The use of cork waste as a sorbent for pesticides and heavy metals generated during wine manufacturing process

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Abstract.
The aim of this study was to evaluate the adsorption capacity of cork wastes for the pollutants generated during wine manufacturing process. Adsorption was focused on four pesticides (aldrin, chlorpyrifos, metalaxyl and tebuconazole) and two heavy metals (Cu (II) and Ni (II)). The final purpose is to use this natural adsorbent as a substrate of a constructed wetland to improve its efficiency as wastewater treatment system. The high efficiency of cork as a sorbent of these pollutants is shown by the fact that equilibrium contact time obtained was 40 minutes. The highest adsorption capacities were exhibited for chlorpyrifos in the case of pesticides and for Ni (II) in the case of heavy metals. Experimental constructed wetlands filled with cork showed great removal efficiencies for these pesticides (more than 95%).
This study demonstrates that cork waste is a potential sorbent for some pesticides and heavy metals and may have relevance in the future treatment of pollutants-contaminated waters.

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1. Introduction

Development of technically simple and economically attractive methods of industrial wastewaters purification is one of the most important priorities of 21st century (Volesky, 2001). Therefore, the best solution is preventing the entrance of pollutants in the ecosystem.
Conventional technologies traditionally used for the removal of some pollutants from aqueous solutions are expensive and becomes less effective. The use of sorbents for the removal of toxic pollutants is one of the most recent developments in environmental water treatments. The major advantages of this technology over conventional ones include its high efficiency and the minimization of chemical or biological sludge (Park et al., 2010).
On the other hand, constructed wetlands are designed to use the natural processes involving wetland vegetation, soils, and the associated microorganisms to assist in treating wastewaters. The combination of both systems, sorbents and constructed wetlands, aims to increase the

efficiency of wastewater treatment. The use of natural sorbents such as cork waste also keeps the sustainability of the process.

Cork is the bark of the cork oak tree (*Quercus suber* L) and is natural, renewable and biodegradable raw material. It has a combination of properties that make it unique and versatile.

Cork oak forests extend over an area of almost 2.2 million hectares, concentrated mainly in the Mediterranean region, in the South of Europe and in North Africa (Portugal, Spain, Italy, France, Algeria, Morocco, and Tunisia). Europe has about 60 % of the total production area (cork forests) and produces more than 80 % of the world's cork. The main use of cork is the manufacture of cork stoppers but not all stripped cork is suitable for that activity. This material is called cork waste and could be used as a sorbent. Different types of biomasses (or sorbents of natural origin) have been studied for the last two decades and the sorption characteristics of many of them have been widely investigated. There are few studies on the ability of cork as a sorbent but these indicate that it might be a good material for its activity (Domingues, 2005, 2007, Chubar et al. 2003, 2004; Hanzlík et al. 2004; Villaescusa et al. 2000,2002).

Winery wastewaters are generated by various processes and operations carried out in wine production. This wastewater is characterized by the high content of organic matter, suspended soils and large variations in a seasonal flow production. Also, heavy metals like copper (Cu) and Nickel (Ni) and some pesticides such as chlorpyrifos and tebuconazole may be present in wastewater generated from the wineries as a result of the control of parasites of grape. These compounds can pass into the environment depending on the technological process (production and waste treatment) and the concentration factor of the fruit (Cabras and Angioni, 2000).

Constructed wetlands may offer an efficient low-cost, low-maintenance and energy alternative for wastewater treatment. Constructed wetlands also have the advantage of being able to accept seasonal flow fluctuations without adversely affecting the functional aspects of the treatment system so, is an alternative for wineries. The use of cork waste as a filling of a constructed wetland tries to be an improvement of the system.

The aim of this work was to evaluate the sorption ability of cork waste for some pollutants (pesticides and heavy metals) generated during wine manufacturing process using batch experiments and a pilot scale constructed wetland filled with cork waste.

2. Material and methods

Reagents

Heavy metals analytical standards were: Copper (II) chloride dihydrate extra pure (Sharlab) and Nickel (II) chloride hexahydrate (Sharlab). Pesticides analytical standards were purchased from Sigma-Aldrich: Aldrin, Chlorpyrifos, Tebuconazole, Metalaxyl and Phenanthrene-d10.To prepare the standard solutions acetone and methanol 215 SpS (Teknocroma) were used.

