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ORIGINAL ARTICLE

Application of hybrid oxidative processes based on cavitation for the treatment of methyl blue solutions

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Abstract

Over the past few decades, the scientific community has developed an increasing interest in high-performance water treatment systems based on cavitational processes. Hydrodynamic cavitation (HC) is one of the promising technologies for wastewater treatment, especially for dyeing solutions, since it shows high efficiency in treating dyes, even at low concentrations. Both strategies have been shown to be efficient ways to get rid of pathogenic bacteria by disinfecting waters and achieving the mineralization of numerous organic pollutants. This makes cavitation-based techniques an attractive choice for use in water treatment facilities' post-treatment stages. Modern techniques have been presented that combine advanced oxidation processes (AOPs) with cavitation for increased oxidation capacity. When used together, cavitation and AOPs (such as O_3, H_2O_2, and Fenton's process) can cause materials to decay much more quickly. This work aims to investigate the degradation of Methyl Blue (MB) with HC and evaluate the effectiveness of a hybrid process (O_3 + HC). The experimental tests were conducted to determine the optimal operating conditions (pressure, pH, O_3 dosage). Furthermore, the feasibility of MB mineralization at a high concentration range (10–100 mg/l) was performed. Cost estimation and energetic analysis were discussed. As a result, the optimal conditions were: P = 4.5 bar, pH 2, O_3 = 7.5 mg/L. For the initial concentration of 10 mg/L, the MB decolorization yield of HC, O_3, and HC + O_3 were 10%, 99%, and 100%, respectively, after 30 min of treatment. The addition of O_3 promoted the degradation efficiency above 95%, decreasing the treatment time. Increasing the O_3 feed rate can reduce the treatment time. A flow rate of 8 L/min of ozone was adopted in the optimal flow value. The hybrid process has an important effect in improving the performance of wastewater treatment by reducing treatment time, causing saving in energy consumption and process cost.

Keywords Hydrodynamic cavitation · Ozone · Hybrid process · Methyl blue (MB) · Venturi tube · Cost estimation

Introduction

In recent years, new classes of chemical pollutants have been identified and classified thanks to improved instruments' analytical sensitivity. These substances are classified as Emerging Pollutants (EPs). These contaminants are chemical compounds that have only recently been regulated and raise concerns regarding their hazardousness to the environment and human health. Among these EPs are included dyes, widely used in the production of textiles since the second half of the twentieth century (Spadaro et al. 1994; Robinson et al. 2001). These kinds of liquid wastes are produced by chemical industries such as the textile, dyeing, paper and pulp, tannery, and paint industries, which are the significant contributors of dyeing effluents to the environment. They have a high environmental impact because many substances enter their production cycle, and some residual dyes are toxic; in addition, dyes are often aromatic organic compounds and, as such, are based mainly on the structure of benzene, which in turn comes from the distillation of either coal or oil, both of which have very energy-intensive processes at their base. Therefore, the textile industry seriously contributes to environmental pollution regarding CO_2 release into the atmosphere. Another environmental problem connected to dyes is when a cloth is thrown away; as a result, several complex substances are released into the environment, eventually entering plant or animal's metabolism and having unknown metabolic effects (Parshetti et al.

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2010; Sharma et al. 2009; Adewuyi 2005). Today's goal is to assess better the possible risks arising from these new substances, set emission limits, and study their reduction and removal techniques. Most treatments designed for this purpose include membrane filtration (Zio et al. 2005; Salladini et al. 2007), adsorption with activated carbon, reverse osmosis, and advanced oxidation processes (AOPs) (Banat et al. 1996; Fung et al. 2012).

Advanced oxidation processes (AOPs) are considered among the most promising techniques. They guarantee the complete mineralization of toxic and refractory compounds from water, avoiding the phase transfer of the pollutants. AOPs can be classified according to the way of generation of the radical species (Gogate and Bhosale 2013; Ince and Tezcanli-Guyer 2004). Among the typical radical species, hydroxyl radicals (·OH) play a role of primary importance, as they possess a very high oxidant power (2.8 V). AOPs can be further classified according to the way of generation of the species radicals in Cao et al. (2022): processes with chemical reagents, photolytic methods (Deshmukh et al. 2020; Siong et al. 2020), and photocatalytic and electrochemical techniques (Cao et al. 2022; Miao et al. 2022).

In the first case, the generation of the radicalic species is obtained from the reaction of some oxidants, used alone or in combination, without using physical promoting agents. In contrast, in the photolytic generation, radicals are obtained by combining chemical reagents with light radiation in the wavelengths of UV and visible. The most consolidated processes are those that use ozone (O_3) (Chu et al. 2007; Mahamuni and Adewuyi 2010) and hydrogen peroxide (H_2O_2) (Bagal and Gogate 2013), often in combination with UV radiation, to favor the photolysis of O_3 or H_2O_2 and the production of radicals (Fernandes et al. 2004). Cavitation-assisted AOPs (either ultrasonic –UC or hydrodynamic cavitation –HC) are promising wastewater treatment technologies (Patil et al. 2021). Mainly, HC shows interesting characteristics in terms of energy efficiency and simplicity of the equipment compared with the other advanced processes (Thanekar and Gogate 2018a). Cavitation includes the phenomena of nucleation, growth, and implosion of cavities in a brief period; usually, milliseconds needed to reach the saturation pressure, which generates enormous energy (Saharan et al. 2013). The effect of HC can be enhanced when it is coupled with others AOPs techniques, such as H_2O_2 and O_3 (Wang et al. 2021; Sun et al. 2021).

