



## Effects of ultrasonic and hydrodynamic cavitation on the treatment of cork wastewater by flocculation and Fenton processes



Zhilin Wu<sup>a,b,\*</sup>, Francisco J. Yuste-Córdoba<sup>c</sup>, Pedro Cintas<sup>d</sup>, Zhansheng Wu<sup>a,e</sup>, Luisa Boffa<sup>a</sup>, Stefano Mantegna<sup>a</sup>, Giancarlo Cravotto<sup>a,\*</sup>

<sup>a</sup> Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, Via P. Giuria 9, I-10125 Turin, Italy

<sup>b</sup> Nanjing Institute of Environmental Science of the Ministry of Environmental Protection of China, Jiangwangmiao Str. 8, Nanjing, China

<sup>c</sup> CICYTEX/Instituto del Corcho, la Madera y el Carbón Vegetal, C/Pamplona s/n, 06800 Mérida, Badajoz, Spain

<sup>d</sup> Dpto. Química Orgánica e Inorgánica, Facultad de Ciencias-UEX and IACYS-Unidad de Química Verde y Desarrollo Sostenible, E-06006 Badajoz, Spain

<sup>e</sup> School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China

### ARTICLE INFO

Dedicated to Professor Bernd Ondruschka on the occasion of his 70th birthday

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### ABSTRACT

This paper reports that ultrasonic (US) and hydrodynamic cavitation (HC) are efficient strategies for the environmental remediation of cork wastewater (CW). It is necessary to remove toxic, inhibitory or refractory organic matter from CW using physical and chemical techniques (pre-treatment) prior to performing conventional biological treatment. After this biological treatment, it is also critical to further decontaminate (post-treatment) in order to meet the discharge limitation. The pre-treatment of diluted CW using Fenton oxidation (FE) alone led to COD and polyphenol (PP) removal values of 30% and 61%, respectively, while HC and US resulted in 83–90% increases in COD reduction and 26–33% increases in PP reduction. Whereas 55% and 91% COD and PP removal were achieved using flocculation (Floc) alone, COD elimination was increased by a further 7–18% under HC and US. No noticeable improvement in PP elimination was observed. US did not enhance the Floc decontamination of the original concentrated CW, however, considerable quantities of white biofilm were surprisingly generated on the CW surface after the pre-treatment, thus indicating the improvement of biodegradability of the resulting liquid. In fact, the post-treatment stage, using FE alone after having filtered the biofilms, led to reductions of 53% in COD and 90% in PP. The HC and US protocols resulted in 26–34% increases in COD elimination. HC further enhanced PP elimination caused by FE, while US resulted in lower levels of PP elimination.

### 1. Introduction

Cork is essentially composed of suberin, which is a hydrophobic, waxy substance present in the walls of the cells, making them resistant and impermeable to water. Cork oak (*Quercus suber*) is native to the Mediterranean area, yet is also cultivated in the United States and India with an annual production of around 200,000 tons worldwide with Portugal (ca. 50%) and Spain (ca. 30%) being the major producers of the actual cork stopper [1]. Although cork is indeed a versatile material that has found widespread use from cloth to furniture, the market is dominated by the production of wine stoppers. Cork wastewater (CW) comes from the cooking of large, curved planks which are immersed in boiling water for one hour in order to improve their physico-chemical characteristics. The immersion water can be generally used for repeated boiling cycles (10–30 times). CW is a black liquor containing a complex mixture of organic substances, including both small molecules and

macromolecules, which often show colloidal behavior, making the degradation and separation processes quite difficult. The polluting nature of CW is readily noticeable in view of its high chemical oxygen demand (COD: ~6500 mg L<sup>-1</sup>) and polyphenol content (PP: ~1000 mg L<sup>-1</sup>), which indicate the level at which CW inhibits the activity of microorganisms [1–3].

The toxicological properties of these effluents and the high volumes produced (~1200 L ton<sup>-1</sup> cork) [1], mean that they must be treated by sophisticated and tedious processes prior to their delivery for human consumption [2,4]. While there is no doubt that the high content of organic matter in cork wastewater and in the effluents of numerous other industries, such as food and paper, is a serious environmental issue, there is, however, a clear increase in interest in reusing water pollutants for nutrient recovery and energy savings [5].