Cork samples

A cork factory supplied the cork waste. Three granulometric fractions: 2-3mm, 3-7mm and 15-20mm were used to select the optimal particle size for the adsorption process.

Batch sorption experiments

In the case of heavy metals, granulate cork (0.06g) is put in contact with 20 mL of solution. The mixture is set under stirring with Rotator Drive STR4 (Stuart Scientific). Once the set time elapsed, aqueous solution was filtered with a cellulose filter. pH was determined with a pH meter Crison BasiC 20. Concentration of metal was analyzed by flame atomic absorption (Varian 220 FS). Calibration standards suitable for measuring the concentration of heavy metals have been used. The appropriate hollow cathode lamp was also used.

In the case of pesticides, granulate cork (0.3g) is put in contact with 100 mL of solution. The solutions were mixed with a Vibromatic oscillating shaker at 700 oscillations/min. Concentration of pesticides were analyzed by solid phase microextraction (SPME) procedure and gas chromatography-mass spectrometry (GC-MS) analysis (GC-MS-SPME). For SPME extraction, 18 mL of each sample were analyzed. The fiber was immersed into the aqueous phase with agitation at 50ºC during 30 min. After extraction, the fiber was thermally desorbed for 10 min into the liner at 250ºC. The splitless time was set at 4 min and desorption time at 10 min. GC was performed with 6890N Agilent chromatograph equipped with a MSP2 Gerstel autosampler and coupled to a MS 5973N mass spectrometer. The separation was achieved using an HP-5MS column (30m, 0.25 mm, 0.25 μm, film thickness) (J&W Scientific, Folsom, CA, USA), and the CG program was: 60°C (1min), increased by 25°C/min to 163ºC, increased by 0.3°C/min to 167ºC, increased by 30°C/min to 210°C (held for 2 min), increased by 5°C/min to 250°C (held for 4min). The carried was helium (99.999%) from Abello Linde with a constant flow rate of 2mL/min. The mass spectrometer was operated in a selected ion monitoring mode (SIM). The monitored ions were of m/z: aldrin 263 and 293; chlorpyrifos 197 and 314; tebuconazole 125 and 250; metalaxyl 250 and 125. The quantification of pesticides was based on comparison of the areas for the monitored molecular ions to that of the internal standard, with calibration response curves generated from six different concentrations characteristic of each pesticide (Mühlen C et al. 2014 and Scheyer A et al. 2005).

Batch experiments were conducted to study the effect of cork particle size, pH (in the case of heavy metals), contact time, amount of organic material (using COD value) and temperature in sorption process. The last two simulates the conditions that could occur during the treatment of water in a wetland. The effect of the presence of organic material or the chemical oxygen demand (COD) value in adsorption process was determined using a synthetic wastewater. This solution was prepared in accordance with the table 1.

Table 1. Composition of synthetic wastewater.

Reagents	Composition 1	Composition 2	Composition 3
Sugar (g/L)	0.3	0.3	0.3
Basic fertilizer (ml/L)	2	3	4
COD (mg/L)	510	574	598

In both cases, heavy metals and pesticides, the results are expressed in percentage of removal and coefficient of variation values.

Constructed wetland filled with cork waste

A first test on the ability of cork waste as a sorbent and a filling of a wetland was carried out. Three constructed wetlands, two horizontal (HW1 and HW2) and one vertical (VW) filled with cork waste were monitored during 16 days, at a mean hydraulic load of 40 ± 4 L/(m^2/day) (VH) and 20 ± 4 L/(m^2/day) (HW1 and HW2). The flown water was winery wastewater with a secondary treatment.

There were two tanks, a control tank with winery wastewater and a pollution tank with spiked winery wastewater: 0.5 mg/L of chlorpyrifos, tebuconazole, metalaxyl, Cu (II) and Ni (II). One horizontal (HW1) and vertical (VW) wetland worked with periods of contamination being fed with the pollution tank and decontamination periods being fed with the control tank. First 8 days, HW1 and VW were fed with the pollution tank and last 8 days were fed with the control tank. The other horizontal wetland (HW2) only operated with the control tank. The sampling was carried out in feeding tank and in the exit of the wetlands. The results are expressed in μg/L and removal percentages.

