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Integrated Physico-Chemical procedures to tackle "Hard COD" pharmaceutical wastewater under Hydrodynamic cavitation and cold plasma

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Abstract

The decontamination of pharmaceutical industry effluents is of paramount importance due to the potential environmental and health risks associated with the presence of active pharmaceutical ingredients (APIs) and other contaminants. In recent years, advanced oxidation processes (AOPs) combined with cavitational treatment (both acoustic and hydrodynamic) have emerged as promising techniques for the effective removal of pollutants from wastewater. Moreover, reactor design for the large-scale operation is another crucial factor monitoring the efficacy and synergistic effects of the hybrid technique and should be aimed at achieving uniform distribution of both cavitation as well as the electrical discharge (ED). The current work investigates the treatment of an "Hard COD" (485 g/L) pharmaceutical industry effluent (PIE) using hydrodynamic cavitation (HC), operated individually or in combination with oxidants and ED cold plasma. An integrated physic-chemical approach has been established to achieve a complete COD and surfactants reduction for the treated PIE by the addition of a final purification step over activated carbon. The research work has clearly established that cavitation in combination with other AOPs can be effectively used for the treatment of PIE with a significant increase in the extent of COD and surfactants reduction for the combined approach.

1. Introduction

Availability of water is becoming an increasing concern in the globalised world, both in developed and in developing countries. A sustainable use of water could result in the search of additional water sources or even in recycling wastewater treatment plant effluents. (United Nations World, 2017) (UN World Water Development Report, 2017; Dagar et al., 2023; Chmielowski et al., 2023). In this context, with the expansion of industrial development and the increasingly serious problems of water pollution and availability, the development of advanced decontamination technologies is strictly required and well documented by the increasing number of articles related to industrial wastewater treatment (from 4000 to 18000 documents by years) reported in literature from 2010 to 2022 (Graphic S1) (Mao et al., 2019; Lofrano et al., 2010). Indeed, every year, many kinds of persistent organic pollutants (POPs) are discharged into water (Richardson et al., 2017) by the major polluting industries, such as pharmaceutical, textile, paper, plastic and dyeing (Choudhary et al., 2020; Bethi et al., 2021). These pollutants are hard to be removed by conventional treatment methods and have caused serious environmental and human health problems and threatened the Target 6.3 in Sustainable Development Goal 6, which have accelerated the establishment of more strict emission and recovery standards in developing countries (Anastopoulos et al., 2015). The requirement to protect the natural environment from POPs has been raising over the past decades leading to the establishment of novel

and effective biological (aerobic oxidation) (Suman Raj et al., 2005) as well as physico-chemical processes for pharmaceutical wastewater treatment (Yu et al., 2019; Bhavya et al., 2021). However, the high chemical oxygen demand (COD) of such wastewaters makes them difficult to completely mineralize by one single approach (oxidation, adsorption, or membrane filtration), and a multi-faceted strategy is often exploited to achieve a certain level of water quality. In this context, advanced oxidation processes (AOPs) have recently proved to be extremely promising in the degradation of different active pharmaceutical ingredients (APIs), including antibiotics, hormones, and analgesics either applying them as single or combined approaches (Taoufik et al., 2021; Smith et al., 2022). The outstanding feature of AOPs is their ability to generate a wide range of reactive hydroxyl radicals (·OH), which can efficiently degrade POPs (Kumar et al., 2022). Although ozone is the chemical commonly used in AOPs, combinations such as O_3/H_2O_2, O_3/UV or O_3/Fe_2O are also used to effectively degrade persistent organic pollutants (POPs) (Bahnmüllera et al., 2015). Beyond ozone, it is important to consider the drawbacks associated with its use at industrial level. These include concerns regarding toxicity, as well as high treatment and maintenance costs, which are considered the major disadvantages of the process. At this regards several other AOPs have been extensively explored, including heterogeneous photocatalysis, electrochemical oxidation, and Fenton processes. Heterogeneous photocatalysis utilizing semiconductor materials, such as titanium dioxide (TiO_2), has shown promising results in the degradation of pharmaceutical compounds (Kanakaraju et al., 2015). Similarly, electrochemical oxidation techniques, such as electro-Fenton and anodic oxidation, have exhibited excellent removal efficiencies for various APIs (Klavarioti et al., 2009). These AOPs offer the advantage of operating under mild conditions, making them energy-efficient and environmentally friendly. In addition, concerning the emerging technologies for the eco-efficient wastewater decontamination, cavitational treatments cannot be overlooked (Ince et al., 2018; Gogate et al., 2004; Calcio Gaudino et al., 2021). In particular, cavitation is defined as the fast generation, growth, and subsequent collapse of microbubbles (or cavities) in a liquid, releasing large energy density in an extremely small interval of time (micro-seconds) and space (Mohod et al., 2023). These localized supercritical conditions generate free radicals, hot spots, and strong turbulence within the liquid. Cavitation-induced phenomena are particularly effective in oxidizing POPs in water through either acoustic (US) or hydrodynamic cavitation (HC) (Movahed et al., 2023; Gogate et al., 2002). However, the exact mechanism responsible for the degradation of organic water pollutants has not been clearly elucidated yet and is typically described through two approaches: (*i*) free-radical attack and (*ii*) pyrolysis. While acoustic cavitation, either alone or in combination with other AOP strategies, has been exploited successfully at laboratory scale to degrade several substances it is currently limited to small-scale operations (Moradi et al., 2020; Wu et al., 2018). Conversely, HC is considered to be more energy efficient (Ranade et al., 2022) and often suitable for the application at industrial scale (Panda et al., 2020; Dixit et al., 2022). In particular, many studies are reported on the removal of single pollutant present in aqueous solution mostly at low concentration ranges (i.e. 10–100 mg/L) using HC (Calcio Gaudino et al., 2021). However, the mineralization degree of complex organic compounds utilizing HC alone is limited and to enhance its efficiency, a combined approach with others advance oxidation strategy has recently been documented (Innocenzi et al., 2019). Among other, Raut-Jadhav et al. (2016) reported the application of HC combined with and H_2O_2 and ozone for the successful treatment of real water effluent containing pesticides with an initial COD of 17000–18000 mg/L. The synergistic HC-AOP approach has the potential to produce an increased amount of oxidizing radicals in water, thereby leading to a heightened rate of degradation for persistent organic pollutants (POPs) (Roy et al., 2019; Gagol et al., 2018; Thanekar et al., 2020).

