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Development of an economically viable process for the integrated management via utility of winemaking industry wastes; production of high added value natural products and organic fertilizer

Review on winery waste management technologies

terra nova

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The present Report was conducted by the scientific team of **TERRA NOVA Ltd.:**

TERRA NOVA Ltd.

39 Kaisareias str. 115 27 Athens, Greece
Tel.: +30 210 7775597, Fax: +30 210 7775572
e-mail: information@terranova.gr

Dr. Argyro Lagoudi
Chemist

Ioannis Spanos
Chemical Engineer

Stauroula Barafaka
Chemical Engineer

Katerina Founda
Chemical Engineer

Ourania Devekou
Environmentalist MSc.

Ioannis Tsikos
Environmentalist MSc.

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CHAPTER 1:
WASTE AND WASTEWATER GENERATION IN WINE MAKING PROCESS WITHIN THE WINERY

Although the wine making process may seem as a straight forward procedure it requires a long time and a big amount of resources and energy until wine is ready for consumption. The wine making process entails the generation of a significant amount of waste and wastewater that should be further treated before being disposed off to the environment.

The management and disposal of the generated waste is a matter of big interest to the winery operators, and so far several methods and equipment have been used for their treatment, some of which without success. Some of the methods that have been used so far were either incapable of meeting the environmental standards or were too expensive for the winery industry's budget.

Finding the most environmentally and economically efficient solution for treating waste is a complex issue, and it gets more difficult when referring to winery waste, since these waste involve some particular aspects:

- **Seasonal Variation:** First of all the quality and quantity of winery waste differs significantly from season to season. Winery waste can be divided into crush season and non-crush season waste (also called vintage and non vintage). The crash season begins in August and lasts until February, whereas the non crash season involves the period from early March till the end of July. Each period generates different types of waste and different qualities and thus waste should be treated separately for each season applying the necessary in every case method. (For instance during the crash period a bigger amount of solid waste is generated comparing to the non crash period that entails bigger quantities of wastewater).

- **Quality:** Winery waste contains high concentrations of certain chemical parameters that make waste treatment more difficult. In particular, wastewater from the wine industry has a high organic content, contains both suspended (TSS) and dissolved solids (TDS) and is usually acidic. (Further description of the winery waste quality is given below)

- **Benefits:** Winery waste and especially grape marc, contains some useful substances with pharmacological activities. As it will be mentioned in the following sections polyphenols that can be found in the winery waste are proved to have some pharmacological activities in treating diseases such as cancer, and thus attempts are being made so as to remove these substances from waste for further use.

1.1 Waste Generation

In this point, we should make a short description of all the different waste streams that arise from the wine making process. Although the wine making process varies depending on the type, the colour and the expected quality of the wine, the typical wine making process may be summarised as follow:

A. Vintage period

Sorting the fruit (1)

1. Grapes are initially collected and processed in the crusher – destemmer machine. This machine separates the grapes from the stems and gently crushes them.

2. When grapes are crushed a juice called 'must' is produced.

3. The juice and natural yeast from the skins are added to a vat or oak barrel to ferment. The yeast converts the grapes' natural sugar into alcohol and carbon dioxide, which then bubbles and dissipates.

4. The juice ferments at controlled temperatures for a couple of weeks until sugar is completely gone.

B. Non Vintage Period

5. The dead yeast is either removed or left in to add complexity.

6. The wine is kept fresh or aged in stainless steel vat/oak barrels.

7. Wine is drained and filtered in order to remove any particles left in it.

8. Wine is finally bottled and labelled and is ready for consumption.

The exact amount and type of waste arising from the wine making process depends on the method and equipment of each winery; however the waste mentioned below is quiet a precise and complete list of winery waste.


Grape Destemming and barrel cellar (2)

1.1.3 Solid waste generation

- Pomace: grape skins, stems, seeds, yeast, and pips (marc)

This waste is generated during the harvest period. For the production of red wine skins, stems, pips and skin are removed after the fermentation of must to wine so as to extract colour pigments. Where as in the case of white wine production stems, pips and skin are removed after the pressing process.

- Lees: wine sediment

Within the term lees all the residues of the tanks, in which fermentation and removal of unfinished wine takes place, are included. Lees consist of a mixture of wine yeast and bacteria.

Fermentation Tanks (3)

- <u>Filtration waste: diatomaceous earth, centrifuge sludge, and bentonite clay</u>

Filter earth such as, bentonite clay, diatomaceous earth and perlite is used to polish or clarify wine of floating organic material (lees). These waste are generated during the post-vintage period when filtration process takes place.

- <u>Wastewater Sludge</u>

In cases where there already exists a wastewater treatment plan, there is an extra production of wastewater sludge that should be further managed.

1.1.4 Wastewater generation

<u>Cleaning Activities & Caustic cleaners</u>

During the wine making process a big amount of water is used in order to clean and sterilize the winery equipment (wash down water). For safety and health reasons (for the consumers) all wine tans and barrels should be cleaned each time after holding vintage. These procedures generate the major part of wastewater within the winery. Wastewater arising from the cleaning activities include:

- barrel washing,
- tank cleaning
- equipment washing,
- bottle washing,
- floor and crush pad washing
- crush pad washing

Cooling

Besides the need for water in cleaning activities, there are some wineries in which water can be used as well as a coolant (chilling and heating procedures). In cases where water is used as a coolant, wastewater is generated from the cooling tower and boiler blow down, due to the fact that a part of hot water should be removed occasionally in order to avoid high concentrations of salts.

Wine ion exchange regeneration.

In some wineries, grape juice and wines are treated by ion exchange. In these cases sulphuric acid is used for the regeneration of the ion exchange column involving the generation of acid wastewater that should be further treated.

For the purposes of this report only waste arising form the main wine making process are taken into account. Waste such as landscaping waste, packaging waste and vineyard waste at this point are beyond our focus.

1.2 Waste & Wastewater quantity & quality

1.2.3 Solid Waste

Solid waste arising from the wine making process can cause bad odours and can contaminate soil and water resources. Solid waste of a winery mainly consists of grape marc waste. According to the Agriculture and Resource Management Council of Australia and New Zealand grape marc forms 9%-13% of the total weight of the grape. Grape marc waste represents one tonne in every fresh 8 tonnes that comes into a winery. If the grapes are stripped from the stalks before processing the residue or marc consists of approximately 25 - 40% seed and 10 - 25% skins and around 50%-65% moisture which may be in the form of unfermented or partially fermented juice or wine.