The process of flocculation (Floc), or coagulation, using common inorganic salts, such as aluminum and ferric chloride, has been known

\* Corresponding authors at: Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, Via P. Giuria 9, I-10125 Turin, Italy.  
E-mail address: [giancarlo.cravotto@unito.it](mailto:giancarlo.cravotto@unito.it) (G. Cravotto).

as a means for removing total solids (TS) and colloidal matter from CW for some time [6,7]. In this process, COD reduction (30–65%) and PP removal (70–90%) can be achieved using Floc [8], however, the remaining contaminants inhibit biological treatment [2]. Ultrasonic cavitation (US) technology has proven itself to be a suitable tool for combination with traditional suspension separation methods [9]. Likewise, a US-chitosan enhanced Floc process for treating algal-bloom-related turbidity in water has also been developed. Turbidity removal (~99%) for the US/Floc of algae was comparable to those of the conventional rapid mix coagulation process, proving that ultrasonic mixing can be used to improve turbidity removal [10–12]. Power densities in the range of 100–250 W L<sup>-1</sup> are sufficient to provide adequate mixing for chemical distribution and flocs formation.

The US driven particle Floc process is a well-known and useful technique for solid-liquid separation and usually works at MHz frequencies. This separation, however, is generally only applicable to particles with diameters similar to, or smaller than, the ultrasound wavelength, as particles are trapped at the pressure nodes or anti-nodes of the standing wave. The flocculation of larger particles (mm-sized) is therefore difficult to achieve using MHz-range ultrasound and would require lower frequencies, although studies into this are scarce and often lead to contradictory interpretation. A recent study, however, showed that the successful Floc of large particles in water at 20.3 kHz most likely arises from a different mechanism involving the adhesion of oriented bubbles to particles, in the acoustic field, which then move to the anti-nodes of the standing waves [11,13,14].

The enhanced, and sometimes synergistic, effects of sonochemical and sonophotocatalytic methods are much more pronounced when used in tandem with advanced oxidation processes (AOPs), such as Fenton oxidation (FE), O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> [15–18]. Moreover, combined AOPs, such as hybrid FE/Floc and Photo-FE processes, have been successfully tested for the COD reduction of CW and have achieved up to 90% COD reduction [19,20]. The maximum degradation (66.4%) of 0.5% (v/v) *p*-nitrophenol was observed using a combined US/FE process [21].

In principle, AOPs whose effectiveness is based on the transient formation of reactive oxygen species can be boosted under cavitation collapse [18,21]. The extreme, localized conditions that occur under bubble collapse – temperatures as high as 4500–5000 K and pressures higher than 1000 atm – cause mechanical and chemical effects that can induce numerous physico-chemical changes. Mechanical effects arise from the turbulent flow, microjets and shear forces which occur at solid-liquid interfaces. The chemical effects are related to the direct pyrolysis of volatile substrates in the collapse cavities [22] and the highly reactive species [23] such as hydroxy (OH) and hydroperoxy (HO<sub>2</sub>) radicals and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which are formed by sonolytic degradation in liquids containing O<sub>2</sub>, O<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>.

Besides ultrasonic cavitation, hydrodynamic cavitation (HC) has also been widely investigated, since 2000, as a means to treat organic wastewater [24]. HC bubbles are generated at large pressure differentials that are induced by an orifice plate, venturi, impeller or rotor within a moving liquid. The collapse of bubbles generates localized hot spots and is accompanied by a number of physical effects, including emulsion and erosion. HC can also bring about a number of sonochemical effects, such as the formation of active oxidants and the oxidative degradation of organic pollutants [25]. The cavitation intensities generated in HC reactors are lower than in their acoustic counterparts, but cavitation yields are higher than in all sonochemical equipment (ultrasonic horn, ultrasonic bath, dual frequency flow cell) [24,26]. Moreover, the energy efficiency (ratio of the energy transferred into the system in relation to supplied electrical energy) is higher in HC reactors [27]. Several reports have documented the efficiency of HC in the degradation of phenolic effluents in the oxidation, ozonation [23,28,29], and FE processes [30–33].

