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A critical review of the current technologies in wastewater treatment plants by using hydrodynamic cavitation process: principles and applications

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(Article begins on next page)

- 32 2. Classification of HC mechanisms on degradation of pollutants.
- 33 3. Methods to evaluate HC efficiency for degradation of pollutants.
- 34 4. Mathematical models to simulate fluid dynamics into HC devices.
- 35

36 1. Introduction

37 In the last years, many researchers worldwide published scientific papers on HC process. Initially, the main
38 research topic was the comprehension of HC negative effects on hydraulic machineries, such as turbines,
39 pumps, valves, etc. [1–6]. With this purpose, researchers have dedicated many efforts to establish the basic
40 mechanisms in HC process generation, in order to overcome some very serious problems related to hydraulic
41 machineries, such as vibrations, erosions and noises [1,5]. Therefore, many studies have been carried out in
42 order to identify methodologies and parameters aimed to predict and, then, avoid cavitation inception [7].

43 Recently, some worldwide widespread problems such as water resources availability, population increase in
44 developing countries and the related water consumption, or more strict legislations on water quality, led to
45 the use of HC as an innovative technique in the field of wastewater treatment. Fig. 1 shows the significant
46 increase in the number of peer-reviewed publications indexed by Scopus databases on innovative wastewater
47 treatments and, moreover, on the application of HC as an innovative technique in the field of wastewater
48 treatment.

49 It has been widely proven that HC is characterized by a very high oxidative capacity, which favours the use of
50 HC, used alone or in combination with other techniques, in a large number of applications in the field of
51 wastewater treatment, ranging from biological processes such as cellular disruption to chemical treatments
52 such as the oxidation of organic pollutants in aqueous effluents, including bio-refractory and toxic chemicals
53 [8–10].

54 In the field of wastewater, the inability of the most advanced oxidation processes (AOP) to completely degrade
55 complex compounds has generally led to the application of cavitation to overcome this limit. For this purpose,
56 the effectiveness of the cavitation process in wastewater treatment has been widely demonstrated using
57 acoustic cavitation (AC) [11,12]. However, in the last decade, restrictions due to high costs related to AC
58 applications have been overcome by the development of HC technologies [13]. Moreover, when compared
59 with other conventional treatment techniques, HC has proved to be characterized by greater pollutants
60 removal efficiencies, lower energy requirements [14,15] and fewer secondary contamination problems.

61 AC has been widely applied to treat wastewater. On the contrary, HC has been applied in a lower number of
62 scientific papers, but it showed promising results in various fields in WWTPs, such as biological treatments
63 (activated sludge [16–19], pre-treatment of biomasses before anaerobic digestion [20], denitrification
64 processes [9], reduction of activated sludge [15], enhancement of sludge dewaterability [21]), removal of toxic
65 carcinogens and dyes [8], pharmaceutical products, toxic cyanobacteria, bacteria and viruses [22].

66

67 2. Brief background of cavitation process

68 Cavitation can be defined as the phenomena of generation (inception), growth, coalescence, fission, travelling
69 and implosive collapse of cavitation bubbles or cavities (Fig. 2) within a liquid in less than a few microseconds.
70 The result is a very high local temperature and pressure [23,24], which induce physical and chemical effects,
71 in addition to the mechanical ones.

72 According to its generation pathway, cavitation can be classified into acoustic cavitation (AC), hydrodynamic
73 cavitation (HC), optical cavitation (OC), particle cavitation (PC) and steam bubbles cavitation. OC and PC occur
74 when a liquid is irradiated with high intensity light or by means of a laser. In OC, photons are used to break the
75 liquid, while in PC other types of elementary particles, such as protons and neutrinos, can accomplish a
76 breakdown in the liquid [25]. In AC and HC, cavities are generated as a result of local pressure drops, due to
77 pressure and speed fluctuations, respectively. Steam cavitation occurs when direct injection of steam into sub-
78 cooled water is provided, producing collapse conditions similar to HC and AC [26]. Although all types of
79 cavitation generate cavitation bubbles, it was found that mainly AC and HC are able to bring to the desired
80 chemical changes in the treated matrixes in the environmental [27,28].

81 Afterwards, the well-known thermodynamic concept of vapor pressure will be used to explain the physical
82 meaning of the cavitation process, based on local pressure drops. As shown in Fig. 3, in the water phase
83 diagram the curve from the triple point to the critical point separates the liquid and vapor domains. Crossing
84 that curve is representative of a reversible transformation in static or equilibrium conditions. The phase
85 transformations from the liquid phase to the vapor phase (evaporation) or vice versa from the vapor phase to
86 the liquid phase (condensation) take place at a specific pressure value, known as vapor pressure, p_v , for each
87 temperature value. Cavitation is very similar to boiling, except that the main driving mechanism is not a change
88 in temperature, but a change in pressure. After cavitation, bubbles grow into the liquid in low-pressure regions
89 and can be transported by convection to higher-pressure regions, where they can collapse [29].

90 When cavitation occurs, it is possible to observe a multi-phase condition into the fluid with gas (vapor and air)
91 and liquid. If the pressure of the mixture is equal to saturation pressure, vapour cavitation occurs. On the
92 contrary, for pressures lower than atmospheric one, a release of air from the liquid can be observed. Since
93 vacuum creation and vacuum filling with vapour and/or air take place simultaneously, the instantaneous
94 saturation of the vacuum can presumably be justified [29].

95 It is widely accepted that cavitation inception is strongly influenced by water quality, especially in relation to
96 the concentration of nuclei into water. Occurrence of cavitation bubbles starts from weak points into the
97 water, namely bubbles nuclei, which break the bond between the water molecules. These nuclei are generally
98 small gas bubbles or solid nuclei.

99 Despite some differences in the generation of cavitation bubbles using AC and HC, the principles governing
100 the hydrodynamic and acoustic growth of bubbles are the same. In AC, when the ultrasonic wave propagates
101 in the fluid, it generates compressions and rarefactions. The compression cycles exert a positive pressure on

102 the liquid, pushing the molecules together, while the rarefaction cycle exerts a negative pressure by pulling
103 the molecules from one another. Due to low pressure, cavitation bubbles are generated in the rarefaction
104 regions. These bubbles grow in successive cycles, reaching an unstable diameter and collapsing violently [30].
105 In HC, due to the presence of a restriction into the fluid, that usually involves a reduction in the cross-section
106 of the flow, low pressures are reached, with consequent generation of cavitation bubbles. Downstream of the
107 constriction, as the cross section expands, the pressure of the flow is restored and this leads to the growth of
108 the bubbles, reaching an unstable diameter, whereby the cavities collapse violently [31]. The bubbles that
109 occur in a cavitating flow are not perfectly spherical. However, it is often said that spherical analysis shows a
110 satisfactory dynamic modeling of higher level bubbles. Furthermore, it is often assumed that there is a growth
111 of isothermal bubbles up to their maximum radius, in which the bubbles are mainly filled with vapor and/or
112 air at equilibrium at room temperature [32].

113 Many studies have been conducted to investigate the dynamics of bubble collapse [33], showing the presence
114 of numerous peculiar phenomena that can occur in a very short period, while the overall environment remains
115 at the ambient atmospheric conditions. After the growth phase, bubbles can collapse, generating new smaller
116 rebound bubbles that can grow and collapse several times. This phenomenon, known as *rebound*, is due to
117 the presence of gas trapped into the bubbles during collapse [34,35]. Rebound bubbles sometimes can also
118 break into different bubbles (*fission* of bubbles). The shape of rebound bubbles depends on the symmetry or
119 asymmetry of the collapse dynamics. A perfectly spherical collapse produces a spherical rebound bubble, while
120 an asymmetry leads to the deformation of the bubble and the generation of a micro-jet emerging from the
121 rebound bubble [35]. A micro-jet can reach velocities in the order of 100 m/s [36], increasing the turbulence
122 and the mass transport coefficient. Because of their high velocity, micro-jets can contribute to changes in
123 water clusters, in the agglomeration of fibers and molecules. During the collapse phase, it is possible to reach
124 very high temperatures, in the order of thousands of K [23], but for a very short period (in the order of micro
125 seconds). Under these conditions, the vapours trapped in the cavitation bubbles can be dissociated, with the
126 consequent generation of free radicals, such as $\bullet\text{H}$ and $\bullet\text{OH}$, which are very strong and non-specific oxidizing
127 species [37,38]. Sometimes both the temperature and the pressure into the liquid are so high that light can be
128 emitted during the collapse phase (*luminescence* [39]).

