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A new winery wastewater treatment approach during vintage periods integrating ferric coagulation, Fenton reaction and activated sludge

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ABSTRACT

A two stage Coagulation- Fenton's-like process was used for the treatment of winery wastewater. The main objective of this sequence was to enhance biodegradability so that a posterior aerobic biological depuration could be possible. The chemical processes (initial pH of 3, $(Fe_2(SO_4)_3) = 1500$ ppm, $(H_2O_2) = 1.18\ L\ m^{-3}_{effluent} L\ m^{-3}_{effluent}$ and 8 h of oxidation procedure) led to global COD removal of 56.6%. Besides, a biodegradability enhancement of 60% was attained reaching a BOD_5/COD ratio of 0.4. The operation costs were assessed for this stage, showing that the proposed methodology entails a cost of 0.27€ per kg of COD removed. Moreover, the further refining of the effluent using a Sequential Batch Reactor (SBR) had a mild positive effect over COD removal. The final COD abatement was 74% (145 mg $O_2\ L^{-1}$). Moreover, dissolved iron reached a value below 1 mg L^{-1} after the biological treatment. Under these conditions, the final stream was within the legal limits for direct discharge into the hydrological resources. Thus, it was concluded that the proposed methodology is able to satisfactorily treat winery wastewater even during the harvesting peak.

1. Introduction

Nowadays, water scarcity is raising some important questions related with the obligation of minimizing consume and safeguard the natural water courses. Liquid effluents reutilization for land irrigation or even for public water supply will decisively contribute for a better management of water resources minimizing the ecological problems associated with the disposal of wastewater into natural hydrological systems [1].

In wine production, vintage occurs for only 3–4 months. During this stage, wastewaters produced encompass massive organic content and high flow rates when compared with the streams coming from the remaining periods of winemaking.

Winery wastewaters (WinW) are characterized by pH 4–5, high biochemical and chemical oxygen demand [2]. Moreover, the high seasonal features of these streams make them difficult to manage. Over the years different treatment methodologies were proposed. Among them, traditional biological anaerobic and aerobic processes are the most widely studied [3].

Nowadays, the wineries wastewater treatment plants (WWTP's) are normally designed for the vintage period. Thus they are oversized during the rest of the year. This design leads to an increase of the foot implantation and high investment costs. The off season period is characterized by lack of sufficient organic load to maintain an adequate biomass concentration in the biological reactors. Besides, these traditional treatment systems are unable to eliminate recalcitrant or high molecular weight compounds. To solve these issues, the advanced oxidation processes arise as suitable alternatives. It should be referred that usually their efficiency increases when associated with a previous coagulation/floculation stage for solids removal and some COD abatement [4–6]. Among these processes Fenton's oxidation [7–10], ozonation [11], electrochemical oxidation [12], electrochemical coagulation [13] and solar photo-Fenton [14–16] can be referred since they operate at room conditions of pressure and temperature.

Fenton oxidation process (using iron and hydrogen peroxide in an acidic solution) is a technique widely used for the destruction of several organic compounds. It is based on the generation of free

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hydroxyl radicals HO•, which have a high oxidation potential. Moreover, at the end of the process, the ferrous/ferric coagulation promoted under alkaline conditions facilitates the separation of some suspended organic matter [17,18]. Fenton process can be extremely costly when the aim is to promote total mineralization. Thus, usually this technology is designed to promote partial oxidation with a corresponding increase of the wastewater biodegradability favoring a posterior biological treatment [2,19,20].

This work has as main purpose to develop a novel methodology able to minimize the harvest peak seasonal impact over the activated sludge reactors in winery wastewater treatment. This new process can be applied for different wineries, as an integrated and compact technology. This study evaluates the integration of coagulation, chemical oxidation and biological treatment for an application at the real scale. A first stage with iron based coagulation was applied, promoting the solids removal and some COD abatement. A certain amount of this iron will remain dissolved and can be directly used as catalyst in Fenton's reaction. The main goal was to verify the possibility of enhancing biodegradability, thus endorsing a substantial more efficient and quick posterior biological treatment [21–23]. In this context, the novelty of this research relates with the development of a compact treatment system able to be adapted to the flow and composition variations of winery wastewater along the year. Moreover, a coagulation step that will also produce the catalyst for the posterior Fenton's peroxidation constitutes an important step in processes integration. This procedure would allow to design the biological tanks for the off season period and apply the chemical process as a pre-treatment during the harvesting period.