Scaling effects have also been reported; whereas a pilot-scale operation using HC/FE and an initial *p*-nitrophenol concentration of

5 g L<sup>-1</sup> gave a maximum removal value of 63.2%, the same method only led to 56.2% degradation in solutions containing 10 g L<sup>-1</sup> of *p*-nitrophenol [34]. The effect of HC combined with chemical oxidation processes, such as hydrogen peroxide (HC/H<sub>2</sub>O<sub>2</sub>), ferrous activated persulfate (HC/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/FeSO<sub>4</sub>), HC/FE (HC/FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>), advanced Fenton (HC/Fe/H<sub>2</sub>O<sub>2</sub>), and Fenton-like process (HC/CuO/H<sub>2</sub>O<sub>2</sub>), have all been investigated in the degradation of 2,4-dinitrophenol (DNP) at optimized conditions of pH 4, 35 °C and an inlet pressure of 4 bar. The experimental results showed that the HC/FE process is more feasible and successful than HC combined with other Fenton-like processes and that it furnishes complete degradation [35–37]. Accordingly, it is fair to say that the US/FE and HC/FE processes are efficient and widely-applicable technologies for removing phenol and phenolic compounds from aquatic effluents.

Cork wastewater generally contains high concentrations of organic matter and impurities which are toxic, inhibitory or refractory for subsequent biological systems [3]. Pre-treatment is therefore necessary to remove the majority of harmful components prior to performing biological treatment. The high initial concentration of organic matter means that it is difficult to meet the discharge standard using pre-treatment and biological treatment alone. It is thus critical that post-treatment is carried out after biological treatment. We report herein the preliminary results of the pre- and post-treatment of several CW batches from a large cork industry with Floc, US/Floc, HC/Floc, FE, US/FE and HC/FE. The extent of COD and PP removal has been tested in order to evaluate the effects of US and HC on the Floc and FE processes.

## 2. Materials and methods

### 2.1. Chemicals and materials

Reagent grade FeSO<sub>4</sub>·7H<sub>2</sub>O (Riedel-de-Haën), 35% H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich), 96% H<sub>2</sub>SO<sub>4</sub> (Carlo Erba) and NaOH (98% purity) pellets (Carlo Erba) were obtained from commercial suppliers and used as received.

The original CW, which displayed a high concentration of organic pollutants, was provided by CICYTEX in Mérida (Spain). Samples used throughout this study were diluted in deionized water. The COD, PP, TS and total suspended solids (TSS) content ranges in the original CW were found to be 5.0–6.5 g L<sup>-1</sup>, 943–1088 mg L<sup>-1</sup>, 2.0–2.8 g L<sup>-1</sup> and 1.0–1.4 g L<sup>-1</sup>, respectively, at pH values of 4–6.

### 2.2. Experimental setup

**Stirring:** Stirring was performed at 500–800 rpm, either at room temperature or 30 °C, using an AREX heating magnetic stirrer (VELP Scientifica, Italy).

**US devices:** 400 and 800 mL CW samples were sonicated at 30 °C in a REUS-US (France) cup horn at 25 kHz and total input power of 150 W. A cooling jacket with circulating water allowed for good temperature control, as described elsewhere [38]. An Elma US bath (Transsonic 460, 35 kHz, 85 W, 2 L) was used to prepare the CW samples from the original CW using US/Floc for post-treatment.

Seeing as the HC reactor has a fixed volume of 800 mL, this volume was selected for US treatment. While a 400 mL solution volume (higher power density) was used to optimize the operative parameters for Floc and US/Floc treatments.

**HC device:** The homemade lab-scale loop-system, which consists of a centrifugal pump, manometers, a flow-meter, a water-reservoir and a heat exchanger as well as being equipped with online instrumentation for measuring conductivity and temperature has been reported previously [32,39]. The core component; the centrifugal pump (GY-028-2, 2750 rpm, ~0.7 MPa, ~1700 L h<sup>-1</sup>), was provided by Speck Pumpen, Walter Speck GmbH & Co. KG (Roth, Germany). HC studies were conducted on 800-mL samples in suction mode with 6 mm throat Venturi at 500 W and 30 °C. A schematic of the 6 mm throat Venturi

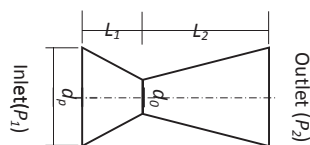


Fig. 1. Schematic diagram of the 6 mm throat Venturi used to create HC.

used for hydrodynamic cavitation is shown in Fig. 1. The dimensions of the convergent-divergent nozzle are  $d_p = 18$  mm;  $d_0 = 6$  mm;  $L_1 = 11$  mm;  $L_2 = 23$  mm. The main operative parameters are highlighted as follows; flow-rate  $990$  L  $h^{-1}$ , liquid velocity at the throat  $8.8$  m  $s^{-1}$ , inlet pressure ( $P_1$ ) 100.

