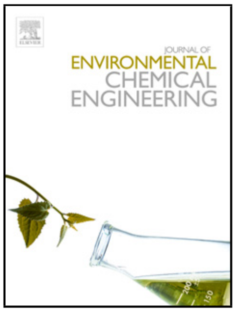

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Optimization of hydrodynamic cavitation process of azo dye reduction in the presence of metal ions

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Highlights

- We study the degradation of methyl orange by using hydrodynamic cavitation (HC) in the presence of ion metals
- We measure the effect of various operating parameters (pH, temperature, inlet pressure) on the decolourization efficiency.
- We carry out a full factorial plan to determine the main effects and mutual interactions among the factors: inlet pressure, temperature, initial dye concentration and treatment time.
- We find that the optimum operating conditions among those investigated are: 5 ppm of, pH=2, 0.6 MPa and 1 hour, independently of temperature.
- We investigated that the hydrodynamic cavitation in the presence of ion metals increased of 5 times the efficiency of the HC compared to the test performed in the absence of metals

Abstract

The aim of this research was to investigate the methyl orange degradation using hydrodynamic cavitation. The synthetic solutions simulated a real textile effluent containing dye and metals (iron and nickel) as a consequence of the corrosion of nickel-plated metal components of the plant during the production of textile materials. In the first series of experiments, the hydrodynamic cavitation was studied in terms of operating inlet pressure and pH of solution. Subsequently, a full factorial plan was performed to determine the main effects and interactions among the investigated factors: inlet pressure (p_{in}), temperature (T), initial dye concentration ($c_{MO}/_0$), and treatment time (t). The results showed that inlet pressure, temperature and concentration had a significant positive effect on dye degradation, as well as the interactions temperature/dye concentration and pressure/time. The optimum operating conditions among those investigated were: $c_{MO}/_0$=5 ppm, pH=2, p_{in}=0.6 MPa and t=1 hour, independently of temperature (T). In the above conditions, the degradation yields were near to 75% and the final concentration was less than 1 ppm. On the contrary, at $c_{MO}/_0$=20 ppm, pH=2, p_{in}=0.6 MPa, 40°C and t=1 hour, the degradation efficiency was about 56% and the final concentration was less than 9 ppm.

A comparison among the experiments carried out in the absence and in the presence of iron and nickel showed that metals acted as catalysts and the energy required for the process with metal ions was 5 times smaller than those required by the experiments conducted without the metals in solution, at the same operating conditions.

Keywords: *Methyl orange dye; Degradation of dye; Hydrodynamic cavitation; Advanced oxidation Processes; Venturi tube; metal ions*

1. Introduction

Textile industry produces wastewaters containing several types of dyes. In the dyeing process, around 15% of the colorants is lost and discharged as industrial residual solutions [1, 2]. The treatment of such liquid wastes is a matter of great concern, due to their colour and toxicity. It is estimated that the annual world production of synthetic dyes in 2009 exceeded 900,000 tonnes and it is expected to grow a million tonnes every year [3-5]. The azo dyes are the most commonly used dyestuff and represent around 50-70% of the total production [6-8].

This type of dyes is characterized by the presence of a double nitrogen bonds (-N-N-) and it is widely used in the textile, paper and cosmetic industries [2, 9]. The release into the environment of azo-contaminated wastewaters poses severe problems of toxicity because of their bio recalcitrance for conventional aerobic wastewater treatment and the toxic aromatic intermediates. Therefore, the developments of effective methods for the removal of such polluting dyes is of major importance. From a literature survey, a lot of papers deals with the traditional decolourization techniques, and the work by Banat and co-workers [10] offers a good review. Physical and chemical processes, often combined with biological treatments dominate the scenery, mainly flocculation, flotation, membrane filtration, ion-exchange, coagulation precipitation, ozonisation and activated carbon adsorption [11]. Some of them showed almost satisfactory performances for the removal of dyes from textile wastewaters, while the process for the removal of sulfonated azo dyes had some lacks in the effective colour reduction. Anyway, the efficiency of the treatments depended on the initial characteristics of the wastewaters; moreover, one of the main drawbacks is the production of chemical sludge that needs to be proper disposed and the high consumption of chemicals which negatively affects the treatment costs. Fung et al. [11] in their paper outlined how to choose the technique based on the characteristics of dyeing wastewater. For an example, ozone treatment could be used to improve the biodegradability only if major pollutants contain conjugated double bonds or aromatic groups [12]; coagulation could be used to remove colloids and suspended solids; other types of bio-treatments could be applied to degrade the wastewater according to the biodegradability of the suspensions [13]; ultrafiltration process are indicated to remove solids (1-20 nm) and dissolved organics and macromolecules with molecular weight between 300 and 300,000 g/mol [14-17].

More recently, the research activities have been focused on the degradation of dyes with using advanced oxidation processes (AOPs) as Fenton’s treatment, photocatalytic oxidation and sonolysis. The results of the specialized literature showed that these types of processes are more suitable than the traditional ones for degradation of dyes, mainly because of their strong oxidative capacity, and the capability of reacting with many substances [18-21].

Among AOPs, some papers have shown the efficiency of the use of zero-valent ions (ZVI) as copper and iron to reduce the azo dyes [22-24]. More details about the process and its efficiency are in the review by Fu et al. [25].

A recent development for the treatment of dye polluted wastewaters, in particular of textile residual solutions, is represented by hydrodynamic cavitation (HC). In this process, the liquid flows at high pressure through one or more holes. Venturi tubes or orifice plates can be used for HC. The passage through the holes causes a substantial pressure reduction that generates bubble cavities. In some cavities (local hot -spots) drastic conditions could be reached (up to 5000 K of temperature and up to 100 MPa of pressure). These conditions induce the collapse of the bubbles and the production of free radical due to the decomposition of water vapor and non-condensable gases inside the bubbles [26-32]. This technique has been successfully tested for degradation of priority pollutants such as ibuprofen and paranitrophenol [33-36] and for production of biodiesel [37]. A literature analysis has shown that HC has been seldom used as a stand-alone process in azo-dye degradation but always in combination with a catalyst (*see Table 1*).

Table 1: Scientific literature relative to the azo-dye degradation using hydrodynamic cavitation

The dye solutions used for the experiments are generally synthetic, prepared by diluting dye in the aqueous phase, neglecting the other substances that could be present in the textile effluents. A review on textile wastewater characterization showed that this type of solutions can contain organic substances as oil, grease, surfactants and metals. The composition of the residual solutions depends on cycle production and metals enter the wastewater in many ways: the incoming water supply, metal parts (like pumps, pipes, valves, etc.) oxidising and reducing substances, electrolyte, acid and alkali, dyes and pigments, maintenance chemicals and other. The main source of heavy metals is the dyeing process even if many of the newly developed dyes are metal-free. [44]

The present work is a part of an ongoing scientific activity aimed to define possible enhanced of the hydrodynamic cavitation for the treatment of real industrial effluents.

The objective of the present work and its novelty with respect to the scientific literature is to investigate the degradation of dye solutions by using hydrodynamic cavitation in the presence of metal ions as iron and nickel. Methyl orange was chosen as model dye and the solutions simulated an effluent that contained metals as a consequence of corrosion of metal components of the plant for the production of textile materials.

In order to investigate the simultaneous effects of various parameters on the dye degradation yields (%) and interaction between variables, two series of experiments have been performed. In the first series it was studied the effect of the inlet pressure and pH solution. The second set of experiments was carried out applying a design of the experiment (DOE) combined with response surface methodology analysis. A full factorial with four factors and two levels has been performed. The investigated factors were: inlet pressure, temperature, dye concentration and time. The results showed which factors and interactions were significant for the process; these data were used to describe an empirical model by statistical approach. The model provided a good correlation between the experimental and predicted yields of degradation. Finally, a comparison between the results in terms of degradation yields with and without metals in the solutions has been described.