2. Materials and methods

2.1. Winery wastewater characterization

The Winery Wastewater (WinW) was collected in March 2011 from a winery located near Sabrosa, Portugal. Its main characteristics are present in Table 1. Briefly, the chemical and physical properties of the WinW were: pH 4.3; Chemical Oxygen Demand (COD) 5180 $mgO_2\,L^{-1}$; total suspended solids (TSS) 556 $mg\,L^{-1}$; total nitrogen content (TN) 55.8 ($mg\,L^{-1}$) and total phosphorous content (TP) 5.49 $mg\,L^{-1}$.

2.2. Reagents

All reagents were industrial grade and used as received. Hydrogen peroxide (49.5%), ferric sulfate, ferric chloride, sulfuric acid (30%) and sodium hydroxide were acquired from Quimitécnica SA.

2.3. Analytical methods

The liquid samples were analyzed regarding COD, TSS, BOD_5, TN and TP. All the parameters were measured in accordance with Standard Methods [24].

Table 1
WinW characterization.

pH	4.3
COD ($mgO_2\,L^{-1}$)	5180
TN ($mg\,L^{-1}$)	55.8
TP ($mg\,L^{-1}$)	5.49
TSS ($mg\,L^{-1}$)	556
BOD_5 ($mg\,O_2\,L^{-1}$)	1296
BOD_5/COD	0.25

COD determination was performed by the 5220D standard method using a COD thermoreactor (HANNA HI 839800) and a HANNA HI 83224 photometer. The dissolved oxygen for BOD_5 analysis was measured using a HANNA HI 4421 measurer while pH was determined using a HANNA HI 4522 pH meter. Hydrogen peroxide concentration was controlled during and after the treatments using test strips. Along the experiments, total nitrogen analysis was accomplished with HI94767 A ($0–25 \pm 0.5\,mgN\,L^{-1}$) and HI94767 B ($10–150 \pm 3\,mgN\,L^{-1}$) kits while total phosphorous concentration was determinate by the HI 94763B ($0–1.15 \pm 0.02\,mgP\,L^{-1}$) and HI 94763C reactants ($0–32.6 \pm 1\,mgP\,L^{-1}$) kits. All measurements involved a HANNA HI 839800 thermoreactor and a HANNAHI 83224 photometer.

Total Suspended Solids (TSS) were obtained by Standard Methods: "2540 D: Total Suspended Solids Dried at 103–105 °C" [24]. Iron content on the liquid phase was measured by atomic absorption in a PerkinElmer 3300 apparatus. Chloride was obtained by ionic chromatography (Waters).

All the referred measurements were determined in non-filtered samples. To check repeatability, some experiments were randomly run in duplicate and the samples were analyzed in triplicate to minimize the experimental error. The deviations between the performed runs were always lower than 5% and 12% for COD and BOD_5 results, respectively.

2.4. Coagulation experiments

Coagulation experiments were performed at ambient conditions using a jar test. Two iron based coagulants ($Fe_2(SO_4)_3{\cdot}5H_2O$ and $FeCl_3{\cdot}6H_2O$) were tested in doses varying within the range 500 and 2000 ppm. The effect of pH (from 2 to 6) over COD and TSS removal was also evaluated. Each coagulant was added to 250 mL of effluent in the mentioned conditions. The experimental process consisted in three steps: flash mixing for one minute (120 rpm) followed by 30 min stirring (20 rpm) in order to promote coagulation. Afterwards, two samples were taken. The first was used to analyze directly the resulting supernatant (after one hour of sedimentation). In the second one, sodium hydroxide was added until reaching a pH value of 10 so that iron precipitation could be promoted. The supernatant was analyzed after 1 h of sedimentation.

2.5. Fenton oxidation

The iron remaining in solution after the coagulation step was applied as catalyst in Fenton's process. The oxidation was carried out in a jar test system. Briefly, 250 mL of wastewater were introduced in the glass reactor. The initial pH was the one coming from the coagulation stage. This parameter was left run freely during the experiments (between 2.4 and 3.2). The reaction (at room conditions) initiates when a specified amount of H_2O_2 was added in the reactor. Along the treatment, samples were withdrawn for analysis. NaOH was introduced to promote the precipitation of iron hydroxides, removing a fraction of the organic matter [25] and also quenching the remaining H_2O_2 [20].

2.6. Biological treatment

Aerobic biological treatment was performed at laboratory scale in a Sequential Biological Reactor (SBR) with an operating volume of 150 mL. Agitation was magnetically promoted at a speed of 150 rpm. An air diffuser was used to maintain aerobic conditions. Temperature was kept around 22 ± 2 °C while pH was maintained around pH 7.5–8.5 by adding H_2SO_4 30% and NaOH (50%).

The biological process was divided into five distinct phases following a controlled time: filling (5 min), aeration-reaction