129 Cavitation can be further classified, according to the degree of its intensity, which depends on the magnitude
130 of the pressure or temperature, in *transient cavitation* or *stable cavitation* [30]. In transient cavitation, the
131 radius of cavitation bubbles expands at least twice its initial size. Thus, cavitation bubbles can collapse to a
132 minute size of its original in a limited period of time, resulting in the absence of mass flow of permanent gas
133 through the liquid-bubble interface [28] and causing a very violent implosion. This gives rise to the release of
134 a significant amount of acoustic energy and the emission of light. In this phase, vapour temperature inside the
135 bubbles can reach several thousand K and the cavitation pressure several hundred atm. In stable cavitation,
136 on the other hand, cavitation bubbles contain more gas and therefore have a less violent collapse than

137 transitory cavitation bubbles. Shock waves and micro-jets caused by implosion of stable cavitation bubbles
138 usually generate lower pressure than transient ones [40–42].

139 It has been experimentally proven that in HC, if the intensity of the turbulence is rather low, the recovery
140 pressure downstream of the constriction can be approximated by a linear expression with respect to the
141 distance downstream of the constriction, where the stable cavitation takes place. When the turbulence
142 intensity increases and the recovery pressure is no longer linear, the behaviour of cavitation bubbles can be
143 defined as transient [43].

144

145 3. HC generation and mechanisms

146 Due to the introduction into the flow of some constrictions, such as orifice plates, Venturi systems or throttling
147 valves, flow velocities and, consequently, flow pressure can be modified, resulting in HC generation. According
148 to the Bernoulli principle (Eq. 1), when the liquid flows through a constriction, the flow velocity (Fig. 4 a) and,
149 therefore, the flow kinetic energy increases at the expense of the flow pressure (Fig. 4 b):

$$150 \frac{V^2}{2g} + \frac{p}{\rho g} + z = \text{constant} \quad \text{Eq. 1}$$

151 where V is the velocity of the flow at a point on a streamline, g is the acceleration due to gravity, z is the
152 elevation of the point above a reference plane, p is the pressure at the chosen point, and ρ is the density of
153 the fluid at all points in the fluid.

154 When the flow accelerates due to the presence of a constriction, the total energy remains constant, but part
155 of this energy is converted into turbulence and heat during the process; therefore, the downstream flow
156 pressure will always be lower than the upstream one. If the restriction throttling is sufficient, the flow pressure
157 at the constriction throat can equal or fall below the vapor pressure of the fluid at the given temperature and
158 vapor cavities can be generated.

159 This condition can be formulated as follows, Eq. 2:

$$160 p_{min} = p_v \quad \text{Eq. 2}$$

161 where p_{min} is the minimum static flow pressure and p_v is the vapor pressure at a given fluid temperature.
162 According to the geometry of the constriction, with further lowering of the pressure, the cavities can continue
163 to grow. They reach their maximum size at the lowest flow pressure and subsequently when the cross section
164 expands, with a consequent decrease in the flow velocity, the pressure flow recovers and this can cause the
165 implosion and the collapse of these previously formed cavities [31,44], (Fig. 4 c).

166 3.1. HC flow regimes

167 In the characterization of cavitating flows, the most used parameter is cavitation number C_v . It is a
168 dimensionless number, that can be expressed as reported in the following equation, Eq. 3:

$$169 C_v = \left(\frac{p_r - p_v(T)}{\Delta p} \right) = \left(\frac{p_r - p_v(T)}{\frac{1}{2} \rho \cdot V^2} \right) \quad \text{Eq. 3}$$

170 where p_r is the recovery pressure [Pa] measured downstream of the restriction, in which the flow becomes
171 again undisturbed (a conventional reference point can be considered where cavitation inception is expected
172 and the flow pressure is easily measurable), p_v the liquid vapour pressure of at the operating temperature T
173 (i.e. 2.35 kPa at 25°C) [Pa], Δp the pressure difference that characterizes the system, and ρ , V are the liquid
174 density [kg m^{-3}] and the flow velocity [m s^{-1}] at the cavitating constriction, respectively.

175 The cavitation number indicates the probability that cavitation takes place in a flow regime. As shown in Eq.
176 3, C_v is can be defined as the ratio between the forces exerted by collapsing cavities with respect to those
177 initiating their formation. Therefore, high C_v values involve more collapsing forces and lower initiating forces,

178 indicating lower cavitation activity. Cavitation may appear, due to a decrease in flow pressure at the
179 reference point or an increase in the Δp -value.

180 Cavitation begins to occur for C_v values below the threshold value, C_v^* . In most of studies it was observed that
181 the cavities formation started at C_v equal to 1 [31]. However, cavitation can also start at C_v greater than 1,
182 because of the presence of dissolved gases into the fluid and other solid particles which can act as pre-nuclei
183 and therefore they can accelerate the phenomena of cavities generation. For example, typical C_v^* values are
184 ranged from 1.0 to 2.5 - 2.79, [18,45].

185 Many reports indicate that when a decrease in C_v below 1 occurs, more cavities are formed, with consequent
186 increase in cavitation effects. It has also been observed that a further decrease in C_v implies the achievement
187 of a condition where the cavities can coalescing with each other, because of the high number and volume
188 concentration of the cavities, forming a vapour cloud (choked cavitation/supercavitation), resulting in a
189 decrease in cavitation intensity [46].

190 The threshold C_v^* depends on all the usual factors considered in fluid mechanics, such as flow geometry,
191 viscosity, gravity, surface tension, turbulence levels, thermal parameters, wall roughness and gas content of
192 fluid, in terms of dissolved and free gases [36].

193 In HC, the comparison between the measured cavitation number and the threshold C_v^* can lead to the
194 identification of five different flow regimes [36]:

- 195 – *Non-cavitating flow*: when the liquid pressure is higher than the saturated vapour pressure, cavitation
196 does not occur ($C_v > C_v^*$). In this flow regime, known as non-cavitating flow phase, there is no evidence
197 of cavitation bubbles into the fluid.
- 198 – *Cavitation inception or limited cavitation*: in this flow regime, the liquid pressure is equal to or lower
199 than the liquid vapor pressure. The cavitation number is equal to or slightly lower than the threshold
200 value ($C_v \leq C_v^*$). Cavitation is barely detectable, with the consequent appearance of scattered
201 cavitation bubbles into the fluid. This phase is always characterized by a loud noise of cavitation
202 bubbles that collapse, due to the instability of the generated cavities.
- 203 – *Developed cavitation*: even lower values of the cavitation number ($C_v \ll C_v^*$) allow the complete
204 development of the cavitation bubbles.
- 205 – *Supercavitation*: this flow regime represents the final state of cavitation ($C_v \lll C_v^*$). In this regime,
206 the pressure in the cavitation area is low and a large fixed cavity is formed. Compared to other types
207 of cavitation, the interface of a supercavitation cavity is stable. The cavity remains attached to the
208 constriction and the cavity closure is downstream.
- 209 – *Desinent cavitation*: ending in this flow regime, cavitation bubbles disappear completely, as the
210 pressure of the downstream flow increases. The desinent cavitation is often considered as a threshold
211 between cavitating and non-cavitating flows.

212 Recently, it has been shown that C_v cannot be used as a single parameter in providing cavitation conditions
213 and there are broad inconsistencies regarding its determination in previous reports [47]. Furthermore, C_v is
214 not always detectable in HC devices, because it is too difficult to measure the flow velocity or the pressure
215 where cavitation occurs (turbulent flow), especially when the complexity of the cavitating device geometry
216 increases [8].

217 3.2. HC types

218 Furthermore, HC can be differently defined, according to different flow configurations. There are two main
219 classification categories: *attached cavitation* and *vortex cavitation* [35].

220 3.2.1. Attached cavitation

221 The attached cavitation is easily identifiable due to the beginning of a region characterized by of a separate
222 flow filled by steam, which partly remains attached to the solid surface. When the cavity becomes so high that
223 it completely envelops the solid body, supercavitation can occur. If this type of cavitation occurs in the
224 propeller blades or hydrofoils (Fig. 5 a), it is known as “sheet cavitation”, while the name of “blade cavitation”
225 can be associated with the attached cavitation occurring in pumps. The attached cavitation can also be
226 detected in bluff bodies (Fig. 5 b).

227 In case the generated transient cavities are of the same order as the main attached cavity, the attached
228 cavitation is also called “cloud cavitation”. Fig. 6 shows the formation (Fig. 6 a), the separation (Fig. 6 b) and
229 the collapse (Fig. 6 c) of a cavitation cloud on a hydrofoil oscillating in pitch. A very common example of
230 imposed fluctuations is the interaction between rotor and stator blades in pumps or turbines. Recently, the
231 developed cavitation has been studied by Petkovšek et al. [48] in a shear-induced HC reactor, in which two
232 facing rotors were spinning in opposite directions: attached cavitation and bubbles shed from the attached
233 cavitation have been observed on the solid surface of the teeth rotors and in the difference between the rotor
234 and the housing. A cavitation cloud was also detected between the aligned grooves.

235 In order to effectively exploit the positive effect of HC, the developed cavitation must be studied and controlled
236 in HC reactors. For example, Dular et al. [22], studying a Venturi device, in which attached cavitation occurred
237 [49], showed the progress of the developed cavitation (Fig. 7).

