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Methyl orange decolourization through hydrodynamic cavitation in high salinity solutions

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ABSTRACT

This paper presents the experimental results obtained on the decolourization of methyl orange (MO) in saline solutions, carried out through hydrodynamic cavitation (HC), used as a stand-alone technique, and in a hybrid configuration coupling with hydrogen peroxide. Experiments were carried out by adding NaCl in a solution in the range of 1.5 to 5 g/L to study the effect of salt on dye degradation by simulating the composition of a real tannery liquid waste. The results showed that the maximum efficiency was about 30% using a Venturi tube at an operating pressure of 0.55 MPa. The presence of hydrogen peroxide allowed the degradation process to be slightly below 70%; the presence of sodium chloride (5.0 mg/L) increased the decolourization efficiency up to about 70% as well, while the combined presence of NaCl and H_2O_2 had a negative outcome. The experiments on synthetic waste allowed to gain a MO degradation slightly below 90%. Process analysis was carried out to evaluate the possible integration of the HC within a real wastewater treatment plant by comparing the traditional treatment train with a new plant configuration, in which HC takes the place of a conventional coagulation tank.

1. Introduction

Advanced Oxidation Processes (AOPs) are a group of technologies based on the generation of hydroxyl radicals and aimed at oxidizing organic pollutants [1,2]. AOPs include heterogeneous and homogeneous photo-catalysis [3], Fenton and Fenton-like processes [4], ozonation [5], ultrasounds [6], microwaves [7], γ-irradiation [8], electrochemical processes [9], and wet oxidation processes [10]. Over the past two decades, the AOP treatments have been studied from both the experimental and the theoretical points of view. Despite their great potential in the field of wastewater treatment and the recent advances in scientific knowledge, AOPs are still scarcely employed on the pilot and industrial scales, mainly because of the high equipment and process costs [11]. The efficiency of processes for organic substances removal improves by combining them. Photocatalytic treatment combined with peroxide ($TiO_2/UV/O_3/H_2O_2$) resulted to be the optimal economic technology, as demonstrated by Fernandes et al. [12,13] in their studies for the degradation of complex model effluents rich in VOCs, as refinery effluents from bitumen production. The results showed a synergistic effect of ozone, hydrogen peroxide with TiO_2, and UV applied for improved COD and BOD_5 removal, as well as the degradation of the organic substances contained in the effluents.

Furthermore, AOPs efficiency is influenced by the wastewater composition, and often their residual streams need to be further treated and managed, requiring the combination of several removal techniques [14]. This is the case with the sludge-containing Fe ions produced by Fenton treatments, whose treatment is expensive and needs many chemicals and manpower [15]. Among AOPs, hydrodynamic cavitation (HC) has been receiving increasing attention and interest in recent years [16,17]. HC is the phenomenon of formation, growth, and collapse of microbubbles or cavities, with the release of a large magnitude of energy in a short span of time. It is generated by the flow of liquid through a Venturi tube or orifice plate under controlled conditions. When the pressure at the throat falls below the vapor pressure of the liquid, the liquid flashes, generating a number of cavities, which subsequently collapse when the pressure recovers downstream of the mechanical constriction [18–21]. The main chemical effects of HC are the generation of highly reactive free radicals in the aqueous environment; it is possible to use these radicals for the intensification of chemical processes such as degradation of the water pollutants [20]. HC technology has thus unique advantages in wastewater treatment, however, HC alone is not efficient and cost-effective enough to provide a satisfactory degradation extent of target compounds [22]. By combining HC with other AOPs, the efficiency of degradation of the hybrid technology can

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be considerably promoted, and the processing time and the amount of oxidant can also be reduced [23–25]. HC combined with other AOPs allowed the degradation of organic substances like pharmaceuticals, dyes, phenols, pesticides, and other chemicals. Cavitation is also used for the disinfection of water [26]. Moreover, HC can be utilized for the activation of persulfate and peroxymonosulfate. Fedorov et al. [27] studied the degradation of benzene, toluene, ethylbenzene and o-xylene in water. HC combined with PS and PMS increased the potentiality of the oxidation process, and the maximum efficiency for all organic substances was more than 90%.

The hybrid systems provide not only better yields than the HC process alone but also reduce the processing time and thus the cost of treating the polluted solution. The lower cost of treatment is definitely a positive aspect for eventual industrial-scale implementation [28]. Despite the highest degradation achieved, the time of treatment is also the shortest compared to other processes. Finally, this rapid process revealed to be the cheapest one with a treatment cost of 0.15 USD/m^3 calculated for degradation efficiency of 100% in a treatment time of 1 min. These results appear to be consistent with the comparison performed for studied processes in terms of electrical energy per order (EEO), where once more, it was proved the effectiveness of combined processes of HC and other external oxidants. A significant difference between EEO for sole ozone (0.74 kWh m^{-3} order^{-1}) and the combined process of HC/O$_3$ (0.03 kWh m^{-3} order $^{-1}$) reinforce the finding that the use of hydrodynamic cavitation and ozone lower the treatment time and consequently the cost of treatment. Rapid degradation of the target pollutant in the present study allows performing the treatment online without the need for high volume tanks due to the short retention time needed. Finally, low costs of treatment make the developed method ideal for implementation in real industrial practice.

AOPs is favored by acidic conditions, usually the pH value is modified by adding inorganic acid. In a recent study [29], the effect of sulfuric, nitric and hydrochloric acid on the radicals formation as well as harmful secondary pollutants (i.e. production of p-nitrotoluene) is reported; sulfuric acid was the best chemical for acidification while avoiding the production of secondary pollutants.

In the present study, the potentiality of hydrodynamic cavitation is analysed for the degradation of azo -dyes from synthetic solutions. Azo dyes are organic compounds bearing the functional group $R-N=N-R'$ (R and R′ are usually aryls) and are widely used to treat textiles, leather articles, and some foods [29]. Many azo pigments are non-toxic, others are mutagenic and carcinogenic; partly after their uses they are discharged in the effluents and could result in environmental damages if are released without any treatment [30]. These effluents are usually treated to remove pollutants by means of chemical/physical processes (flocculation, coagulation, membrane filtration, and adsorption) [31]. But the above mentioned treatments often offer unsatisfactory removal for the presence of some types of colour pigments, hard to degrade. Moreover, some of these methods have important disadvantages *i.e.* high-energy requirements and production of toxic sludge or other waste material that needs further treatment methods [32]. Hence alternative processes to remove dyes become necessary.

As for the degradation of dye using hydrodynamic cavitation, most scientific papers describe experimental activity carried out mainly at the laboratory scale on synthetic solutions. A review of the articles available in the literature concerning HC applied to the treatment of dye solutions is reported in previous works [22] which showed that HC alone has degradation yields not particularly high and thus to improve the dye removal efficiency, the process should be performed adding for example hydrogen peroxide, ozone or a catalyst for increasing the oxidative capacity [33]. Moreover, most of the papers present experimental activity carried out on synthetic solutions (water with a specific dye), with the aim to individuate the effects of operating conditions and understanding the phenomenology. Few works report treatment of real wastewater from dye processing, some of these are reported below.

Rajoriya et al. studied the HC process for the purification of textile dyeing industry in combination with other oxidants reagents, as air, oxygen, ozone and Fenton's reagent [34].

HC device was a slit Venturi having a throat of 3.14 mm for width, 1 mm of height and for length. The initial effluent contained a green olive color, with total suspended solids of 2634-3167 mg/L, total dissolved solids of 2935-4386 mg/L, COD comprised between 2560-4640 mg/L and TOC of 556-1184 mg/L. The degradation yields were 17%, 12% and 25% for TOC, COD and color, respectively, by using HC alone at 5 bar and pH of 6.8. The hybrid system HC with Fenton's reagent allowed to reach a degradation efficiency of 48% for TOC in 15 min, 38% for COD after 120 min and 98% of decolorization of the effluents. HC + oxygen (2 L/min) produced a degradation of 48% for TOC, 33% for COD and 62% for dye; HC + ozone allowed to reach a reduction of 48% for TOC, 23% for COD and for dye.