2. Materials and Methods

2.1 Materials

Methyl orange dye was provided by Carlo Erba (0.1% in water). The synthetic solutions of methyl orange were prepared using distilled water. The experiments were conducted working with two concentrations of methyl orange c_{MO}=5 and 20 ppm, as provided by experimental plan. Sodium hydroxide (Fluka Chemika, >97%) and sulphuric acid (Carlo Erba, 96%) were used for adjusting the solution pH (2 – 6). Iron and nickel were added as sulfates with commercial grade. These compounds in the solution simulated a textile effluent that contains metals as a consequence of corrosion of metal parts of nickel steel (*i.e.* pumps, valves, fittings). The concentrations of Fe and Ni were kept constant for all experiments and equal to 20 and 10 mg/L, respectively.

2.2 Experimental apparatus

The lab scale experimental apparatus is constituted by a Venturi reactor with a recycling line, as shown in Figure 1.

Figure 1: Layout of the experimental apparatus used for the hydrodynamic cavitation tests

The system includes a feed tank with a volume of 1000 mL (T1), a centrifugal pump (P1) and two valves (V1 and V2). The feed flowrate crosses the principal pipe and passes through the Venturi tube (VT1) therefore reaches up to the tank T1. In order to control the liquid flowrate in this main line an additional pipe (by–pass line) with a valve (V2) is provided. The diameter of the main and by-pass line is equal to 12 mm. The centrifugal pump (Fluid -o – Tech, TMFR2) has a maximum electric power of 375 W and a speed pump of 1100-3500 rpm.

The flow was measured by an automatic flow meter (Comac Cal, Flow 38) while the pressure was checked by two electric manometers M1 and M2, (Barksdale Control Products, UPA2 KF16809D). The pressure signals were sent to a computer and recorded by process software Labview.

The geometrical characteristics of the Venturi are shown in Figure 1A (supplementary material); the divergence angle value is 5.74°. These dimensions of the Venturi assured the cavitation process as suggested by the scientific literature [45]. The Venturi is made of plexiglass. All other system components are in Rilsan and stainless steel.

2.3 Experimental methodology

2.3.1 Preliminary tests: hydraulic study of the system

The preliminary tests with distilled water were carried out for analysing the hydraulic characteristics of the system. The pump speed was set to 1100 rpm and the inlet pressure to the Venturi has been varied up to 0.66 MPa, checking the water flowrate through the line. The test was repeated for pump speed of 1500 and 2000 rpm. According to the technical manual, the flow meter guaranteed accuracy of measurements of 0.5%.

2.3.2 Hydrodynamic cavitation of Methyl orange

The degradation of methyl orange (MO) using hydrodynamic cavitation was performed at different inlet pressures (p_{in}=0.2-0.66 MPa) to the cavitation device and a solution pH varying in the range 2-6 to establish the optimal conditions for the degradation of dye. The pH was adjusted using sulphuric acid and sodium hydroxide. The concentration of methyl orange was $c_{MO}/_0$=5 ppm for all experiments of the first series. The solutions were circulated in the plant for 60 minutes as required by the experiments. The temperature was maintained constant (T=20°C) by cold water that crosses in the jacketed system of T1. The samples were collected at regular intervals of 10 min and the analysed to quantify the extent of MO degradation.

After these experiments, a full factorial design was developed to investigate the effect of four factors: pressure, temperature, dye concentration and time. Process conditions are listed in Tables 2 and 3. The goal of these experiments was to check which was the effect of the factors not studied in the previous tests and if which were the interactions among the several operating conditions. Pressure was studied in the range 0.2-0.6 MPa, to avoid critical conditions recorded at a pressure greater than 0.6 MPa. The solution pH was maintained constant at 2. This value was the optimized value found in previous experiments.

Table 2: Factors studied in the experiments according to the full factorial plan

Table 3: Full factorial design

All the experiments were performed with 600 mL of solution.

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. The concentration of dye was then calculated by the calibration curves.

The decolourization efficiency was determined according to equation (1), [46]:

$$Decolourization\ rate\ (\eta) = \frac{c_{MO/t}}{c_{MO/0}} \tag{1}$$

Where $c_{MO/t}$ and $c_{MO/0}$ were the concentration of methyl orange at a generic time (t) and at the initial time, *i.e.* the initial concentration of methyl orange, respectively.

Total organic carbon (TOC) content of MO was measured by using a TOC analyser (Kit Lange LCK 381).

3. Results and discussion

The efficiency of hydrodynamic cavitation depends on Venturi geometrical parameters (cavitation number and geometry of the device) and operating conditions (such as inlet pressure and properties of the liquid) [27]. Hence, several experiments were performed at different operating conditions in order to evaluate the efficiency of the process in degradation of methyl orange. Experimental tests have been so conceived: hydraulic tests to define the hydraulic features of the system; hydrodynamic cavitation tests of methyl orange in which several operating conditions were investigated.

3.1 Hydraulic study of the experimental apparatus

Figure 2 shows the results of the hydraulic study, in particular the values of flowrate as a function of the inlet pressure, for the experiments performed with using a pump speed of 1100 rpm. Similar trends (not reported in this work) were obtained also for the experiments conducted with 1500, 1750 and 2000 rpm. By varying inlet pressure in the range 0.3-0.66 MPa, it was possible to span the flowrate in the interval 4 – 6 L/min.

Figure 2: Hydraulic features of the system (See Fig 1): flow rate and cavitation number C_v as a function of the inlet pressure. Pump speed equal to 1100 rpm

Figure 3 also reports the cavitation number (C_v) as a function of the inlet pressure, as defined in the following equation (2), [47]:

$$C_v = \frac{P_2 - P_v}{0{,}5\rho v_0^2} \tag{2}$$

where C_v is a dimensionless number, specific for this type of apparatus. P_2 is the downstream pressure, P_v is the vapor pressure of the liquid, v_o is the fluid velocity at the convergent and ρ is the liquid density The analysis of the trends showed that as the inlet pressure increased the flowrate increased, on the contrary as expected the C_v decreased because of the higher kinetic energy of the liquid flow. Moreover, it was observed an increase in the turbulence as a consequence of the more bubbles in the flow [43].

3.2 Hydrodynamic Cavitation of Methyl orange

3.2.1 Effect of the inlet pressure on the methyl orange degradation

Experiments for measuring the potential MO degradation were conducted at different inlet pressures ranging from 0.2 to 0.66 MPa and a corresponding cavitation number in the range 0.21–0.095. The pH of the solution was kept constant at 2.0 in all the experiments. Figure 3 shows the results of the experiments. As can be observed, the degradation of MO increased with increasing the inlet pressure to the Venturi tube, reaching a maximum at 0.6 MPa and then decreased. The yields had a similar trend at 0.3 and 0.4 MPa, more differences were recorded at 0.5 and 0.6 MPa. After 1 hour the minimum and maximum degradation yields were 40% and 74% at 0.2 MPa and 0.6 MPa, respectively.