Concentration of pesticides was analyzed by the same methodology described above and concentration of metal was analyzed by an inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

The first part of the study was determined the best optimal conditions for target pollutants adsorption such as cork particle size, contact time, pH (in the case of heavy metals), composition and temperature.

3.1 Effect of particle size

The effect of cork particle size on the adsorption of Cu (II) was investigated and the results are presented in Figure 1A. Medium particle size (3-7mm) and small particle size (2-3mm) presented similar results with percentage of removal higher than 50%. The same has been observed in the case of chlorpyrifos where the percentage of removal increased as smaller was the particle size (from 75.4 to 100%) (Fig. 1B). It was chosen the smallest particle size (2-3mm) to continue the study.

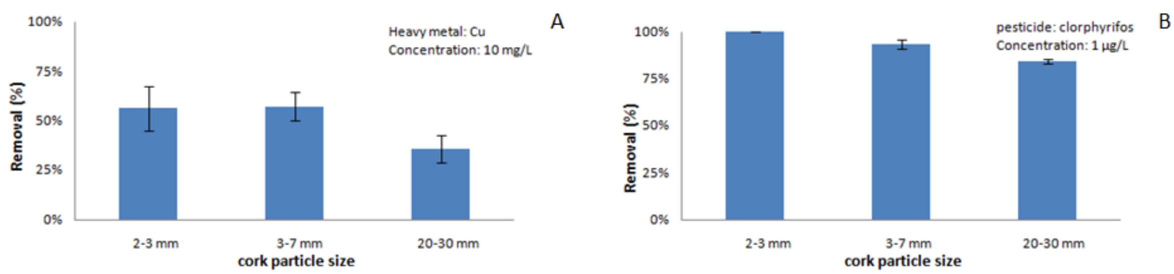

Fig. 1. Effect of particle size on amount of adsorption of Cu (II) (A) and chlorpyrifos (B) by cork waste at initial concentration: 10 mg/L and 1 µg/L, respectively; agitation time: 180 min.

3.2 Effect of contact time

The effect of contact time on the adsorption of Cu (II), Ni (II) and chlorpyrifos was investigated at different time intervals in the range of 0 to 300 min at 9.5, 8.75 mg/L and 1 µg/L, respectively. The results were presented for three pH in the case of heavy metals (5, 6 and 7) and three particle size (2-3, 3-7 and 20-30 mm) in the case of chlorpyrifos.

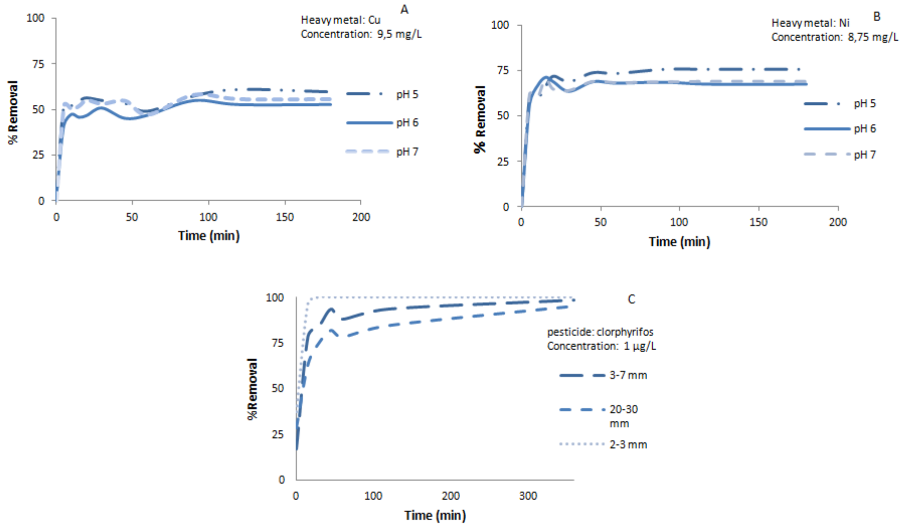

Fig. 2. Effect of contact time on amount of adsorption of Cu (II) (A), Ni (II) (B) and chlorpyrifos (C) by cork waste at initial concentration: 9.5, 8.75 mg/L and 1 µg/L, respectively.