Wang et al. [35] studied the HC process combined with ozone (2 L/min) of real effluents from the secondary sedimentation unit of a textile wastewater treatment plant in China. The initial solutions contained residual dyes, with COD and TOC comprised between 54–68 mg/L and 25–32 mg/L, respectively. Venturi tube had internal and external diameters of 25 mm and 20 mm, respectively. The degradation yields of HC + O$_3$ were 36% for COD, 23% for TOC, 71% for UV$_{254}$, and 90% for color. These were higher than the single treatment. HC + O$_3$ was the most energy-efficient.

Zampeta et al. [36] describe their study about a pilot-scale novel hydrodynamic cavitation reactor used for the degradation of industrial-grade dyes and of real ink wastewater from the printing process. The HC device included a Venturi tube containing an orifice plate. Experimental results showed that 4 bar was the optimal inlet pressure for dye degradation. The process yields were relatively low, the combination of HC and hydrogen peroxide allowed to increase the degradation. Under the optimal conditions (4 bar, HC+ 1 g/L of hydrogen peroxide), COD removal was analyzed for both real grade dyes and wastewater. COD removal was 100% for black, and 38%, 25%, 67% and 78% for the red, yellow, cyan and green dyes, respectively, whereas 55% COD removal was observed for the wastewater treatment [37].

The cited articles describe the efficiency of the HC alone and in combination with other oxidant reagents, no data about the effect of salinity on degradation yield was investigated.

Among the different compounds that are present in a real tannery waste, perhaps the presence of salts in solution affects sonochemistry the most, but until now no consensus has been reached. Particularly, it is well recognized that the presence of a high NaCl concentration in aqueous solutions modifies the water vapor pressure, the surface tension and the number of bubbles [38], thus influencing the yields. As for the degradation of Rhodamine B in aqueous solution, a research study showed that there may be an optimum amount of NaCl to increase removal rate [39]. Other studies on the same molecule by other research group found that Rhodamine B degradation was favored by an increase in electrical water conductivity produced by the presence of NaCl up to a maximum followed by a decrease [40]. No studies have been so far conducted on the effect of NaCl on MO degradation by using HC.

In the present paper, to enhance the oxidative degradation efficiency of HC, a combined process (HC with hydrogen peroxide) is tested for the degradation of a MO in a solution of high salinity, to complete a previous experimental activity in which MO degradation was studied in the presence of metal ions (iron and nickel, [41]) and with hybrid treatments (HC + Fenton and HC + H$_2$O$_2$). A lab-scale apparatus with a cavitation device (Venturi) is used to carry out experimental runs on pollutant degradation, by varying the main process operating variables (temperature, pressure, dye concentration) in the hybrid process (HC/hydrogen peroxide) and with adding NaCl to the MO solution at a concentration varying in the range 1.5 – 5 g/L. The aim of the research is process optimization to find the best experimental conditions among those studied, also in the presence of salts in the solution. Moreover, a test on a synthetic waste with the simultaneous addition of 4.44 g/L di NaCl, 0.20 g/L di NH$_4$Cl and 1.10 g/L di Na$_2$SO$_4$ allowed to quantify the

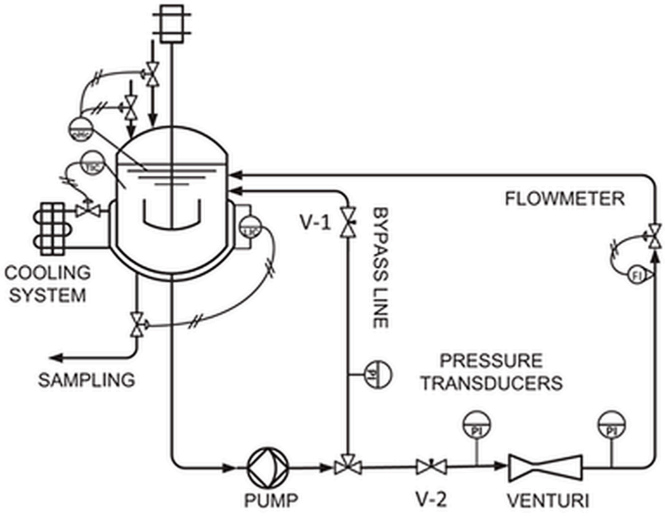

Fig. 1. Scheme of the laboratory apparatus used for the hydrodynamic cavitation experiments.

degradation efficiency in the presence of several salts to simulate a real dyeing wastewater. Finally, a process analysis is carried out to evaluate the possible integration of the hydrodynamic cavitation within a real wastewater treatment plant, by comparing the traditional treatment train with a new plant configuration, in which HC takes the place of a conventional coagulation tank.

2. Materials and methods

2.1. Materials

Methyl orange dye was used to perform hydrodynamic cavitation tests. The solutions of dyes were prepared using distilled water for all the experiments. Sodium hydroxide (Fluka Chemika, >97%) and sulphuric acid (Carlo Erba, 96%) were used for adjusting the pH solution. Hydrogen peroxide (30% v/v, Carlo Erba) has been added in order to test their ability to improve the oxidant capacity of the process. NaCl (Carlo Erba, 96%) was used to simulate a real effluent with high salinity.

2.2. Experimental apparatus

Hydrodynamic cavitation experiments have been performed by using the lab-scale experimental apparatus showed in Fig. 1, consisting in a closed loop circuit.

It incorporates a stirred reactor with cooling system, a recycling line, a centrifugal pump, pressure and flow meters. The main branch passes through a convergent–divergent nozzle (Venturi tube), in which cavitation occurs, and ends into the tank. The reactor has a volume capacity of 1 L and it has a thermostatic system to keep constant the temperature, in this work at T=20 °C. The pump (Fluid-o-Tech, TMFR2) has a maximum electrical power absorption of 375 W and rotation speeds in the range of 1100–3500 rpm. The system is equipped with a flow meter (Comac Cal, Flow 38) and two manometers (PI, Barksdale Control Products, UPA2 KF16809D). The cavitation device is in Plexiglass having the converging and diverging section of 32 mm and 46 mm, respectively. The orifice is 2 mm and the divergence angle of 5.74°. The dimensions of Venturi were extrapolated by Bashir et al. [42] and it was used for other research activity [23,41]. Venturi tube has a maximum diameter of 12 mm as piping diameter, while the minimum one is 2 mm, resulting in β=0.167. The system is equipped with control valves V-1 and V-2 to regulate inlet pressure and consequently, the flow rate through the device. The pipeline is in Rilsan material, fitting is in polyprolene, valves and pump is in stainless steel.

2.3. Experimental methodology

Preliminarily, even if the research apparatus has been already used in a previous experimentation, a new rotary gear pump has been inserted in the lab-scale apparatus, hence a study of the hydraulic curve of the circuit has been carried out; this to choose the best rotation speed of the new pump, that was fixed at 2000 rpm. Afterwards, four series of experimental runs have been performed. In a first series of experiments, the degradation of methyl orange (MO) by using hydrodynamic cavitation was performed at an inlet gauge pressure p in the range 0.3 to 0.6 MPa and pH equal to 2, as defined in previous studies [23,41]. A blank test was carried out at a very low pressure value, when no cavitation occurred, to verify the eventual spontaneous degradation of MO, due to exposure to light. This was quantified in 2-3%, as reported elsewhere [23].

In a second series of experiments, the synergistic effect of HC combined with different amounts of hydrogen peroxide was investigated on dye degradation of aqueous solutions having MO concentration equal to 5 ppm.

In a third series the MO degradation in NaCl solution having concentrations in the range 1.5 to 5.0 g/L was evaluated.

Afterwards, a double test on a synthetic solution which simulate a real tannery waste has been carried out, in which different salts have been added (4.44 g/L di NaCl, 0.20 g/L di NH_4Cl and 1.10 g/L di Na_2SO_4), reproducing a liquid waste composition taken from the literature [43].

All the experiments have been performed by using the Venturi tube as HC device (Fig. 1). The solutions were circulated in the plant for 60 min as required by the experiments. The temperature was maintained constant (T = 20 °C) by cold water that crosses in the jacketed system of the reactor. The samples were collected at regular intervals of 10 min and the analysed to quantify the extent of MO degradation.

2.4. Analytical procedure

The collected samples were analysed using UV-Spectrophotometer (Cary 1E, UV Visible spectrophotometer Varian) in order to observe a change in the absorbance of methyl orange with time at a specific wavelength (λ), that depended on pH value. At the operating pH value (pH = 2), the absorption spectrum of the dye was characterized by a peak in the visible region with a maximum of absorbance at 507 nm.