Recent studies have unveiled the application of HC in conjunction with electrical discharge (ED) cold plasma for flow-mode water treatment (Abramov et al., 2022; Abramov et al., 2021). The combination of cavitation and ED could create a synergistic effect on the degradation of POPs due to the enhancement of highly reactive oxygen species formation in water by means of cavitational effects coupled with UV-light emission (Fang et al., 2019; Verdini et al., 2023; Sarani et al., 2010). However, developing more effective and safer ED cold plasma technologies for use in pollutant-treatment applications is still a challenge, and this is especially

true for the development of efficient application-based instruments. In particular, reactor design for the large-scale operation is a crucial factor for monitoring the efficacy and synergistic effects of the hybrid technique and should be aimed at achieving uniform distribution of both cavitation as well as the ED. In this work, we therefore present an integrated physic-chemical fast approach to treat an "hard COD-PIE" with a combined HC/ED cold plasma. The HC/ED cold plasma degradation efficiency has been monitored in term of PIE-COD reduction. The effects of the HC/ED cold plasma reactor inlet pressure and ED frequency have been evaluated both in absence or in presence of external additives (oxidant agents). Base on the result achieved with the hybrid HC/ED treatment, a complete COD reduction have been investigated combining a subsequent absorption step using different activated carbon. Moreover, the amount of cationic, anionic and non-ionic surfactants present in so treated PIE have been monitored during the hybrid and physic-chemical integrated treatment.

2. Materials and methods

2.1 Materials

The real pharmaceutical industry effluent (PIE) was provided by a local pharmaceutical company. The COD and TOC of the wastewater were 485 g/L and 352 g/L, respectively. The pH of the wastewater was 10.5. The COD kit HI93754B-25 was purchased from Hanna Instruments. Oxone®, Norit® SX ultra, Darco® G-60 were purchased from Sigma-Aldrich.

2.2 Chemical oxygen demand (COD) analysis

The COD was measured following the EPA 410.4 method using the kit COD HI93754B-25 (Hanna Instruments, USA), which allowed the COD determination in a range of 0-1500 mgO_2/L. The accuracy of the measurement was ±4% as declared by the manufacturer. For the COD quantification, both untreated and treated samples of PIE were diluted 1:1000.

2.3 Pilot scale HC/ED treatments

PIE was treated inside a pilot scale reactor which combines HC with ED cold plasma (Verdini et al., 2023). 7 L of diluted PIE samples were treated under HC alone (with inlet pressure of 60 bar), hybrid HC/ED plasma (45, 50 and 60 bar) and HC/ED combined with oxidizing agents (60 bar), with ED amplitude frequencies of 48 kHz or 10 kHz both in flow and loop (30 minutes) configurations. 35 mL of a 1 M solution of H_2O_2, 5 grams of Oxone® and Fenton (Fe^{2+}:H_2O_2 with 1:10 ratio) were used separately as chemical oxidizing agents. Temperature of recirculating effluent was kept constant at 30 °C with fluctuations of ± 2°C using a heat exchanger connected to a chiller unit (H150-1000, LabTech, Italy). The cavitation number (Cv) of the system was calculated in a previous work (Abramov et al., 2021) and it was approximated to 0.0027 for this paper.

2.4 Active carbon treatments

Active carbon treatments were conducted exploiting different activated charcoals (Norit® SX ultra, Darco® G-60 and A.C.E.F EP fine). The wastewater previously treated under HC/ED was moved inside a Falcon tube and then, different AC quantities were added to perform the adsorption step at different AC concentrations: 20, 40 and 60 mg_{AC}/mL_{WASTE}. Subsequently, the samples were placed in a *Synthesis 1* vortex mixer (Heidolf Instruments) and kept under a vibration frequency of 700 rpm for 10 minutes. AC was removed at the end of the treatment using a 0.22 µm PTFE syringe filter.