Figure 3: Degradation of methyl orange with time for different levels of inlet pressure (p_{in}=0.2, 0.3, 0.4, 0.5, 0.6 and 0.66 MPa); pH = 2 and $c_{MO}/_0$ = 5 ppm

The experimental data were used to describe the dye degradation using a first-order reaction (equations 3-5), [48]

$$-\frac{d[MO]}{dt} = k[MO] \tag{3}$$

$$[MO] = [MO]_o \exp[-kt] \tag{4}$$

$$\ln[MO] = -kt + \ln[MO]_o \tag{5}$$

where: $[MO]_o$ and $[MO]$ are the initial concentration and the concentration of methyl orange (mol/L) at zero and "*t*" time, respectively; *k* is the degradation rate constant (min^{-1}) and *t* is the time (min). A linear fit of the experimental data in a logarithmic plot gives from the slope the *k* values, as reported in Table 4. Figure 4 shows as an example the kinetic analysis obtained for the experiments conducted at p_{in}=0.2 MPa. It was found that the data were well fitted by the equation (5) with a regression coefficient greater than 0.99 and the slope of the line, hence the decolourization rate, is 0.0089 min^{-1}. The same trend was obtained for the other pressures (here not reported).

Figure 4: First order decolourization of MO using HC;

$c_{MO}/_0$=5 ppm, pH=2, p_{in}=0.2 MPa

Table 4: Decolourization rate constant, k, and yields at various inlet pressures (standard deviation for the decolourization efficiency= 2- 7%)

As a consequence of an increase in the inlet pressure (or a decrease in C_v), a higher number of cavities formed, hence more collapsing events occurred, which generated additional OH radicals for reacting with the dye. At the same time the solution flowrate and the number of passes in the

Venturi increased. This enhanced the exposure time of methyl orange to the cavitation conditions which resulted into a higher decolourization yields.

The positive effect recorded between the pressures 0.2-0.6 MPa was then suppressed at a value of the inlet pressure equal to 0.66 MPa. It could be supposed that under this pressure the conditions of chocked cavitation occurred. In this situation, the formation of a large number of cavities had a negative effect on hydrodynamic cavitation process because they coalesced each other to form vaporous bubbles that not collapsed, hence not reacted with the dye. The same trends were observed by other authors during the degradation process of reactive orange 4 dye [38] reactive red 120 [41], dichlorvos [38]. p- nitrophenol [33] and ibuprofen [34-36].

3.2.2 Effect of solution pH

Table 5 reports the conditions adopted during the following experiments in which the effect of solution pH on degradation of methyl orange was investigated. All the tests were conducted at the initial pressure of 0.6 MPa (optimal pressure, *see Section 3.2.1*). Every 10 minutes, the samples were collected and then analysed to measure the degradation of dye. Figure 5 shows the results of these experiments.

Table 5: Experiments performed during the second series of test to investigate the effect of pH solution on decolourization of methyl orange

Figure 5: Degradation of methyl orange as a function of time at different pH solution ($c_{MO}/_0$ *= 5 ppm;* p_{in} *= 0.6 MPa)*

It was observed that the degradation yields of methyl orange increased with a reduction of solution pH and a maximum decolourization of the methyl orange of 73% was reached at pH = 2 after 60 minutes. At pH 4 the decolorization yields significantly decreased and after 1 hour the efficiency of the process was less than 20%.

The yields calculated for pH values greater than 4 were not reported since they were near to zero. It was clear that the acidic medium was favourable for degradation of methyl orange using hydrodynamic cavitation. The same phenomenon was presented by several authors and it can be explained as follows [38, 49-50]:

- in the acidic medium the recombination of generated OH radicals is less favoured, hence more radicals are available for the degradation of methyl orange;
- in the acidic medium the dye substance form changes from ions to molecular, it is less hydrophilic and more soluble in the aqueous liquid bulk. As a consequence, the OH radicals fail to react with the molecules of dye that is not degraded.

3.2.3 Full factorial experiments

The effect of pressure, methyl orange concentration, temperature and time and their interactions on the degradation yield (%) were investigated using a full factorial plan (*see Table 2 and 3*). Figure 6 reports the MO decolorization yields obtained during the experiments.

Figure 6: Degradation of methyl orange obtained during the hydrodynamic cavitation experiments at different operating conditions (treatments, see Tables 2 and 3)

The maximum decolourization yields (near 80%) were obtained in treatments “ad” and “abd”, when the pressure was at high level (0.6 MPa), the concentration was at low level (5 ppm) and at 1 hours. The minimum efficiency of the process was obtained in the treatment “c”, performed in the following conditions: p_{in}=0.2 MPa, T=10°C, t=20 min and $c_{MO}/_0$= 20 ppm. Analysis of variance (ANOVA) was carried out using degradation yield data. Yates’ algorithm was used to evaluate whether effects and interactions among factors were significant with respect to the experimental error. This value was calculated using the variance of the fourth and third order which were found to be not significant. The variance of the experimental error calculated was 8.682 with 5 degrees of freedom. The significance of the main factors and their interactions was assessed by F-test method with a confidence level of 95% [51]. Figure 7 shows the effects and interactions of the factors on MO degradation yield. Significant level of 95% (straight line) is also indicated: every effect higher than those lines is significant, according to F-test utilised. The corresponding lines on the negative effect plane are also shown.

Figure 7: Effects and interactions of the factors studied (A = p_{in}*; B = T; C =* $c_{MO}/_0$ *and D = t) on the decolorization yield of methyl orange; straight line = significant level of 95%*

ANOVA shows that pressure, temperature and concentration had a significant positive effect on MO degradation, as well as interaction BC (temperature and MO concentration) and AD (pressure and time). It means that increasing the value of one factor, A, B the degradation of dye increased. Factor C and CD had a significant negative effect. Other interactions did not show significant effects.

The interactions were studied using the two – way table. Figure 8 (a) shows the interaction BC (temperature – dye concentration).

Figure 8: Two-way table. a) BC interaction; b) AD interaction and c) CD interaction.

(A = p_{in}*; B = T; C =* $c_{MO}/_0$ *and D = t)*

When the factor C (dye concentration) was at low level equal to 5 ppm, the effect of temperature was negligible and the average degradation yields ranged from 40 to 45%. While when the concentration of dye was 20 ppm (high level of factor C), the effect of factor B (temperature) was evident: the average yields increased of about 10% at high temperature respect to low temperature. It is clear that in the investigated conditions, temperature had a positive effect on the degradation yields. The effect of temperature was explained in the paper by Vichare Gogate et al. [52]: a higher temperature in a certain degree leads to an increase in the cavitation intensity that contributes to the degradation of the dye. The same phenomenon was described by Yang et al. [43].

Figure 8 (b) shows the interaction AD. It can be seen observed the positive effect of time and pressure. The maximum degradation yields were obtained working at 0.6 MPa and 1 hour. When the pressure was at 0.2 MPa the degradation yields increased from around 16% until 40% by increasing the time from 20 to 60 minutes, respectively. When the factor A was at high level (0.6 MPa), the degradation yields increased from around 26% until 62% by increasing the time from 20 to 60 minutes, respectively. Time had a positive effect on methyl orange degradation that increased by increasing the pressure.

Figure 8 (c) shows the interaction CD (dye concentration – time). Also, in this case it was clear the positive effect of time and the negative effect of dye concentration on the decolorization efficiency. The maximum degradation yields were obtained working with 5 ppm of MO and 1 hour. When the concentration of MO was 20 ppm (high level of factor C) the average degradation yields increased from around 16% until 40% by increasing the time from 20 to 60 minutes, respectively.

When the factor A was at high level (0.6 MPa), the degradation yields increased from around 26% until 62% by increasing the time from 20 to 60 minutes, respectively. Time had a positive effect on methyl orange degradation that increased by increasing the pressure.