Photos 1&2: grape marc waste

The characteristics of the marc vary depending on the variety of grapes, the climate, the production techniques used and the final product (white or red wine). When white wine is being produced the crushed grapes are pressed and the juice is pumped into a fermentation vat where fermentation of the juice takes place. The marc is generated before fermentation takes place and is known as sweet since the sugar rich juice has not been fermented. On the other hand when red wine is being produced the marc is generated after the fermentation is started or completed and the marc is characterised as 'dry'.

When referring to the quality of solid waste arising from a winery it is also worthwhile mentioning the presence of some substances such as phenolic compounds, tannins and tartaric acid that are found in big concentrations and characterise the type of waste.

- The phenolic concentration varies among different varieties of grape. Almost 20% of the total phenolic compounds found in the grape cluster is concentrated in the grape stalk. In the case of Cabernet Sauvignon grapes at maturity, phenolic composition is as follows (4):

Vintage	**Anthocyanins (mg / 100 berries**	**Tannins (g/100 berries)**	
		Seeds	**Skin**
1985	148	0.35	0.39
1983	132	0.25	0.44
1984	129	0.33	0.52

- Tannins are substances that give grape the red colour and can be removed so as to be further used as colourings.

- Tartaric acid represents on average 90% of the organic acids found in grapes and is mainly deposed on the stalks and skins. Tartaric acid is also found in big concentrations in filtration waste, filter earth.

1.2.4 Wastewater

Wastewater production varies from season to season (peak harvest period) and between wineries (wine making method and winery size). For instance for a medium - size winery the wastewater quantity is in the order of 2 to 14 litres for every litre of wine produced (evaporation during ageing is not taken into account).

Wastewater from the wine industry has a high organic content, contains both suspended (TSS) and dissolved solids (TDS) and is acidic. The wastewater is high in sulphide compounds which may lead to odour problems and in nitrogen concentration that can cause eutrofication of water sources. Increased concentrations of TDS can close the soil pores and limit the aeration of soil and the flow of water through soil.

Also, the quality of wastewater varies from season to season depending on the process that takes place in the winery. For instance pH levels on the wastewater can vary from 2.5 to 11 whereas concentrations for Nitrogen from 1 up to 40 mg/ l. The fluctuation of the most important parameters of a typical winery wastewater stream for every season is given in the following table (5):

Parameter	Crush Season Range	Non-Crush Season Range
pH	2.5 - 9.5	3.5 - 11
BOD_5	500 - 12000 mg/L	300 - 3500 mg/L
Dissolved Oxygen	0.5 - 8.5 mg/L	1.0 - 10 mg/L
Settleable Solids	25 – 100 mg/L	2 – 100 mg/L
Total Suspended Solids	40 – 800 mg/L	10 – 400 mg/L
Total Nitrogen	1- 40 mg/L as N	1 – 40 mg/L as N
Nitrate	0.5 - mg/L as N 5	--
Phosphorus	1 - 10 mg/L	1 – 40 mg/L
Sulfate	10 - 75 mg/L	20 - 75 mg/L
Total Dissolved Solids	80 – 2900 mg/L	80 – 2900 mg/L
Sodium	35 – 200 mg/L	35 - 200 mg/L
Chloride	3 - 250 mg/L	3 - 250 mg/L

Source: California Regional water quality control Board, Central Cost Region, 'General Waste Discharge Requirements for Discharges f winery waste'

The level of BOD in the wastewater stream can be very high because of the sugar content inherent in the winemaking process. In effect BOD level in winery waste is often stronger than the one in waste produced from petroleum refineries, food processors and other manufacturers. Wastewater arising from the crushing operations of a typical winery (15,000-20,000 case-per-year) often contains the equivalent organic load of a city of almost 2,000 people.

1.2.3 Presency of polyphenols in the winery waste

When referring to the quality and synthesis of winery waste, a matter of high significance is the presence of some antioxidant compounds in them, known as polyphenols. Polyphenols can be found in the skin and seeds of grapes and are substances that protect cells from oxidative damage caused by molecules called free radicals. Free radicals can damage important parts of cells, including proteins, membranes and DNA. Cellular damage caused by free radicals has been implicated in the development of cancer.

Wine Waste anti-oxidants applications for further use

Research on the antioxidants found in red wine has shown that they may help inhibit the development of certain cancers. Red wine contains more polyphenols than white wine because the making of white wine requires the removal of the skins after the grapes are crushed. The phenols in red wine include:

- Catechin,
- Gallic acid
- vanillic acid
- protocatechuic acid
- Quercetin
- Caffeic acid
- Ferulic acid
- And epicatechin.

CHAPTER 2: WASTE MANAGEMENT

One of the major problems in the operation of wineries is the disposal of large quantities of wastewater containing a medium to high content of biochemical oxygen demand (BOD). Noted problems with winery wastewater include acidity, high levels of organic materials and nutrients as well as seasonal flow variation which create several problems in the use of conventional treatment methods. The general objectives for wastewater management are:

- Reduce of organic load
- Prevent odors
- Avoid nutrient runoff into surrounding waters

On the other hand, a great amount of solid waste derived from winery process including mostly grape marc and filter earth by-products should be treated following the appropriate management practices. The primary concern is the high biological oxygen demand related to the skins and lees, which could lead to a depletion of dissolved oxygen in surrounding streams, rivers and other waters.

Reduction of waste at source is the most environmentally preferable and efficient option, followed by reuse and then recycling. However, an appropriate treatment should be implemented for the waste that are unavoidable, so as to eliminate environmental hazards. The main strategies of waste management are described below.