2.5 Surfactants analysis

2.5.1 Cationic and anionic surfactants

The quantification of anionic and cationic surfactants was performed with MBAS Spectroquant® and CTAB Spectroquant® Merck kit, respectively.

2.5.2 Non-ionic surfactants

Non-ionic surfactants were detected by a volumetric titration. The test samples were titrated with tetrakis-(4-fluorophenyl)borate ($5x10^{-4}$ M) by biphasic titration (Tsubouchi et al., 1985), following the addition of 1,4-diclorobutane (1,4-DCB), potassium hydroxide (KOH) and "Victoria Blue" indicator (44045 Color index, 0.04% solution in ethanol). The titrant solution was previously normalized using a reference surfactant (nonylphenol ethoxylate). 0.5 g of KOH, 4 drops of Victoria blue and 8 mL of 1,4-DCB were sequentially added to 20.0 mL of the reference surfactant solution (100 mg/L). The titration with tetrakis-(4-fluorophenyl)borate of the reference surfactant solution ended at the turning point, which corresponds to the change in color of the organic phase from pink to blue-violet. A blank test on 20 mL of water was also performed. The same procedure was applied for the titration of 20 mL of PIE samples. Nonionic surfactant concentration was expressed as nonylphenol ethoxylate with 10 moles of ethylene oxide (NF/10 EO) (or equivalent). The detection limit is 0.05 mg of nonionic surfactant, present in the volume undergoing titration (corresponding to 2.5 ppm if a volume of 20 mL is used).

3. Results and discussion

3.1 Hard COD pharmaceutical industry effluent decontamination: pilot scale integrated HC/ED treatments

To investigate the effectiveness of the ED cold plasma as a candidate in the replacement of chemical oxidizing agents in the field of AOPs, a hybrid HC/ED pilot scale device was exploited to treat the supplied hard COD PIE.

3.1.1 HC alone compared to hybrid HC/ED cold plasma treatment

Based on preliminary results achieved on laboratory scale treatment performed under HC alone or combined with external oxidant agents (more details are reported in Supplementary Material (Paragraph S2, Figure S1, S2, S3, S4, S5, S6 and Table S1) the first set of degradation experiments was carried out on the diluted PIE (1:100). To demonstrate the effectiveness of the combined approach based on HC and cold plasma, 7 L of PIE were first treated under pilot scale HC alone with an inlet pressure of 60 bar. A maximum COD reduction of 46% was achieved after 30 minutes of treatment. Subsequently, the same volume of fresh PIE was treated with the combined HC/ED technology with the same inlet pressure but simultaneously merging the cold plasma generated with a ED frequency of 48 kHz (default frequency value set). For both HC alone and combined HC/ED the value of the input pressure (60 bar) was chosen because at higher pressures (>60 bar), the formation of foam, which hindered the propagation of the ED plasma, could be clearly observed. The combined HC/ED allowed to reduce the starting COD by a value of 47% in flow configuration, while the highest COD reduction (54%) was observed after only 10 minutes of treatment (Figure 1). Nevertheless, for longer treatment times, the COD reduction decreased probably due to a partial breakdown of organics to simpler molecules that could not be oxidized by dichromate (COD-oxidation resistance). In general, the combination of HC and ED enhanced the degradation observed with the pilot scale HC alone, especially in flow mode and after 10 minutes of treatment, with an increase of COD reduction by a value of 194% and 80%, respectively. Moreover, due to the different design, geometry and configuration of the pilot scale unit compared to the lab scale unit, an abatement of the starting COD value was gained exploiting the pilot scale HC alone.

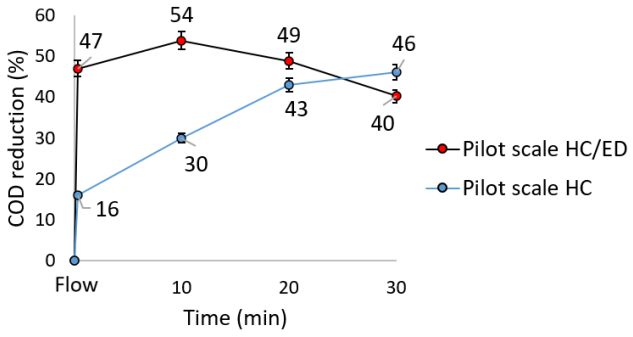

Figure 1. Comparison between HC alone and HC/ED treatments conducted at 60 bar, with an ED frequency of 48 kHz for the HC/ED process.