238 Elements with different shapes and sizes can differently influence the attached cavitation, mainly due to the
239 onset of a pressure difference between the external flow and the inner part of the attached cavitation. As a
240 result, the formation of a stagnation point and different forms of the attached cavitation, due to the different
241 tested cavitation conditions, were observed. All the phases involved in the generation of the attached
242 cavitation, in terms of cavitation inception, cavities reshape and rupture, were repeated periodically (Fig. 7 a).
243 Supercavitation (Fig. 7 b) was also observed in the experiment, because of a decrease in flow pressure and,
244 therefore, to an increase in flow velocity.

245 3.2.2. Vortex cavitation

246 When a linear vortex is generated into the liquid, the static pressure in the core is depressed if compared with
247 the pressure far from the axis of the vortex. When the pressure in the vortex core falls below the liquid vapour
248 pressure, the vortex cavitation can occur. In such situation, the entire vortex core may become filled with
249 vapour. Fig. 8 shows some examples of vortex cavitation in a hydrofoil (Fig. 8 a), in a propeller (Fig. 8 b) and in
250 a turbine (Fig. 8 c), respectively. It may happen that vortex cavitation bubbles remain smaller compared to the
251 vortex core radius, with nearly spherical rapidly growing and collapsing bubbles entirely within the confines of
252 the vortex core. However, at lower flow pressures the initially near-spherical bubble can expand and elongate
253 to fill the core of the vortex and continue to grow along the vortex axis, becoming highly elongated [50].

254

255

256 4. Modeling

257 In the last decade, HC has been deeply studied by many researchers worldwide. As reported in the following
258 sections, it was observed that essential parameters and operating conditions can deeply influence HC intensity
259 and the way in which it can be generated. The definition and the characterization of these parameters (i.e.
260 flow velocity, flow pressure, etc.) present some difficulties basically due to the presence of turbulent flows in
261 cavitation conditions in addition to the complexity of the geometry of most of the HC devices. Moreover, as
262 highlighted by Šarc et al. [47], these parameters were measured using different procedures by researchers,
263 resulting in large inconsistencies reported in the scientific reports. For this reason, experiments and observed
264 results are often not repeatable. To confirm this, it was observed that flow velocity and flow pressure
265 measurements can be easier made in simpler geometries such as hole orifice plates, nozzles or Venturi
266 systems. On the contrary, in cavitating devices with a more complex geometry, it is rather difficult to perform
267 measurements on these variables, resulting in an incomplete or incorrect characterization of the HC process.
268 To overcome these limitations, in the last years there is an increasingly interest in developing mathematical
269 models with the main goal to define a powerful tool able to provide information on hydraulic parameters and
270 on the fluid dynamics into HC devices. Indeed, many researchers are focusing their attention on mathematical
271 modelling and many attempts have been made in order to build models in which HC is taken into account.
272 Again, the complexity of the geometry of some HC reactors and the presence of turbulent conditions in the
273 fluid can increase the difficulty in defining the mathematical model.

274 Simple geometries (i.e. orifice plates, nozzles and Venturi systems) were modelled by Palau-Salvador et al. [51]
275 by performing a computational fluid dynamic (CFD) analysis with FLUENT 6.1 in order to prevent the cavitation
276 inception in the studied cavitation systems. The influence of different geometric parameters such as orifice
277 thickness, hole inlet sharpness and wall angle on the cavitation behaviour was investigated by Simpson and
278 Renade [52] in an orifice device.

279 Pawar et al. [53] compared four different HC devices characterized by different geometries, observing
280 different behaviours of flow into the devices. In order to calibrate and validate the mathematical model
281 (FLUENT 6.3), their methodology involved also the use of high-speed photographs observations. Navickas and
282 Chen [54] studied the internal flow characteristics of a Venturi system by means of a three-dimensional fluid
283 flow program (FLOW-3D). According to their results, numerical methods were effective in figure out how
284 different parameters may affect the performance of the cavitating device. In order to optimize a multi-hole
285 injector nozzle, He et al. [55] modelled the three-dimensional nature of the flow in the nozzle investigating the
286 effect of the geometry and dynamics factors on the spray characteristics in cavitating conditions. A numerical
287 model was develop by Müller et Kleiser [56] for a vortex breakdown in a non-cavitating flow. Ashrafizadeh and
288 Ghassemi [57] performed an experimental and numerical investigation on the performance of small-sized
289 cavitating Venturi. Badve et al. [58] made a mathematical model investigating on the variation of pressure in

290 HC rotor-stator reactor. Mancuso [59] implemented a three-dimensional CFD analysis of a swirling jet reactor
291 in order to analyse the fluid dynamics into the reactor.

292 Thanks to the quick development of computational resources, there have been attempts to model the flow
293 unsteadiness during cavitation using the Large Eddy Simulation (LES), which present an alternative way of
294 improving qualitative and quantitative aspects of complex turbulent flow predictions for both research and
295 engineering purposes. LES can explicitly simulate the large scale of a turbulent multiphase flow while modelling
296 the small scales. Despite some yet unresolved issues, LES is currently considered the most promising method
297 for studying complex multiphase flows. Moreover, numerical results of studies on HC by using LES have
298 showed a very good agreement between mathematical models and the experimental data [56,57].

299 Therefore, an accurate mathematical model could be used as a useful tool in order to optimize parameters,
300 operating conditions and geometry of the cavitating device with the main aim of improving performances of
301 HC devices in terms of generated cavitation intensities.

302

303 5. Methods to evaluate the efficiency of cavitation

304 In the last years, in order to investigate the efficiency of different HC systems in WWTPs in terms of both
305 pollutants removal efficiency and total energy supplied to the system, many methods have been proposed,
306 depending mainly upon the treated matter characteristics.

307 5.1. Pollutants degradation in wastewaters

308 HC technique has recently been used alone or in presence of additives to degrade toxic and carcinogenic
309 compounds in polluted water bodies. In different studies, the degree of the degradation of pollutants, such as
310 for Rhodamine B (RhB) and Rhodamine 6G (Rh6G) [8,14,60–62], orange 4 dye, orange acid II [63], brilliant
311 green [63], reactive brilliant red K-2BP [64], methylene blue (MB) dye [65], pharmaceuticals [66] and
312 pharmaceutical micro-pollutants [66,67] has been evaluated by considering the extent of degradation (ED), as
313 a percentage of removal. ED can be calculated as reported in Eq. 4:

$$314 \quad ED(\%) = \frac{(c_0 - c)}{c_0} \cdot 100 \quad \text{Eq. 4}$$

315 where c_0 [mg L^{-1}] is the initial pollutant concentration and c [mg L^{-1}] is the residual pollutant concentration at
316 the generic instant. All studies reported that for higher ED, higher HC efficiencies, in terms of extent of
317 pollutant degradation, have been observed.

318 Another parameter that has been taken into account is the cavitation yield, $C.Y.$ [8,14,60,63,68,69],
319 calculated as reported in Eq. 5, and defined as the ratio of the observed cavitation effect, in terms of amount
320 of degraded pollutant (usually expressed in mg L^{-1}) by using HC, to the total energy supplied to the system:

$$321 \quad C.Y. = \left(\frac{\text{Degraded matter}}{\text{Power density}} \right) \quad \text{Eq. 5}$$

322 where the degraded matter is the amount of pollutant [mg L^{-1}] removed during the HC treatment, while the
323 power density, [J L^{-1}], is represented by the following equation Eq. 6:

$$324 \quad \text{Power density} = \frac{P_{abs} \cdot t}{V} \quad \text{Eq. 6}$$

325 where V is the volume of the treated matter [L], P_{abs} is the pump absorbed power by the HC system [W] and t
326 is the treatment time [sec]. Higher $C.Y.$ values imply higher HC efficiencies, in terms of both degradation and
327 total energy supplied to the HC system. Nevertheless, $C.Y.$ can be used to compare two or more different HC
328 systems with each other only if the treated pollutant is the same. On the contrary, treating different
329 contaminants with different HC systems, it is not possible to make a comparison between their treatment
330 efficiencies because of the different properties and molecular structures of pollutants, which can provide a
331 different resistance to the HC treatment.