Several researchers studied these so-called hybrid HC processes for industrial wastewater treatments, demonstrating that the combination HC + H_2O_2 /HC + O_3 has the most effective synergistic degradation rate (Rajoriya et al. 2018). For example, the combination of HC with H_2O_2 reaches 64.58%, and HC with O_3 is 95.4% for the degradation of carbamazepine (Boczkaj et al. 2018; Thanekar et al. 2018). Kumar et al. (Kumar et al. 2017) discovered that the maximum degradation of Methyl Blue (MB) occurred at an inlet pressure of 5 bar and a pH of 2. The amount of MB decolorization after 60 min was 94.64% at the molar ratio of MB/H_2O_2, of 1:20. Compared to the combination of hydrodynamic cavitation and TiO_2 photocatalytic process, cavitation and H_2O_2 demonstrated a higher level of synergy.

The present study is based on the treatment of the Methyl Blue dye, the first synthetic compound in the history of medicine to be used as an antiseptic (Rumbeiha and Oehme 1992). Besides its biomedical applications, MB is widely employed by textile industries for various purposes, such as coloring paper, dyeing cotton, wool, silk, leather, and coating for paper stock. Therefore, MB is abundantly present in the textile industry wastewaters. Since it is environmentally persistent, toxic, carcinogenic and mutagenic, it must be efficiently removed from wastewater before discharge into a water body (Khan et al. 2022).

As an intensification process technology, HC plays a critical role in dye degradation, particularly in treating wastewater containing a low concentration of dyes (Innocenzi et al. 2019). The advantages of HC technology include a sizeable operational scale, high energy efficiency, and simple equipment (Saharan et al. 2011; Thanekar and Gogate 2018b). HC is frequently combined with other chemical reagents or AOPs in dyes wastewater treatment, which can significantly reduce chemical consumption, improve energy efficiency, and reduce investment and operation costs (Mahamuni and Adewuyi 2010; Bhat and Gogate 2020). Many studies have been conducted to investigate the MB degradation using HC coupled with the AOPs process. Wang et al. (Wang et al. 2022) found that when HC and O_3 were combined at a pH of 5.7, the degradation rate increased in the presence of ozone, indicating a positive synergistic effect. The O_3 feeding rate was 0.12 g/h, with 99.0% of degradation rate after 30 min of treatment, and the synergy index was 3.58. The ozonation is thus an effective method that can reduce the MB in wastewater (Hassan and Nemr 2017; Banat et al. 2005; Al-Anber 2018).

Materials and methods

Materials

Methylene blue (MB; C16H18N3ClS; molecular weight: 319.85 g·mol^{-1}) and distilled water were used to prepare the dye solutions. Figure 1 shows the molecular structure of MB. Initial solution concentration varied between 5 and 100 ppm, according to the adopted experimental procedures. Sodium hydroxide (Fluka Chemika, > 97%) and sulfuric acid (Carlo Erba, 98%) were used to adjust the pH of the solution.H_2O_2.

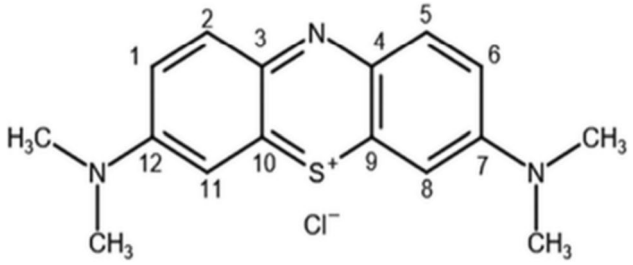

Fig. 1 Chemical structure of Methylene blue (MB)

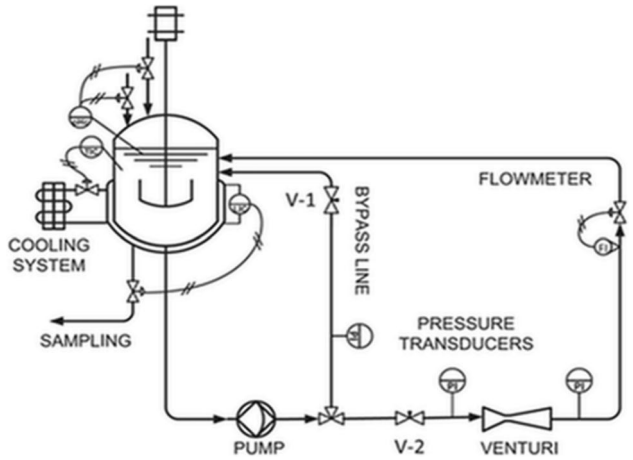

Fig. 2 Layout of the experimental apparatus used for the hydrodynamic cavitation tests