For sake of comparison, Chakinala et. al. (2008) treated 4 L of two real industrial effluent characterised by a starting COD value of 42 g/L, using HC (liquid whistle reactor) alone or in conjunction with H_2O_2. The authors firstly performed a HC treatment alone on the 10 times diluted wastewater (COD=4.2 g/L) with an inlet pressure of 100 bar for 150 minutes, with a consequent COD reduction by a value of 42%. Subsequently, the effluent was diluted 50 times and treated in presence of H_2O_2 (1.9 g/L solution) periodically added inside the reactor. The further dilution of the sample and the addition of a concentrated H_2O_2 solution allowed to observe a highest COD removal of 85%. A similar oxidation treatment on 4 L of a real industrial wastewater (pH=9.7) was performed by Thanekar et. al. (2019), exploiting an HC unit alone or in combined mode with external oxidation-inducing agents (HC+H_2O_2, HC+O_3, HC+Potassium persulphate and HC+H_2O_2+O_3) with an inlet pressure of 4 bar after acidification of the effluent to pH=4. The author firstly investigated the effluent dilution effect on the HC alone, establishing that the highest COD reduction of 7.9% was achieved after 120 minutes in the treatment of effluent diluted for 10 times, while it was only 4% for undiluted effluent. With a H2O2 loading of 5 g/L (HC+H_2O_2) the maximum COD reduction was 40.30% while the approach of HC+O_3 (3 g/h) enhanced COD reduction by almost 5 times as compared to HC operated individually (~35%). Further combination of HC+H_2O_2 (5 g/L loading)+O_3 (3 g/h) has also been applied for COD reduction and the COD reduction obtained was 60.8%. On the other hand, no synergism between HC and potassium persulphate (2.0 g/L) was observed due to the comparable COD removal rate observed during the HC alone treatment. Effect of H2O2 and Fenton reagent loadings with HC were also investigated by Joshi et. al. (2019) to treat industrial wastewater with initial COD of the sample as around 100 g/L and initial pH of 13.2. The maximum COD reduction of 30% was achieved at 15 g/L loading of H_2O_2. Keeping 15 g/L as the constant loading of H_2O_2, optimization of Fenton based treatment was performed with variation of Fe^{2+}:H_2O_2 molar ratio in the range of 1:10–1:30, obtaining a maximum COD removal of 42% at best molar ratio of 1:20. Despite the ED cold plasma technology is already widely used for the treatment of pharmaceuticals, dyes and pesticides in simulated wastewaters (Aggelopoulos et al., 2022), based on the authors' knowledge of the work presented, there are no studies available where cold plasma technology is applied to real industrial effluents. In consideration of the comparison between literature data and the results obtained from the treatment conducted with the innovative HC/ED technology, it can be affirmed that the innovative technology itself enables the enhancement and intensification of advanced oxidation processes on real industrial wastewaters in shorter times without the need for oxidizing chemical compounds to increase the oxidation level or for effluent pH adjustments prior to treatment.

3.1.2 Influence of HC/ED inlet pressure

Due to the production of a large amount of foam observed during the treatment performed at 60 bar with consequent possible limitation in the ED cod plasma propagation through the cavitation bubbles, a further degradation treatment was conducted on 7 L of 1:100 diluted wastewater with an inlet pressure of 50 bar under combined HC/ED plasma. As summarized in Figure 2a, the lowering of the inlet pressure from 60 to 50 bar did not influence conspicuously the COD reduction during the flow mode treatment. In fact, the lower inlet pressure (50 bar) allowed to slightly increase the COD reduction of 47%, observed at 60 bar, to a value of 49%. However, during the treatment performed in loop configuration, a decrease of the COD reduction from 49%, obtained in flow mode, to constant values of 40% was observed. As already discussed in *section 3.1.1*, the decline in COD reduction observed during the treatment at 50 bar may have been a result of the partial decomposition of contaminants into simpler molecules, which exhibited resistance to oxidation by dichromate. Due to the notable COD reduction achieved after 10 minutes of treatment under a pressure of 60 bar (54%), the inlet pressure of 60 bar was selected as the optimized operational parameter (inlet pressure).

3.1.3 Influence of oxidizing agents combined with the hybrid HC/ED treatment

To improve the degradation observed during the hybrid HC/ED treatments conducted on the PIE at 60 bar and 48 kHz (*section 3.1.1*), H_2O_2, Oxone, and Fe^{2+} were combined separately with HC/ED technology. Considering the capability of the ED plasma in the production of H_2O_2 (Pereira et al., 2023), an attempt of Fenton-like reagent generation was performed adding to the wastewater a solution of Fe^{2+} without H_2O_2. The combination of HC/ED and chemical oxidizing compounds did not allow to observe an intensification of the

oxidation treatment performed with the HC/ED plasma alone. On the contrary, the addition of oxidizing compounds negatively affected the degradation process overall, with a decrease of COD reduction values observed with HC/ED plasma (Figure 2b).

3.1.4 Influence of ED cold plasma amplitude frequency

For sake of comparison, the combined HC/ED treatments described in *section 3.1.1 and 3.1.2* were also performed with an ED amplitude frequency of 10 kHz instead of 48 kHz. As reported in Figure 2c, the lower amplitude frequency negatively affected the process conducted at 60 bar, especially for the flow treatment, with a decrease of the COD reduction from 47% to 33%. In respect to the test conducted at 50 bar, the 10 kHz frequency did not affect the flow treatment but allowed to observe an increase of pollutant degradation after 10, 20 and 30 minutes of treatment, with increments of the COD reduction by values of 10%, 15% and 20%, respectively. The negative influence of the 10 kHz frequency on the degradation process conducted at 60 bar may be attributed to large amount of foam generated inside the reaction chamber during the treatment. Probably, the discharge frequency of 10 kHz, compared to the 48 kHz, is not sufficiently high to ensure the propagation of ED cold plasma through both the cavitation bubbles generated by the HC and the air bubbles of the foam, with a consequent limited generation of oxidant compounds.

