23.26 μmol/g), in line with very good selectivity properties.

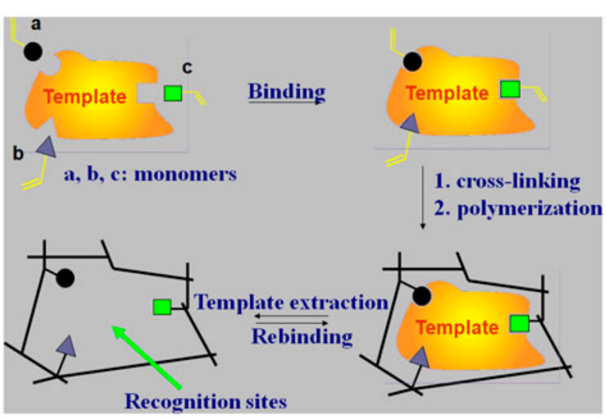

Fig. 5. Molecular imprinting technique.

6. Conclusions

Authors gratefully acknowledge Mr Polychronis Simeonidis (owner of the "Simeonidis Winery," Kavala city, Greece) who provided personal information based on his professional experience. Furthermore, The support for this study was received from the State Scholarships Foundation (IKY) of Greek Ministry of Education and Religious Affairs (in the framework of the Hellenic Republic - Siemens Settlement Agreement) through the research program "IKY Fellowships of Excellence for Postgraduate Studies in Greece - Siemens Program" under the title "Advanced Molecularly Imprinted Polymers (MIPs)" as materials for the selective binding and recovery of various high-added value environmental targets with application to industrial-scale adsorption columns.

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