2.1. Pollution prevention

2.1.1 REDUCTION OF WASTEWATER AT SOURCE

Principle of the method	Pollution prevention looks at the following options: • Identify less polluting materials that can be substituted in the process • Use the existing materials in ways that create less waste Pollution prevention includes: • process modification • raw material substitution • product and administrative development, in order to minimize the resource use, the quantity of waste generated and their content of environmentally harmful substances
Main alternatives and procedures recommended	• Reduction of water consumption in the different phases of the production procedure (fermentation tanks, barrel washing, barrel soaking, bottling line, cellars, and crush pad) o Regularly check for and repair all leaks o Monitor water usage monthly: unusual water usage can be an early indicator of maintenance needs o Document all clean-up policies, including water conservation cleaning measures o Save the rinse water from the final rinse of tanks for reuse; use recycled water for the first rinse of tanks o Automate cleaning. Use of cleaning chemicals and water can be reduced. This is particularly applicable for barrel washing. o Do not clean tanks and vessels by overflowing with water for extended periods. o Use high pressure, low volume cleaning equipment for water cleaning o Use mops and buckets rather than hoses for cleaning floors o Use aboveground holding tanks as they are easier to inspect for leaks o Use hot water for cleaning, thus significantly reducing the need to use caustic soda o Fit flow-restrictors in taps and other water fixtures. These are pressure sensitive washers that expand as flow increases, maintaining a stable flow rate. o Dry-sweep spills where possible using brooms, scrubbers and squeegees. This reduces both water use and organic load of the wastewater. o Spot mop and clean up spills promptly before they spread

	over a larger area. o Install automatic shut off valves on hose outlets. This will reduce water waste, as hoses will not run when not required. o Reuse the water from barrel leak testing. Significant volumes of water are used during leak testing and recycling can reduce net water use. o Eliminate unnecessary production runs. This will reduce cleaning requirements. • Manage storm water (rainwater) properly: - Separate storm water from washing water - Collect and use stormwater for applications ranging from vineyard irrigation to cleaning and wash-down in the winery • Skins, pips and lees need to be heaped on an impenetrable layer (such as cement or plastic) and covered against rain, so that organic acids cannot run off and have a negative effect on soil. Also, all crushing, processing, bottling, effluent solids collection and storage areas will be located on a impenetrable layer that will be drained so that all wastewaters are diverted to the waste water treatment system. • Install mesh sieves over drainage channels and pits to prevent organic material (grapes, skins, stalks, etc) entering the effluent stream.

2.1.2 REDUCTION OF SOLID WASTE AT SOURCE

Principle of the method	Reduction of the amounts of solid waste generating from different phases of the production procedure.
Hints for reducing Solid Waste	• Buy materials (e.g. cleaning chemicals, additives) in bulk containers where possible. • Use reusable, returnable, refillable or recyclable containers. • Consider alcohol recovery from marc and tartrate recovery from diatomaceous earth and bentonite (generally only viable for high tonnage wineries). • Compact waste to reduce disposal volumes and costs.

2.2 Wastewater treatment

The type of wastewater management system used at a facility is based on evaluation of a number of factors. Site factors include:

- property size/available land onsite for disposal,
- proximity to nearby surface waters and natural surface drainage,
- depth of groundwater, soil type and permeability.

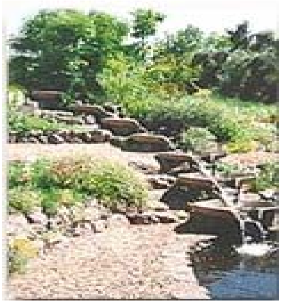
Other factors include:

- winery wastewater load,
- waste constituent levels,
- economic considerations,
- seasonal load variation,
- future plans for expansion,
- adjacent land uses,
- efficiency,
- legislative considerations,
- proximity to residents.

The most common waste management system practiced by wineries is based on biological treatment and disposal of the treated effluent for irrigation. Some of the most commonly used wastewater management and disposal methods in wineries are:

- Subsurface applications such as septic tanks/leach fields,
- Aerated ponds or aerobic facultative lagoons,
- High-Rate system bio reactors/activated sludge, or bio digesters;
- Recycling and reuse
- Land surface applications such as vineyard and field irrigation,

Also, combined systems and more sophisticated solutions can be applied as well as some more Advanced Aesthetic Treatment Systems including constructed wetlands or water gardens. The most common applications are presented in the following sections.



Traditional solutions Modular treatment Systems Aesthetic Treatment Systems (6)

2.2.1. Biological treatment

2.2.1.1 ANAEROBIC DIGESTION

Principle of the method	In anaerobic treatment, organic substances are degraded by fermentation to intermediate products such as acids and alcohols. The final product of the treatment is biogas (CH_4 and CO_2).
Main characteristics	Anaerobic digestion is usually combined with other techniques such as: - Sedimentation – precipitation – flocculation - Aerobic digestion The most critical point in this technique is the effectiveness in biodegradation of organic pollution load and production of methane. A variety of systems based on anaerobic treatment have been applied. Some of them are just as simple as a small pond and some are much more complicated as they could adopt a bioreactor in the process. Based on the above each one of the anaerobic applications have different advantages and disadvantages and the feasibility of each treatment system should be studied by case. The most common advantages and disadvantages of anaerobic digestion regardless the system applied are presented below.
Advantages	- production of biogas with high methane content - lower sludge production compared to aerobic digestion - lower requirement for nutrients compared to aerobic digestion - can be left dormant for months and recover quickly compared to an aerobic system
Disadvantages	- lower substrate removal rates compared to aerobic digestion - an anaerobic treatment can be highly efficient only by using advanced systems
Applications	***Anaerobic lagoon*** A conventional treatment system that has been practiced by small wineries for many years. It can just consist of a large pond which may or may not be covered in its simplest scheme, providing: - low biosolids production - good equalization characteristics - simplicity of operation - low capital and operating costs - ability to degrade suspended solids.

ANAEROBIC DIGESTION

The main disadvantages include:
- large land area requirements
- may have to dredge eventually
- gas collection difficulty

Bio-digester

In larger wineries the whole progress of organic degradation takes place in a properly designed reactor.

Anaerobic digestion has several advantages compared to other biological treatment methods, including:

- it takes up much less land than settling ponds
- significant reduction of pollution load
- production of methane that can be burned on site to produce energy
- odour-free operation

However, there are several difficulties in the application of this method in small and medium size wineries due to the high construction and operation cost.

Some industries are still reluctant to use anaerobic treatment plants, probably because of the counterpart of their efficiency: they can become unstable under some disturbances like changes in the quantity (*i.e.*, hydraulic overloading) or quality (*i.e.*, organic overloading) of the wastewater to be treated (7).

Combined systems

Furthermore lagoons can be used as a pretreatment method which is followed by a bioreactor.