The concentration of dye was then calculated by the calibration curves. The decolourization efficiency η was determined according to Eq. (1):

$$\eta = decolourization\ efficiency = \frac{[MO]_0 - [MO]_t}{[MO]_0}\ x\ 100 \tag{1}$$

Where $[MO]_t$ and $[MO]_0$ were the concentrations of methyl orange in ppm at a generic time (t) and at the initial time.

In each test, the average experimental error recorded was 5%.

2.5. Process analysis

2.5.1. Scope definition and background on process

Scientific literature shows that HC can actually be used for industrial wastewater treatment as an alternative to more traditional processes [37], anyway there are no scientific articles comparing the various process alternatives. Hence, the scope of the proposed process analysis is to show even if in a preliminary way an economic comparison between a traditional process based on coagulation and a treatment based on hydrodynamic cavitation. Two alternative processes have been proposed to treat dyeing wastewaters. The first one is drawn from the paper by Lofrano et al. [44] (Process A), while the second process has been proposed in according to the experimental results reported in the present work (Process B). In details, Process A includes coagulation by

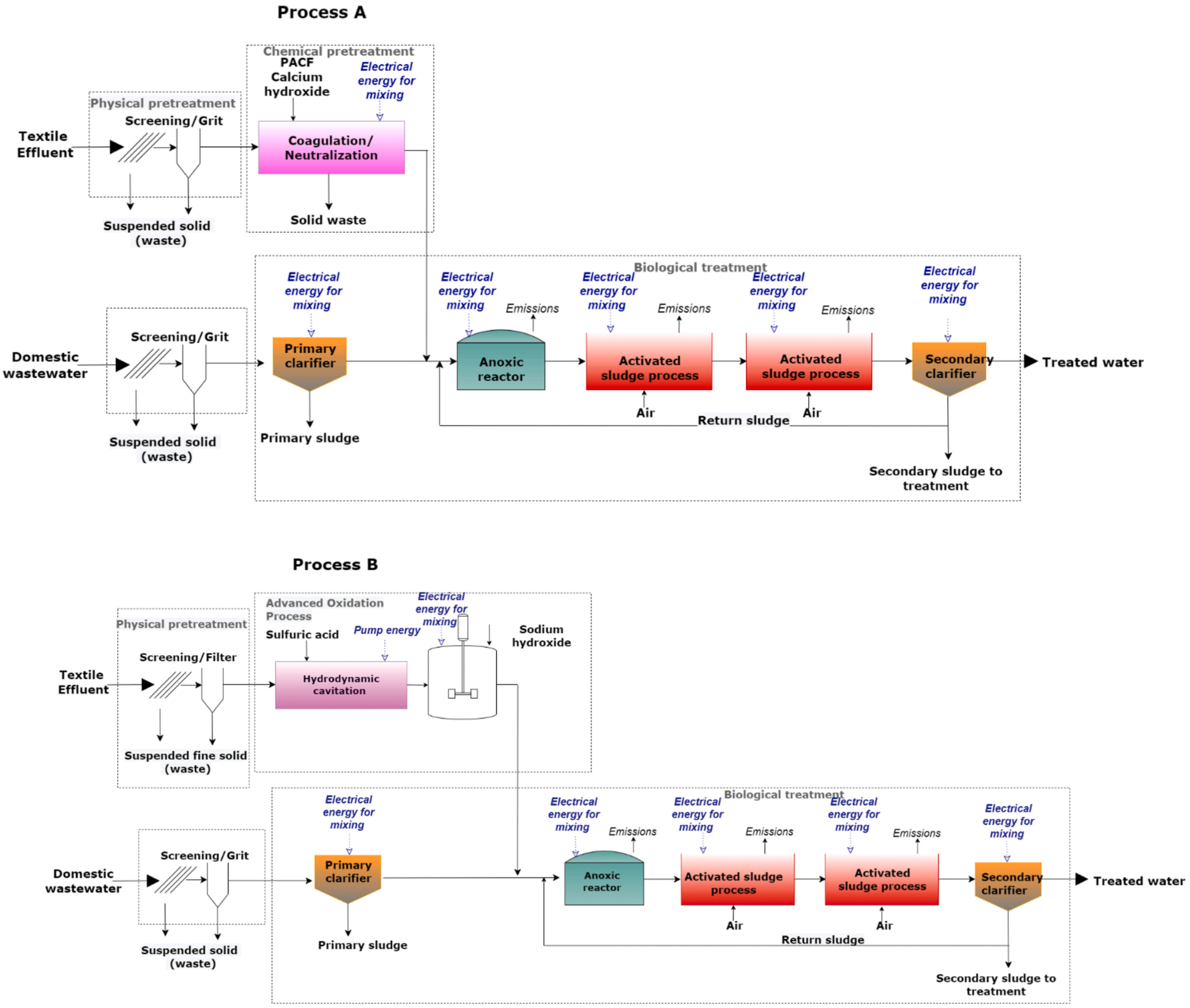

Fig. 2. Block scheme of the Processes A and B.

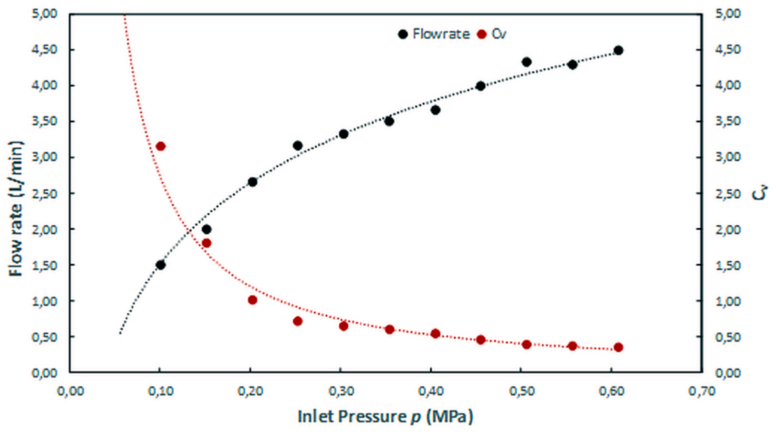

Fig. 3. Hydraulic curve of the liquid pumping circuit.

aluminium ferric chloride (PAFC) and basification up to pH = 8.5 with adding calcium hydroxide. After this pre-treatment the effluent requires a biological treatment for COD reduction. Process B operates with hydrodynamic cavitation to remove the dye, but also in this case the treated water cannot be discharged as COD and other substances exceed the legal limits to the discharge (Dlg. 152/06). It is supposed that after

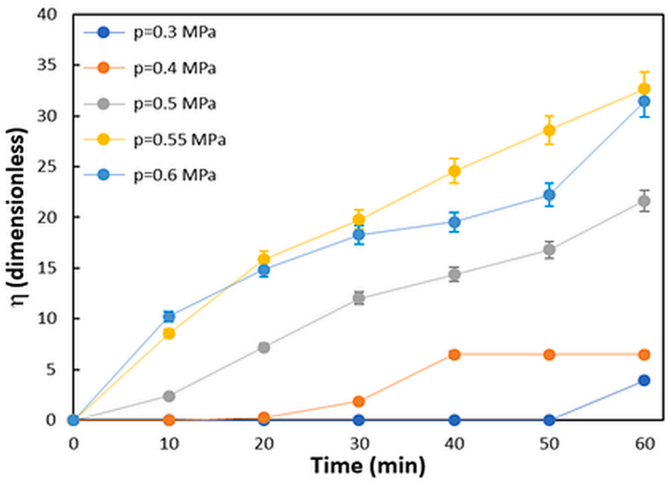

Fig. 4. Effect of inlet pressure on MO degradation efficiency.