Experimental apparatus

Laboratory-scale hydrodynamic cavitation plant

The laboratory scale hydrodynamic cavitation system (Fig. 2) includes a wastewater storage tank with a cooling jacket, in which coolant water circulates to maintain the temperature at 20 °C; a volumetric rotary pump in stainless steel with a variable speed motor (Fluid-o-Tech -TMFR2); two control valves and a Venturi tube as a cavitation device. The system also has two piping lines, with an internal diameter (ID) of 12 mm: the main line that crosses the cavitation device and a bypass line equipped with a hand valve for flow and pressure regulation in the primary circuit. The pump rotation speed of 1100–3500 rpm. The flowrate is measured by a flowmeter, while the pressure with two pressure gauges placed upstream and downstream of the cavitation medium. The system components are made of stainless steel, polypropylene, and glass.

The Venturi tube was obtained through innovative technology, such as 3D printing with a photopolymer resin, allowing excellent tensile strength and rigidity. The tube has a maximum diameter of 12 mm, to the pipe diameter, and has a minimum diameter of the throat section equal to 2 mm, while the divergent area is 5,74°.

Ozone generating module

An ozone generating module (Triogen LAB2B, power: 230 V-1PH-50HZ) was fed with dry air input of 4–10 L/min. The maximum ozone output was 4 gm/h. The Triogen LAB2B consists of a ceramic dielectric with 316 stainless steel electrodes within an aluminum-finned outer heatsink housing. The module end caps are manufactured from PTFE with stainless steel tubing connectors to PVDF External inlet/outlet connectors. The shrouded housing has thermostatic protection to stop ozone production if the module temperature rises due to the failure of the cooling fan.

Experimental procedure

The experimental plan was organized into different tests to find the best conditions among those studied. At first, it has been studied the hydrodynamic cavitation process alone (Sect. "HC experiments"), then the oxidation process only with ozone (Sect. "Ozone experiments"), and finally, the combined process HC + ozone (Sect. "Hybrid process: HC + Ozone").

HC experiments

The experiments conducted with only HC were divided into two groups. In the first group, the effect of inlet pressure on the HC device on dye degradation has been studied (P_{in} between 0.81 and 5.5 bar) to identify the optimal pressure value. The experiments were carried out with an initial solution concentration of 5 mg/L at pH 2, and the tests had a treatment time of 60 min with sampling every 10 min. This experimental condition was reported by several researchers and was explained by the fact that the dye molecule is in a molecular state with significant hydrophobicity in the acidic solution. Thus,·OH recombination is inhibited and as a result, a large number of hydroxyl radicals are produced, which accelerate dye degradation (Barreto et al. 1994).

In the second group of experiments, the decolorization yield was analyzed by varying the initial solution concentration (5–25 mg/L) while keeping the pressure constant (at the optimal value found in the first series) and the solution of pH (pH 2).

All experiments have been performed for a treatment time equal to 60 min, sampling every 10 min for the MB analysis.

The degradation rate η is defined as (Innocenzi et al. 2018):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where c_0 and c_t (in mg/L) are the MB concentrations at the initial time and sampling time, respectively.

Ozone experiments

The second series of experiments with only ozone has been organized in two sets; at first, experiments were performed varying the effect of ozone flow 7 to 8.2 mg/L (4–10 L/min) at the P_{min} and optimal pressure, maintaining constant the initial solution concentration (10 mg/L) and the pH of the solution (pH 2). The ozone was directly injected into the tank solution. Then, another set of tests was conducted at the optimal ozone flow (found in the previous experiments), varying the solution's pH (MB = 10 mg/L, pH between 2 and 8). The scope was to identify the effect of pH on dye degradation.

Hybrid process: HC + Ozone

The last series of experiments have been carried out to study the performance of the hybrid process, HC combined with ozone. Firstly, the decolorization yields as a function of initial solution concentration (10–100 mg/L) have been analyzed by keeping constant the pH value (pH 2) and the flow of ozone 3 g/h (8 L/min). In the last group of tests, the degradation process was repeated under the same conditions mentioned above, combining hydrodynamic cavitation applied at the optimum pressure.

Analytical procedure

With a maximum wavelength of 663 nm, the UV–VIS spectrophotometer (Cary 1E, UV Visible spectrophotometer Varian) is used to analyze the shifting peak characteristics during the degradation of MB. (Innocenzi et al. 2018; Tang et al. 2021).