### 2.3. Analysis

**Determination of COD:** A Hanna HI839800 COD Test Tube Heater and a photometer HI 83214 COD were used to perform COD analyses in agreement with EPA 410.4 and ISO 15705:2002 standards. COD reagents and the medium-range EPA dichromate method (25 test vials, HI 93754B-25) were used to measure COD in the 0–1500 mg  $L^{-1}$  range.

**Determination of PP:** PP content was determined using the Folin–Ciocalteu method, as developed by Cicco et al. [40]. Spectrophotometric measurements were recorded at 725 nm in a 1-cm-cuvette with a Cary 60 UV–Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

**Optical microscopy:** Examinations of the biofilms generated in the liquids after pre-treatment were carried out on a DM2500 microscope (Leica, Germany) equipped with a Motic 480 camera.

### 2.4. Experimental protocols

**Flocculation processes:**  $FeSO_4 \cdot 7H_2O$  (3.6 or 7.2 mmol) was added to CW (400 or 800 mL, respectively). Reaction mixtures were mixed using three separate methods; stirring at 500 rpm (Floc), sonication (US/Floc) and hydrodynamic cavitation (HC/Floc) for 30 min at 30 °C. After mixing, the pH values were adjusted to ca. 10 via the addition of a 2 N NaOH solution in order to achieve flocculation.

**Fenton processes:**  $H_2O_2$  (40.7 or 81.4 mmol) was slowly added at pH 3.5 after the addition of the above-mentioned Fe(II)-containing mixtures (3.6 or 7.2 mmol, respectively). FE, US/FE, and HC/FE processes were then separately carried out for 30 min at 30 °C. After oxidation, the pH values were then adjusted to ca. 10 via the addition of a 2 N NaOH solution to achieve flocculation. The relative standard error of the processes was less than 5% for all experiments.

The efficiency of the Fenton oxidation process primarily depends on the  $H_2O_2$ :COD and  $Fe^{2+}$ : $H_2O_2$  ratios. In this study, the  $H_2O_2$ :COD and  $Fe^{2+}$ : $H_2O_2$  ratios were set at 2.18 (by weight) and 0.15 (by weight), respectively. In this respect, Anabela M.F.M. Guedes, et al. reported the effect of  $H_2O_2$  and  $Fe^{2+}$  concentration on the Fenton oxidation of cork cooking wastewater [3]. The  $H_2O_2$ :COD and  $Fe^{2+}$ : $H_2O_2$  ratio ranges were set at 0.78–2.76 (by weight) and 0.11–0.50 (by weight), respectively. The optimal  $H_2O_2$ :COD and  $Fe^{2+}$ : $H_2O_2$  ratios were demonstrated to be 2.12 and 0.20, respectively. Under these optimal conditions, about 66.4% of total organic carbon (TOC), 87.3% of chemical oxygen demand (COD) and 70.2% of biochemicaloxygen demand ( $BOD_5$ ) were removed and an increase in the  $BOD_5$ /COD ratio, from 0.27 to 0.63, was achieved. In addition, E. Chamarro, et al. reported that refractory organics were efficiently removed using Fenton oxidation, at  $Fe^{2+}$ : $H_2O_2$  ratios of 0.001–0.1 (by mol.), i.e., 0.0016–0.16 (by weight), and that the lower  $Fe^{2+}$ : $H_2O_2$  ratio also worked very well [41].

**Preparation of CW samples using US/Floc for post-treatment:** CW (1.0 or 2.0 L) was treated with  $FeSO_4 \cdot 7H_2O$  and then subjected to US/Floc for 15 min at 30 °C in an ultrasonic bath (Elma, Transsonic 460, 35 kHz, 85 W).