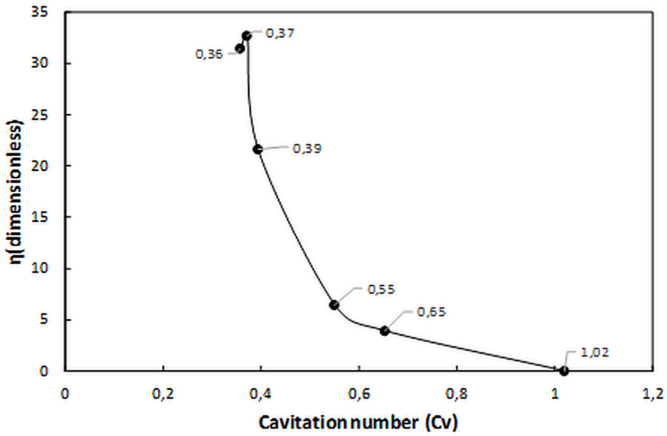

Fig. 5. Effect of cavitation number on MO degradation efficiency.

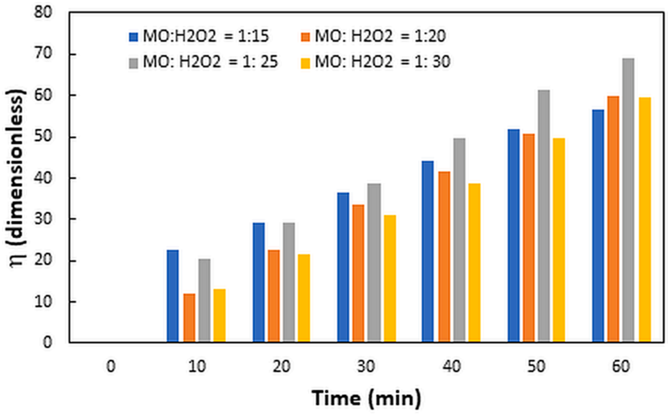

Fig. 6. Effect of hydrogen peroxide on MO degradation efficiency.

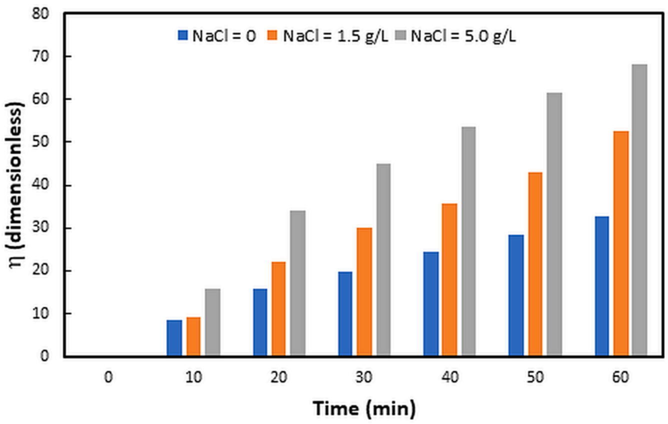

Fig. 7. Effect of NaCl on MO degradation efficiency as a function of treatment time.

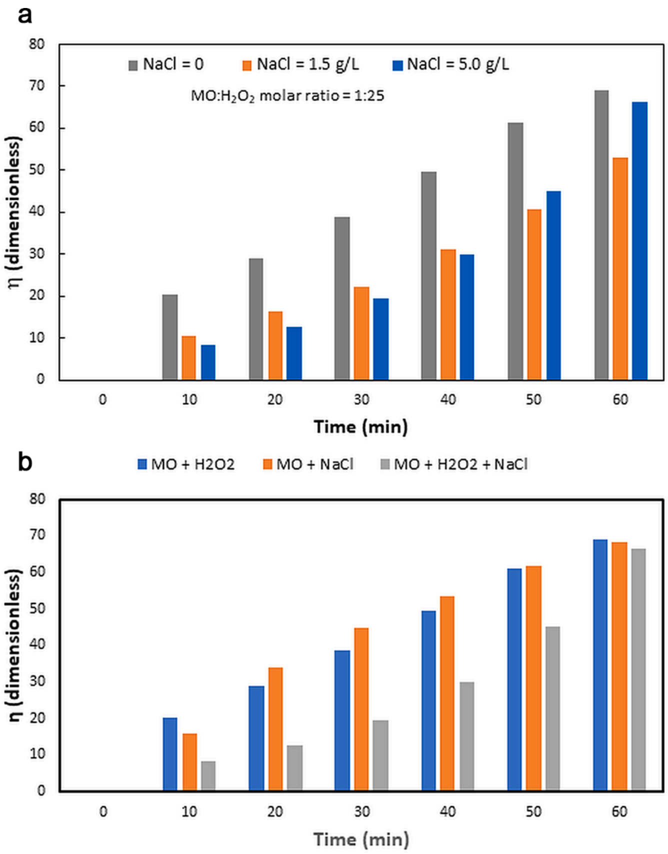

Fig. 8. (a) Combined effect of NaCl and H_2O_2 on MO degradation efficiency as a function of treatment time. (b) MO degradation efficiency comparison between H_2O_2 (MO: H2O2 molar ratio = 1:25), NaCl (5 g/L) and H_2O_2 (MO: H_2O_2 molar ratio = 1:25), + NaCl (5 g/L).

this pre-treatment, as for Process A, a biological treatment is necessary to reduce pollutant concentrations.

The proposed schemes include the combination of a pre-treatment followed by the biological process to refine the effluent purification process. AOPs and biological process is a sequence that is very often used for wastewater treatment [45]. The oxidation processes allow the destruction of organic matter into intermediates that can be more easily digested by bacteria, as by- products nitro-products can be formed due to chemical oxidation reactions [46], so the downstream biological treatment is also useful to reduce the possible production of nitrogen products.

Mass and energy balances have been performed considering a wastewater treatment plant that works in a continuous mode with a maximum plant capacity of 10368 m^3/d. The effluents are for the 50% constituted from tannery and textile wastewaters, the remaining 50% is civil wastewater, as in a real wastewater treatment plant located in the south of Italy [47].

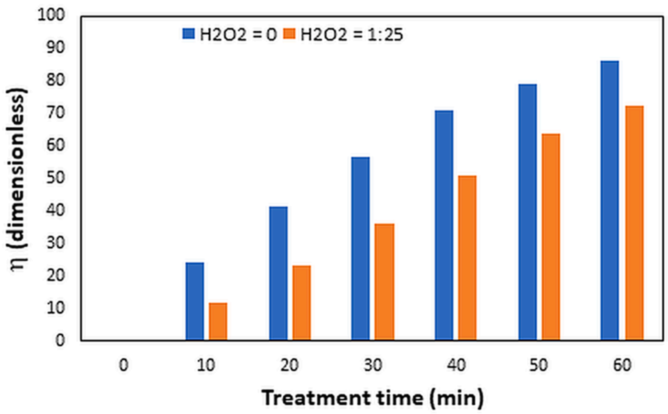

Fig. 9. MO degradation efficiency as a function of treatment time for a synthetic real waste in the absence and in the presence of hydrogen peroxide.

As proposed by Lofrano *et al.* [44], industrial wastewater can be treated by coagulation adding PAFC (900 mg/L). Calcium hydroxide is also added to adjust the pH values from 4-5 until 8.5. This stage ensures significant removals of COD and TSS, higher than 60% for both parameters [44], Process A. Alternatively, this step can be replaced by hydrodynamic cavitation operation (Process B). Experimental results (see Section 3) showed that HC effectively removes the dye, but COD remains almost unchanged while increases the biodegradability of the wastewater, therefore favouring the subsequent biological processes [48].

After these treatments (coagulation for Process A, or HC for Process B), the industrial wastewater is sent to the biological section of the plant constituted by a sedimentary clarifier, an anoxic process followed by two aerobic bioreactors which also receives the municipal effluent. This sequence of operations allows to reduce the pollutant concentrations.

Fig. 2 shows the block scheme of the Process A and Process B.

Processes A and B have been simulated by Intelligen's SuperPro Designer (SPD), a specific software for the simulation of biological and chemical processes. The input data are the initial volume, compositions of the industrial and municipal effluents. For the biological sections the checked default input of the software were used for simulation. The output of the software are the mass and energy balances and the equipment size. These data have been used to perform a technical and economic analysis in order to define the optimal process configuration for the wastewater treatment plant.

All data are the basis of utility consumptions and equipment cost used for the estimation of the economic feasibility of the simulated processes.