Results and discussion

HC results

Effect of the inlet pressure

The oxidizing capacity of HC depends on inlet pressure and cavitation number (C_v) defined as follows:

$$C_v = \frac{P_2 - P_v}{0.5\rho v_0^2} \quad (2)$$

where P_2 is the pressure measured downstream of the Venturi tube (Pa), P_v is the vapor pressure of the aqueous solution (Pa), ρ is the aqueous solution density (kg/m^3), and v_o is the flow velocity (m/s). C_v is a dimensionless number used to describe the cavitation conditions. The cavitation occurs when $C_v \leq 1$ in the ideal conditions, but in some cases, it could also happen for values greater than 1, for example, when there are dissolved gases or suspended solids that act as cavitation nuclei. For our HC system, the C_v number is 0.5–0.27 for 0.3–0.6 bar, respectively. The details about C_v values are reported in a previous work (Innocenzi et al. 2018).

The pressure effect was studied in the P_{min}=0.81 bar to 5.5 bar to determine the optimum pressure. The results (Fig. 3) show an increase (from 4% to around 33%) in the degradation rate of MB as a function of the inlet pressure. Beyond 4.5 bar, a decrease in the degradation rate has been noticed, reaching about 17% and 21% at 5 and 5.5 bar, respectively. Thus, the pressure that will be considered an optimal parameter for the next series of experiments will be 4.5 bar. This trend is in line with what has been reported in the scientific literature; more in detail, the more pressure increases, the more significant number of radicals that are generated, but beyond the optimal pressure, the incomplete collapse occurs, followed by a decrease in degradation rate (Yu et al. 2022; Joshi and Gogate 2012). Using a single orifice, Patil and Gogate (Patil and Gogate 2012) studied the impact of inlet pressure in the operating range of 1–8 bar on the degradation of methyl parathion. It was found that at greater pressures, the rate of growth reduces from 1 bar to the ideal value of 4 bar. An increase in cavitational activity at higher operating pressures can be the cause of the observed rise in degradation as the pressure climbs from 1 to 3 bar. When operational pressures are raised, the cavity collapses more quickly and violently, producing a stronger pressure pulse.

Kumar et al. (Kumar et al. 2017) investigated the degradation of methyl blue dye at various inlet pressures ranging from 1 to 10 bar. They reported that a decolorization of about 32% was observed at the optimal pressure of 5 bar. Similar observations have been noticed during this investigation as compared to earlier results. When the input pressure was increased beyond the optimal value, a reduction in the rate of degradation of MB dye was detected. Thus the cavitation number increased linearly with input pressure, demonstrating that cavity formation becomes easier as inlet pressure increases (Li et al. 2015). However, an undesirable consequence could be produced by the rapidity with which cavities form when inlet pressure monotonically increases, resulting in cavity clouds with much lower cavitational collapse intensity (Goel et al. 2004). Figures 3, 4 report the results of this series of experiments.

The data have been used to estimate the kinetic constants using the pseudo-first-order kinetic model, following the Eqs. (3, 4, 5)

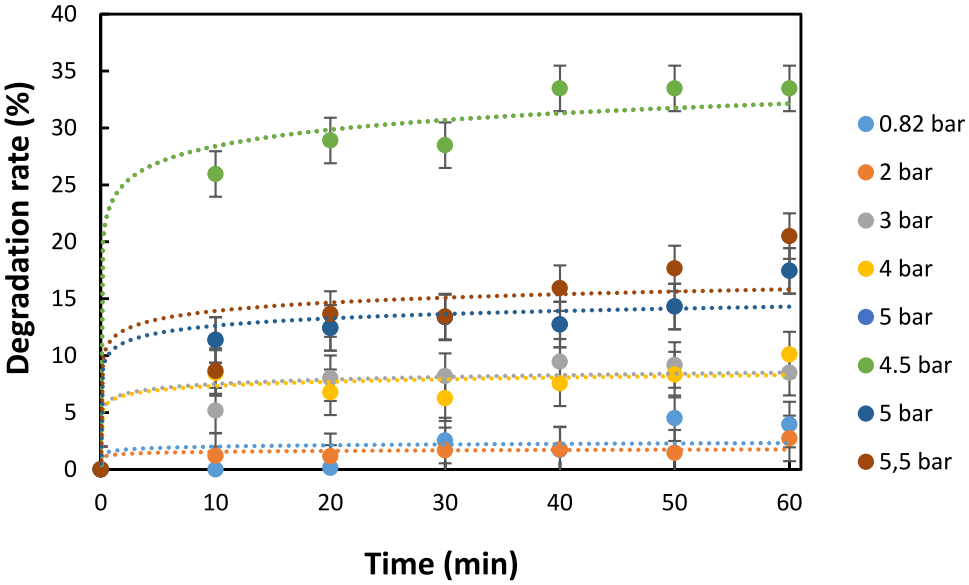

Fig. 3 Effect of the inlet pressure on MB decolorization. (C_0 = 5 mg/L, V = 1 L, pH 2, T = 20° ± 2 °C)