2.2.1.2 AEROBIC DIGESTION	
Principle of the method	In aerobic treatment, organic substances are quickly and efficiently digested by microbes and enzymes in a highly- aerated environment.
Main characteristics	Aerobic digestion is usually combined with other techniques such as: - sedimentation – precipitation – flocculation - anaerobic digestion. The most critical point in this technique is the high BOD reduction rates that can be obtained per day. As in anaerobic digestion, a variety of aerobic systems have been practiced, each of them having different benefits as it is analysed below. The most common advantages and disadvantages of aerobic digestion regardless the system applied are presented below.
Advantages	- fast rate of biological growth - relatively high reduction of organic load depending on the technique -
Disadvantages	- the operation of the aerobic treatment is very sensitive to flow fluctuation as well as to periodical use, a significant problem with wineries taking into account that they work seasonally. - the winery's wastewater quality and quantity show significant differences (pH ranging from 4.5 (wine or high sugars from crush) to 10 or more with caustic cleaning of tanks) which means that a pretreatment is necessary. - high production of biological sludge compared to anaerobic digestion - require long retention times compared to anaerobic digestion

AEROBIC DIGESTION

Applications	*Aerobic Pond*

Applications

Aerobic Pond

Wineries traditionally treat their wine process wastewater with aerobic (aerated) ponds to biologically degrade the biochemical oxygen demand (BOD) (8). The majority of the wineries collect their wastewater in primary aeration ponds and then pump to a secondary settling pond to remove solids before they can discharge the water to the vineyard for irrigation.

The main advantage of this method is its low cost compared to more sophisticated biological treatment techniques. However, these systems are subject to upsets under sudden heavy load or when neglected and require large surface area, especially when natural oxidation ponds are used. Also, the performance of such a system is not high and therefore the treated effluent cannot be discharged to water resources. It can only be used for irrigation in a field which means that a large surface area is needed for the application of the effluent. Furthermore the adoption of an aeration system can be expensive.

Activated sludge treatment

The system consists of an aeration basin (cement vault or tank), an aeration source (high volume low pressure blowers) and a clarifier.

As the effluent passes through the clarifier the microbes settle and concentrate, and pumped back into aeration basin. This is known as a Return Activated Sludge system.

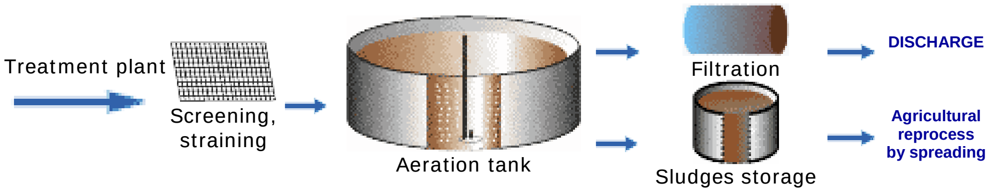
A pH level of 7,0 and a dissolved oxygen (DO) level of 2,0 ppm are the otimum conditions for BOD digestion.

BIO ARMOR Environment, a French waste treatment company, has developed a specific wastewater treatment facility which uses a Bio Reactor with rotary blowers and fine bubble diffusers to achieve an efficient way of converting electricity into dissolved oxygen (9).

The abatement achieved by the proposed system ranges from 95 % to 99 % on: COD, BOD_5, suspended solids.

AEROBIC DIGESTION

Applications	

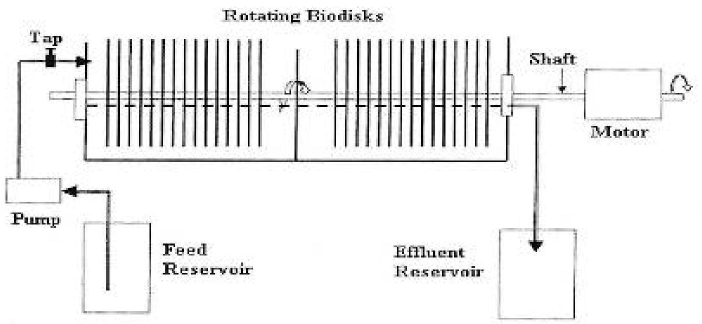


Main advantages:
- significant reduction of pollution load
- relatively odour-free operation
- rapid adjustment to changes in loading and temperature
- performances no affected by climatic conditions
- treatment plants can be designed to accept load variations

Main disadvantages:
- difficulties in the application in small and medium size wineries due to the expertise needed for the effective operation of the unit
- pure oxygen systems are expensive
- high energy consumption

Rotating Biological Contractor (RBC)

The system proposed by a research programme (10) is based on a microbial biofilm that develops on the surface of disks mounted onto horizontal shaft with at least 40% of the disks submerged in the wastewater. Rotation of the shaft results in alternating contact of the disks with wastewater and air that allows for the aerobic growth of the micro-organisms on the surface of the disks.



Main advantages:
- easy to operate
- has a short start-up
- requires little maintainance
- effectively oxygenated with little sloughing of biomass
- does not occupy too much land
- relatively odour-free operation

AEROBIC DIGESTION	
Applications	*Main disadvantages:* - difficulties in the application in small and medium size wineries due to high cost - pure oxygen systems are expensive - high energy consumption Given the seasonal fluctuations in wastewater discarded by wineries, the RBC could therefore be an effective primary treatment system to lower the COD to more acceptable levels for secondary treatment by constructed wetlands or other biological processes. ***Combined systems*** More complicated systems have been developed that include the combination of lagoons as mixing clarifiers, as activated sludge ponds and as clarifiers (11). Furthermore lagoons can be used as a pretreatment method which is followed by a bioreactor.

2.2.2 Disposal of the treated effluent

The main disposal alternatives of the treated effluent include:

(1) reuse in the winery

(2) agricultural crop irrigation or

(3) discharge to a water resource.

Wastewater must be treated and discharged into a water resource to sustain the environment or to be available for a potential downstream user. It is important for winery management to take into account that the treatment systems do not always guarantee a proper quality of the effluent that could allow its discharge to a natural water resource. Therefore, the most common method proposed and practiced in large scale by the wineries is irrigation.

2.2.2.1 IRRIGATION	
Principle of the method	The treated winery wastewater is used for irrigation. The discharge level of BOD as well as the restriction of standing water in an irrigation field is regional dependent and is regulated by European and National Legislation.
Main characteristics	Where wastewater irrigation of crops is not feasible, constructed wetlands offer an alternative for wineries that have sufficient land area available for wetland creation. A wetlands ecosystem acts as a water 'filter'. Water quality improves as surface water moves through soils, plant stems and plant roots, and is acted on by microorganisms living in the system. The required land area is deduced from the volume and characteristics of the winery effluent, climatic data and evaporation rates at different times of the year as well as characteristics of the soil and the corps. The winery should monitor the impact of wastewater on soil, water resources and vegetation.
Advantages	- low running cost

IRRIGATION	
Disadvantages	- if the discharge levels of BOD exceed certain concentrations, the irrigation water can create an odour in the irrigated fields - if the discharge levels of BOD exceed certain concentrations, the irrigation water can develop a slime layer just under the soils surface, which 'plugs' the field - irrigation with treated wastewater disposal is prohibited prior to predicted storms - need large area of land
Applications	When irrigation in vineyards is not feasible the construction of a wetland is a common practice. Constructed wetland include wetland plant species and stay wet through application of water. In this case, the objective of a constructed wetland is to mimic the filtering activity of natural wetlands to manage wastewaters (12).