In respect to the treatments conducted at 50 bar, the 10 kHz frequency allowed to slightly increase the degradation of organic compounds observed at the same inlet pressure with ED frequency of 48 kHz. Nevertheless, the optimized degradation process consists in the combination of an inlet pressure of 60 bar and an ED amplitude frequency of 48 kHz for 10 minutes of treatment. In conclusion, the effect of frequency variation is more easily observable at high inlet pressure values (60 bar), while it is less intense for lower applied pressure values (50 bar). However, no study has ever provided a thorough explanation of the frequency effect in the field of ED plasma, thus further research is needed for detailed explanations of the phenomenon.

3.1.5 Influence of PIE dilution

In the view of intensification and sustainability of the degradation process, further experiments were performed on 7 L of 1:50 diluted PIE with both 10 and 48 kHz of ED frequencies. To avoid the generation of foam and subsequent inhibition of ED plasma propagation, the experiments were conducted with an inlet pressure of 45 bar. As reported in Figure 2d, both experiments performed at 10 and 48 kHz on the PIE allowed to reach similar COD reduction values observed during the optimized conditions (1:100, 60 bar, 48 kHz). In detail, the flow treatments conducted on the PIE (1:50) samples degraded the same amount of contaminants observed in the flow treatment under the optimized operative conditions (46-47%). In general, the highest COD reduction of 56% was observed after 10 minutes of treatment on the 1:50 PIE with an ED frequency of 10 kHz. For longer treatment times (i.e 20 and 30 minutes) the COD reduction values were similar to the ones observed during the treatment performed at 48 kHz.

However, the increase in COD removal from 54% to 56% (both observed after 10 minutes of treatment) achieved by reducing the frequency from 48 kHz to 10 kHz is not significantly high enough to warrant the need for setting a different frequency than the default one set on the device. Thanks to the treatments just described, it was possible to demonstrate the reactor's efficiency in reducing contaminants even in wastewater with a high COD load (due to lower dilution), especially at lower inlet pressure, with resulting lower mechanical stress on the entire system. Further treatments with lower dilution rates were tried but the amount of foam generated was so high that it prevented the generation of ED plasma inside the reaction chamber, even at lower inlet pressure than 45 bar. To further increase the COD removal, an additional treatment was performed on the PIE 1:50 at 45 bar and 48 kHz in combination with Oxone. As shown in Figure 2e, the combined HC/ED+Oxone treatment did not allow to observe an improvement of the treatment performed without the use of chemical oxidizing agent, confirming what was already discussed in *section 3.1.3*.