The optimum operating conditions among those investigated for methyl orange degradation were:

- $c_{MO}/_0$=5 ppm, pH=2, p_{in}=0.6 MPa, t=1 hour independently of temperature. That's an advantage because the decolorization process can be performed at room temperature. In these conditions the degradation yields were near to 75% and the final concentration was less than 1 ppm.
- $c_{MO}/_0$=20 ppm, pH=2, p_{in}=0.6 MPa, t=1 hour, T=40°C. In these conditions the degradation efficiencies were near to 56% and the final concentration was less than 9 ppm.

Data obtained from the factorial plan were used to develop a statistical model useful for the estimation of the degradation efficiency when the operating conditions change in the range just studied. The response of the system was found as a function of the significant factors and interactions. The not significant terms were not considered by stepwise method. The independent variables were X_1 = pressure, X_2 = temperature, C = MO concentration, D = time. It was found the following relation [51]:

$$Y = A_0 + A_1 X_1 + A_2 X_2 + A_3 X_3 + A_4 X_4 + A_{23} X_2 X_3 + A_{14} X_1 X_4 + A_{34} X_3 X_4 \qquad (6)$$

where

Y = degradation of methyl orange %, $A_0 = 36.19$, $A_1 = 7.87$, $A_2 = 2.22$, $A_3 = -7.76$, $A_4 = 14.82$, $A_{23} = 2.87$, $A_{14} = 3.22$, $A_{34} = -2.98$.

Figure 9 shows the scatter diagram relative to statistical model. In the graph the decolorization yields were reported plotting predicted against empirical data. The values were rather correlated as confirmed by high value of R^2 (equal to 0.99).

Figure 9: Scatter diagram for the decolorization of methyl orange

The model was used to graph the response of the system as a function of the effects. For example, Figure 10 shows the methyl orange degradation as a function of the dye concentration and pressure. Temperature and time were kept constant and equal to 20°C and 60 min, respectively.

Figure 10: MO degradation as a function of dye concentration and pressure (20°C and 60 min)

The decolourization yields were comprised between 20-80%. The maximum extractions (70-80%) were obtained performing the hydrodynamic cavitation at pressure higher than 0.5 MPa with a concentration of MO near to 5 ppm. At the same pressure, increasing the concentration of dye the degradation decreased until to reach almost 50%. The minimum decolorizations (20-30%) were obtained working with high concentration of methyl orange (20 ppm) and 0.2 MPa.

Figure 11 shows the methyl orange degradation as a function of temperature and pressure. Other conditions were constant and equal to 5 ppm and 60 min, respectively.

Figure 11: MO degradation as a function of temperature and pressure (5 ppm and 60 min)

The decolourization yields were comprised between 50-80%. Also, in this case it was clear the positive effect of the pressure, while the temperature had not a significant effect. The maximum decolorization efficiencies were obtained (70-80%) were obtained performing the hydrodynamic cavitation at pressure higher than 0.5 MPa, regardless of temperature. The minimum decolorizations (50-60%) were obtained working with pressure lower than 0.45 MPa, for temperature between 10-40°C.

The statistical model provided to estimate the efficiency of the hydrodynamic cavitation under specific conditions. So, for example, it is possible to consider the following conditions: 5 ppm, 20°C, 5 bar and 1 hours; in these conditions the empirical decolorization yield was 67.8%. At the same conditions, the experimental results (*see Fig. 4*) the efficiency was 65.3%. The values were very closely with one another: this confirm that the mathematic model, described using the experimental results of the full factorial plan, efficiently estimated the decolorization efficiency when the operating conditions change in the range just studied.

3.3 UV-vis spectra change during treatment

The UV-vis spectra analysis was performed to evaluate the methyl orange degradation. As an example, Figure 2A (supplementary material) shows the spectrum changes of the dye solution before (pink vial) and after (transparent vial) cavitation for the test concluded at the following conditions: pH = 2, $c_{MO/0}$=5 ppm, p_{in}=0.6 MPa bar and t= 1 h. Before the cavitation the absorption spectrum of the dye was characterized by a peak in the visible region with a maximum of absorbance at 507 nm; moreover, another band was present in the ultraviolet region at a wavelength less than 300 nm. The highest peak was associated to the aromatic rings connected through the azo bond, while the other small peak was due to the presence into the molecule of a benzene- like structure. It was observed that after cavitation the peak at 507 nm decreased to zero after 60 minutes. The change of the smallest peak was mainly due to the degradation the dye and its intermediates [42].

The decomposition pathway of methyl orange was already studied by other authors [53, 54].

The final products are some intermediates, carbon dioxide and water.

The intermediates are expected to be aromatic compounds [42], which also accounts for the TOC of the solution. The measurement of dye concentration by spectrophotometer does not guarantee the complete mineralization of the dye, hence the TOC measure in our experimentation was performed for the test that gave the maximum MO decolourization (p_{in}=0.6 MPa, pH =2, $c_{MO/0}$=5 ppm, t=1 hours). The measure showed a negligible reduction. Comparing the results in term of decolourization yield (%) and TOC reduction (%), after 60 min it was observed that the decolourization of dye was a relatively fast process as compared to the mineralization process. The same trend was reported in literature [39, 55]. Further oxidation of the aromatic intermediates could produce carboxylic acid, as formic and acetic acid.

3.4 Comparison with the results obtained in the absence of metal ions

A final experiment was conducted using solutions in the absence of metal ions in solution, at the same conditions. Table 6 shows the results and compared the results obtained in the previous series.

The energy efficiency of experimental apparatus was also evaluated on the basis of the concentration and type of pollutant. The experimental data were also used to define the cavitation yield (*eq. 7*) [56].

$$Cavitation\ yield\ [mg\ L\ J^{-1}\ ] = \ (amount\ of\ dye\ degradated)/\frac{P_E\ t}{V} \tag{7}$$

where P_E is the power of the pump, t is the operation time, and V is the volume of pollutant solution.

Table 6: Comparison of the results of the hydrodynamic cavitation performed with and without metal ions (standard deviation for dye degradation = 2-7%)

The maximum cavitation yield of unit energy input is achieved in the experiments conducted in the presence of metals. It was also estimated the required energy to achieve 95% of dye degradation. The time for 95% ($t_{95\%}$) decolourization in the cavitation zone can be found as (*eq. 8*) [56]:

$$t_{95\%} = \frac{2.996}{k} \tag{8}$$

Where k is the rate constant.

The electric energy in kWh (E) required for 95% degradation is calculated as [56]:

$$E = \frac{P_E\, t_{95\%}}{60\times 1000} \tag{9}$$

The energy required, therefore the operating costs, for the dye degradation in the experiment conducted in the presence of metals (iron and nickel) was 5 times smaller than the test conducted without any metal in solution.

From these data it can be seen that the metal ions in solutions were acting as catalysts for the dye degradation, increasing the efficiency of the hydrodynamic cavitation process at the same operating conditions.

Conclusion

Methyl orange dye degradation using hydrodynamic cavitation process was investigated. The experiments were conducted using synthetic solutions in which the dye and metal ions (iron and nickel) were added. The objective of the research was to define the effect of the metal ions in the aqueous phase on dye degradation: the solutions simulated an effluent that contained metals as a consequence of corrosion of nickel-plated metal components of the plant for the production of textile materials. Several experimental series were performed: in the first one the effect of some parameters as inlet pressure and solution pH was studied, keeping constant the initial dye concentration (c_{MO}=5 ppm) and the temperature (T=20°C). A maximum decolourization (~ 74%) of methyl orange was obtained at pH=2, p_{in}=0.6 MPa after 60 minutes of HC. In a second series of experiments, the optimal conditions for dye degradation were determined with the aid of a full factorial plan in which the effect of the inlet pressure, temperature, dye concentration and time was investigated. The results showed that pressure, temperature and concentration had a significant positive effect on MO degradation, as well as the interactions T - c_{MO} and p_{in} - t.