2.3. Solid waste management

The most commonly used methods for the solid waste treatment may be summarised as follows:

Grape marc waste

- Treatment of grape marc waste by distillation
- Energy recovery infrastructure
- Reuse on vineyards
- Grape marc waste material composting
- Grape seed oil production.
- Reuse grape marc as stock feed
- Combination of treatment methods for grape marc such as distillation and re-use on vineyards.

On the same time the grape marc waste treatment entails some difficulties including:

- Management/Processing Costs and economies of scale.
- Composting of grape marc is not a winery or vineyards core business.
- Seasonality of waste availability (for processing).
- Possible spread of phylloxera.
- Need to monitor the effects of re-using grape marc in vineyards.
- Inappropriate disposal of grape marc (eg dumping in a paddock).

Filter earth (bentonite clay and diatomaceous earth)

- Filter earth is collected for the recovery of tartrate (tartaric acid)
- Filter earth is disposed to landfill
- Filter earth is sent with grape marc for distillation processing, and is mixed with grape marc for re-use on-site.
- Combination of disposal methods such as tartaric acid extraction prior to landfilling

The most important solid waste management methods are analysed in the following sections.

2.3.1. Management of grape marc

2.3.1.1 DISTILLATION PROCESS	
Principle of the method	Grape marc generated from the crushing, draining and pressing stages of wine production is collected for distillation processing into alcohol.
Main characteristics	The still produces 'low wine' which is subsequently rectified to a high strength spirit. Sweet marc must be inoculated with a yeast culture to ensure complete fermentation or the grape sugars in order to achieve maximum alcohol recovery during processing (13).
Advantages	- 'low wine' produced from this process can subsequently rectified to a high strength spirit - 'low wine' is sold in some countries as 'Grapa' (in Italy) and 'Marc' (in France) - in Australia rectified grape spirit is used principally for fortifying sweet or dessert wines - grape spirit could also be used as a source of renewable power - recovery of tartrates from marc is carried out in conjunction with distillation processing - the processing of marc for alcohol and tartaric acid recovery results in the generation of spent marc that is supplied to feedlots and horticultural enterprises or returned for application to vines
Disadvantages	- grape marc availability for distillation processing is seasonal and is dependent on the length and size of the vintage for the industry - decrease in alcohol sales may result in the collection of grape marc from certain regions no longer being economically viable - grape spirit has to compete against other spirits which are often much cheaper to produce and can be used in many products
Applications	Generally grape marc from the larger wineries is collected for distillation processing, although in addition, they may retain a small percentage for re-use on their vineyards. It is estimated that approximately 90% of grape marc generated by the South Australian wine industry is collected for distillation processing into alcohol (13).

2.3.1.2 ENERGY RECOVERY	
Principle of the method	Biomass is the name given to any recent organic matter that has been derived from plants as a result of the photosynthetic conversion process. Biomass energy is derived from plant and animal material, such as wood from forests, residues from agricultural and forestry processes, and industrial, human or animal waste including **grape marc.**
Main characteristics	There are several methods that can be used in order to convert biomass energy into a usable energy source: **Burning :** biomass can be burned in special plants to produce steam for making electricity, or it can be burned in order to provide heat for industries and homes. **Bacterial Decay:** the anaerobial decay of biomass (agricultural waste) produces methane. **Fermentation:** Adding a yeast to biomass produces an alcohol called ethanol. This is how wine, beer, and liquor are made. Wine is just fermented grape juice. Also, biodiesel can be produced with this method. Therefore grape marc can be used in order to produce energy through either incineration or anaerobic treatment.
Advantages	o Use marc as a renewable energy source o Economical benefits from marc sales as a fuel or from energy production on site (through either incineration or production of methane). The economics of biomass electricity generation depend on several factors, including technology and fuelstock. Also the cost of the fuel depends on the location of the residue incinerator in comparison to the wine industry.
Disadvantages	- The use of an incinerator must be combined with an expensive air pollution abatement system otherwise a significant air pollution problem can be created - The construction cost of an incinerator or an anaerobic treatment system for the production of methane is too high.

2.3.1.3 ON SITE REUSE	
Principle of the method	A common practice of dealing with waste grape skins and lees is plowing skins back into fields and discharging lees to its irrigation system.
Advantages	- low application cost - easily applied in areas showing low rainfall and high evaporation rate - spent marc residue from distillation process can be re-used on vineyards provided that the phenolic leachates have been removed - the seeds in the marc are very tough and decompose very slowly and their size is ideal for improving soil structure by creating macro press where water and air can be retained in the soil for utilization by plants and soil biota
Disadvantages	- high biological oxygen demand related to the skins and lees, which could lead to a depletion of dissolved oxygen in surrounding streams, rivers and other waters - inadequate on-site stockpiling and mulching methods for fresh grape marc at vineyards could potentially cause environmental issues such as odour, soil and surface water contamination with acid leachates, fire hazards and breeding of vermin - marc should not be applied fresh as without any pretreatment the phenolic leachates are reported to seriously inhibit root growth
Applications	The on site reuse of grape marc sourced directly after wine production on vineyards is likely to remain the favored treatment option for smaller scale wineries where the solid production is limited.