332 5.2. Biological wastewater treatments

333 In the field of biological treatments, HC efficiency can be evaluated by measuring (i) the improvement of
334 solubilisation of the activated sludge in terms of soluble chemical oxygen demand (SCOD) increase, Eq. 7, (ii)

335 the ratio of change in soluble chemical oxygen demand (*SCOD*) after cavitation to particulate chemical oxygen
 336 demand ($PCOD_0 = TCOD - SCOD_0$), Eq. 8, and (iii) the ratio of change in ammonia after cavitation to initial
 337 organic nitrogen content ($Norg_0 = TKN_0 - NH_4^+ - N_0$), Eq. 9:

$$338 \quad \Delta SCOD(\%) = SCOD_{cav} - SCOD_0 \quad \text{Eq. 7}$$

$$339 \quad DD_{PCOD}(\%) = \frac{SCOD_{cav} - SCOD_0}{PCOD_0} \times 100 = \frac{SCOD_{cav} - SCOD_0}{TCOD - SCOD_0} \times 100 \quad \text{Eq. 8}$$

$$340 \quad DD_N(\%) = \frac{NH_4^+ - N_{cav} - NH_4^+ - N_0}{Norg_0} \times 100 = \frac{NH_4^+ - N_{cav} - NH_4^+ - N_0}{TKN_0 - NH_4^+ - N_0} \times 100 \quad \text{Eq. 9}$$

341 where $SCOD_{cav}$ is the soluble COD of the treated sludge by using HC [$mg L^{-1}$] at the time t , $SCOD_0$ is the soluble
 342 COD of the untreated sludge [$mg L^{-1}$], $TCOD$ is the total COD of the untreated sludge [$mg L^{-1}$], $NH_4^+ - N_{cav}$ is the
 343 ammonia content of the treated sludge by using HC [$mg L^{-1}$] at the time t , $NH_4^+ - N_0$ and TKN are the ammonia
 344 and total Kjeldahl nitrogen content of the untreated sludge [$mg L^{-1}$].

345 Another important index reported in different studies on sludge disintegration is the sludge disintegration
 346 degree calculated as the ratio of SCOD-increase by cavitation to the SCOD-increase over the chemical
 347 disintegration, Eq. 10:

$$348 \quad DD_{COD NaOH}(\%) = \frac{SCOD_{cav} - SCOD_0}{SCOD_{NaOH} - SCOD_0} \times 100 \quad \text{Eq. 10}$$

349 where $SCOD_{NaOH}$ [$mg L^{-1}$] is the soluble COD of the reference sample obtained with a strong alkaline
 350 disintegration (NaOH digestion).

351 Furthermore, HC efficiency can be evaluated, according to Eq. 11, as percentage of biogas yield increase by
 352 HC pre-treatment [70] [ref]:

$$353 \quad \eta_{CH_4}(\%) = \frac{Y_{biogas\ with\ HC} - Y_{biogas\ without\ HC}}{Y_{biogas\ without\ HC}} \quad \text{Eq. 11}$$

354 where $Y_{biogas\ without\ HC}$ is the biogas yield from activated sludge without HC treatment [$ml\ gVS^{-1}$],
 355 $Y_{biogas\ with\ HC}$ is the biogas yield from activated sludge with HC treatment [$ml\ gVS^{-1}$].

356 However, HC efficiencies should be always referred to other indexes that consider the energy consumption in
 357 each HC system. Many studies report the specific supplied energy (SE), defined as the energy required by the
 358 HC system to the initial amount of total solids Eq. 12:

$$359 \quad SE \left(\frac{kJ}{kgTS} \right) = \frac{P_{abs} \times t}{V \times TS} \quad \text{Eq. 12}$$

360 where P_{abs} is the power absorbed from the pump [W], t is the treatment time [sec], V is the volume of the
 361 treated sludge [L] and TS is the activated sludge solids content [$g L^{-1}$].

362 Similarly, the energy efficiency (EE), expressed as $mg\ DSCOD\ kJ^{-1}$, has been calculated as the mg of SCOD-
 363 increase per unit of energy supplied, Eq. 13, [71]. Higher EE values correspond to higher removal efficiencies.

$$364 \quad EE \left(\frac{mg\ \Delta SCOD}{kJ} \right) = \frac{V \times \Delta SCOD}{P_{abs} \times t} \times 1000 \quad \text{Eq. 13}$$

365 **6. The effect of various parameters on HC effectiveness**

366 A significant number of parameters exist that can affect HC effectiveness, influencing the number of generated
367 (reactive) bubbles and collapse conditions. As showed in Fig. 9, an overview of the effective parameters in HC
368 has been suggested by Braeutigam et al. [72].

369 The main factors that govern HC and its effectiveness are (i) construction parameters, (ii) technological process
370 parameters of the HC device, and (iii) properties of the liquid [73]. The influence of all these aspects on HC
371 effectiveness is separately analysed in the following paragraphs.

372 **6.1. Construction parameters of cavitating devices**

373 A first group of factors that influences HC effectiveness include parameters linked to the structural
374 characteristics of HC reactors, and more in details of the cavitation inducer and the flow chamber.

375 **6.1.1. Influence of geometry of cavitating devices**

376 HC effectiveness depends on size and shape of cavitation inducer and flow chamber, which can both affect
377 the number of cavitation bubbles and the collapse intensity. Recently, many researchers have focused on the
378 optimization of geometry of cavitating devices to obtain the highest cavitational effects, in terms of both
379 number of cavitation events and significant pressure drops, also resulting in a decrease in energy requirements
380 of the HC process. With this purpose, different HC devices have been developed. A first HC reactors
381 classification has been provided by Gogate et al. [74], and successively reported by Manickam and Ashokkumar
382 [75], and adapted in this review:

- 383 a) *high pressure hydrodynamic cavitation reactor*, which is a high pressure positive pump with a throttling
384 device [74] or a blade [76] designed to operate at high pressure ranging from 50 atm to as high as 300
385 atm;
- 386 b) *low pressure hydrodynamic cavitation reactor*, where the flow through the main line is forced to pass
387 through a geometric constriction, such as single-hole orifice or multiple holes on an orifice plate [8,72]
388 (Fig. 10 a), a Venturi [16,46,47] (Fig. 10 b), a blade, and where the local velocities suddenly increase
389 due to a reduction in the flow area resulting in lower pressures;
- 390 c) *low pressure swirling cavitation reactor*, where cavitation is generated by using a vortex flow swirl
391 chamber [77] (Fig. 10 c) in which a central vortex with a core pressure lower than the vapour pressure
392 of the liquid is formed, thus inducing cavitation bubbles formation in the vortex, and where the liquid
393 is then ejected from the chamber through the exit orifice into a volume of liquid where the cavitation
394 bubbles collapse;
- 395 d) *high speed homogenizer*, which consist of rotating equipment (Fig. 10 d). Generally a roto-stator
396 assembly is used [19], that operates at rotating speeds of 4000 rpm to as high as 20000 rpm, causing
397 a pressure drop near the periphery of the rotor.

398 In the first three groups the passage of the liquid supplies the energy needed to induce cavitation (static
399 hydrodynamic cavitation devices) while in the fourth group the energy required is furnished by the help of a
400 rotating inducer (dynamic hydrodynamic cavitation devices).

401 Further, different geometrical configurations of each device have been investigated in wastewater treatment
402 field. Following are discussed some examples of different HC reactors reported in literature.

403 Several researchers investigated the influence of the geometry of orifice plate systems on HC intensity [14,78],
404 testing plates with different thickness [8,78] and with different numbers, shapes and sizes of holes [14,78,79].
405 It was observed that the highest cavitation intensity was generated by using the lowest free area in the orifice
406 plate system. However, keeping constant the free area, orifice plates with higher diameter and lower number
407 of holes showed lower intensities [12,14].

408 Šarc et al. [47] compared four very similar Venturi shapes, considering the same operating conditions (constant
409 values for flow pressure, flow velocity, and temperature, respectively). Significant differences in typology,
410 dynamics and intensity of cavitation were found. By using a high-speed camera, they observed how cavitation
411 size and appearance could vary significantly when the divergence angle of the Venturi system was changed.
412 Similarly, Kim et al. [16] investigated the effect of different Venturi outlet inclination angles on the
413 performance of their HC system, which was used to increase sludge solubilisation. Rajoriya et al. [80] used a
414 slit and a circular Venturi, respectively, to generate cavitation and, thus, to degrade Rhodamine 6G.
415 Considering the same operating conditions, the degradation rate of the dye was marginally higher in the case
416 of slit Venturi as compared to the circular one. In another study [81], the authors checked the influence of
417 geometrical parameters on decolorization of reactive blue 13 in a polluted aqueous solution. With this
418 purpose, eight cavitating devices i.e. six orifice plates having different perimeter and flow area, and slit and
419 circular Venturi were tested, showing that the HC efficiency was strongly influenced by the geometrical
420 parameters. Carpenter et al. [82] provided a detailed geometrical analysis of HC devices in order to investigate
421 the effect of geometry of orifice plates and Venturi of different shapes and geometrical parameters on the
422 formation and stability of mustard oil in water nanoemulsion.

423 A swirling jet cavitation device has been investigated by Wang et al. [60,83]. Recently, Mancuso et al. [8,9] and
424 Langone et al. [84] proposed a modified swirling jet-induced cavitation reactor, in which cavitation was
425 generated by using a modified Ventury system. The authors studied the influence of the injection slots number,
426 the geometry of the system, and the number of HC devices in series on the HC effectiveness, highlighting how
427 different geometries of the cavitating device influenced the HC effectiveness. A comparison between orifice
428 plates and a vortex diode system on degradation of different organic solvents such as acetone, methyl ethyl
429 ketone, and toluene was carried out by Suryawanshi et al. [85].