The optimum operating conditions between those investigated were:

- c_{MO}=5 ppm, pH=2, p_{in}=0.6 MPa, t=1 hour, independently of temperature. In these conditions the degradation yields were near to 75% and the final concentration was less than 1 ppm.
- c_{MO}=20 ppm, pH=2, p_{in}=0.6 MPa, t=1 hour, T=40°C. In these conditions the degradation efficiencies were near to 56% and the final concentration was less than 9 ppm.

Finally, the efficiency of the hydrodynamic cavitation process for dye degradation in the absence of the metals in solutions was evaluated, at the same operating conditions. The results showed that metals were acting as catalysts and the energy required, therefore the operating costs, for the process in the experiment conducted in the presence of metals (iron and nickel) was 5 times smaller than the test conducted without the metals in solution.

With respect to the potential for hydrodynamic cavitation process in the treatment of dye solutions that simulated textile effluents, the final implications of this research were diversified: although decolorization of methyl orange in specific operating conditions was satisfactory, the TOC degradation was near to zero. It meant that there was not the complete degradation of dye in water and carbon dioxide, but reaction intermediates were formed that may be of regulatory concern and require further treatment that will be objective of the future trials.

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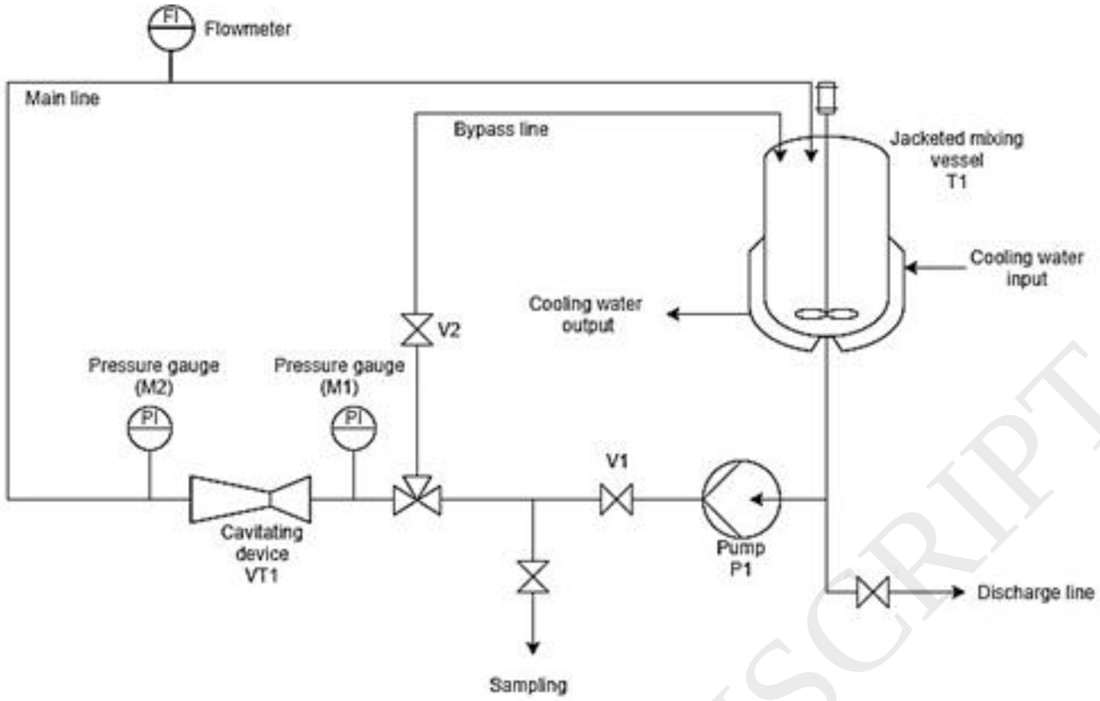


Figure 1: Layout of the experimental apparatus used for the hydrodynamic cavitation tests

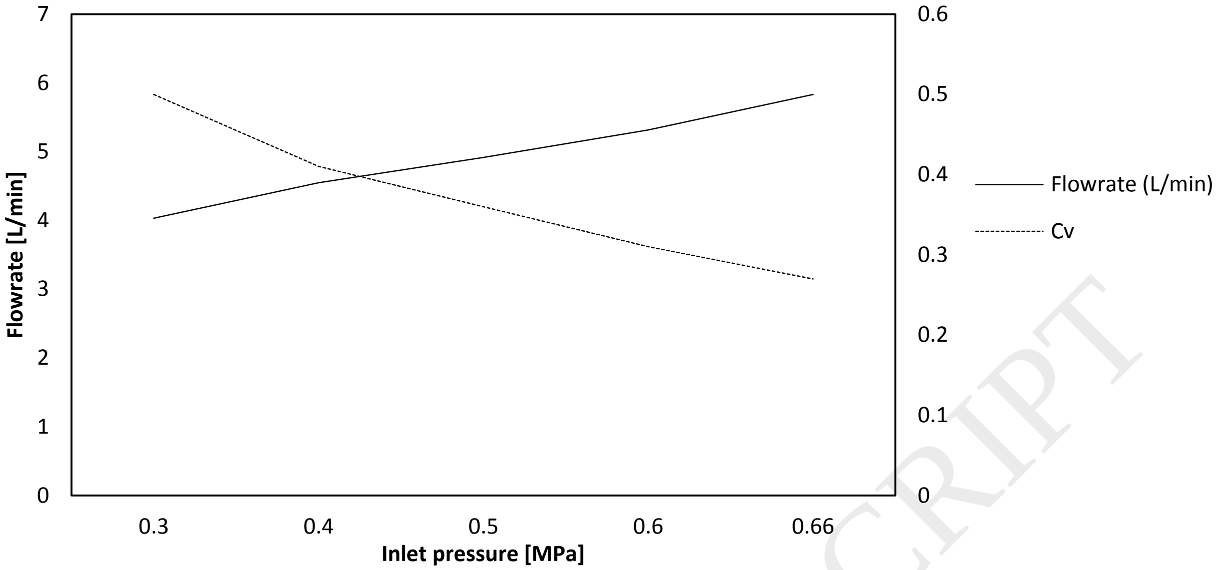


Figure 2: Hydraulic features of the system (See Fig 1): flow rate and cavitation number C_v as a function of the inlet pressure. Pump speed equal to 1100 rpm