2.3.1.4 COMPOSTING	
Principle of the method	Composting is a biological decomposition of organic waste by bacteria, fungi, worms, and other microorganisms occurring under controlled aerobic conditions. The organisms use carbon, nitrogen and other nutrients released from the organic matter during the decomposition progress.
Main characteristics	The composting process occurs in two major phases. In the first stage, microorganisms decompose the composting feedstock into simpler compounds, producing heat as a result of their metabolic activities. In the second stage, microorganisms deplete the supply of readily available nutrients in the compost, which, in turn slows their activity. As a result, heat generation gradually diminishes and the compost becomes dry and crumbly in texture. Optimum moisture, aeration, temperature, particle size and carbon to nitrogen ratio are important for efficient composting: - temperature: 45 - 60^{o}C - oxygen: 10% (concentration in the air within the compost pile) - moisture: 45-60% (water concentration in the pile) - C/N ratio: 30:1 - particle size: 1,5 – 3,5 cm - pH: 6 – 7,5
Advantages	- relatively low cost - easily constructed and maintained - the resulting composting can be sold to other users as an agricultural additive (composts are often referred to as high performance soil conditioners) - grape marc is low in sodium and chloride and has a higher nutrient value than other organic waste - the negatively charged colloidal surfaces of humus retain moisture, which reduces the risk of crops and vines from suffering from moisture stress between irrigation events
Disadvantages	- potential environmental and nuisance impacts to nearby communities such as odour and dust nuisance in case of open-composting systems - siting restrictions (sites required close to wineries and vineyards) - a number of compost producers have stated that the absence of seeds from their compost product would improve the marketability of the product. However, the suitable machinery is too expensive to be used for this purpose. - marketing of compost products faces competition of chemical alternatives (farmers often don’t trust compost products due to ignorance)

Applications	Suggestions include the production of compost pellets that could be produced by using a blend of grape marc and other winery waste such as winery filter cake and sludge in order to compete better with chemical alternatives in terms of performance and application. Composted marc can be incorporated into the soil at the end of vintage when the soil is being worked and prepared for sowing cover crops. Alternatively, compost can be applied when cover crop is turned in. The agricultural sector is potentially the major consumer of compost. More specifically, compost can be used: ▪ to enrich soil with organic matter and increase soil fertilization ▪ to improve soil aeration ▪ as biocide ▪ to decrease soil erosion ▪ to decrease soil need for chemical fertilization and peat ▪ to increase water holding and irrigation capacity of the soil ▪ to increase the soil capacity for nutrient absorbance and assimilation.

2.3.1.5 GRAPESEED OIL PRODUCTION

Principle of the method	The seeds contained in pomace can be separated, and then used for producing grapeseed oil.
Main characteristics	Grape seeds have a high energy content concentrated in their oil. Seeds are crushed to extract the oil and then filtered before bottling.
Advantages	Grapeseed oil has numerous applications and therefore is a valuable product.
Disadvantages	- the oil content varies from grape to grape (the oil content should be high enough in order to make a good quality cold-pressed oil) - grape marc is vulnerable to infection from a number of damaging moulds, which can cause degradation of oil and occupational health and safety risks if not handled promptly and effectively.
Applications	Grapeseed oil has numerous applications: - it is sold as a gourmet food item in specialty shops, used for mild food flavoring, and also may have health benefits - it can also be used as a beauty product and is absorbed quickly to the skin - it has been used as a semi-drying oil in paints since the late 1700s - it is being marketed as a cheaper alternative to olive oil. France and Italy are the worlds' largest producers of grapeseed oil. The European Union provide tax benefits to improve the economic viability of producing grapeseed oil and to therefore relieve a critical oversupply of grape marc in Europe (4).

2.3.1.6 ANIMAL FEED

Principle of the method	Use of marc as a stock feed. Washed skins are dried and used for animal feed.
Main characteristics	Seeds are crushed so that grape seed oil is recovered and the remaining proteins are used for animal feed (14). The protein content of grapeseed renders the press-cake (meal) as a useful ruminant feed. The grapeseeds can form a useful component of lamb diets as both oil and protein are readily digested (4). It is suggested that seeds could profitably be included at reasonably high levels in ruminant diets. In a study, carried out in Cyprus, dried grape pomace was fed as 15 and 30 percent of calf fattening diets in order to determine the nutritional value of this by-product. Urea was added to compensate for the low digestibility of grape pomace protein. On a dry-matter basis, crude protein was 12,3% and it was 19,5% digestible (15).
Advantages	- low cost - economical benefits from animal feed sales
Disadvantages	- a number of fungicides and insecticides used in grape production have restrictions that do not allow the feeding of marc to livestock
Applications	Several wineries use marc with certain specifications for animal feed.

2.3.2 Management of other solid waste

2.3.2.1 TARTARIC RECOVERY	
Principle of the method	Use of filter earth for tartaric recovery
Main characteristics	Filter earth such as bentonite clay, diatomaceous earth and perlite is used to polish or clarify wine from floating organic material (lees). Solid potassium bitartrate and lees or diatomaceous earth containing high concentrations of potassium bitartrate can be sent in a solid or liquid paste form for tartaric acid recovery. Other treatment methods for filter earth include: ▪ disposal to landfill ▪ sent with grape marc for distillation, and ▪ mixed with grape marc for re-use on site
Advantages	- tartaric acid recovery, which is used to adjust the wine acidity in wine industries - economic benefits
Disadvantages	- solids with low concentration of potassium bitartrate can not be used for tartrate recovery and should be disposed off in a landfill or mixed with grape marc for distillation - generally, smaller size wineries may not generate enough filter earth waste to justify its transportation for tartaric acid recovery.
Applications	In some cases wineries use a combination of disposal methods. For example filter earth waste are sent for tartaric acid extraction prior to landfilling, while waste that do not contain significant amount of potassium bitartrate are sent directly to landfill. Some larger wineries are using high speed centrifuges in order to eliminate the use of filter earth. Sludge produced from this process is generally distilled and sent for tartrate recovery.

2.3.2.2 SOIL ENHANCEMENT	
Principle of the method	Wine filtering byproducts are used as soil enhancement.
Advantages	- low cost disposal method - economical profits - the filter cake is diverted from a waste to a beneficial product
Disadvantages	- the suitability of filter earth as an additive to mulches and composts should be determined through on-site trials
Applications	Applications of these byproducts include: – Mixture of wine filtering byproducts with cow manure in order to be used as soil enhancement (12). – Mixture of filter earth with grape marc for reapplication in vineyards (13).

2.3.2.3 ANIMAL FEED	
Principle - Main characteristics	Several solid byproducts (waste) from the winery production procedure can be used as animal feed. These include the filtered solid from the fermentation procedure as well as the dewatered sludge (plankton) derived from the biological treatment of wastewater (16).
Advantages	- low cost - economical benefits from animal feed sales
Disadvantages	- the solid waste derived from winery process does not always reach the qualification standards so as to be incorporated in feedstuff

CHAPTER 3:

TECHNOLOGIES USED FOR THE EXTRACTION OF PHENOLS

Polyphenols, existing in wine wastewater, consist a major problem mainly due to their toxicity for the ecosystems. These compounds are hardly degraded and therefore their existence in wastewater is one of the reasons why these waste cannot be discharged to the environment. Thus, the removal of phenols from these wastewater is very critical for their proper management.