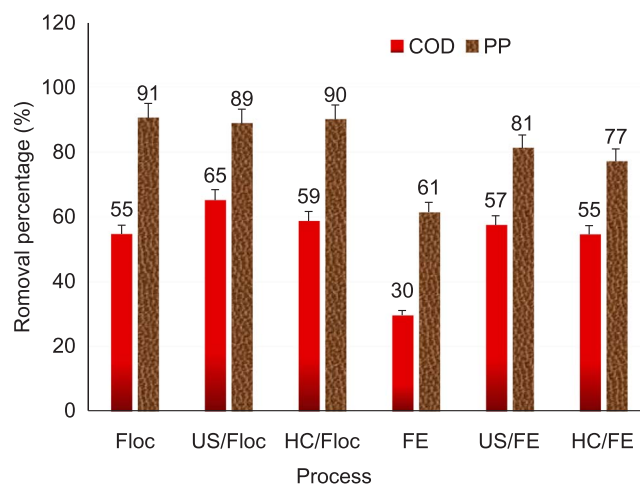


Fig. 2. Comparison of COD and PP removal after the various FE- and Floc-based pre-treatments (Conditions: 800 mL of diluted CW was processed with 7.2 mmol  $FeSO_4 \cdot 7H_2O$  and 81.4 mmol  $H_2O_2$  at pH 3.5 (FE, US/FE, HC/FE) or without  $H_2O_2$  at pH 4.0 (Floc, US/Floc, HC/Floc), at 30 °C for 30 min. The input power density of US was 187.5 W  $L^{-1}$ ; that of HC was 625 W  $L^{-1}$ ).

## 3. Results and discussion

### 3.1. Pre-treatment using US and HC to improve the Floc and FE processes

#### (1) Effects of US and HC on the treatment of diluted CW

Our preliminary screening started with diluted CW samples (800 mL), which showed COD and PP values of 1584 and 236 mg  $L^{-1}$ , respectively. The subsequent addition of Fe(II) (7.2 mmol) was carried out both in the absence and presence of hydrogen peroxide (81.4 mmol) at pH 3.5–4.0, 30 °C for 30 min. NaOH solutions were used to raise the pH of the CW, form colloidal particles and precipitate the hydroxide salts out of solution with added  $FeSO_4$ . The yellow supernatants were filtered and collected for further analysis.

The results of the Floc and FE processes, both with and without US and HC, are shown in Fig. 2. Whereas FE alone gave relatively low COD (30%) and PP (61%) removal, US and HC provided significant increases in COD removal (57% and 55%, respectively), with similar figures being obtained for PP elimination. These improvements can be clearly ascribed to cavitation effects, as noted in the introductory remarks, and most notably the generation of reactive species, such as  $OH^\cdot$  and  $H_2O_2$  [42].

The use of Floc on its own warrants further comment as it led to higher COD and PP removal (55% and 91%, respectively) than the FE processes. Moreover, both US- and HC-assisted Floc substantially increased COD removal, although no PP removal effect was observed. At this stage, the soluble organic matter released from the suspended solids should be further investigated. The highest COD removal was achieved by the US/Floc treatment, which is most likely due to the enhanced mass transfer caused by cavitation agitation. Moreover, oxidation by the generated hydroxyl radicals and the pyrolysis of organics also cause the reduction in COD, to a certain extent. Accordingly, this treatment would appear to be the method of choice for CW pre-treatment from both technical and economical viewpoints.

#### (2) Removal of COD and PP from original CW using US/Floc process

The influence that US/Floc has on COD and PP removal was also investigated on the original CW without further dilution. In a typical run, 1.6 L of original CW, with COD and PP contents of 6336 and 943 mg  $L^{-1}$  respectively, was introduced into an ultrasonic bath (operating at 35 kHz and 85 W). In a separate trial, 72 mmol of  $FeSO_4 \cdot 7H_2O$  was dissolved in 0.4 L of original CW, which was then

**Table 1**

COD and PP removal after the US/Floc treatment of 2.0 L of the original CW sample with 72 mmol of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  at 30 °C for 15 min and the subsequent filtration of the supernatant biofilms (Sonication was conducted in an ultrasonic bath at 35 kHz with an input power density of 34  $\text{W L}^{-1}$ ).