430 Badve et al. [86] and Patil et al. [20] developed an efficient stator and rotor assembly, where rotor is a solid
431 cylinder which has indentations on its surface, and can be rotated at different speeds of rotations. Afterwards,
432 a novel stator and rotor configuration has been proposed by Petkovšek et al. [19] based on two facing rotors

433 with special radial grooves spinning in the opposite direction: the authors studied the effect of different shapes
434 of the teeth of their rotor on the cavitation process [48]. Another reactor, which can generate shear cavitation,
435 was recently proposed by Petkovšek et al. [19]. The main feature of this device is that it works both as
436 cavitation generator and as driving pump, avoiding additional pressure drop. Jain et al. [87] studied the
437 influence of the reactor geometry by comparing an HC rotating device with an orifice plate system for water
438 disinfection.

439 **6.2. Technological process parameters**

440 This second group includes operative parameters of the technological process, such as flow velocity or kinetic
441 energy of the liquid, pressure at the inlet to the HC system, temperature of the liquid, pH of the liquid, and the
442 HC “processing” time (the number of times the liquid passes through the cavitation device).

443 **6.2.1. Influence of flow velocity**

444 In an HC device, the number of cavitation bubbles is mainly related to an increase of the flow velocity or the
445 kinetic energy of the liquid. Increasing the flow velocity, higher local pressure oscillations are expected, and
446 pressure may fall below the vapour pressure of the liquid at the operating temperature, causing partial
447 vaporization of the liquid and the generation of cavities. As can be deduced from Eq. 3, an increase in flow
448 velocity implies a decrease in the cavitation number, resulting in an increase of cavitation effects. Higher
449 flow velocities further can imply higher turbulence levels.

450 Flow velocity can be varied either by adjusting the pump flow rate (and thus the pressure at the outlet of the
451 pump) or by changing the geometry of the cavitating device (i.e. reducing or increasing the constriction area).
452 Šarc et al. [47] reproduced different cavitation conditions by varying the flow velocity at the throat of a Venturi
453 system for different values of inlet pressure, while keeping constant the cavitation number and the geometry
454 of their HC system. They observed that cavities slightly grew when the flow velocity was increased.

455 A Venturi system was used by Saharan et al. [46] to investigate the effect of the flow velocity on degradation
456 of RR120. It was observed that the degradation rate increased with an increase in the flow velocity reaching a
457 maximum and then it dropped, due to the onset of the supercavitation. Similar results were reported by
458 Prajapat and Gogate [88] and Gore et al. [69] using conventional Venturi systems.

459 Similarly, Joshi and Gogate [89] investigated the influence of flow velocity at the throat of a single orifice plate
460 by adjusting the flow rate. In their study, increasing the flow velocity up to an optimum value, an increase in
461 the extent of degradation of dichlorvos was detected. Higher flow velocities promoted an increasingly violent
462 collapse of cavities, and thus an increasingly hydroxyl ions generation, resulting in an increment in the extent
463 of degradation. However, for flow velocities higher than the optimum value, the extent of degradation
464 decreased due to the onset of supercavitation, resulting in an extremely rapid growth of bubbles downstream
465 to the orifice plate with the subsequent splashing and vaporization of the flow.

466 Wang and Zhang [90] reported a continuous increase in the degradation rate of alachlor by using a swirling
467 jet-induced reactor and increasing the flow, while keeping constant the geometry of their HC system. These
468 results are in agreement with the study of Mancuso et al. [9] that, studying a modified swirling jet-induced
469 cavitation reactor to improve the sludge disintegration, observed an increase in sludge solubilisation with an
470 increase of the flow velocity into the liquid. However, using the same HC device to treat a polluted dye aqueous
471 solution by Rhodamine B, supercavitation occurred and an optimum value for flow velocity was detected [16].
472 In a rotor-stator system, Badve et al. [58] varied the velocity of the liquid on the surface of the rotor by
473 adjusting the rotational speed of the rotor. Their results showed that an increase in the rotational speed led
474 to an increase in velocities of the liquid surface and to a decrease of the cavitation number.
475 Nevertheless, also the geometry can deeply influence the flow velocity, resulting in different cavitation
476 effects. Sivakumar and Pandit [14], using multiple hole orifice plates and operating at the same inlet pressure,
477 observed an increase in the cavitation process efficiency increasing the flow velocity for different geometries
478 of their HC system. By using a swirling jet-induced reactor, Mancuso et al. [9] obtained an increase in HC
479 effectiveness, in terms of activated sludge solubilisation, for the highest flow velocity achieved by decreasing
480 the number of the injection slots at the same inlet pressure.

481 **6.2.2. Influence of inlet pressure to the HC system**

482 Inlet pressure can influence both the number of generated cavitation bubbles and their collapse intensity. In
483 HC systems, an increase in inlet pressure always implies an increase in flow rate, and vice versa. As seen in
484 section 6.1.1, higher inlet pressures involve higher flow rates and thus higher flow velocities, increasing
485 turbulence levels and local pressure oscillations. Therefore, increasing the inlet pressure an enhancement of
486 HC effectiveness is expected. Furthermore, higher inlet pressures involve higher pressure drops through HC
487 devices. This increase in pressure can lead to higher shear forces that are able, especially for HC applications
488 in WWTPs, to break down bacterial cell walls and to increase the release of organic matter [9,91]. However,
489 at very high inlet pressures cavities can start coalescing with each other and supercavitation can be detected,
490 resulting in a progressive decrease in the HC effectiveness. By using both a multi-hole orifice plate system and
491 a swirling jet reactor, Mancuso et al. [8] observed that higher inlet pressures allowed to achieve higher extent
492 of degradation rates in polluted aqueous solutions containing Rhodamine B. Similarly, Kumar and Pandit [92]
493 found an increase in the pressure drop across their Venturi system due to higher inlet pressures to the HC
494 system, resulting in an increase in the cluster collapse pressure. Two different systems (slit and circular) were
495 used by Rajoriya et al. [80] to treated wastewater polluted by Rhodamine 6G. The Authors observed an
496 increase in the extent of degradation by increasing the inlet pressure up to an optimum value of 5 bar.
497 However, lower decolourization rates were detected by considering inlet pressures beyond 5 bar, due to the
498 inception of choked cavitation.

499 Similar findings were reported from Kumar et al. [65] that treated polluted aqueous solution by methylene
500 blue dye by means of a Venturi system. In their experiments, the inlet pressure was varied from 1 to 10 bar,

501 showing an optimum at 5 bar in terms of extent of dye degradation. Thanekar et al. [93] investigated the effect
502 of inlet pressure on degradation of carbamazepine. The cavitation intensity increased with an increase in
503 pressure from 3 bar until an optimum of 4 bar. Further increase in pressure beyond optimum value led to the
504 formation of cavity cloud which in turn reduced cavitation intensity, resulting in a decrease in the extent of
505 degradation. Carpenter et al. [82] used two Venturi systems and single orifice plates with different shapes in
506 order to produce highly stable oil in water emulsion. For all devices, increasing the inlet pressure from 5 to 10
507 bar, a significant increase in HC efficiency was observed by the authors, but further increasing the pressure
508 from 10 to 15 bar, only a marginal or no further increase in HC efficiency was observed. Choi et al. [94] tested
509 different inlet pressure from 30 to 70 bar for the degradation of bisphenol A. Again, the degradation rate
510 increased from 30 to an optimum of 50 bar, then, for a further increase in the inlet pressure, the downstream
511 area into the Venturi system was completely filled with cavities, which began to coalesce with each other and
512 formed a cavity cloud, resulting in a decrease in the extend of degradation. The effect of inlet pressure on the
513 degradation of Rhodamine B was investigated by Tao et al. [95] over the range of 60 - 120 bar. An increasing
514 degradation rate for Rhodamine B at higher inlet pressure was observed from the authors. In this case,
515 supercavitation was not detected simply because inlet pressure was not high enough or most likely due to the
516 capacity of jets impingement to divide cavitation bubbles into micro-bubbles and then to prevent coalescence
517 between them.

518 **6.2.3. Influence of cavitation number (C_v)**

519 Cavitation number, C_v , is inter-correlated with the other two parameters previously described: flow velocity
520 and inlet pressure. Up to now, many studies on the influence of C_v on the effectiveness of cavitation have
521 been carried out. However, missing or inaccurate information about the position at which the pressure and
522 the flow velocity were measured or calculated implies that researchers commonly use inappropriate values of
523 C_v , taking advantage that there are no standard methods for its determination [47]. Most of the studies on HC
524 are not repeatable because of a not detailed definition of the C_v in the published research. Nevertheless, for
525 completeness of the contents of this work, some results on the influence of C_v on the HC effectiveness have
526 been reported.