Also, grape marc, the waste from wine production, has long been a problem for wineries. Once the juice has been extracted, the skin, stalks and seeds are all redundant. In total, more than 20 per cent of wine production is waste, comprising thousands of tonnes. The marc, if not treated effectively, can cause a number of environmental hazards ranging from surface and groundwater pollution to foul odours. Historically, winemakers produced grape spirit from grape marc. However taking into account that the amounts of waste produced every year are huge new uses of waste must be found. As it was mentioned in the previews chapter these waste can be used in order to produce compost or fertiliser. However, the value in both soil nutrition and cost terms makes composting a marginal proposition.

Taking into account that grape seeds have high energy content, several valuable compounds could be extracted from these waste, such as grape seed oil, tannins (in order to produce colours) and polyphenols. Several attempts are in progress mainly in pilot stage globally aiming to produce valuable by-products from grape marc. An Australian company has made an attempt to produce an essence of wine. This essence is really recovered from the skins of the wine and it contains the key red colours and this is added to wine to give it a deeper colour and a rich wine feel turning a cheap cask wine into a grange.

Also, as it was mentioned above, the antioxidant properties of polyphenols make them a valuable by – product. However, technologies for the extraction of polyphenols from wastewater and waste have been used only in laboratory or pilot scale until now. Technologies for the extraction of polyphenols are used successfully in other applications as for example in the removal of haze from wines or fruit juices. In general the existing technologies include:

- Membrane separation (Ultrafiltration/ Nanofiltration)
- Use of absorbent resins
- Extraction (solid phase extraction, liquid/liquid extraction, supercritical fluid extraction)

In this chapter, the use of grape marc and wastewater from wine for the extraction of polyphenols is further discussed.

3.1 MEMBRANE SEPARATION (ULTRAFILTRATION / NANOFILTRATION)	
Principle of the method	Membrane separation involves separating components from liquid fluid or gaseous streams by means of forcing the stream to flow under pressure over the surface membrane. Membranes operate in cross flow filtration mode where the liquid flow is parallel to the membrane surface. This creates two outlet streams, the permeate, which passes through the membrane and the concentrate, which is retained by the membrane. The techniques that can be used are reverse osmosis, ultrafiltration, nanofiltration and microfiltration. Ultrafiltration separates dissolved solutes of 0.005 to 0.1 microns, which corresponds to a molecular weight cut-off of about 1,000 to 500,000. Depending on the molecular weight cut-off selected, the membrane will concentrate high molecular weight species while allowing lower molecular materials to pass. The nanofiltration membrane rejects the pass of organic molecules in a molecular weight range between 200 – 300. The type of membrane that will be used determines the selectivity of particular compounds.
Main characteristics	The performance of a membrane system is determined by: - Membrane selectivity - Permeate flux (lt/m^2/h) – typical values lye between 20 – 2,000 l/m^2/h (17).
Advantages	Significant selectivity in the separation of certain compounds. Improvements in the design and decreasing costs in membrane filtration technology have made possible a multitude of applications for this technology. Wine industries are familiar with membrane technology and therefore the use of membranes for the treatment of wastewater is quite easy for them.

MEMBRANE SEPARATION (ULTRAFILTRATION / NANOFILTRATION)	
Disadvantages	The greatest disadvantage is the problem associated with flux reduction (flux is the rate of filtration) and fouling. These factors can significantly increase the cost of operating a membrane filtration system unless preventative measures are taken. Initially, the system will have a relatively high flux that will quickly diminish as the membrane is fouled. Cleaning does not return the flux to the initial rate but to a value considerably lower. More frequent the cleaning, the lower the expected membrane life. Also, plugs of trace contaminants in the system can dramatically reduce membrane life. Proper pre-treatment is an economical and effective way to reduce cleaning frequency and membrane replacement. Also, there is high consumption of energy in order to achieve the pressure needed for the treatment. Finally membrane selectivity/sensitivity can create major problems in the treatment of wastewater. Most commercial membranes do not show good results in the removal of organic load from wastewater.
Cost	*Construction cost: it* depends on the type of membranes the treatment rate and other parameters. The construction cost for a simple membrane system for the treatment of 6 m^3/h: 44,000 €. However this cost for a complex system for the treatment of heavily polluted wastewater can increase significantly. *Operating cost:* 1.2 €/m^3. The operating cost includes mainly consumables and energy cost.
Applications	Commercial membranes are used widespread in food industry in order to remove undesirable compounds as for example in: o milk industry o fruit juice and syrup industry for the clarification of juices (removal of impurities such as yeasts, moulds, bacteria, colloids and solids as well as proteins, polyphenols, tannins, polysaccharides helping in this way to impart stability to the final juice whilst still allowing sufficient transfer of colour (use of UF membranes) o wine and vinegar industry for clarification of the product (17) According to measurements, the reduction of polyphenol content in apple juice using a commercial cellulose UF membrane (10 kDa) is approximately 12%. Selective removal of polyphenols from apple juice using PES/PVP ultrafiltration membranes has been achieved in a laboratory scale (operation pressure 1 bar) (18). The removal percentage of polyphenols using this technique is approximately 35%. These membranes can be regenerated with NaOH.

Based on the above mentioned a UF membrane could be used for the separation of polyphenols from winery's wastewater. However, it must be mentioned that the quality of the inflow to the membrane separation system in the clarification procedure of wine or apple juice differ significantly from the quality of wastewater from wineries.

Also, laboratory results show potentials in the use of membrane separation for the removal of polyphenols from wastewater, however there are several problems in the application of this technique including difficulties due to the character of phenols: due to their small size, phenols are captured based on their size by RO membranes. In order to separate phenols using membranes with larger pore size and less sensitive than RO, special type of membrane material must be used. Great difficulties exist in finding the proper type of membrane for the separation of phenols existing in wastewater.

Also, the construction and operating cost for this technique seems to be quite high.

Also, membranes can be used in wastewater treatment systems as a final step. An application has been tested in pilot scale in a European project where a bioreactor was used in combination with a membrane filtration system for the treatment of wastewater from wine and juices (19).

In this case the membrane filtration system can be used in order to further treat the outflow after the biological treatment. This is very important taking into account that the organic load in these waste is quite high. Therefore, in most of the cases biological treatment can not reduce BOD and COD levels so much in order to allow the disposal of the outflow into natural receivers or its recirculation in the production procedure. The use of membrane filtration system as a final step can improve the quality of the final outflow significantly.