	Concentration (mg L <sup>-1</sup> )		Removal percentage (%)	
	COD	PP	COD	PP
Original CW	6336	943	–	–
After US/Floc	2864	110	55	88
After filtering the biofilms	2085	86	27	22
Accumulated removal	–	–	67	91

placed into the ultrasonic bath and the 2 L of mixture was sonicated at 30 °C for 15 min. As noted above, flocculation was accomplished in a basic medium after the addition of aqueous NaOH solutions (2 N). The US/Floc results are gathered in Table 1.

As shown in Table 1, 55% COD and 88% PP were removed after US/Floc treatment leading to substantial pollutant removal. However, US/Floc on the original CW, which is much more concentrated, gave lower COD and PP removal percentages than those for diluted samples. This difference is probably related to poor ultrasonic performance as power density decreases through the acoustic field causing turbulence and lowered mass transfer. The power density was calculated to be 42.5  $\text{W L}^{-1}$  when 2 L wastewater was processed in the ultrasonic bath at 85 W of total input power, while the power density was 187.5  $\text{W L}^{-1}$  when 800 mL wastewater was processed in the cup horn at 150 W. Moreover, the physical properties of the original CW, such as suspended solid amounts and viscosity, are quite different from those of the diluted samples. Original CW generally contains 1.1 to 1.5  $\text{g L}^{-1}$  of total solids [43], but the high values of TS, TSS, volatile solids and volatile suspended solids can reach 5.13, 4.05, 0.58 and 0.15  $\text{g L}^{-1}$ , respectively [1]. In this study, TS and TSS in samples were measured to be about 2.8 and 1.4  $\text{g L}^{-1}$ , respectively.

### (3) Formation of biofilms after pre-treatment of original CW

It is worth noting that the decontamination of original CW using US/Floc pre-treatment led to the curious formation of white biofilms in the supernatant phase, as long as the reaction vessel was protected from sunlight for ca. 7 days (Fig. 3). This indicates the enhanced biodegradability effect that the process has on CW, as such a phenomenon would not be observed in the original untreated CW. The biofilms were examined by optical microscopy as shown in Fig. 4, although both the identification of the microorganisms and their viability lie beyond the scope of this study and will be reported in future work.

COD and PP further decreased to 2085 and 86  $\text{mg L}^{-1}$ , respectively, after the microorganism films were filtered meaning that the accumulated removal of COD and PP amounted to 67 and 91%, respectively (Table 1). Taken together, these results indicate that US/Floc pre-

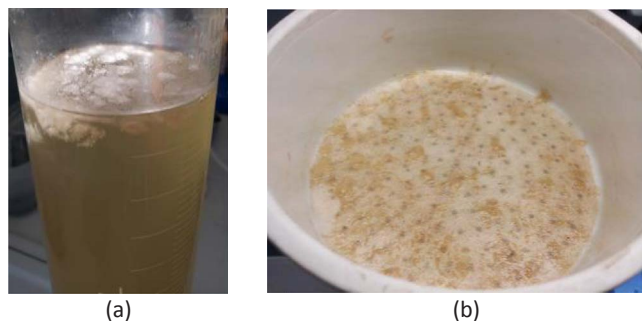


Fig. 3. Biofilms generated in the supernatant phase of CW by the US/Floc pre-treatment after 7 days stored in the dark; (a) before filtering; (b) after filtering.

treatment not only eliminates toxic substances but also contributes to creating more biodegradable wastewater.

### (4) Optimization of US/Floc process for treating original CW

The US/Floc process was examined using an orthogonal array testing technique ( $L_4 2^3$ , 3 factors with 2 levels) on original CW in order to gain further insight into the parameters affecting the removal, such as the treatment mode, reaction time and amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  used.

In a typical run,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (mass specified in Table 2) was dissolved in 80 mL of the original CW (with 4968  $\text{mg L}^{-1}$  COD and 1088  $\text{mg L}^{-1}$  PP) under stirring, which was then combined with an additional volume (320 mL) of the original sample, giving rise to pH values in the 4.4–4.8 range. The resulting mixture was then processed either using mechanical agitation (Floc) or US/Floc at 30 °C. The pH value was adjusted to ca. 10 with an aqueous NaOH solution (2 N) after treatment and the yellow supernatant was filtered and collected for further analysis after solid precipitation. The results of these optimizations are shown in Tables 2 and 3.