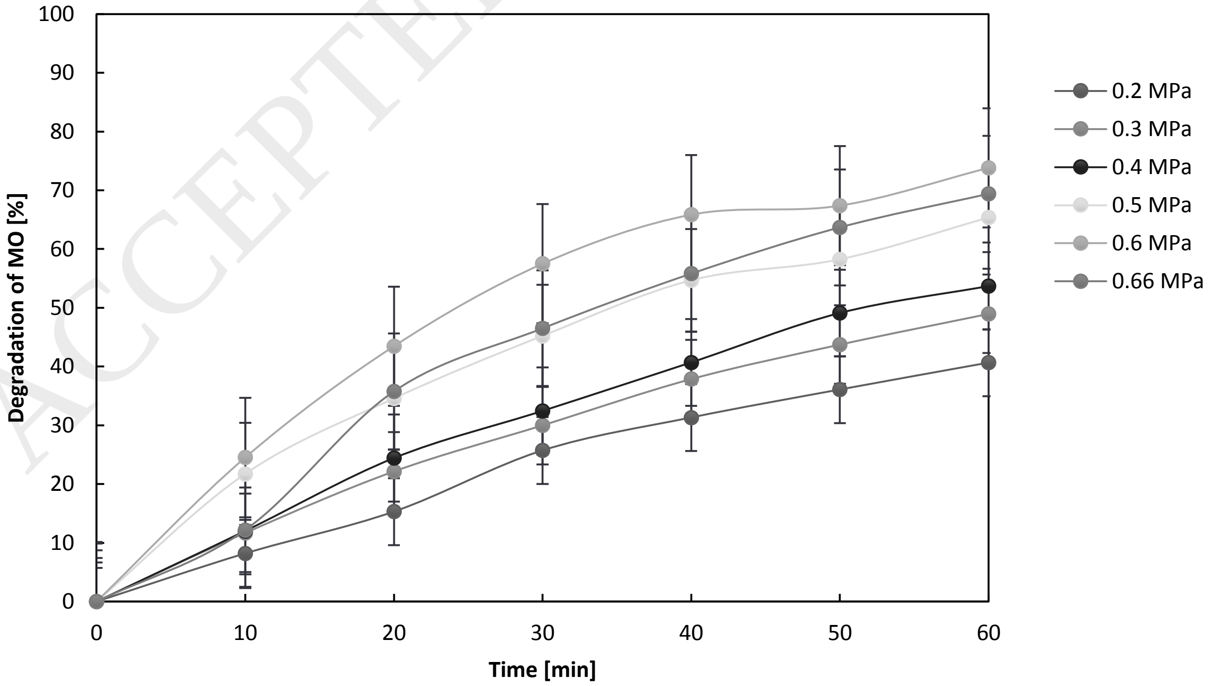


Figure 3: Degradation of methyl orange with time for different levels of inlet pressure (p_{in}=0.2, 0.3, 0.4, 0.5, 0.6 and 0.66 MPa); pH = 2 and $c_{MO/0}$ = 5 ppm

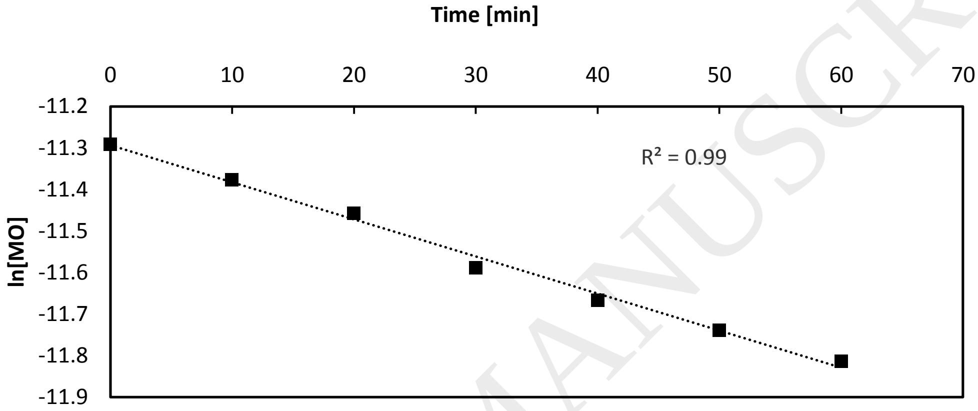


Figure 4: First order decolourization of MO using HC; $c_{MO/0}$=5 ppm, pH=2, p_{in}=0.2 MPa

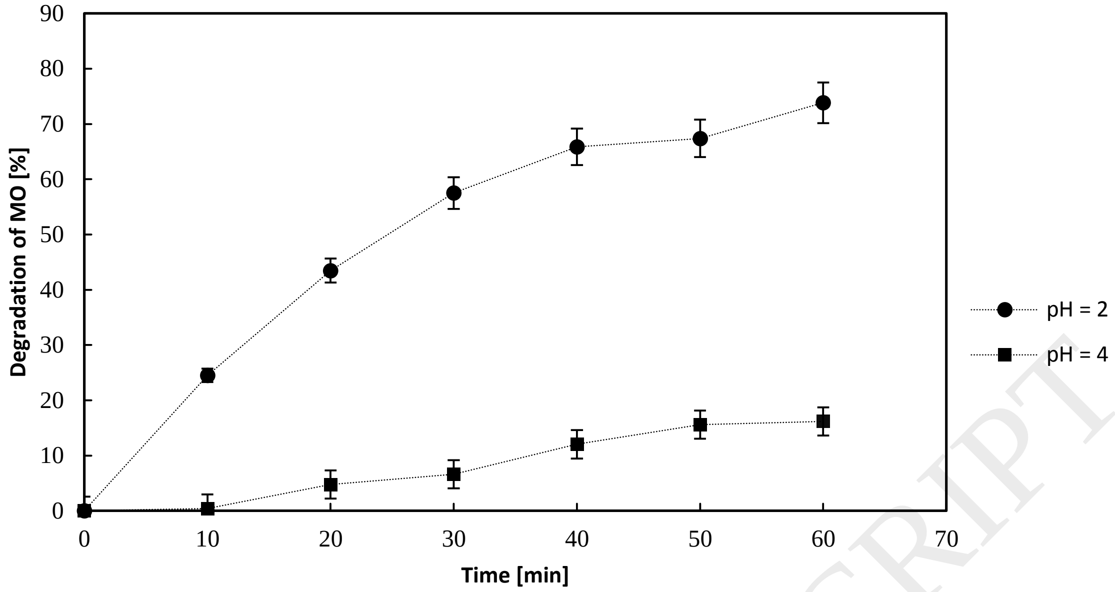


Figure 5: Degradation of methyl orange as a function of time at different pH solution ($c_{MO}/_0$ = 5 ppm; p_{in} = 0.6 MPa)

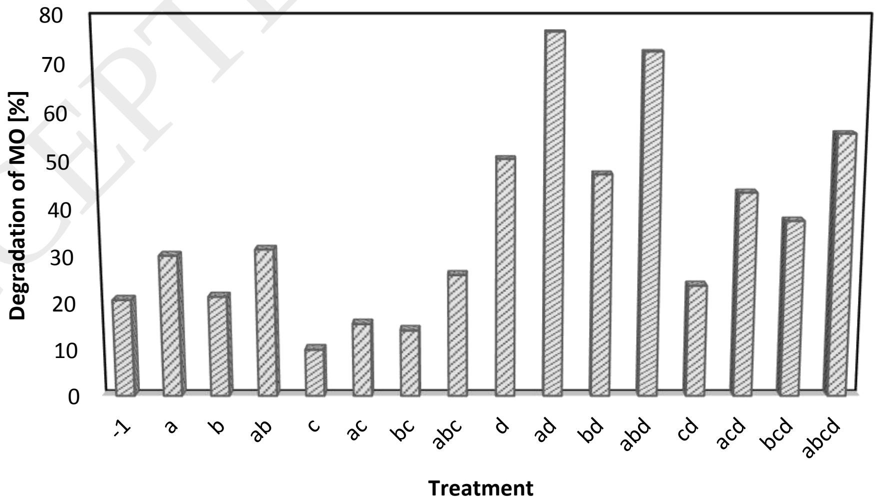


Figure 6: Degradation of methyl orange obtained during the hydrodynamic cavitation experiments at different operating conditions (treatments, see Tables 2 and 3)