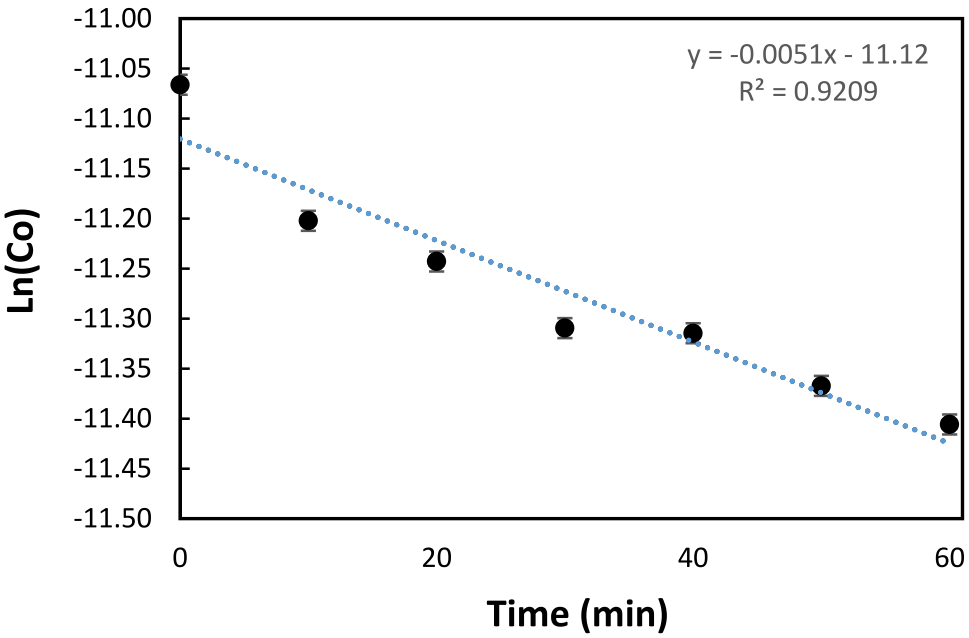

Fig. 4 Kinetic analysis for the experiment conducted at 4.5 bar

$$-\ln\left(\frac{C_0}{C_t}\right) = kt \tag{3}$$

$$C = C_o \exp[-kt] \tag{4}$$

$$\ln C = -kt + \ln C_o \tag{5}$$

where C (mol/L) is the concentration of MB, t is time, and k is the kinetic constant.

Figure 4 shows the kinetic analysis for the experimental test performed at 4.5 bar. The data fitted through Eq. (4) and the slope described the kinetic constant. The same study has also been conducted for the other experiments. The minimum kinetic constant rate obtained at 0.82 bar was 0.0009 min^{-1}, and the maximum at 4.5 bar was equal to 0.005 min^{-1}. The degradation yields were compared with the results obtained in a previous campaign of tests (Innocenzi et al. 2022), in which the degradation of another dye was studied, the methyl orange (Fig. 5).

It is possible to observe that the optimal inlet pressure to maximize the production of the radicals is 4–4.5 bar. It mainly depends on the geometrical structure of the Venturi tube; the difference in yields between the two dyes lies in the chemical structure, since methyl blue is more difficult

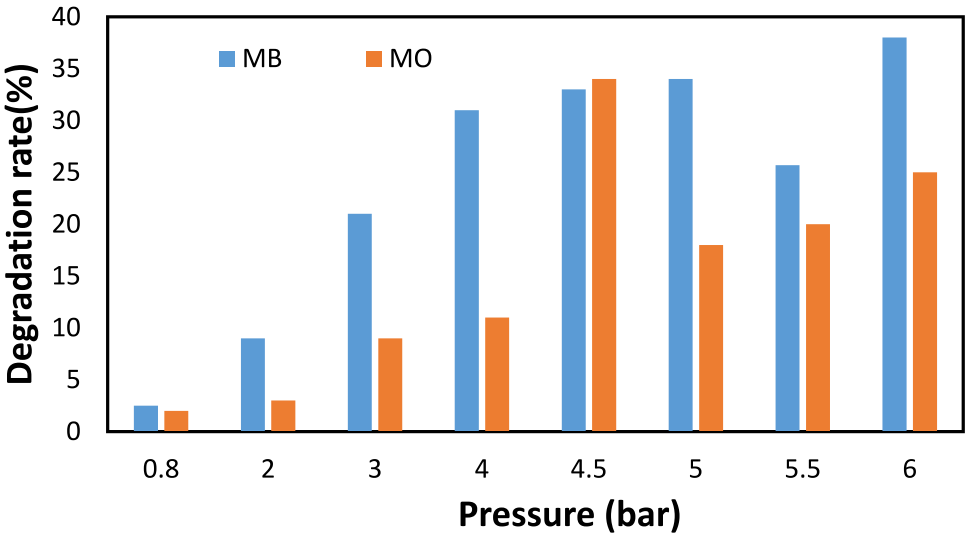

Fig. 5 Comparison between methyl orange (MO) and methyl blue (MB)

to degrade with respect to methyl orange (Innocenzi et al. 2018, 2022).