As shown in Tables 2 and 3, the amounts of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  used during the protocols, rather than treatment method and reaction time, largely determine the COD and PP removal. US does not enhance the removal percentage in original CW in combination with the Floc method, even when sono-processing is performed at high input power density (375  $\text{W L}^{-1}$ ) for prolonged treatment times. As noted above, one could speculate that the higher viscosity and solid concentrations of the original samples significantly hamper the mechanical effects of cavitation agitation. It has been demonstrated that particle size and viscosity exert very strong influences on the outcomes of ultrasonic irradiation [44]. This positive relationship between pollutant removal and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  amount is further demonstrated in the Floc process and in the salt concentrations that vary from 2.5 to 12.5  $\text{g L}^{-1}$ ; 5.0  $\text{g L}^{-1}$  is the optimal amount for decontaminating the original CW sample. At concentrations below 5  $\text{g L}^{-1}$  of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , the flocculates cannot be separated from the bulk CW by spontaneous precipitation, meaning that 5.0  $\text{g L}^{-1}$  is probably the minimum quantity required to induce flocculation. Conversely, the removal do not significantly increase at salt concentrations above the mentioned threshold. The point was further investigated by adding the optimal amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to 1 L of original CW under stirring at 700 rpm, at room temperature for 15 min, which was followed by Floc with solid NaOH (1.7g). After separation and analysis, COD and PP content levels were 2036 and 58  $\text{mg L}^{-1}$ , which represent removal of 59 and 95%, respectively.

### 3.2. Post-treatment using US and HC to improve Floc and FE processes

Analyses of CW after pre-treatment, primary biodegradation and filtration showed that the COD content is still around 2000  $\text{mg L}^{-1}$ , meaning that difficult and time-consuming elimination protocols would still be required to meet the necessary standards. It would therefore be beneficial to include an additional physico-chemical post-treatment prior to the secondary biodegradation process. Cavitation assisted FE and Floc processes have therefore been investigated to this end.

A diluted CW sample was obtained after pre-treatment and biofilms filtering, and presented COD and PP contents of 834 and 35  $\text{mg L}^{-1}$ , respectively. The Floc and FE processes were investigated on these samples using the stirring, US and HC methods separately. The experimental protocols are as follows; a CW sample (800 mL) was treated with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (3.6 mmol) both in the absence and presence of  $\text{H}_2\text{O}_2$  (40.7 mmol) at pH values of 3.5 and 5.0 at 30 °C for 30 min. Precipitation with a NaOH solution was carried out before the analyses, just as for the pre-treatments. Fig. 5 shows that relatively low COD removal was achieved using the Floc method, regardless of the use of either US or HC, suggesting that most of the suspended solids had been

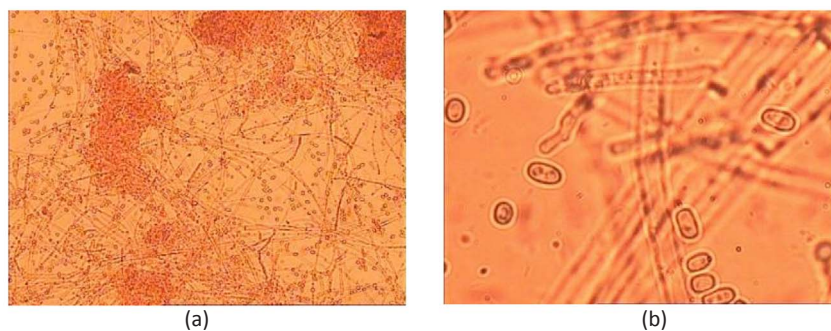


Fig. 4. Biofilms viewed under optical microscopy at different magnification levels; (a) 10 $\times$ , (b) 63 $\times$ .

Table 2

Orthogonal array testing for COD removal using Floc and US/Floc treatment protocols; (400 mL of original CW was processed at pH 4.4–4.8, 30 °C and 375 W L<sup>-1</sup> input US power density).