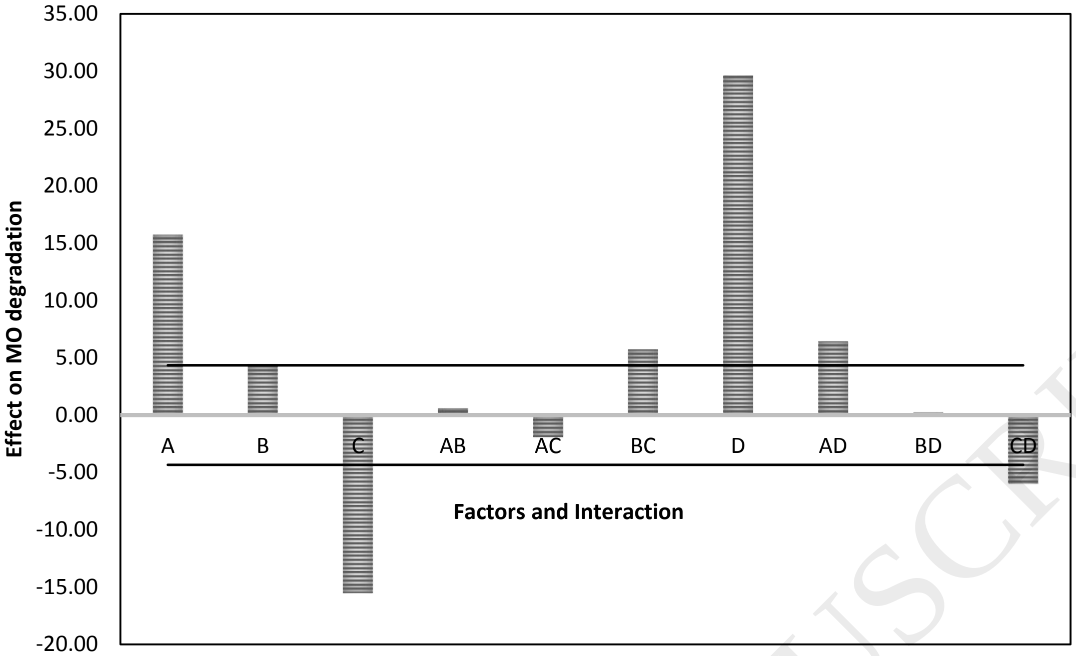
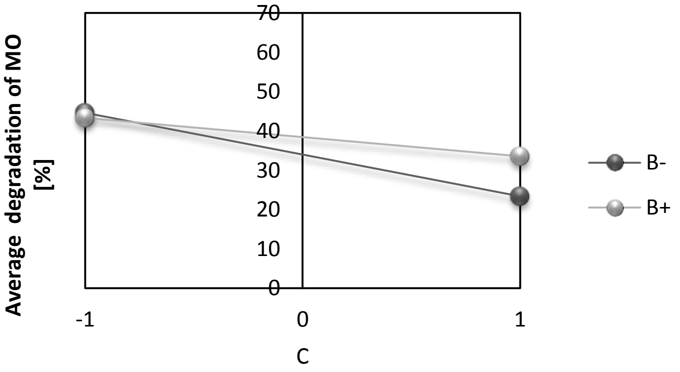
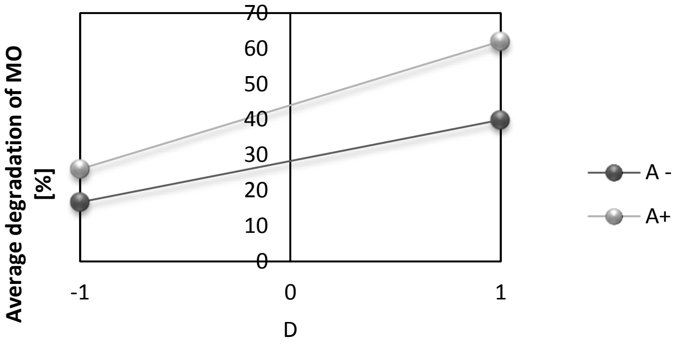


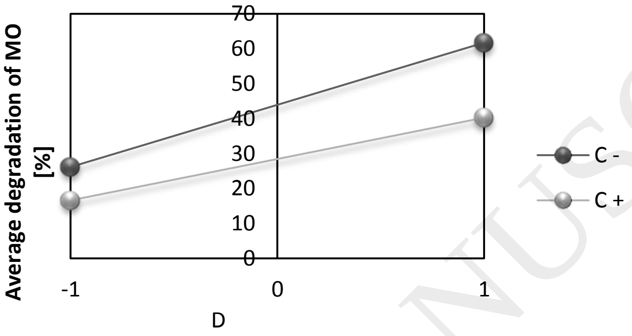
Figure 7: Effects and interactions of the factors studied (A = p_{in}; B = T; C = $c_{MO}/_{0}$ and D = t) on the decolorization yield of methyl orange; straight line = significant level of 95%



(a)



(b)



(c)

Figure 8: Two-way table. a) BC interaction; b) AD interaction and c) CD interaction.

(A = p_{in}; B = T; C = $c_{MO/0}$ and D = t)

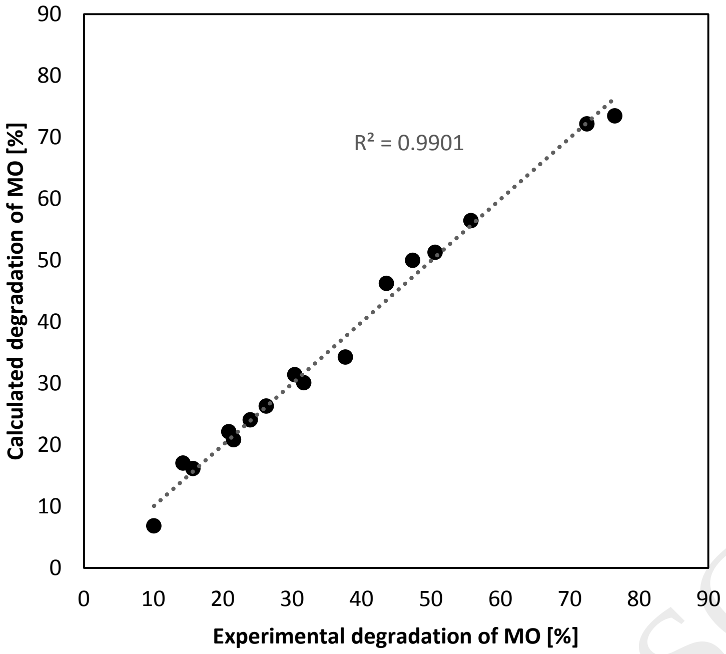


Figure 9: Scatter diagram for the decolorization of methyl orange

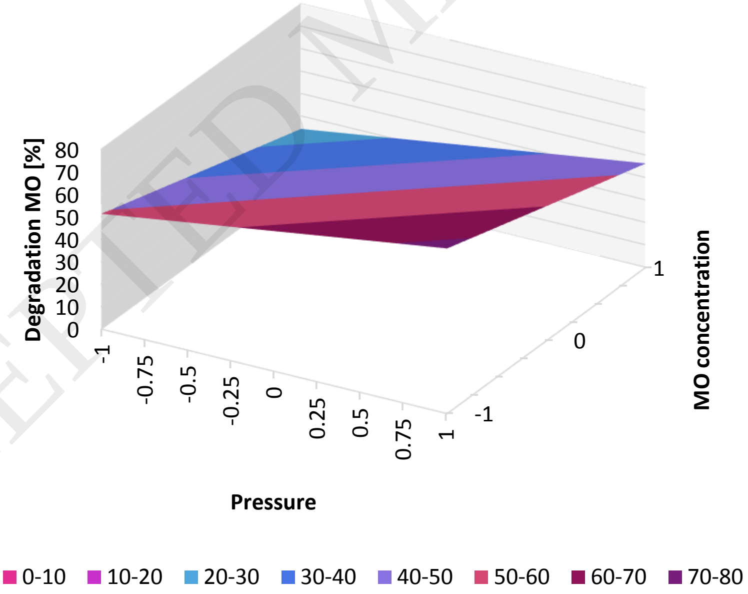


Figure 10: MO degradation as a function of dye concentration and pressure (20°C and 60 min)