2.5.2. *Preliminary economic feasibility*

The data from process simulation has been used to perform an economic analysis of the process schemes A and B, considering the costs of equipment, raw material and energy consumption personal and solid waste management. Economic analysis includes the operation and maintenance costs (OPerating EXpense, OPEX), and the non- recurring costs (NRC) or capital costs (CAPital Expenditure, CAPEX) [49–51]. OPEX has been calculated starting from the mass and energy balances, while the CAPEX is estimated from the equipment cost (PEC), on the basis of which the total construction cost (TCC) and total investment cost (TCI) are calculated. PEC have been estimated considering the specific literature and have been discounting to 2021 considering the inflation in Italy [52].

Once the construction costs of the main treatments units (as biological reactors, clarifier) are estimated, the additional construction costs (as for screening, sand trap, control and maintenance buildings and storage facilities, chemical dosing units and sludge dewatering as filter press, decanters, ..), can be calculated by multiplication with a costing factor (F_{ac}). F_{ac} is a function of the size of wastewater treatment plant, and in the specific case F_{ac} is equal to 1.4. Another factor is F_i, a factor whose value considers other costs as design and engineering, site preparation, contingency, start-up of the plant and miscellaneous. In the specific case, as suggested by the literature, F_i is 1.7 [52]. Hence, TIC is estimated using the following relation:

$$\mathrm{TIC} = \mathrm{TCC} \times F_{ac} \times F_i \tag{2}$$

Annual operating costs have been estimated taking into account the following items: personnel, maintenance and insurance, chemicals consumptions, utilities, electrical energy mainly for aeration, sludge disposal, effluent discharge.

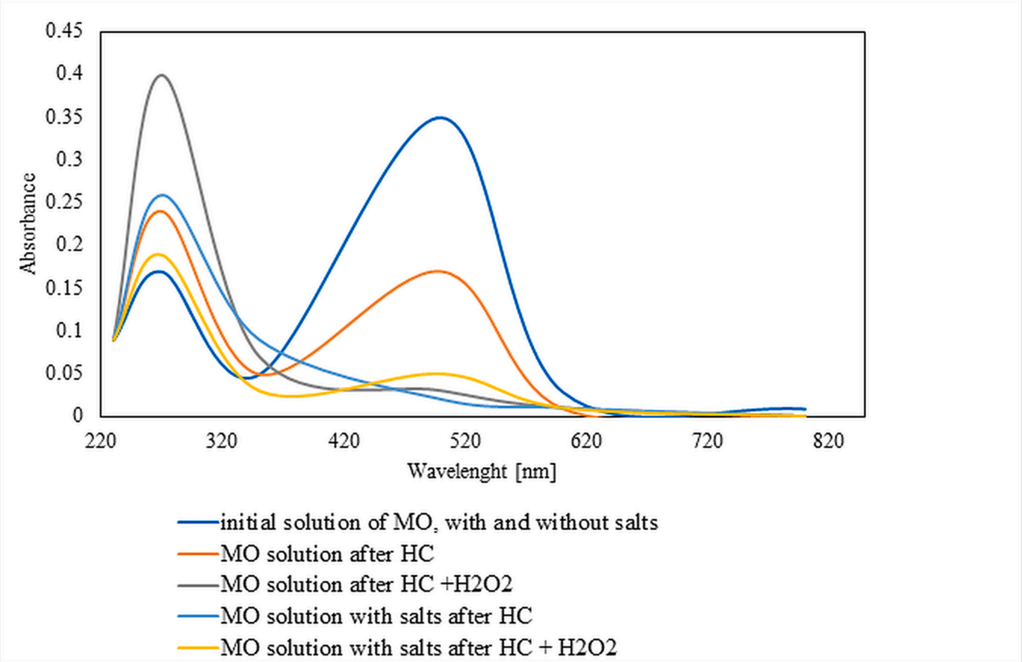

Fig. 10. Uv-vis spectra of MO degradation after HC treatments.

Table 1
Mass Balances of the Processes A and B.

PROCESS A			
Input	**t/h**	**Output**	**t/h**
Pre-treatment process by coagulation			
Industrial wastewater	215.198 (216 m^3)	Solid from screening/grit	0.341
Calcium hydroxide	0.001	Wastewater	201.659
PACF	0.194	Sludge from clarifier	13.666
Sum			
Biological section			
Wastewater	201.659	Sludge from grit/primary clarifier	1.082
Municipal wastewater	213.853	Sludge from secondary clarifier	2.693
Oxygen	0.1472	Air emission	0.1478
		Treated water	411.724
Sum		**Sum**	
PROCESS B			
Input	**kg/batch**	**Output**	**kg/batch**
Pre-treatment process by hydrodynamic cavitation			
Industrial wastewater	215.198 (216 m3)	Solid from screening/grit	0.341
Sulfuric acid (98%)	0.009	Wastewater	201.659
Sodium hydroxide (solid)	0.0086		
Sum			**120**
Biological section			
Wastewater	201.659	Sludge from grit/primary clarifier	1.082
Municipal wastewater	213.853	Sludge from secondary clarifier	1.894
Oxygen	0.1472	Air emission	0.1467
		Treated water	425.736
Sum		**Sum**	
Process A	**kWh/m^3**	**kWh**	
Coagulation	0.02	4.32	
Screening		6	
Primary clarifier		0.5	
Anoxic reactor	1	433	
First aerobic reactor	2	866	
Second aerobic reactor	9.5	866	
Secondary clarifier		0.5	
Total		**9970.32**	

Table 2
Energy consumption.

Process B	**kWh/m^3**	**kWh**
Pump		42
Screening/filter		6
Primary clarifier		0.5
Anoxic reactor	1	466
First aerobic reactor	2	933
Second aerobic reactor	2	933
Secondary clarifier		0.5
Total		**10767**

3. Results and discussions

3.1. Characterization of hydraulic curve of the liquid pumping circuit

The hydraulic curve of the HC experimental apparatus is shown in Fig. 3.

As it appears from the analysis of the Fig., at the chosen pump speed rotation (2000 rpm), the cavitation number (C_v), defined in Eq. (3), varies in the range between 0.4 and 3.2 in the investigated inlet pressure range (0.10-0.61 MPa):

$$C_v = \frac{P_2 - P_v}{0.5\rho v_o^2} \tag{3}$$

Table 3
Estimation of the total investment cost.

PROCESS A		
	Size	**Cost**
Coagulation	487 m^3	326,046.50 €
Primary clarifier	483 m^3	323,368.50 €
Anoxic reactor	443 m^3	216,135.40 €
First aerobic reactor	965 m^3	548,964.00 €
Second aerobic reactor	965 m^3	548,964.00 €
Secondary clarifier	978 m^3	654,771.00 €
TCC		2,113,478.40 €
TIC		5,030,078.58 €
PROCESS B		
	Size	**Cost**
Hydrodynamic cavitation section	42 kW (for pump)	81,000.00 €
Primary clarifier	483 m^3	323,368.50 €
Anoxic reactor	475 m^3	225,371.93 €
First aerobic reactor	1037 m^3	572,921.32 €
Second aerobic reactor	1037 m^3	572,921.32 €
Secondary clarifier	1050 m^3	683,281.56 €
TCC		2,468,989.64 €
TIC		5,876,195.35 €

where p_2 and p_v are the pressure downstream of Venturi device and the vapour pressure of the liquid, respectively; v_o is the fluid velocity at the convergent. From the graphs it can be seen that as the pressure upstream of the Venturi increases, the flow rate increases too and the cavitation number decreases due to the greater kinetic energy of the circulating liquid, falling below the unity for an inlet pressure above 0.2 MPa. As C_v decreases and becomes less than one, fluid velocity grows, resulting in an increased turbulence and, therefore, cavitation occurs with the formation and subsequent implosion of the cavitation bubbles. Therefore, to be sure to work in cavitating conditions, experiments are conducted for an inlet pressure above 0.2 MPa.

3.2. Effect of the inlet pressure on methyl orange degradation

The first series of experiments of hydrodynamic cavitation has been performed to define the effect of the inlet pressure on dye degradation. The initial methyl orange concentration was 5 ppm and the tests have been carried out at an inlet pressure on cavitation device varying in the range 0.3 – 0.6 MPa for a treatment time up to 60 min. For pressures below 0.3 MPa dye degradation is very low and it is not shown. The results obtained are shown in Figs. 4 and 5, which show the behaviour of degradation efficiency as a function of the treatment time with varying the inlet pressure (Fig. 4), and as a function of the cavitation number, as defined in Eq. (3) (Fig. 5).