Effect of initial dye concentration

The concentration of the dye is an important parameter to be considered in the study. The experiments were performed with HC only at $P_{optimal} = 4.5$ bar with a variation of MB concentration from 2.5 to 25 mg/L at pH 2 for one hour of treatment time, with sampling every 10 min. As a result, the degradation yield decreased by increasing the initial concentration from 2.5 mg/L to 25 mg/L. This is since, above a specific concentration, considered as critical, the number of generated radicals is fixed with a higher substrate loading (Wang et al. 2021). In Fig. 6, the experimental results of the decolorization tests showed that when the concentration increased from 2.5 mg/L to 25 mg/L, the degradation rate decreased from 56% to 2.5%.

Ozone experimental results

Effect of O_3 dosage

Ozone has a strong oxidation potential (Sun et al. 2021). It has been reported that ozone could be an effective remediation for dye mineralization. Methyl blue decolorization tests carried out through ozonation were carried out by varying the O_3 dosage at the levels 8.2 mg/L, 8 mg/L, 7.5 mg/L, 7 mg/L (4 L/min, 6 L/min, 8 L/min, 10 L/min, respectively)

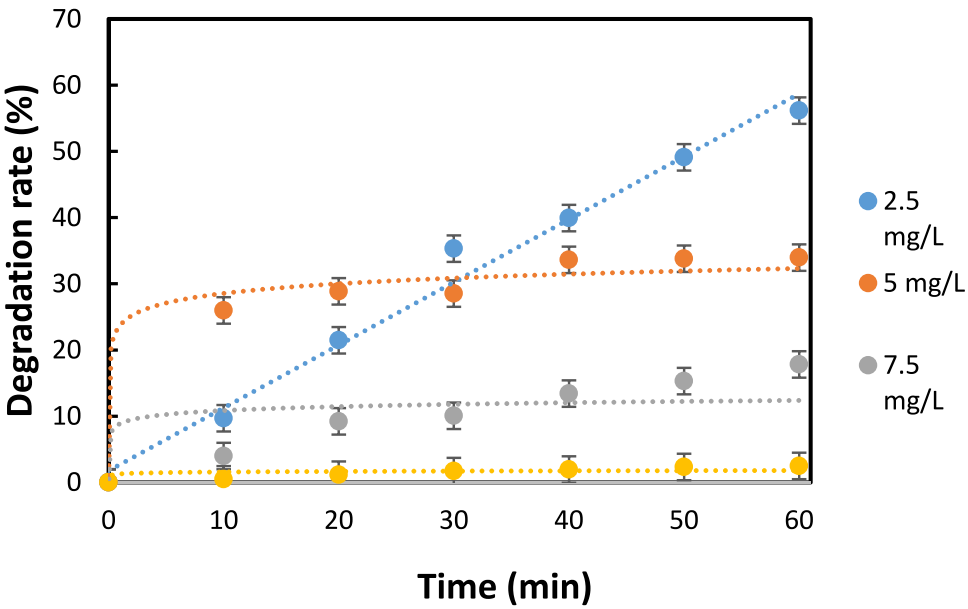

Fig. 6 Effect of the initial solution concentration (in ppm) on the degradation of MB. ($P_{in} = 4.5$ bar; V = 1 L; pH 2; T = 20 ± 2 ℃)

with C_0 equal to 10 mg/L at pH 2, to identify the optimal dosage of ozone under the investigated conditions.

The results obtained are reported and compared in Fig. 7. For the initial O_3 concentration equal to 8.2 mg/L and 8 mg/L, the decolorization of MB obtained in 20 min was equal to 81% and 95%, respectively. For an amount of ozone equal to 7.5 mg/L, the degradation yield reached 99% in about 20 min.

In the case of an initial concentration of O_3 equal to 8.2 mg/L and 8 mg/L, a complete discoloration of the methyl blue was obtained in a time equal to 30 minutes. Thus, increasing the O_3 feed rate can reduce the treatment time. A dosage of 8 L/min of ozone was adopted for the subsequent experiments, as it resulted in the optimal flow value.

Effect of the initial pH

The pH is a conducting parameter in our experiments. The initial pH was studied in the range of 2–8 with 7.5 mg/L of O_3 feeding rate at $C_0 = 10$ mg/L. The Fig. 8 shows the effect of pH in the degradation, with the degradation rate that reached the maximum at pH 2. This results showed that an acidic medium is favorable condition for degrading dyes (Innocenzi et al. 2018). This result has been reported by several authors and was explained by the fact that in the acidic medium, the dye molecule is in a molecular state with high hydrophobicity. The recombination of ·OH is prevented. As a consequence, a high amount of hydroxyl radicals is generated, which enhances the degradation of