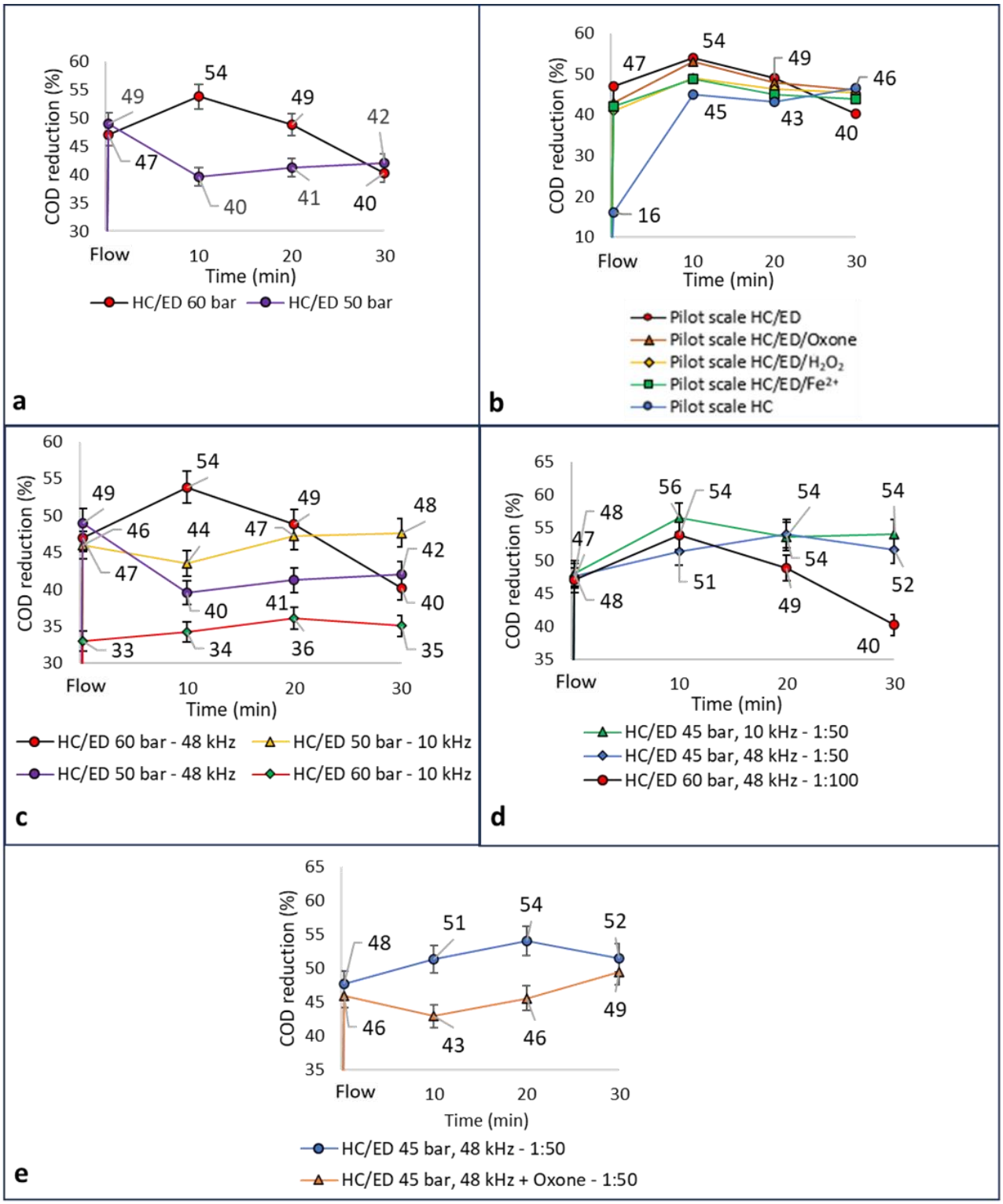

Figure 2. a) Influence of the inlet pressure (50 and 60 bar) during the HC/ED treatments (48 kHz). b) Influence of Oxone, H_2O_2 or Fe^{2+} addition during the HC/ED treatment on PIE (60 bar, 48 kHz). Error bars are not reported for better clarity of the graph. c) Influence of ED frequency (10 or 48 kHz) in the HC/ED treatments performed at 50 and 60 bar. d) Comparison of HC/ED treatments performed on 1:100 diluted PIE at 60 bar (48 kHz) and 1:50 diluted PIE at 45 bar (both 10 and 48 kHz). e) Influence of the Oxone addition to the recirculating PIE during the HC/ED treatment performed on 1:50 diluted PIE.

3.1.6 Integrated physico-chemical PIE treatment: HC-ED treatment coupled with a post active carbon filtration step

Although the treatments performed in the pilot scale reactor in the optimized operative conditions have made it possible to remove about half of the contaminants present in the PIE without the use of chemical oxidizing agents, further treatments with activated carbon were carried out as an attempt for the complete removal of contaminants. In detail, the PIE treated with an ED frequency of 10 kHz (*section 3.1.5*) for 30 minutes (54% of COD reduction) was collected and subsequently subjected to adsorption treatments with different concentrations (20, 40, 60 mg/L) of three activated carbons (Norit® SX ultra, Darco® G-60 and A.C.E.F EP fine) in a vortex mixer under a vibration frequency of 700 rpm for 10 minutes. At the end of the adsorption treatment, the PIEs were filtered with a 0.45 um PTFE filter and subsequently characterized in terms of COD. Among the ACs tested, the A.C.E.F EP fine AC has proven to be the best in the adsorption of organic contaminant residues at the same concentration of Norit® SX ultra and Darco® G-60 ACs. As shown in Figure 3, the A.C.E.F AC allowed to observe a COD reduction increment of 67, 83 and 85% using a concentration of 20, 40 and 60 mg_{AC}/mL_{PIE}, respectively, which were higher to the ones observed with both Norit (37, 63 and 80%) and Darco (37, 61 and 78%) ACs. The proposed wastewater treatment approach demonstrates a pioneering integration of combined HC/ED technology and biomass-derived active carbon, paving the way for a novel purification strategy in treating complex and recalcitrant industrial wastewater effluents. In the context of future biorefinery concepts, it is envisioned that residual lignocellulosic biomasses, after undergoing appropriate pre-treatment processes for the valorisation and extraction of their main components (i.e cellulose (Verdini et al., 2021), monosaccharides, tannins and polyphenols (Aimone et al., 2023), could serve as a valuable source of lignin-rich residues for obtaining active carbon (Gul et al., 2021) for wastewater purification in a sustainable way.