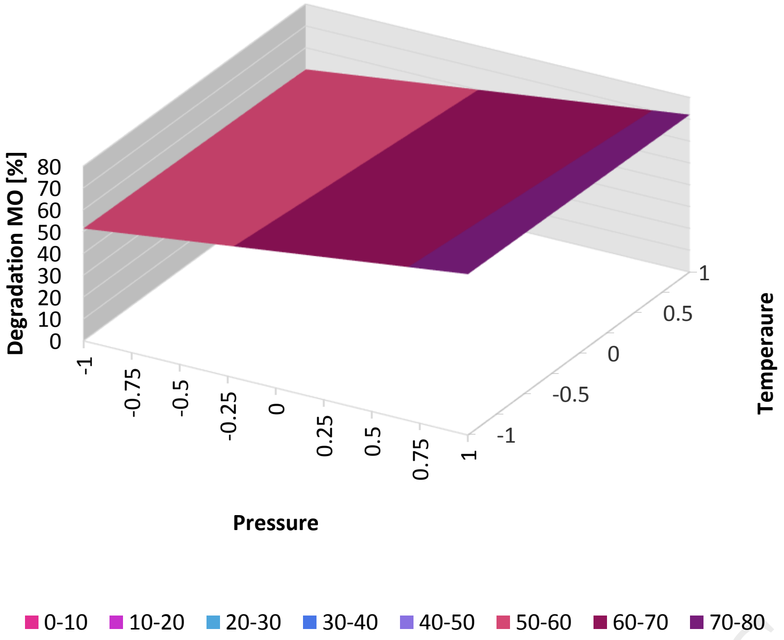


Figure 11: MO degradation as a function of temperature and pressure (5 ppm and 60 min)

Table 1: Scientific literature relative to the azo-dye degradation using hydrodynamic cavitation

Scientific work	**Dye**	**Hydrodynamic cavitation-based hybrid techniques**	**Maximum yields**	**Optimal conditions**
Saharan et al. [37]	Acid Red 88	HC + H_2O_2 + Fe-TiO_2 nanoparticles	HC alone 92% HC + H_2O_2 99% (4000 µM) HC + H_2O_2 (100 µM) + Fe-TiO_2 (1.8 g/L) complete dye decolorization	Dye concentration= 100 µM pH = 2 Inlet pressure = 5 bar Temperature = 35 °C 120 minutes Note: the rate of decolorization of dye enhanced (by about 45-60%) by the addition of Fe-TiO_2.
Gore et al. [38]	Reactive Red 4 (RO4)	HC + H_2O_2 + Ozone	HC alone 37.23 HC + H_2O_2 99% (molar ratio RO4/ H_2O_2 = 1/30) 99.56% HC + H_2O_2 + Ozone complete dye dcolorisation within 5 minutes	Dye concentration= 40 ppm pH = 2 Inlet pressure = 5 bar Time = 120 minutes
Saharan et al. [39]	Reactive Red 120	HC + H_2O_2	HC alone 60% HC + H_2O_2 (2024 µM) 100%	Dye concentration= 50 ppm pH = 2 Inlet pressure = 5 bar Temperature = 30-35°C Time = 180 minutes

Wang et al. [40]	Rhodamine B	HC + H_2O_2	HC + H_2O_2 (150 mg/L) 99.1%	Dye concentration= 10 ppm pH = 3 Inlet pressure = 6 bar Temperature = 50°C Time = 180 minutes
Mishra and Gogate [41]	Rhodamine B	HC + H_2O_2 + CCl_4 + Fenton's reagents	HC alone 25% HC + H_2O_2 (200 mg/L) 99.9% HC Fenton's reagents 100% (in 15 min at 40°C) HC + CCl_4 (1 g/L) 82%	Dye concentration= 10 ppm pH = 2.5 Inlet pressure = 4.8 bar Temperature = 30-45°C Time = 120 minutes
Li et al. [42]	Methyl Orange	HC + Cu^0 nanoparticles	HC alone 6.8% HC + Cu^0 nanoparticles (40 mg/L) 83%	Dye concentration= 10 ppm pH = 3 Inlet pressure = 4 bar Temperature = 25°C Time = 180 minutes
Yang et al. [43]	Methyl Orange	HC + ClO_2	HC + ClO_2 (8 mg/L) 83%	Dye concentration= 10 ppm Inlet pressure = 4 bar Temperature =38°C Time = 60 minutes

Table 2: Factors studied in the experiments according to the full factorial plan

Factor		**Levels**	
		-1	**+1**
A	Pressure (MPa)	0.2	0.6
B	Temperature (°C)	10	40
C	Metyl orange concentration (ppm)	5	20
D	Time (min)	20	60

Table 3: Full factorial design

Treatment	**Coded factor**				**Factors**			
	A	B	C	D	A (MPa)	B (°C)	C (ppm)	D (min)
-1	-1	-1	-1	-1	0.2	10	5	20
a	+1	-1	-1	-1	0.6	10	5	20
b	-1	+1	-1	-1	0.2	40	5	20
ab	+1	+1	-1	-1	0.6	40	5	20
c	-1	-1	+1	-1	0.2	10	20	20
ac	+1	-1	+1	-1	0.6	10	20	20
bc	-1	+1	+1	-1	0.2	40	20	20
abc	+1	+1	+1	+1	0.6	40	20	60
d	-1	-1	-1	+1	0.2	10	5	60
ad	+1	-1	-1	+1	0.6	10	5	60
bd	-1	+1	-1	+1	0.2	40	5	60
abd	+1	+1	-1	+1	0.6	40	5	60
cd	-1	-1	++1	+1	0.2	10	20	60
acd	+1	-1	+1	+1	0.6	10	20	60
bcd	-1	+1	+1	+1	0.2	40	20	60
abcd	+1	+1	+1	+1	0.6	40	20	60

Table 4: Decolourization rate constant, k, and yields at various inlet pressures (standard deviation for the decolourization efficiency= 2- 7%)

Inlet pressure [MPa]	**Flow rate [L/min]**	**C_v [-]**	**Decolourization in 60 min [%]**	**Decolourization rate constant, *k* [min^{-1}]**
0.2	-	-	40.00	0.0089
0.3	4.03	0.50	48.97	0.011
0.4	4.55	0.41	53.69	0.013
0.5	4.92	0.36	65.35	0.017
0.6	5.32	0.31	73.83	0.022
0.66	5.83	0.27	69.39	0.020

Table 5: Experiments performed during the second series of test to investigate the effect of pH solution on decolourization of methyl orange

Test	**Initial MO concentration [ppm]**	**pH**	**Inlet pressure [MPa]**
1	5	2	0.6
2	5	4	0.6
3	5	6	0.6

Table 6: Comparison of the results of the hydrodynamic cavitation performed with and without metal ions (standard deviation for dye degradation = 2-7%)

Experimental conditions	**Metals ions**	**Dye degradation [%]**	**Decolourization Constant rate k [min^{-1}]**	**Cavitation yield [mg L J-1]**	**Electric energy [kWh]**
5 ppm of MO 0.6 MPa 1 hour 20°C	-	22.51	0.0044	2.39E-07	4.26
5 ppm of MO 0.6 MPa 1 hour 20°C	20 mg/L Fe 10 mg/L Ni	75%	0.022	8.87E-07	0.85