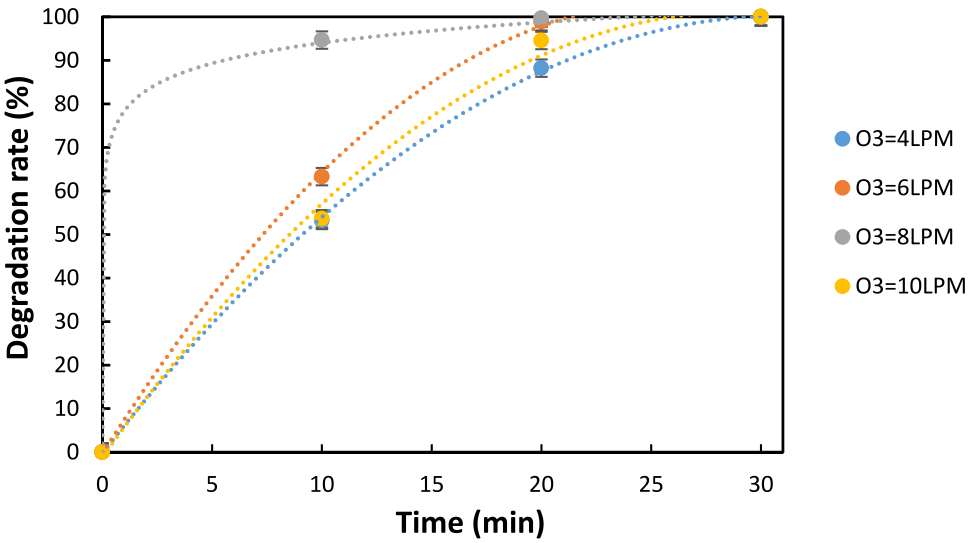

Fig. 7 Effect of O_3 dosage on the degradation of MB. ($C_0 = 10$ mg/L; V = 1 L; pH 2; T = 20 ± 2 ℃)

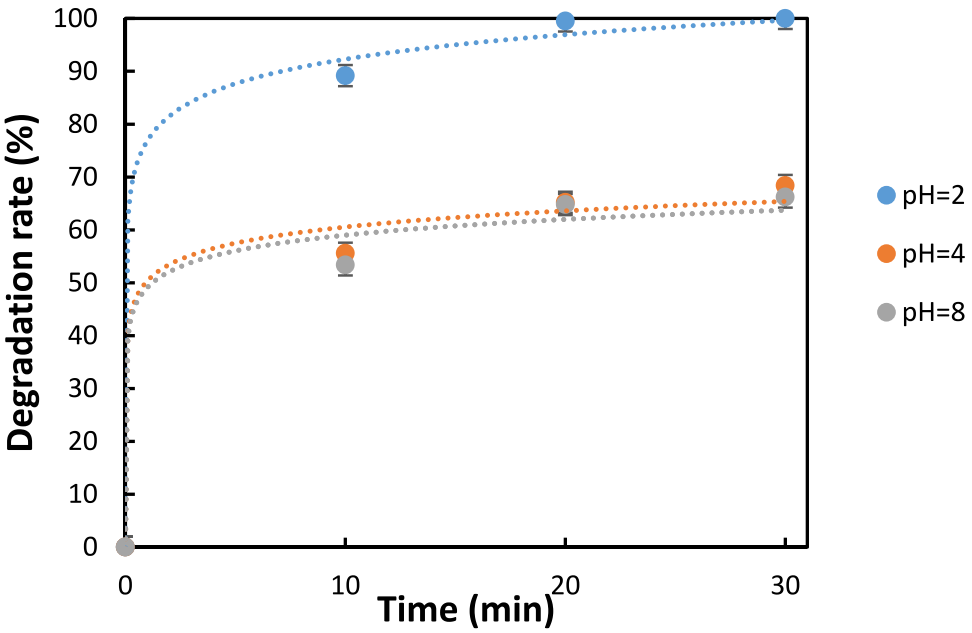

Fig. 8 Effect of pH on the degradation of MB. ($C_0 = 10$ mg/L; $O_3 = 8$ LPM; V = 1 L; pH 2; T = 20 ± 2 ℃)

dye (Li et al. 2015; Goel et al. 2004; Ku et al. 1997). Wang et al. (Wang et al. 2022) reported that the greater degradation rate under acidic circumstances is due to two factors: (I) under acidic conditions, the production of hydroxyl radicals (OH) in the HC system is more beneficial because it precludes ·OH recombination; at the same time, the oxidation potential of ·OH in acidic conditions is greater than that in alkaline ones (Innocenzi et al. 2019; Wang et al. 2022). (II) the enhancement of degradation rate is mostly determined by whether the dye molecules are in the molecular or ionic states. In acidic solutions, MB tends to exist in the molecule state. Because of the molecule's hydrophobicity, MB is mostly found near the gas–liquid interface between the cavity and water (Wang et al. 2022).

MB occurs in an ionic form in alkaline circumstances, then becomes hydrophilic and mostly exists in solution. Due to the short half-life, only about 10% of the generated ·OH diffuses into the main body of the solution. Based on these experimental results, the following experiments were carried out under the condition of solution pH 2.0.