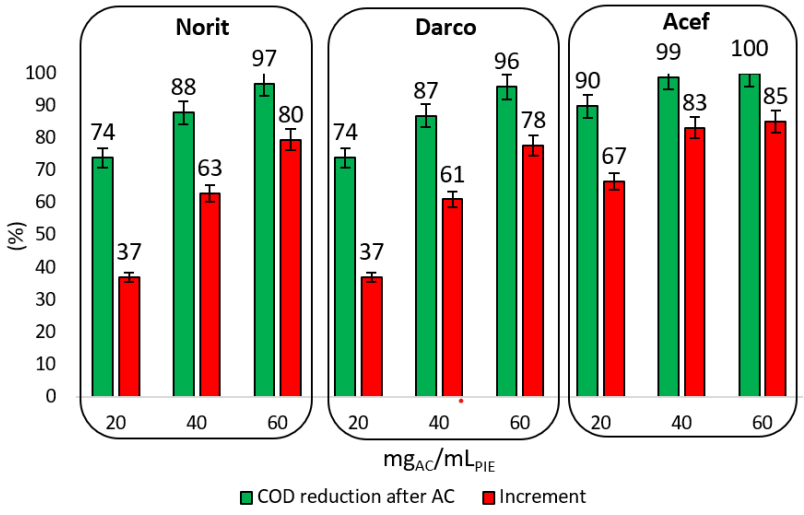

Figure 3. COD reduction and COD reduction increment values of PIE wastewater after AC treatments (Starting COD reduction, reference: 54%)

3.1.7 Surfactants removal

Considering the amount of foam generated inside the pilot scale reactor during the treatment discussed in *section 3.1.5*, a quantitative determination of non-ionic, cationic, and anionic surfactants on both PIE and treated PIE was performed. The concentrations of the anionic, cationic and non-ionic surfactants inside the PIE were 10.50, 4.00 and 15.00 g/L, respectively. The presence of a total concentration of 34.50 g/L of surfactants explained the necessity of performing the HC/ED treatment with a lower inlet pressure (45 bar) for the 1:50 diluted PIE than the treatment conducted at 60 bar for the 1:100 diluted PIE. To demonstrate the capability of the pilot scale reactor in degrading surfactants, the PIEs treated at 45 bar with and ED frequency of 10 kHz for 10 minutes, also in presence of Oxone, H_2O_2 and Fe^{2+}, were characterized in terms of surfactants contents (Table S2). As reported in Figure 4, the HC/ED alone and in presence of oxidizing agents, allowed to observe a quantitative degradation of both anionic and non-ionic surfactants (>98%). Regarding

the cationic surfactant removal, the HC/ED alone treatment allowed to decrease the starting cationic surfactant concentration (4.00 g/L) by a value of 69%. On the contrary of what observed for the anionic and non-ionic surfactants, the presence of chemical oxidizing agents allowed to enhance the degradation of cationic surfactants observed during the HC/ED treatment (69%). In fact, the addition of Oxone, H_2O_2, Fe^{2+} allowed to decrease the starting concentration by values of 81, 80 and 82%, respectively.

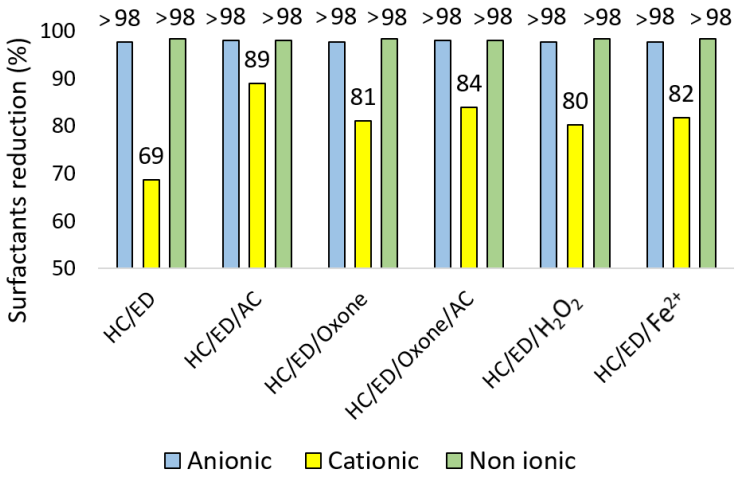

Figure 4. Surfactants reduction of PIEs treated under HC/ED, HC/ED/Oxone, HC/ED/H_2O_2 and HC/ED/Fe^{2+}.