Fig 2A and Fig 2B shows the effect of contact time amb pH on adsorption of Cu (II) and Ni (II) using cork waste. The results showed that the percentage of metal ion adsorption increase with increasing time and equilibrium was reached at the plateau value at 40 min. Thus, it has been chosen 180 min as equilibrium time to ensure the equilibrium in all concentration and experimental conditions. Due to the pH dependence of metal sorption, the sorption of both metal ions was studied at three different pH values (5, 6 and 7). The maximum removal (about 62%) for Cu (II) were found a pH 5 and differences on removal percentage were not found for Ni (II) at the different pH studied (from 65.3 to 68.6%). After the contact with cork waste, metallic solutions had a equal final pH of 6.5 independently the value of initial pH, indicating a buffering behavior of cork. The study continued at initial pH within the range of 5 to 6.
The effect of contact time on the adsorption of chlorpyrifos using cork waste at different granulometries was investigated and the results are presented in Fig 2C. The chlorpyrifos was totally sorbed rapidly within 30 min in particle size 2-3 mm (100% of recovery). Equilibrium time was reached within 120 min in higher particles size. As in the case of heavy metals, for pesticides it has been chosen 180 min as experimental time to ensure the equilibrium in all experimental conditions.

3.3 Effect of the amount of organic material
In order to take into account the adsorption conditions that could occur during the treatment of water in a wetland, the presence of organic material using COD value was tested. Table 1 shows the differences regarding the value of COD in the three types of synthetic wastewater.
Fig 3. shows the effect of chemical oxygen demand on the adsorption of Cu (II), Ni (II), aldrin, chlorpyrifos and tebuconazole onto cork. There was a reduction in the adsorption of Cu (II) and Ni (II) onto cork as the COD value increases (598 mg/L or composition 3). The removal percentage of Ni (II) decreases from 43 to 32% and for Cu (II) decreases from 54.2 to 31.8% among composition 1 to 3 (Figure 3A). A slight increase in COD value results in significant decreases on metal ions removal. Thus, the presence of high concentration of COD would have a negative effect in metal elimination on the wetlands.

COD studied values did not affect the ability of cork waste as adsorbent of targeted pesticides. The percentage of removal was from 98.6 to 100% for aldrin, from 39 to 54.5% for tebuconazole and 100% for chlorpyrifos for composition 1, 2 and 3 (Figure 3B). It seems that the presence of organic material do not affect pesticides removal on wetlands.

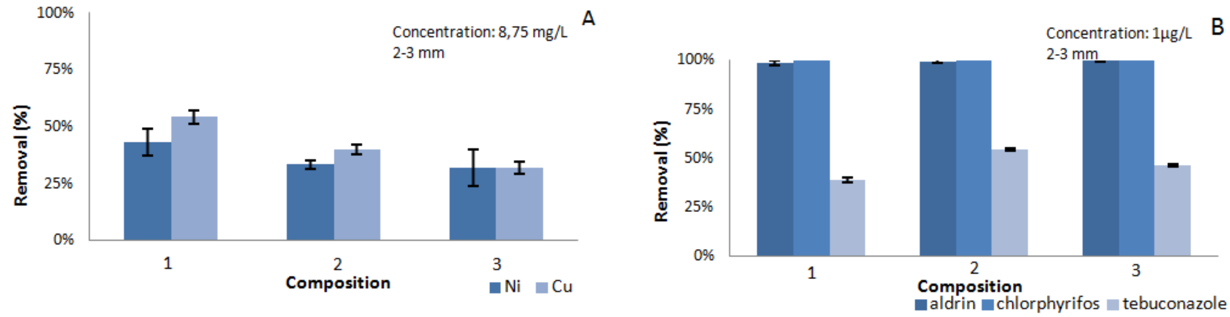

Fig. 3. Effect of organic material on amount of adsorption of Cu (II) (A), Ni (II) (B) and aldrin, chlorpyrifos and tebuconazole (B) by cork waste at initial concentration: 8.75 mg/L and 1 µg/L, respectively; agitation time: 180 min.

3.4 Effect of temperature

As in the case of COD, temperature was taken into account to evaluate the effect of the wetland conditions in adsorption. Two temperatures, 5 and 20ºC was chosen, simulating winter and summer climatic conditions. As seen in Fig. 4, removal percentages of heavy metals (Fig 4A) and pesticides (Fig 4B) were maintained regardless of the temperature.