As can be seen from Fig. 4, with increasing the inlet pressure, the degradation efficiency increases as well, up to an inlet pressure p=0.55 MPa; for higher pressure, there in an inversion in this trend, and the degradation efficiency decreases. This is a trend already observed in previous works and quite common in cavitation investigations. When pressure increases, the yield of degradation is reduced because super cavitating conditions occur which disturb the growth of the bubbles downstream the orifice. The production of numerous cavities results in the formation of a large vapor pocket, where a lower formation of OH radicals takes place. Hence in this work, hereinafter the HC process has been performed at an optimum inlet pressure of 0.55 MPa. In these conditions, for the same initial concentration of dye (5 ppm), the maximum degradation yield was slightly above 30% after 60 min of treatment by using HC alone. Fig. 5 clarify what happens with decreasing pressure; the cavitation number decreases and for a $C_v \leq 1$ (for $p \leq 0.2$ MPa, see Fig. 3), no cavitation occurs, as a consequence no degradation takes place. Also in this representation, it is well visible the inversion of the efficiency trend that happens at p=0,6 MPa.

Table 4
Operational cost for the Process A and B ([37]; * Italian market. Average (day/night) electricity price; ** [68]).

Operational cost item	Range*	Unit of Measure	Chosen value		
				PROCESS A	**PROCESS B**
Personnel	2-5%	€/y	2.5%	125,751.96 €	146,904.88 €
Operation	0.5-1.5%	€/y	1%	50,300.79 €	58,761.95 €
Maintenance - civil	0.5-1%	€/y	0.75%	11,317.68 €	13,221.44 €
Maintenance – mechanical/E&I	1-2.5%	€/y	1.5%	52,815.83 €	61,700.05 €
Insurance	0.2-0.4%	€/y	0.3%	15,090.24 €	17,628.59 €
Electrical energy	0.18*	€/kWh		3,431,621.38 €	3,751,207.20 €
Chemical consumption				357,758.40 €	83,834.95 €
Sludge transport & disposal (coagulation)	500 (dry sludge)**	€/t		5,388,714.00 €	
Sludge transport & disposal (Biological section)	60-500	€/t TSS	280 €/t TSS	222,311.06 €	804,710.03 €
TOC				**9,655,681.33 €**	**4,937,969.09 €**

Table 5
Chemical consumption for the Process A and B (data from vendors).

Raw materials	**Process A**		**Process B**	
	€/kg	€/y	€/kg	€/y
Calcium hydroxide	0.1	876.00 €		-
PACF	0.21	356,882.40 €		-
Sulfuric acid		-	0.19	15,279.19 €
Sodium hydroxide		-	0.91	68,555.76 €
Total		357,758.40 €		83,834.95 €

3.3. *Effect of hydrogen peroxide and NaCl on methyl orange degradation*

Since the main driving mechanism for the degradation of pollutants by using hydrodynamic cavitation is the formation and subsequent reaction of hydroxyl radicals with the pollutant molecules, if hydrogen peroxide is added to the solution, an increase in the degradation yields would occur, due to the supplementary source of OH radicals [53]. It is to point out that previously two blank tests of dye degradation have been performed in the absence of any cavitation device, with adding hydrogen peroxide alone, at a MO concentration=5 ppm, pH=2, 20°C, t=60 min and H_2O_2 concentration = 0.005%v/v. The maximum degradation yield for the blank test with hydrogen peroxide alone was 6%. That is hydrogen peroxide, despite being an oxidant agent, when used alone did not produce sufficient OH radicals to degrade the dye. An intensification in the production of OH radicals can be carried out combining HC and H_2O_2.

The following Fig. 6 shows the experimental series obtained by measuring the MO degradation efficiency as a function of time when growing amounts of hydrogen peroxide are added to the cavitating solution, molar ratio MO:H_2O_2 in the interval of 1:15-1:30. The inlet pressure was fixed at 0.55 MPa, while the initial methyl orange concentration was fixed at 5 ppm.

The analysis of the figure allows to clearly see that there is a decay in the degradation yield of the dye when exceeding the value of MO: H_2O_2 molar ratio equal to 1:30, that appears to be as the optimal dosage. The worsening of performance at higher hydrogen peroxide concentrations is due to the recombination of OH radicals, a possible negative outcome of the oxidant which may react with the hydroxyl radicals thus decreasing the radicals present in solution, destined to degrade methyl orange. Recombination reactions are those listed below (Eqs. (4)–(6)), [54]:

$$OH + OH \rightarrow H_2O_2 \tag{4}$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{5}$$

$$OH + HO_2 \rightarrow + H_2O + O_2 \tag{6}$$

This is a confirmation of the results obtained in previous experiments carried out at a different inlet pressure, that is in the hybrid technique HC/H_2O_2, the optimal dosage of H_2O_2 to gain a better efficiency is not trivial and must be experimentally detected. The optimal amount of oxidant agent is responsible for an improvement in degradation: an excessive H_2O_2 concentration produces lots of radicals and the rate of reaction between OH radicals and dye molecules is surpassed by the rate at which OH radicals get scavenged by H_2O_2 itself [55].

Fig. 7 shows the experiments carried out on a synthetic solution in which NaCl is added to generate a high salinity, typical of a real tannery waste. In details, two sodium chloride concentrations have been tested, 1.5 g/L and 5.0 g/L, representative of the conditions of a medium and high salinity real tannery liquid wastes.

It can be observed that with respect to the degradation in the absence of sodium chloride, the adding of NaCl has a positive outcome on the decolourization of the dye, that grows up to about 70% after an hour of treatment time.

Properties as viscosity and surface tension of solutions affect the hydrodynamic cavitation. An increase in viscosity has a negative effect on the process due to the reduction of cavitational effect on bubble growth and collapse [24].

In the specific case the change in viscosity does not change significantly, so the effect can be neglected, considering also that the aqueous solution is a Newtonian fluid for which an increase in liquid viscosity does not significantly affect the collapse pressure of cavities [26].

The positive effect of NaCl on hydrodynamic cavitation can be due to the reduction of vapor pressure and increase of superficial tension of the solution, thus promoting a more violent collapse of the cavitating bubble [56,57].

Another article reported that the presence of chloride ions improves the degradation process, due to the scavenging effect of OH radicals in the chlorine pathway, which implies the formation of species with a lower oxidation potential [58].

Fig. 8 shows the results obtained on MO degradation with using the optimal dosage of hydrogen peroxide previously found (MO:H_2O_2 molar ratio = 1:25) when NaCl is added in solution. In the plot, the