For sake of comparison, the degradation of a typical anionic surfactant, sodium dodecyl sulfate (SDS), was performed by Mondal et. al. (2019) exploiting a UV/H_2O_2 AOP process. The authors observed a complete degradation of the surfactant (100 mL of a 0.1 g/L solution) after 5 minutes of treatment conducted in a UV reactor (450 mJ/cm^2 fluence) with the addition of a 0.1 g/L solution of H_2O_2.
Although a complete conversion was achieved in a short time, when 10 times higher starting SDS concentration (1 g/L) was used, the degradation of the sample after 5 minutes was only about 10%. SDS (1 L of a 2.5 mg/L solution) was also quantitative degraded (>96%) by Arslan et. al. (2018) exploiting the combination of UV, H_2O_2 (0.34 g/L) and O_3 (10 mg/L dosage) for a total treatment time of 55 minutes. The same anionic surfactant (SDS) was treated for the first time by Mukherjee et. al. (2020) exploiting the HC technology coupled to H2O2 and Fenton reagent. The authors firstly optimized the operative conditions for the degradation of a SDS 10 mg/L solution during the HC treatment alone, reaching a maximum SDS degradation of 65% after 120 minutes of treatment using an orifice plate with an orifice opening of 1.6 mm, at pH=2 and an inlet pressure of 5 bar. The combined HC+H_2O_2 treatment was performed using the previously HC optimized parameters with the addition of a H_2O_2 5 g/L solution, which allowed the SDS complete degradation after 60 minutes. HC was also coupled to Fenton reagent ($FeSO_4$:H_2O_2 = 1:3 ratio, $FeSO_4$ concentration: 1 g/L) and the SDS complete degradation was observed after 60 minutes of treatment, which allowed to reduce the quantity of H_2O_2 in respect to the HC+H_2O_2 treatment. Regarding non-ionic surfactants, Pagano et al. (2008) treated separately 10 non-ionic surfactants (C12E23 (Brij 35), C16E10 (Brij 56), C18E10 (Brij 76), C13E18, C8PhE9.5 (Triton X-100), C9PhE9 (Tergitol NP-9), C9PhE5 (Igepal CO-520), C9PhE40 (Igepal CO-890), C12E4, C12E10) with both Fenton and UV/H_2O_2 treatments. The Fenton process, performed on 29 mL of a 14 mg/L of each surfactant allowed to reduce the starting concentration by 96-99% values in presence of H_2O_2 (9 mg/L) and Fe^{2+} (10 mg/L) after 5 minutes of treatment ([Surfactants]/[H2O2]/[Fe^{2+}] equal to 1/0.7/0.7). The UV/H_2O_2 process required 30 minutes to reach the same surfactant removal rate observed at the end of Fenton treatment (96-99%) for the treatment of 100 mL of a surfactant 14 mg/L solution, using a 3.5 g/L H_2O_2 solution. To compare the treatment efficiency on a real wastewater matrix, at the end of the processes conducted on the synthetic matrix, surfactants were subsequently dissolved in an effluent collected from a municipal wastewater treatment plant. The authors observed a decrease in process efficiency and, consequently, they increased the [Surfactant]/[H_2O_2]/[Fe^{2+}] from 1/0.7/0.7 ratio to 1/17/12 to achieve quantitative degradation. A mixture of surfactants (C_0=3.2 mg/L) from a real effluent was successfully treated with HC combined with O_3 by Pereira et. al. (2022). For this purpose, 2.4 L of effluent were firstly recirculated inside an HC reactor equipped with a 1.5 mm diameter holed plate for a total time

of 120 minutes with an inlet pressure of 4.5 bar under acidic conditions (pH=2), reaching a 37% surfactants reduction. Degradation efficiency was increased to 88.6% when O_3 (3.1 g/h flow rate) was associated with HC. In recent years, ED plasma technology is increasingly used for wastewater treatments in the field of AOPs. Brisset et al. (2016) exploited the gliding arc technology to generate a plasma cloud in air for the degradation of SDS. The authors observed an abatement of the SDS concentration by about 90% after 8 hours of treatment inside the circulating reactor. ED plasma was also used by Lee et. al. (2020) to perform a corona discharge plasma-based degradation of simulated residual sodium linear alkylbenzene sulphonate (LAS) and sodium dodecyl benzene sulfonate (DBS) surfactants dissolved in water (3% w/w). In detail, the authors generated plasma in air using a 20 kV DC power supply (with an ED frequency of 58 kHz), with different input currents (1.00, 1.25 and 1.50 A) and at various electrode-to-sample distances (20, 25 and 30 mm). Under optimal treatment conditions (1.5 A current and 20 mm electrode-to-sample distance), the tested DBS and LAS surfactants were maximally degraded to about 57% following the plasma treatment for 120 min. Comparing the existing AOP and ED plasma methods for the surfactants degradation with the pilot scale HC/ED technology, it is possible to admit that the HC/ED innovative technology outperforms current alternatives by facilitating the comprehensive degradation of substantial volumes of surfactants solutions, even at remarkably elevated concentrations inside a complex matrix of a real industrial wastewater without the use of chemical oxidizing compounds in a very short treatment time.

Conclusion

In this work a new advanced and sustainable cavitational process was investigated at pilot-scale for an “Hard COD” pharmaceutical wastewater treatment in absence of any catalyst or oxidating agent exploiting a combined hydrodynamic cavitation and electrical discharge combined process. The tests were conducted with a real pharmaceutical industry wastewater characterized by high COD (485 g/L) value. However, this innovative HC-Plasma combined treatment could guarantee high performances also with low transmittance wastewater. Thus, the integrated HC/ED cold plasma process can be considered as a valuable alternative to conventional oxidation wastewater processes. An integrated physic-chemical approach has been established to achieve a complete COD and surfactants reduction for the treated “hard COD” PIE by the addition of a final purification step over activated carbon. The research work has clearly established that cavitation in combination with other AOPs can be effectively used for the treatment of PIE with a significant increase in the extent of COD and surfactants reduction for the combined approach. Moreover, this work points to the possibility that HC/ED integrated process is suitable for real applications as it is easily scaled, robust, it can operate in continuous mode and has in many cases higher removal efficiency than acoustic cavitation. However, a techno-economic feasibility study on a full-scale reactor is still needed for employment of the technology into water treatment practice.

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