3.2 USE OF ADSORBENT RESINS	
Principle of the method	The mechanisms for removal polyphenols by resins include adsorption, size exclusion and ion exchange. Organophylic adsorption occurs when two non-polar molecules are held together by Van der Waal forces. The benzene rings on the synthetic resins and phenolics enhance this particular adsorption.
Main characteristics	To select a synthetic adsorbent the main things that must be checked are its adsorption capacity and its effect on other components included in the wastewater. The main characteristics that show interest in the selection of an adsorbent are: - Porosity – pore size distribution - Surface area - Pore diameter - Hydrophobic or hydrophilic properties - Particle size - Density - Pressure drop due to fluid flow through an adsorbent - Ability to remove certain organic compounds - Desorption and regeneration ability - Catalytic activity The adsorbents used to separate phenols from various media are usually polymeric with high surface area, hydrophobic surface able to concentrate organic compounds. Characteristis resins that are used for the removal of polyphenols and proteins from apple juices and wine in fluidised bed form are (20): - Amberlite XAD 16 (Rohm & Haas): is a styrene/divinylbenzene based material that is a nonionic, hydrophobic, crosslinked polymer with a surface having an aromatic nature. The adsorptive properties come from its macroporous structure, which contains both a continuous polymer phase and a continuous porous phase. Pore size ranges from 2 to 300 Angstroms; the surface area is 800 m^2/g. The distribution of pore size shows its application for adsorption of low to medium molecular weight organic compounds, especially proteins - XUS40285 (Dow Chemical): dimethylamine functionalized chloro-methylated copolymers of styrene and divinylbenzene. This resin has high surface area and high porosity. It is a weak base anion exchange resin. The protein removal mechanisms include ion exchange, size exclusion, and possible adsorption. - XU43520 (Dow Chemical): is a macroporous adsorbent resin, a styrene-divinylbenzene polymer - Polyamide resins which have show great ability to adsorb polyphenols

USE OF ADSORBENT RESINS	
Main characteristics	Also, polymer additives such as polyvinylpyrolidine (PVP or PVPP (Polyclar AT) or polymer materials containing silica gel can be used for the adsorption of phenols. These additives can be added to the wastewater in insoluble form and then, after the adsorption of phenols, can be removed through filtration or sedimentation.
Advantages	The main advantage of this method is the ability to remove polyphenols with a low cost compare to other methods.
Disadvantages	The efficiency of this method depends on the type of the selected adsorbent. The main disadvantages of this technique include: - Difficulties in the selected adsorption of polyphenols taking into account that wastewater contain several organic compounds having a significantly high organic load. - Problems with pressure drop /adsorption efficiency due to the nature of waste water (high organic load, density of wastewater) - Difficulties in the recovery of polyphenols - Lower efficiency in removal/recovery of polyphenols compare to other methods (as for example SPE).
Cost	Construction cost for a unit of 6 m^3/h separation rate: 32,000 € Operating cost: 0.89 €/m^3
Applications	Resins are commonly used in wineries in order to clarify wines from haze (protein and polyphenol removal). Traditionally the clarification of wines is performed using bentonite. Tests conducted at the Viticulture and Enology Research Center (VERC) (14), with support from CATI and the American Vineyard Foundation, focused on three commercially available resins (Amberlite XAD, XUS40285, XU43520). Wine and juice samples were pumped slowly through columns of resin, then heated and analyzed for haze formation, as well as for protein and phenolic content. Levels of pH, brix, titratable acidity and metals also were measured. All three resins were found to have effectively stabilized the grape juices and wine. Also, it was found that DOW XUS40285 was more efficient in the removal of phenols and the least efficient in the removal of proteins (20). Based on the above mentioned, the use of resins for the removal of polyphenols from wineries waste and wastewater seems to be a very attractive method.

3.3 EXTRACTION

Main characteristics	Polyphenols can be extracted from grape marc using solid phase extraction or liquid extraction (21). A method showing several advantages compared to conventional solid and liquid extraction, is supercritical fluid extraction. Supercritical fluid extraction (SFE) is an extraction technique that uses the unique properties of a supercritical fluid (carbon dioxide) to selectively extract and fractionalize valuable non-polar components from feed streams. A typical SFE process shown consists of two major segments, the extractor and the separator. The material to be extracted is packed into the extractor and supercritical carbon dioxide enters the extractor where it dissolves the volatile material in the plant. The CO_2 and the extract then goes to the separator where the pressure is below critical thereby allowing the CO_2 to revert to the gas phase and deposit the extract. The CO_2 can then be recycled to the extractor vessel. In order for the CO_2 to be in the supercritical state, the pressure and temperature must be above the critical point of CO_2 i.e. 31^{o}C and 74bars.
Advantages	SFE provides significant advantages including: increased selectivity, automatability and environmental safety, in addition to a dramatically decreased use of organic solvents. Carbon dioxide is cheap, inflammable, and leaves no detectable residue.
Disadvantages	Although the extraction results in products are of superior quality compared to other methods such as resins, the capital cost associated with setting up an SFE processing plant is high.
Cost	The cost of the equipment is high however the operation cost is low since carbon dioxide is not expensive. For example, two laboratory scale SFE units which have extractor vessels with capacities from 25ml to 300ml cost 120000 €. This cost does not include all the other equipment needed for the extraction procedure.
Applications	Supercritical fluid extraction is used in various pharmaceutical or food applications such as: • decaffeinating coffee • extraction of essential oils and aroma material from species • extraction of edible oils and producing cholesterol-free egg powder • distillation of crude oil • regeneration of used oils/lubricants • elimination of residual solvents from wastes • purification of contaminated soil • separations of biological fluids

	However the use of SFE for the extraction of polyphenols from wine has been tested only in laboratory scale till now and therefore we do not know its results in real scale. The biological activity of polyphenols extracted from grape marc was studied with a view to finding a new use for this winery waste in a laboratory scale in Spain. Polyphenols were extracted by using an alternative supercritical-fluid extraction method based on the use of a liquid trap that allows extracted polyphenols to be retained in a saline buffer, thus avoiding the need for the organic solvent required to elute polyphenols from a solid trap. The major extraction variables influencing the performance of the liquid trap were optimized. The proposed method was applied to the supercritical-fluid extraction of 0.3 g grape marc with CO_2 modified with 3% methanol at 350 bar at 50 ^oC for 20 min, using a liquid flow-rate of 0.9ml/min. The polyphenol extracts thus obtained exhibited cytotoxic effects that induced apoptosis in tumour cells (22). Similar trials have been performed also from other scientists (23).

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