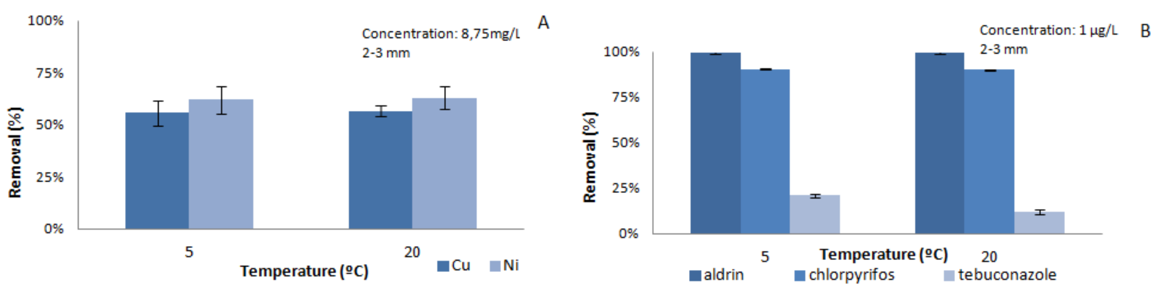

Fig. 4. Effect of temperature on amount of adsorption of Cu (II) (A), Ni (II) (B) and aldrin, chlorpyrifos and tebuconazole (B) by cork waste at initial concentration: 8.75 mg/L and 1 µg/L, respectively; agitation time: 180 min.

Temperature value did not affect the ability of cork waste as adsorbent of heavy metals and pesticides.

3.5 Cork waste as a constructed wetland substrate for pesticides and heavy metal removal

Three constructed wetland, two horizontal (HW1, HW2) and one vertical (VH), filled with cork waste were monitored during 16 days. Table 2 presents the removal percentages of each target pollutant for each type of wetland after 16 days of operation.

Table 2. Removal percentage of pesticides and heavy metals in each type of wetland

	% REMOVAL (16 days)		
	HW 1	**HW 2 control**	**VW**
Metalaxyl	99,6		99,6
Chlorpyrifos	100,0		100,0
Tebuconazole	99,4		99,2
Cu (II)	98,1	85,4	98,0
Ni (II)	98,1	71,9	97,5

The results showed that cork as a filled of horizontal and vertical wetland presents percentages of pollutant removal from 71.9% to 100%. The percentage removals were high for both pesticides and heavy metals. The horizontal wetland (HW1) (from 98.1 to 100 %) seems to be a bit more efficient than the vertical wetland (from 97.5 to 100%).
The initial concentration of heavy metal could affect the removal capacity of cork waste considering the results obtained for the control wetland (HW2). HW2 was only fed from winery wastewater without fortification. In this case, it was observed that the initial water had already traces of Cu (II) and Ni (II) (7.2 µg/L and 4.3 µg/L, respectively) and that were eliminated by filled cork (85.4 and 71.9%, respectively).
The concentration of pesticides and heavy metal in wetlands effluents throughout the study showed in Fig 5 and Fig 6.

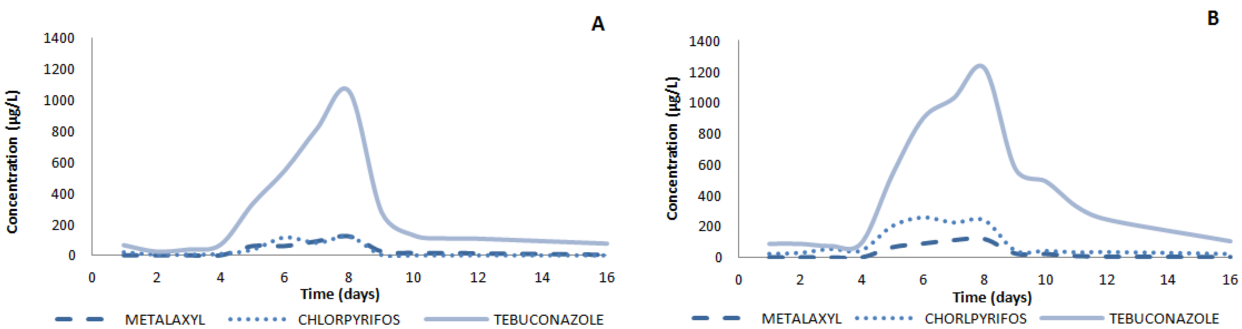

Fig. 5. Concentration of metalaxyl, chlorpyrifos and tebuconazole of wetland water effuent, HW1 (A) and VW (B), throughout its operation.