527 Tao et al. [32] recently investigated the effect of the C_v on degradation of Rhodamine B by using a novel device
528 based on double cavitating-jets impingement. A decrease in the C_v from 0.0486 to 0.0246 implied an increase
529 in Rhodamine B degradation. However, in their results the authors reported that the pressure in the main
530 chamber was just approximatively 10 bar. This inaccuracy was due to the difficulty to get an accurate value of
531 the pressure, and hence of the C_v (see definition of this parameter above in Eq. 3), most likely due to the
532 presence of cavitation conditions that made measurements more difficult. As expected, Rajoriya et al. [81]
533 observed a decrease in C_v with an increase of the inlet pressure for different geometries of their HC system in
534 order to treat a polluted solution by reactive blue 13. In their study, it was found that the decolorization rate
535 increased with a decrease in C_v till an optimum value and then further decreased or remained constant for all

536 the cavitating devices used, due to the inception of choked cavitation. Saharan et al. [46] used a Venturi
537 system to degrade Reactive Red 120 dye. It was observed that the rate of degradation increased with a
538 reduction in C_v , reaching a maximum and then dropping. In their findings, authors distinguished two different
539 stages depending on cavitation number: firstly, a decrease in cavitation number led to an increase in the
540 number of generated cavitation bubbles, resulting in an increase in the number of cavitation collapse
541 pressure pulses as well as in the generation of more $\bullet\text{OH}$ radicals that increased the degradation rate; then,
542 the degradation rate decreased with further decrease in C_v . This may be because of reduced cavitation
543 intensity due to excess numbers of cavities inside the Venturi system at very low C_v . Indeed, when there are
544 too much cavities, these can start coalescing to form a larger cavitation bubble that can get away from the
545 liquid without collapsing or result into an incomplete collapse, resulting in a reduction of generated $\bullet\text{OH}$
546 radicals.

547 Gore et al. [69] investigated the influence of the C_v , ranged from 0.210 to 0.095, on degradation of reactive
548 orange 4 dye using a Venturi system. Also in this case, it has been found that the decolourisation rate increased
549 with a decrease in the C_v , reaching to the maximum at 0.15 and then decreased. Authors attributed these
550 findings to an increase in the number of cavities and thus of the number of collapsing events, resulting in the
551 generation of more $\bullet\text{OH}$ radicals. However, a further decrease in the C_v below 0.15 implied a decrease in the
552 extent of degradation due to the occurrence of choked cavitation/supercavitation conditions, where cavities
553 no longer behaved as individual cavities. They coalesced with each other to form larger vaporous bubbles,
554 which were carried away with the flowing liquid without collapsing.

555 All studies on wastewaters contaminated by soluble pollutants confirm that for a decrease in C_v , an increase
556 in the number of cavities is expected, resulting in an increase in overall collapse intensity of cavities [46,69,81].
557 However, depending on the specific HC device configurations, after certain value of C_v , the number of cavities
558 can become very high, so these cavities can start coalescing with each other and form a cavity cloud [46,69,81],
559 compromising HC effectiveness. Energy produced by the collapse of some cavities can be taken up by the
560 neighbouring cavities, resulting in a cavity cloud formation (choked cavitation). Hence, the importance of
561 optimizing HC cavitation devices in order to operate between these two limits, i.e. cavitation inception and
562 choked cavitation/supercavitation, to get the maximum effect.

563 By applying HC treatment to sludge, C_v greater than 1 have been reported, because of the presence of solid
564 particles into the flow which can act as pre-nuclei and therefore they can accelerate the phenomena of cavities
565 generation. Lee and Han [18] estimated a cavitation number of 2.79 using a multiple-orifice plate to treat
566 activated sludge for methane production. However, very few studies reported C_v values when sludge is treated
567 by HC, mainly because of the difficulty to evaluate the various parameters. Further, it should be noted that in
568 order to compare two or more HC systems each other, rather than C_v , other parameters, such as for instance
569 vibrations and noise measurements, and some indexes (see section 5) could be used to measure the intensity
570 and efficiency of HC systems.

571 **6.2.4. Influence of liquid temperature**

572 The influence of temperature on HC is complex, which can have both positive and negative effects on HC
573 treatment efficiency. Temperature affects the dynamics of cavities through the properties of the liquid such
574 as viscosity, vapor pressure, and surface tension. As shown in the phase diagram of water (Fig. 3), the vapour
575 pressure of a fluid depends on its temperature and it increases exponentially with temperature. Thus, an
576 increase in operating temperature can both enhance the probability of vaporous cavities generation due to
577 entrapment of vapours and influence the kinetic rate. The increase of temperature implies a decrease of the
578 viscosity and surface tension, leading to an easier bubble formation [73]. However, these generated bubbles
579 are richer in vapour content, which reduce the intensity of bubbles collapse due to the “cushioning” effect of
580 their implosion [73]. A rise in temperature reduces gas solubility, which is the chief source of cavity nuclei and
581 thus reduces the rate of occurrence of cavitation events.

582 It is then likely that an optimum operating temperature might exist in specific conditions. When the
583 temperature of the solution increases beyond the optimum value, the increase in vapor pressure of liquid
584 might result in higher vapor content in cavitation bubbles leading to a cushioning effect and thus to an HC
585 effectiveness reduction.

586 With this background, Wang and Zhang [90] have reported a positive effect on the degradation of alachlor
587 with an increase in temperature from 30 to 40°C, but the degradation rate decreased with a further increase
588 in the temperature over a range of 40 - 60°C. Joshi and Gogate [89] investigated the effect of operating
589 temperature over the range of 31 - 39°C. In their experiments on degradation of dichlorvos, the maximum
590 degradation rate was achieved at the lowest temperature. Mancuso et al. [9] investigated the influence of
591 temperature, ranged from 20 to 35°C, on sludge disintegration. The authors observed that for this range of
592 temperature, the higher the temperature, the more efficient HC (in terms of sludge solubilisation) was. Similar
593 results were reported by Choi et al. [94] for the degradation of bisphenol A by using HC, where an increasing
594 temperature from 10 to 50°C implied an increase in the extend of degradation. Šarc et al. [47] proved that the
595 magnitude of pressure oscillations, which occurs due to cavitation bubbles collapse, increased for
596 temperatures up to 40°C, but then dropped significantly for higher temperatures.

597 **6.2.5. Influence of liquid pH**

598 Typically, acidic or basic conditions are favourable to the degradation of chemical pollutants using HC reactors.
599 The optimal pH value depends on the pollutants to be treated. Their degradation is strongly dependent on
600 medium pH, as pH can influence the presence of •OH free radicals available for pollutants removal. Moreover,
601 it is possible to get changes in pollutants structure for different pH, obtaining more biodegradable forms, which
602 can be easily attacked by •OH free radicals. Usually, acid conditions are recommended for pollutants
603 degradation by HC, because such conditions favours generation of hydroxyl radicals and impedes any reaction
604 of recombination among free radicals [69].

605 Many studies have been carried out to remove dye pollutants from wastewaters. Saharan et al. [46]
606 investigated the effect of pH on Reactive Red 120 dye degradation by carrying out experiments at different pH
607 ranged from 2 to 11. Their results indicated that the rate of degradation increased with a decrease in the pH
608 of the solution, confirming that acid conditions implied higher degradation rates for the Reactive Red 120 dye.
609 Also Kumar et al. [65] observed a decrease in the rate of decolourization of polluted solution by methylene
610 blue dye with an increase in the pH from 2 to 10, indicating that also the state of the molecules of this dye can
611 change from ionic to molecular or vice versa depending on the solution pH and thus different rates of
612 decolourization can be detected. These findings are in agreement with results of Rajoriya et al. [81], where the
613 authors investigated the influence of pH solution, ranged from 2 to 8, on decolourization of reactive blue 13
614 dye by using a slit Venturi to generate cavitation. Their results depicted that the extent of decolorization
615 increased with a decrease in solution pH. Gore et al. [69] studied the effect of pH, ranged from 2 to 10, on
616 degradation of reactive orange 4 dye using a Venturi system. The authors, starting from a neutral polluted
617 solution, observed an increase in the decolourisation rate by either increasing or decreasing the pH of the
618 polluted solution. However, the highest extent of degradation was obtained working at lower pH solutions,
619 indicating a lower rate of recombination among generated $\bullet\text{OH}$ radicals in acid conditions and, hence, the
620 presence of more $\bullet\text{OH}$ radicals available for the dye oxidation. Moreover, the increase in the degradation rate
621 can be also attributed to the change of state of the orange 4 molecules from ionic to molecular under acidic
622 conditions. This alteration in the state of the molecules makes them hydrophobic and more easily attacked by
623 $\bullet\text{OH}$ free radicals. On the contrary, in the basic medium, the extent of degradation of orange 4 was not so high
624 as in acid conditions because dye molecules remained in ionic state, resulting in an increase in their hydrophilic
625 behaviour that implied their persistence in the liquid bulk.