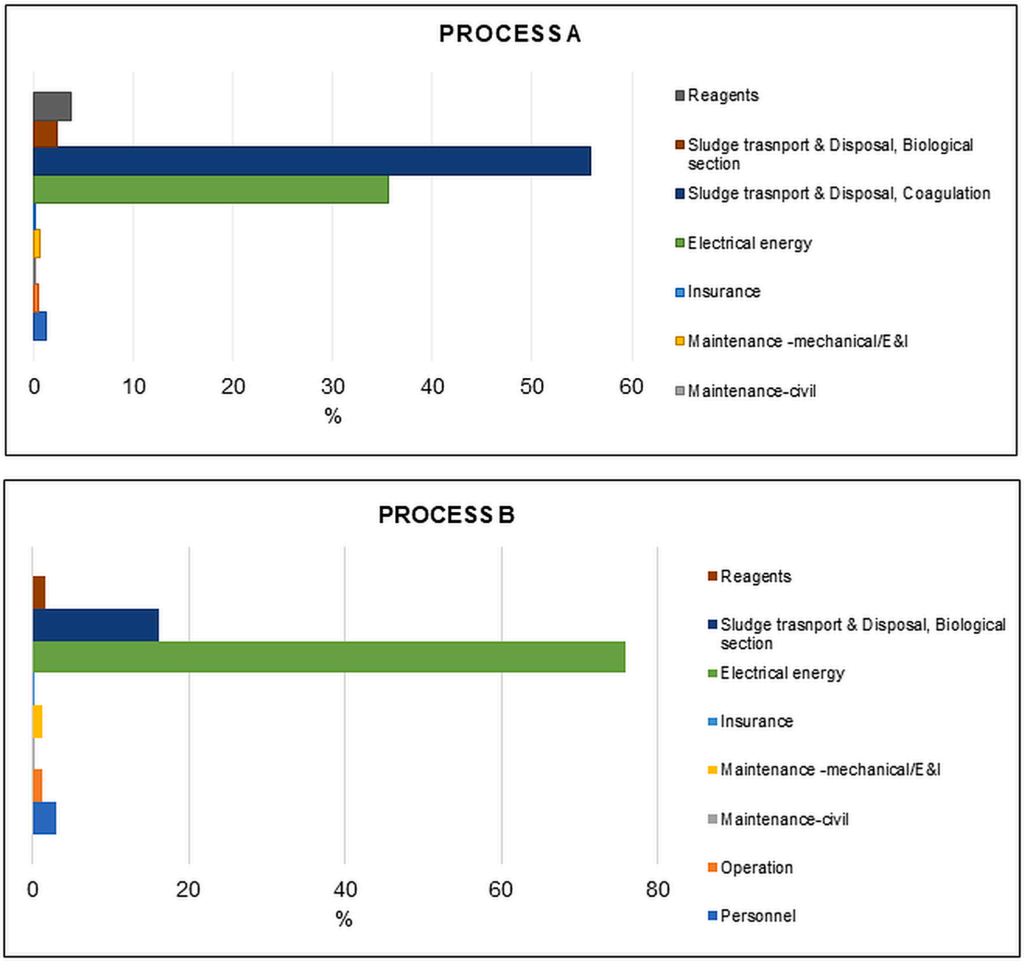

Fig. 11. TOC distribution for the Process A and Process B.

experiments without NaCl (Fig. 4) are here reported for a comparison.

As can be seen, the combined presence of NaCl and H_2O_2 has a bad influence on decolourization efficiency. The presence of hydrogen peroxide increases the amount of OH radicals, it can be assumed that salt reacts with these radicals reducing the free *OH* for degradation process of dye [59].

Finally, Fig. 9 shows the MO degradation efficiency as a function of the treatment time for a liquid waste simulating a real tannery wastewater, in which 4.44 g/L di NaCl, 0.20 g/L di NH_4Cl and 1.10 g/L di Na_2SO_4 were added, according to a research article on tannery wastewaters [43]. As can be noted, once again the presence of H_2O_2 get worse the degradation efficiency, that after an hour of treatment time reaches 86% with using HC alone, while it is slightly above 70% when hydrogen peroxide is added to the solution.

3.4. Analysis of degradation mechanism

The absorption peaks are in the visible and ultraviolet area due to presence of azo group and benzene ring in the structure of methyl orange [60]. The oxidation the process breaks down dye molecules (azo group) in aromatic intermediate compounds such as dimethyl-aniline, aniline, benzene sulfonic acid and others. The last products are aliphatic acids and at the end of reaction carbon dioxide.

Fig. 10 reports the UV-spectra of the dye solutions before and after HC treatment.

More in details, the *initial solution* (dark7 blue curve) is the aqueous solution containing the MO before the HC treatment, the UV profile being the same with and without salts, since the added substances are colourless. It is possible to observe two main peaks at 270 nm (benzene rings) and 507 nm (azo groups); the second one is due to the chromophoric group of methyl orange. The orange curve shows the absorbance profile of the solution without salts after the HC treatment at the optimal condition (0.55 MPa, decolourization yield of 30%); the grey curve reports the absorbance of dye solution without salts after treatment of HC combined with hydrogen peroxide under optimal conditions (0.55 MPa and optimal molar ratio of dye: H_2O_2 = 1:25, decolourization yield of 70%); the light blue curve represents the profile for the synthetic solution with salts, mimicking the real waste, after HC treatment (0.55 MPa, decolourization yield of 86.13%); and the last one (yellow curve) shows the absorbance values of the synthetic solution with salts after HC and hydrogen peroxide combined treatment (0.55 MPa, optimal molar ratio of dye: H_2O_2 = 1:25, decolourization yield of 72.6%).

The peak at 507 nm decreases in all treatments and this is most evident in the combined processes when the dyeing solution is treated with HC and hydrogen peroxide and in the experimental test on the synthetic solution with salts, treated with HC alone. The reduction of this peak indicates that the azo groups are destroyed by hydrodynamic cavitation. In the solution with MO without salts, an almost complete destruction of these groups occurs by adding hydrogen peroxide, which increases the efficiency of the oxidation process. The same results are obtained for the treatment of the salted dyeing solution by using HC alone. For this kind of solution, mimicking a real liquid waste, the hydrogen peroxide addition during HC seems to worsen the process. This confirms what was previously discussed, that is the presence of a negative interaction between hydrogen peroxide and anions and cations, that reduces the efficiency of the advanced oxidation process. It is also

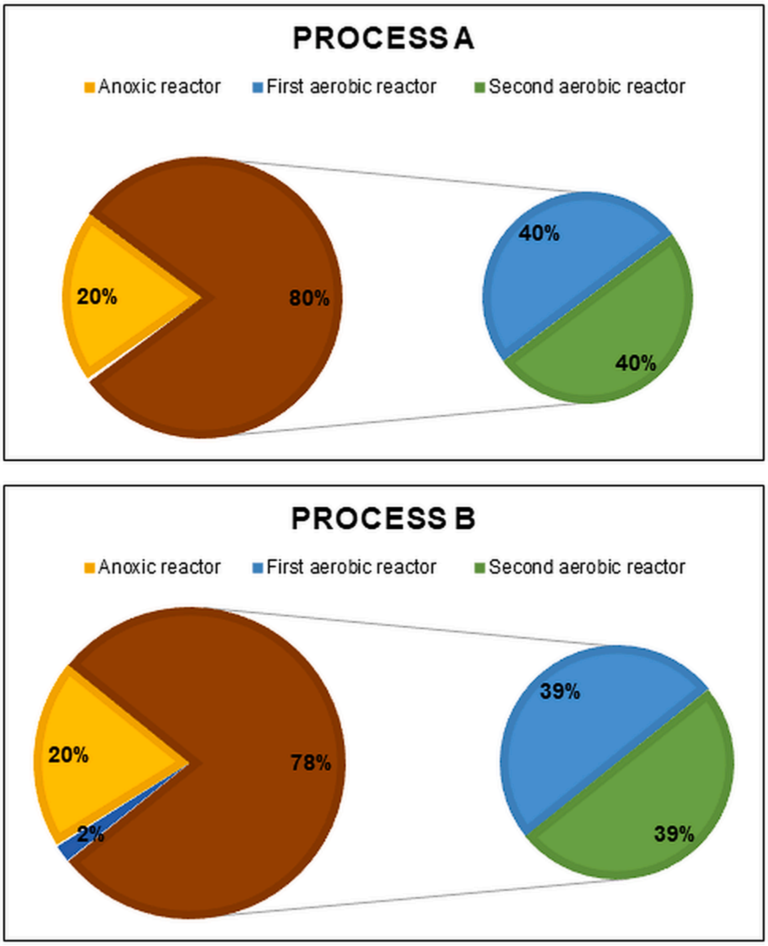

Fig. 12. The main items of the electrical energy consumption for the Processes A and B.

Table 6
Total annualized cost for Process A and B.

Process A		
ai,n	11.25	civil works
ai,n	9.12	mechanical and E&I installations
AIC	134,042.69 €/y	civil works
AIC	386,011.26 €/y	mechanical and E&I installations
TOTAL AIC	520,053.95 €/y	
TOC	9,655,681.33 €/y	
TAC	10,175,735.27 €/y	
Process B		
ai,n	11.25	civil works
ai,n	9.12	mechanical and E&I installations
AIC	156,590.21 €/y	civil works
AIC	450,942.77 €/y	mechanical and E&I installations
TOTAL AIC	607,532.97 €/y	
TOC	4,937,969.09 €/y	
TAC	5,545,502.07 €/y	

possible to observe the increase in the peak in the UV region which corresponds to the presence of aromatic substances, due to the degradation reactions. In the experiments conducted with dye solutions without other substances, the presence of hydrogen peroxide increases the efficiency of the oxidative process, while again it turns out that the combination HC + H_2O_2 is disadvantageous for the degradation process in the case of salted dyeing solutions.