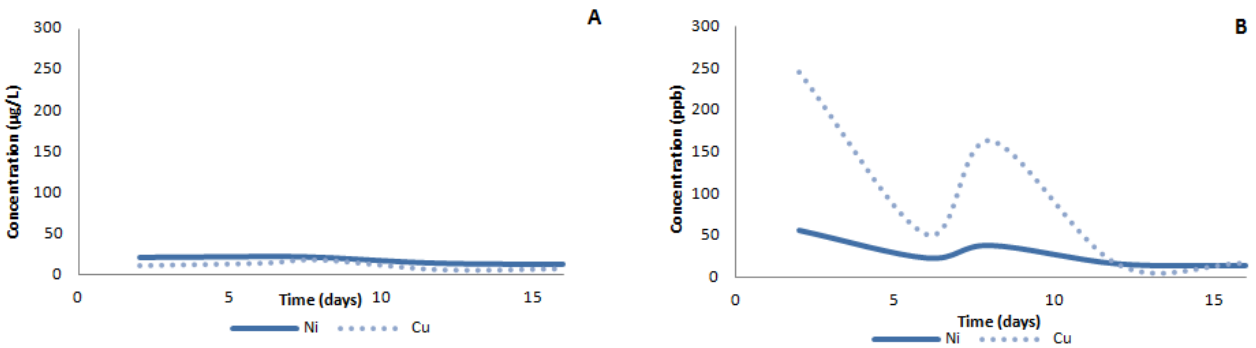

Fig. 6. Concentration of Cu (II) and Ni (II) of wetland water effuent, HW1 (A) and VW (B), throughout its operation.

In the case of pesticides, the effluent concentrations increased during the contamination period and then decreased over time. The effluent concentrations of pesticides in control wetland (HW2) were lower to the limit of detection (data not shown). In both wetlands, concentrations of all pesticides reached the maximum values at day 8 coinciding with the last contamination. For HW1 (Fig 5A), the effluent concentrations of metalaxyl (from 122.0 to 0 µg/L) and chlorpyrifos (from 123.8 to 1.9 µg/L) were lower than tebuconazole (from 1057.6 to 23.9 µg/L). For VH (Fig 5B), also the concentration of metalaxyl (from 118.6 to 0 µg/L) and chlorpyrifos (from 239.5 to 20.3 µg/L) were lower than tebuconazole (from 1223.0 to 75.2 µg/L). In batch experiments, tebuconazole also presented the lowest removal percentages. According to these results, cork waste seems to be more efficient for the adsorption of chlorpyrifos and metalaxyl than for tebuconazole.

The evolution of the effluent concentration of Cu (II) and Ni (II) depends on the type of wetland. For HW1 (Fig 6A), heavy metal concentrations had remained constant throughout the period of contamination and decontamination. The ranges were from 13 to 22 µg/L in the case of Ni (II) and from 5.6 to 18 µg/L for Cu (II). For VH (Fig 6B), Cu (II) and Ni (II) initial concentrations were higher than HW1, then decreased to increase again and finally decreased. This behavior was more evident for Cu (II) than for Ni (II). The ranges were from 14 to 56 µg/L in the case of Ni (II) and from 15 to 245 µg/L for Cu (II).

Conclusions

- ✓ Cork waste particle size affects the adsorption efficiency of targeted pesticides and heavy metal adsorption. The best tested size was 2 -3 mm.
- ✓ The high efficiency of cork waste as a sorbent of these pollutants was obtained after 40 minutes of contact.
- ✓ The presence of organic matter leads to a decrease in the quality of metal ions adsorbed and did not affect the pesticides removal.
- ✓ Temperature did not affect the removal percentage of pesticides and heavy metal studied.
- ✓ In the case of pesticides, cork waste was more adsorbent for chlorpyrifos and aldrin than for tebuconazole.
- ✓ Cork waste as a substrate of horizontal and vertical wetland allowed the removal of tebuconazole, metalaxyl, chlorpyrifos, Cu (II) and Ni (II) present in polluted winery wastewater.
- ✓ The horizontal wetland seemed to be a bit more efficient than vertical wetland for the removal of selected pollutants.

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