626 Same findings have been reported by some researchers that studied the degradation of Rhodamine B.
627 Mancuso et al. [8] treated polluted aqueous solutions by Rhodamine B using a multi hole orifice plate system,
628 and observed the highest degradation rate of the dye at pH 2, while it dropped significantly and remained
629 constant for pH ranged from 5 to 8. This was due to the prevalence in the acid conditions of Rhodamine B in
630 the cationic form rather than the zwitterionic form [96]. Previous studies on Rhodamine B reported that the
631 cationic form is easier to degrade [60], and thus at low values of pH the oxidation of Rhodamine B can be
632 higher. Similar results were obtained by Mishra and Gogate [62] using a Venturi device, by Wang et al. [60]
633 using a swirling jet-induced cavitation system, and by Tao et al. [95] using a novel reactor based on double-
634 cavitating-jets impingement, respectively. A different trend of results on the effect of the pH was reported by
635 Rajoriya et al. [80], studying Rhodamine 6G degradation. In this case, the observed results showed an increase
636 in the extent of degradation with a pH increase in the solution from 2 up to an optimum value of 10. Then, the
637 decolorization rate decreased. Under acidic pH Rhodamine 6G molecule became hydrophilic in nature, and
638 thus, the dye remained in bulk of the solution where concentration of $\bullet\text{OH}$ radicals was minimum. On the
639 other hand, under basic conditions Rhodamine 6G molecule became hydrophobic. Under such conditions, the

640 dye was in its molecular state and located itself at the cavity-water interface where the concentration of $\bullet\text{OH}$
641 radicals was maximum. Recently, HC has been applied to treat water solutions contaminated with insecticide
642 and pharmaceutical compounds, and the pH effect on pollutant degradation have been also investigated. Joshi
643 and Gogate [89] investigated the influence of pH on degradation of dichlorvos, a household and public health
644 fumigant. Using an orifice plate system as cavitating device, they found that lower pH provided higher extents
645 of degradation. Studying the degradation of pharmaceutical compounds, Thanekar et al. [93] found that the
646 efficiency of carbamazepine removal was maximum for a pH of 4 and minimum at 11. However, a decrease
647 from 4 to 3 showed a worsening of the degradation process.

648 When treating activated sludge, it was observed that alkaline conditions were more suitable to enhance
649 organic hydrolysis [97]. Optimal results in terms of organic matter release have been obtained when HC was
650 assisted with NaOH pre-treatment, then working at basic conditions with a pH of about 9 or 10, resulting in
651 an increase in biogas production in the anaerobic digestion process [69].

652 **6.2.6. HC schemes**

653 In order to treat wastewaters, different HC experimental schemes have been proposed. Usually, HC devices
654 require low amounts of supplied energy to work and, therefore, they are generally applied to closed loop
655 circuits, where the liquid to be treated is recirculated several times through the HC reactors (Fig. 11) [8,14,22].
656 Fig. 11 shows an example of a closed loop circuit where HC has been taken into account. This scheme
657 comprises a main tank (1), a pump (2), control valves at appropriate places (V_1, V_2, V_3, V_4, V_5), a cavitation
658 reactor (4), sampling ports (5) and gauges (P_1, P_2) to measure hydraulic parameters. Control valves (V_1, V_2, V_3)
659 are placed in order to control the flow rate through the mainline.

660 However, HC closed loop circuits cannot be considered into scaling-up actions in real WWTPs due to the higher
661 volumes of liquid to be treated, leading to the application of other configurations called “one-shot treatment”
662 [98]. In these configurations, HC treatment is applied as single unit of the WWTP, and it takes place with a
663 single pass without any recirculation of the solution to be treated. However, these HC schemes can be
664 implemented when the HC devices are able to transfer high power during only one passage, resulting in the
665 effectiveness of the HC process.

666 About the closed loop circuits, both the HC efficiency and the extent of degradation can significantly increase
667 with an increase in the number of passages through the HC reactors [8,99,100]. It is substantially due to longer
668 exposure times of pollutants to HC conditions [69]. If the inlet pressure to the HC system is constant, the
669 number of passes is directly correlated with the process treatment time.

670 These considerations were confirmed by Save et al. [101] that used an HC reactor based on a throttling valves
671 system to disrupt cells. Their results showed as an increase in the number of passes and, then, of the time of
672 treatment, led to a corresponding increase in the extent of cell disruption. However, at low inlet pressures,
673 the effect of the number of passes was marginal, but was slowly increased at higher inlet pressures.

674 **6.3. Properties of the liquid medium**

675 This last group includes parameters characterizing the properties of the liquid medium, mainly pollutant
676 concentration, viscosity of the liquid, surface tension and dissolved gas content.

677 **6.3.1. Influence of pollutant concentration**

678 When cavitation conditions are not varied, the amount of $\bullet\text{OH}$ radicals produced in the HC system should be
679 constant as well. Therefore, for an increase in initial pollutant concentration, a decrease in pollutant removal
680 rate is expected as hydroxyl radicals may not be sufficient to degrade the pollutant completely.

681 This is true in the case of removal of chemical pollutants dissolved in water solutions. Parsa et Zonouzian [78]
682 studied the effect of the initial dye concentration on degradation of Rhodamine B by using a submerged multi
683 hole orifice plate system. In their experiments, the initial dye concentration was ranged from 2 to 14 mg L⁻¹.
684 They found that the efficiency of the process was inversely proportional to the initial dye concentration. In
685 justifying this result, the authors explained that it might be imputed to an increase in the total amount of dye
686 molecules, while the total amount of free hydroxyl radicals remained constant. These findings are in
687 agreement with other studies on degradation of Rhodamine B [8,60,61,95], Rhodamine 6G [80], reactive blue
688 13 [81], tetracycline [102], and other organic solvents such as acetone, methyl ethyl ketone, and toluene [85],
689 respectively, where the authors observed an increase in the extend of degradation with a decrease in initial
690 dyes concentration.

691 Treating activated sludge, the solid content (TS) concentration may influence the HC effectiveness, and thus
692 the sludge disintegration degree. Kim et al. [16] investigated the influence of initial TS concentration, ranged
693 from 5 to 40 g L⁻¹, on sludge solubilisation by using a Venturi system as cavitating device. The authors observed
694 an increase in sludge solubilisation by increasing the initial TS concentration. These results are in agreement
695 with the study carried out by Mancuso et al. [9], where the authors, ranging the initial sludge concentration
696 from 7 to 40 g L⁻¹, observed the highest COD solubilisation for the highest initial sludge concentration. The
697 increase in TS content provides more cells and aggregates and thus a higher viscosity of the sludge, due to the
698 inter- and intra- particle interactions. It was observed that both growth and collapse of cavities can be reduced
699 by considering higher viscosities [49]. However, the increase in TS enhances the possibility of collision between
700 sludge flocs and cavitation cavities, resulting in an increase in sludge disintegration. Therefore, the negative
701 effect of high TS concentration on sludge degradation can be negligible if compared to the positive ones. In
702 addition, it was observed that the presence of solids can influence the initial size of the HC nuclei [13].

703 **6.3.2. Influence of liquid viscosity**

704 The rheology of the treated matter can be characterized by its viscosity. This important parameter can
705 influence HC intensity and the way in which a polluted liquid flows into HC devices. The main parts affected by
706 viscosity are the nuclei distribution and the bubble dynamics. Generally, an increase in viscosity, regardless of
707 whether fluids are Newtonian or non-Newtonian, can reduce the efficiency of cavitation due to a decrease in

708 both growth and collapse of bubbles [49]. For these reasons, in most of the studied HC applications, water was
709 selected as the liquid medium due to its low viscosity, which ensures higher possibilities to cavitation to occur.
710 However, HC process has been used in fluids other than water. For instance, HC was used as a pre-treatment
711 technique to treat activated sludge in WWTPs. In the activated sludge, the viscosity increases with an increase
712 in TS concentration, due to the inter- and intra-particle interactions [16]. Experimental results showed that the
713 negative effect of viscosity on the sludge solubilisation is negligible compared to the positive effect of sludge
714 concentration for cavitation development [9,16].

715 When the activated sludge is treated by HC, its viscosity decreases. Consequently, it can be heated, mixed and
716 pumped more easily, resulting in a decrease of the supplied energy in the anaerobic digestion process [103].
717 A decrease in viscosity was observed by Kim et al. [16] in the first 30 min of treatment by using a Venturi
718 system as cavitating device, whereas the viscosity was constant for a treatment time between 30 and 60 min.
719 Garuti et al. [98] applied HC as full-scale application to treat agro-industrial sludge, achieving a decrease in the
720 apparent viscosity in the range of 23-27%. This result was mainly attributed to an increase in temperature,
721 shear forces and cavitation bubble collapse due to the HC treatment. In agreement with this study, Mancuso
722 et al. [9] observed a decrease in viscosity by using a swirling jet-induced cavitation to increase the sludge
723 solubilisation. As the viscosity decreased during their HC tests, it was necessary to progressively reduce the
724 frequency of the pump inverter in order to keep constant the inlet pressure, and thus the flow rate and flow
725 velocity. Using the same experimental HC device for treating cattle manure, Langone et al. [104] proved that
726 the apparent viscosity dropped about 21, 38, and 40% for samples HC treated at 6.0, 7.0, and 8.0 bar,
727 respectively, as compared the untreated manure. This was due to a progressive alteration of the rheology of
728 the activated sludge, resulting in a decrease of its viscosity during the HC treatment. Similarly, Prajapat and
729 Gogate [88] investigated the effect of inlet pressure on depolymerisation of aqueous polyacrylamide solutions
730 by using a Venturi system. Their experimental results showed an increase in intrinsic viscosity reduction with
731 an increase in inlet pressure. Mohod et al. [105] used an high speed homogenizer for the intensification of
732 biodiesel production. In their study, HC combined with an increase in temperature till an optimum resulted in
733 reduced viscosity of the oil phase and enhanced miscibility of the reactants, leading to an increase in the
734 biodiesel yield.