It is clear that the processes studied lead neither to complete decolorization and degradation of the dye, since the yields are not 100% and the two characteristic peaks do not disappear. The treatment succeeds in breaking the complex dye molecule into less complex molecules that can be further treated by a downstream process for example biological, as suggested in the process analysis.

3.5. *Comparison study on removal treatment of methyl orange and toxic dyes*

Solutions contaminated by toxic dyes can be treated by using different technologies as membrane filtration, ion exchange, adsorption and AOPs. Usually, these processes are followed by biological treatments. As regards HC, the process alone does not achieve comparable yields with the other listed technologies. Indeed, removal yields near to 100% and greater than 80% can be obtained by membrane processes (nanofiltration and reverse osmosis) and ion exchange [61–63]. Similar yields can be obtained by combining HC with other oxidants such as hydrogen peroxide, ozone. As regards the technical aspects, each process has advantages and disadvantages. Adsorption has a high adsorption capacity for dyes, as demonstrated by the high removal efficiency, but has low surface area and high cost of the adsorbents. There is no loss of material in the case of ion exchange but this technology cannot be used with disperse dyes. Membrane filtration has a high removal yields but there is a production of sludge. Anaerobic processes produce by-substances that can be used as an energy source, but have a long time processing. Aerobic degradation has the advantage of low treatment costs, but provides suitable environment for growth of microorganism and the treatment time is long. In general, the biological treatment poses a risk of microbiological contamination and a relevant production of sludge to dispose [64,65]. Among the AOPs, photocatalyst has a low cost operational and economically feasible, ozonation does not produce sludge but has high operative costs. The main disadvantages is due to the release of by-products that can be treated by biological processes. Hydrodynamic cavitation is an innovative AOPs, it is technically a simple system that needs a static equipment (cavitation device), so the fixed costs are low, electrical consumption is mainly due to the pumping system. The advantage of the hybrid system is that no sludge is produced and the consumption of additives is reduced, since the oxidation process is intensified precisely by the phenomenon of cavitation. AOPs allow complex dye molecules to be broken down, and the degradation byproducts can then be further degraded by biological processes [66].

3.6. Process analysis

In this section a process analysis is presented, carried out to evaluate the possible integration of the hydrodynamic cavitation within a real wastewater treatment plant. At the scope, the traditional treatment train (Process A, described in the Section 2.5.1) is compared with a new plant configuration (Process B, described in the Section 2.5.1), in which HC takes the place of a conventional coagulation tank. A cost analysis is performed to choose the most cost-effective configuration. Tables 1 and 2 report the mass balances and the energy consumption of the Process A and B, respectively. The data for the energy consumption are extrapolated from Enerwater [67].

Table 3 shows the cost of the main equipment of the wastewater treatment plant.

The equipment cost for the pre-treatment section of Process A is higher than the cost of Process B, because in the first flowsheet the coagulation equipment is more expensive than the hydrodynamic cavitation section constituted by recycling pump (approximately, 10,000 €), reactor and hydrodynamic cavitation device. For these last section it has been estimated the cost of the reactor according to its volume, while for HC device a cost equal to half of the reactor purchase cost. Despite this difference in pre-treatment costs, the TCC of Process B is higher than the TCC of Process A because the equipment of the biological sections treats a greater flow of industrial waste from pre-treatment (200 m^3/h and 216 m^3/h for Process A and B, respectively).

The operational costs are reported in Table 4.

Details about the chemical consumption are reported in the following Table (Table 5).

It is possible to observe that the sludge disposal and electrical energy cost are the main items which have the greatest impact on TOC for Process A and Process B, as shown in Figs. 11 and 12.

The main items for energy consumption are clearly linked to the aerobic processes, the incidence of other treatments such as screening, coagulation, pump and clarifiers is less than 0.2%, for this reason are not reported in the Fig. 12.

A relevant aspect in the design optimization procedure is the calculation of the total annual treatment cost (TAC), composed of the annualized investment cost (AIC) and the operational costs (TOC). Hence, TIC is annualised over the expected lifetime of the treatment plant, transforming them into net present value (financing or annualized investment costs). The following formula has been applied [52]:

$$\mathrm{AIC} = \mathrm{TIC} / \mathrm{a}_{\mathrm{i,n}}$$

Where AIC is the annualized investment costs (depreciation), $a_{i,n}$ is the annualization factor and i is the interest rate, and n is the economic lifetime of the treatment plant in years. $a_{i,n}$ is calculated as follows:

$$\mathrm{a}_{\mathrm{in}} = [(1+\mathrm{i})^{\mathrm{n}} - 1] / [\mathrm{I} * (1+\mathrm{i})^{\mathrm{n}}] \quad (7)$$

Often a distinction is made between the economic lifetime of the civil part and the mechanical and E&I part: for an example, 30 years for the civil part and 15-20 years for the mechanical and E&I part. Hence, TIC is divided into different fractions, for instance, 35-60% for the civil works and 25-40% for the mechanical equipment, and 15-25% for E&I equipment.

In this specific case, it has been chosen I = 8%, the expected economic lifetime of the civil works of 30 years and 17 years for mechanical and E&I installations. The data are reported in Table 6.

TAC can be used to calculate the treatment cost for a cubic meter of total effluent, in particular, it is estimated a cost of 2.7 €/m^3 and 1.5 €/m^3 for Process A and B, respectively.

4. Conclution

In the present work, the efficiency of the hydrodynamic cavitation for the decolourization of methyl orange has been studied by using a Venturi device. The effect of inlet pressure, hydrogen peroxide concentration and the salinity of the solutions on dye degradation (5 ppm of MO) has been investigated. The experimental results showed that the inlet pressure had a positive effect on the efficiency of HC, and the maximum efficiency was about 30% at operating pressure of 0.55 MPa. The hybrid system HC and hydrogen peroxide, at the optimal molar ratio of dye: H_2O_2 = 1:25, allowed to increase the decolourization removal up to slightly below 70%; the same effect has been observed in the experiments performed with 5 g/L of NaCl, while the combined presence of NaCl and H_2O_2 had a negative outcome.

In a second phase of the research activity, HC process was tested for the treatment of synthetic solutions having the characteristics of tannery wastewater, hence some salts as NaCl, NH_4Cl, and Na_2SO_4 have been added. The presence of these compounds far from having a negative outcome, indeed substantially improved the dye decolourization, which reached about 90%. This result shows that HC could be a real alternative to the more traditional processes for the treatment of this type of wastewater. For these reasons a process analysis has been carried out to evaluate the possible integration of the hydrodynamic cavitation within a real wastewater treatment plant, by comparing the traditional treatment train with a new plant configuration, in which HC takes the place of a conventional coagulation tank. More in detail, two case studies for the treatment of tannery wastewater have been studied. The first (Process A) includes coagulation by aluminum ferric chloride (PAFC) and basification up to pH 8.5 adding calcium hydroxide. After this pre-treatment, the effluent needs further treatment by a biological process to reduce the amount of COD. Otherwise, the second case study (Process B) consists of hydrodynamic cavitation to remove the dye, also in this case the treated water cannot be discharged and as for Process A, a biological treatment is necessary to reduce the concentration of pollutants. The economic analysis showed that the annual treatment cost was 2.7 €/m^3 and 1.5 €/m^3 for Process A and B, respectively. For Process A, sludge disposal of residual solid, from the coagulation section, was determined to be the major component of the total annualized, instead for Process B, the electrical energy consumption, mainly for the aerobic section, had a higher incidence on the annual treatment cost. The results of the experimental activity and process analysis encourage to continue the research of the cavitation process for the treatment of industrial wastewater as an alternative to traditional ones, studies that should still be carried out in the laboratory scale to investigate other operative parameters, and using real wastewater and then test the processes at the pilot-scale to confirm the efficiency of the process.

Credit author statement

Conceptualization, V.I, M.P.; methodology, A.C., V.I, M.P.; experimental tests, A.C.; analytical measurements, A.C.; investigation, A.C, V. I., M.P; data curation, V.I, M.P; writing-original draft preparation, V.I., M.P. writing-review and editing, V.I., M.P; supervision, M.P.

Declaration of Competing Interest

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

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