Test No.	Factor			COD removal (%)
	Treatment mode	Treatment time (min)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)	
1	Floc (Agitation)	15	2.0	60.1
2	Floc (Agitation)	30	4.0	62.3
3	US/Floc	15	4.0	62.9
4	US/Floc	30	2.0	55.5
Average 1		61.5	57.8	–
Average 2		59.2	58.9	–
Difference	2.0	2.6	4.8	–

Table 3

Orthogonal array testing for PP removal for Floc and US/Floc treatment protocols; (400 mL of original CW was processed at pH 4.4–4.8, 30 °C and 375 W L<sup>-1</sup> US input power density).

Test	Factor			PP removal (%)
	Treatment mode	Treatment time (min)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)	
1	Floc (Agitation)	15	2	94.9
2	Floc (Agitation)	30	4	96.4
3	US/Floc	15	4	96.1
4	US/Floc	30	2	94.7
Average 1	95.65	95.50	94.80	
Average 2	95.40	95.55	96.25	
Difference	0.25	0.05	1.45	

eliminated during the pre-treatment step. Obviously, the PP content that remained after the pre-treatment was completely eliminated in this step using US/Floc, which proves the efficiency of sonication in this particular case.

Interestingly, COD and PP removal reached 53% and 90% respectively under post-treatment with FE alone. The combined use of FE with either US or HC yielded higher COD removal, which highlights, once more, the physical and chemical effects that cavitation collapse has on this process. However, sonication rather unexpectedly resulted in considerably lower PP removal. Polyphenols are most likely generated during the oxidation process, at least to a certain extent, as indicated by color changes from pale yellow to dark yellow in CW.

#### 4. Conclusions

We have demonstrated that both US and HC significantly enhance the removal of COD and PP pollutants in diluted CW samples, when FE

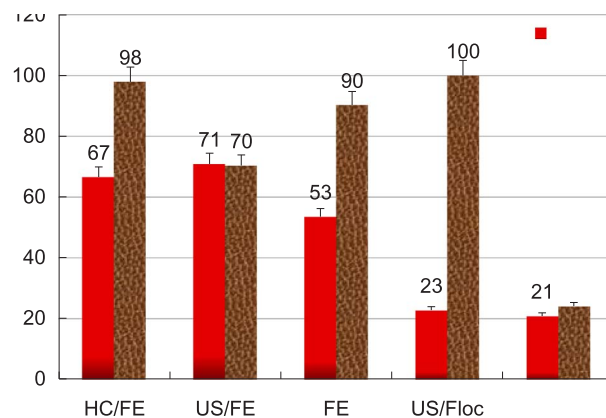


Fig. 5. Comparison of COD and PP removal by the various FE and Floc-based post-treatments. 800 mL of diluted CW was processed with 3.6 mmol FeSO<sub>4</sub>·7H<sub>2</sub>O and 40.7 mmol H<sub>2</sub>O<sub>2</sub> at pH 3.5 (FE, US/FE, HC/FE) or without H<sub>2</sub>O<sub>2</sub> at pH 5.0 (US/Floc, HC/Floc), 30 °C for 30 min. The US input power density was 187.5 W L<sup>-1</sup> and the HC input power density was 625 W L<sup>-1</sup>.

is used as pre-treatment. Cavitation also increases COD removal, although it gave no significant effect on PP removal in combination with the Floc process. Over 55% COD and 90% PP was eliminated from the original CW using US/Floc, although sonication did not appear to play a significant role. CW was particularly prone to biodegradation after pre-treatment with US/Floc. In post-treatment, cavitation no longer has an effect on the COD removal produced by Floc, but can still enhance its elimination by the FE process.

Cavitation chemistry clearly provides unique and salient opportunities for improving the degradation and reuse of highly polluted effluents, such as those from the cork industry for which the strategy is unprecedented. Although conventional pre-treatment by coagulation/flocculation is largely used, furnishes high COD removal and is still very much at the forefront of numerous decontamination processes, they are processes which also produce chemical sludge, extensively use chemical reagents and concomitantly form side products. The present study indicates that optimal CW degradation/purification can be successfully achieved using Floc and US/Floc pre-treatment; precipitation and filtration, primary biodegradation and further filtration, post-treatment, preferably via HC/FE, and finally a secondary biodegradation protocol.

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