735 **6.3.3. Influence of surface tension**

736 Surface tension can affect the HC process, influencing the number and the size of both vapour nuclei and gases
737 into the liquid [74]. Higher values in surface tension lead to a lower number of gas nuclei and to a faster
738 dissolution of them into the liquid. For this reason, at the very beginning of the HC process, cavitation
739 efficiencies may be affected due to a low presence of gas nuclei into the liquid. However, during the collapse
740 phase, cavities becomes nuclei and they can be cyclically used, resulting in an increase in cavitation
741 effectiveness over time.

742 The surface tension depends on the type of liquid and its temperature; an increase in temperature implies a
743 decrease in the surface tension, resulting in easier evaporation of the liquid [73]. By using very small amounts
744 of surfactants, it is possible to reduce the surface tension and thus to decrease the cavitation threshold,
745 resulting in an easier generation of bubbles and hydroxyl radicals.
746 However, while a decrease in the surface tension of the liquid can imply an easier generation of cavitation, it
747 should also be noted that a decrease of surface tension can affect the collapse of cavities, which would be less
748 violent.

749 **6.3.4. Influence of dissolved gas content**

750 Cavitation nuclei are provided by the gas released due to the reduction in pressure or by the partial
751 vaporization of liquid. The dissolved gas content can influence the rate of nucleation, and thus the cavitation
752 intensity. Depending on the typology of the dissolved gas, different parameters such as thermal conductivity
753 and liquid surface tension can be affected, leading to different ranges of temperature for the HC hot spots. In
754 addition to the gas typology, also the amount of dissolved gas inside the cavity can affect the final collapse
755 temperature and pressure [74]. The dissolved gas such as oxygen can also participate to chemical reactions
756 that can enhance the production of free radicals. Most of the HC applications are carried out in the presence
757 of gas atmosphere; however, the effect of presence of various gases (i.e. argon, air) has also been investigated
758 [106]. It was observed that different properties of dissolved gases, such as the gas solubility, can significantly
759 affect the cavitation process, leading to an alteration of the concentration gradient around the cavitating
760 bubbles, and the mass transport to and from the cavitating bubbles [74].

761

762 7. Mechanisms of degradation of pollutants

763 HC can have both mechanical and chemical effects in the system, Fig. 12. The violent collapse of cavities in HC
764 systems can cause the formation of hydrogen atoms and reactive hydroxyl radicals and can give rise to thermal
765 hot spots, which can produce pyrolytic cleavage of chemicals [107]. The two main chemical mechanisms for
766 pollutants degradation using HC are the thermal decomposition of volatile pollutant molecules trapped inside
767 the cavity during the cavity collapse and, secondly, the reaction of the radicals $\bullet\text{H}$ and $\bullet\text{OH}$ with the pollutant
768 that occurs in the cavity-water interface. In the case of non-volatile pollutants, the main mechanism for their
769 degradation will be the attack of pollutants molecules by hydroxyl radicals in the cavity-water interface and in
770 the bulk fluid medium.

771 Also, the mechanical effects are significant: (i) generation of shock waves from the collapsing cavity, (ii)
772 creation of liquid micro-jets and (iii) formation of interfacial turbulence and powerful hydraulic tensions, due
773 to the high flow velocity. The mechanical effects can directly break the molecular bonds on the main
774 macromolecular chain, in particular the complex compounds of great molecular weight, thus degrading the
775 refractory organic materials. The decomposed intermediates are more susceptible to $\bullet\text{H}$ and $\text{OH}\bullet$ attacks and
776 biological oxidation, which can further improve the rate of oxidation/mineralization of pollutants [46].
777 Furthermore, the high velocity of micro-jets (>100 m/s [36]) disturbs the boundary layer on the solid surface,
778 leading to the breakage of the liquid film responsible for the resistance to mass transfer.

779 The chemical and mechanical effects are also responsible for the improvement of heat transfer, whose rate is
780 almost twice as high in the presence of cavitation [108].

781 The HC technique has been successfully applied in the field of wastewater treatment, treating contaminated
782 wastewater and sludge and biomasses.

783 When HC is applied to contaminated wastewater the main aim is the removal of contaminants, such as dyes,
784 pharmaceutical and toxic compounds. In this applications, chemical mechanisms, both thermal decomposition
785 of volatile pollutant molecules and the reaction of the radicals $\bullet\text{H}$ and $\bullet\text{OH}$ with the pollutant, are prevalent
786 as compared with the mechanical effects. However, the generated mechanical effects, as described before,
787 can enhance the overall efficiency of the HC treatment.

788 HC is applied to activated sludge [9,21], manure and biomass [98,104] as a pre-treatment, with the main
789 purpose to improve hydrolysis and the solubilization of organic matter, and, thus, the aerobic or anaerobic
790 biodegradability. When applied as sludge pre-treatment, HC acts by destroying the walls and membranes of
791 bacterial cells with consequent release of intracellular and extracellular matter [91,109]. Many of the
792 intracellular constituents, including cytoplasm and nucleic acids, are readily biodegradable, resulting in
793 acceleration of both aerobic and anaerobic digestion processes in sludge treatment or in promoting
794 denitrification in wastewater treatment processes [9]. Furthermore, an enhancement in sludge dewatering
795 performance was also observed after HC treatment as a result of the destruction of extra-cellular polymeric
796 substances (EPS) and cells by highly reactive radicals [21]. When applied as biomass/manure pre-treatment,

797 HC reduces the structural and compositional barriers present in the lignocellulosic biomass and exposes the
798 polymer chains of cellulose and hemicellulose to microbial breakdown as well as enhances the rate of biomass
799 degradation and biogas yield [20].

800

801 **8. HC combined to advanced oxidation processes (AOPs)**

802 As discussed above, HC has a potential in degrading organic pollutants effectively to a certain level. The
803 efficiency of the process depends on the typology of pollutants to be treated, operating conditions, number
804 of hydroxyl radicals that are being generated and their effective utilization.

805 Hence, in this regard, various researchers have investigated on the synergetic effect of HC coupled with AOPs
806 such as H_2O_2 , O_3 , Fenton's reagents, photocatalysis, etc. in order to improve the efficiency in terms of increase
807 in $\bullet OH$ radicals' generation and their effective distribution. These combined methods have shown higher
808 efficiencies when compared to HC or other AOPs techniques used as individual operation.

809 Table 1 depicts some of the applications of HC combined with existing AOPs for the wastewater treatment
810 illustrating the typology of pollutants, used equipment, operating parameters and removal efficiencies.

811 Further, some researcher have also investigated on the synergetic effect of HC in presence of additives in
812 combination with other techniques such as acoustic cavitation [110,111] and ultraviolet irradiation [93].

813

814 **9. Concluding comments**

815 HC technology seems to be very effective for intensification of chemical and mechanical processing in the
816 specific area of wastewater treatment. Among mechanical treatments, this innovative process is taking a more
817 prominent role, mainly due to the ease of operation, flexibility and capability to vary the required intensities
818 of cavitation conditions.

819 In the present work, the importance of the HC phenomena in wastewater treatments engineering has been
820 exemplified, explaining the principles of the process and critically examining the aspects related to the use of
821 different types of HC. The efficiency of the HC process has been reported as function of several parameters
822 that characterize HC devices and the wastewater to be treated. The optimum selection of the HC device and
823 of the operating parameters will help to obtain more overall advantages for specific applications. According to
824 the reviewed literature, there is still no fully comprehensive method to evaluate the efficiency of HC. However,
825 some main methods commonly used for this purpose have been reported.

826 This work provides a useful guideline for HC applied to wastewater treatment and acts as a starting point for
827 the HC process optimization. Moreover, the provided framework could form an origin for future literature
828 studies, focusing on several aspects, among them modeling. Mathematical models can be used as useful tools
829 to gain a better understanding of how HC devices operate in cavitating conditions and, further, to optimize
830 performances of these devices in terms of cavitation effectiveness.

831

832

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843 **Declaration of interests**

844

845 The authors declare that they have no known competing financial interests or personal relationships that
846 could have appeared to influence the work reported in this paper.

847

848 The authors declare the following financial interests/personal relationships which may be considered as
849 potential competing interests:

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854 **References**

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