Effect of initial dye concentration

The scope of the first series of experiments is to evaluate the efficiency of O_3 alone at different initial solution concentration before the combination with the hybrid process. In this current investigation, the feeding rate was equal to 8 L/min of ozone. The inlet pressure was fixed at 4.5 bar and the pH 2 while the concentration of MB was varied from 10 mg/L to 100 mg/L. The results are presented in Fig. 9. It can be seen that after 1 h of treatment with O_3 alone, the degradation rate reached 99.6% for an initial concentration of 25 mg/L. For the other concentrations, the rate varied between 99.3%, 85%, and 84.7% for 50, 75, and 100 mg/L, respectively.

Factorial plan

The experimental results were reorganized according to a factorial plan with three factors and multiple levels to identify the effect of the quantities studied in the various experiments. In particular, the following factors were: dye concentration, factor A (10–50–100 ppm); time of treatment, factor B (10–30–60 min); and the type of treatment, factor C (only ozone- ozone/hydrodynamic cavitation). The degradation yields were used for the statistical analysis of the data. The significance of the factors and interactions was determined by the F-test method with 95% confidence levels. The third-order interaction was used to estimate the experimental error. Table 1 summarizes the experimental data.

The data have been used for the Analysis of Variaces (ANOVA) (Table 2).

The results of the ANOVA show that the Factors A (dye concentration), B (time) and C (type of the treatment) influence the dye oxidation process. The AB interaction is also significant. Figure 10 shows the graphs for the three effects and the AB interaction for practical interpretation of the experiment.

It is possible to observe that the factors B (time) and C (type of the process) had a positive effect: an increase in the variable, in the specific case of the factor C, the use of the combined treatment O3 and HC, shifts the mean deviation from the target toward the increase (thus increases the degradation yield). Instead, an increase in factor A (dye concentration) had a negative effect on the degradation process.

HC combined with O_3

Experimental results

Coupling ozone and hydrodynamic cavitation are beneficial in reducing the dose of O_3 and, subsequently, the operative

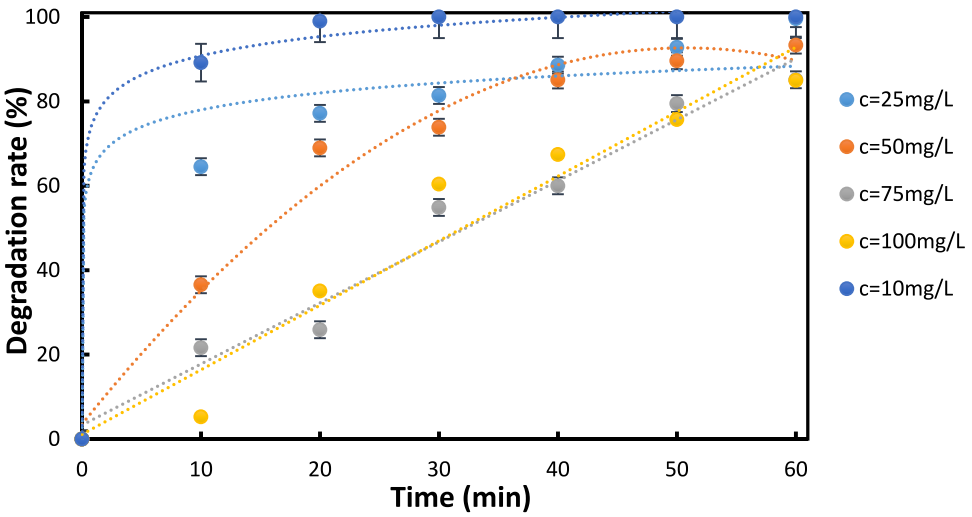

Fig. 9 Effect of O_3 on the degradation of MB at high concentration. (P_{in} = 4.5 bar; O_3 = 8 LPM; V = 1 L; pH 2; T = 20 ± 2 ℃)

Table 1 Factorial plan and experimental results

A, ppm	B-time					
	10 min		30 min		60 min	
	C-Treatment		C-Treatment		C-Treatment	
	O_3	O_3/HC	O_3	O_3/HC	O_3	O_3/HC
10	89.2	89.2	100	100	100	100
50	36.6	65	73.9	86.4	93.3	93.6
100	5.26	28.5	60.4	73	85	85.9

Table 2 Analysis of the variance

	Sum Square (SS)	Freedom degree (df)	Mean Square = SS/df	F value = MS/MSE	P value	Significance (%)
A	4823.49	2.00	2411.75	108.45	7.62E–05	**99.99**
B	5335.71	2.00	2667.85	119.96	5.95E–05	**99.99**
AB	1748.33	4.00	437.08	19.65	2.93E–03	**99.71**
C	337.48	1.00	337.48	15.17	1.15E–02	**98.85**
AC	170.40	2.00	85.20	3.83	9.80E–02	90.20
BC	212.21	2.00	106.10	4.77	6.93E–02	93.07
	12,627.61					
Err	111.20	5.00	22.24			
TOT		18				

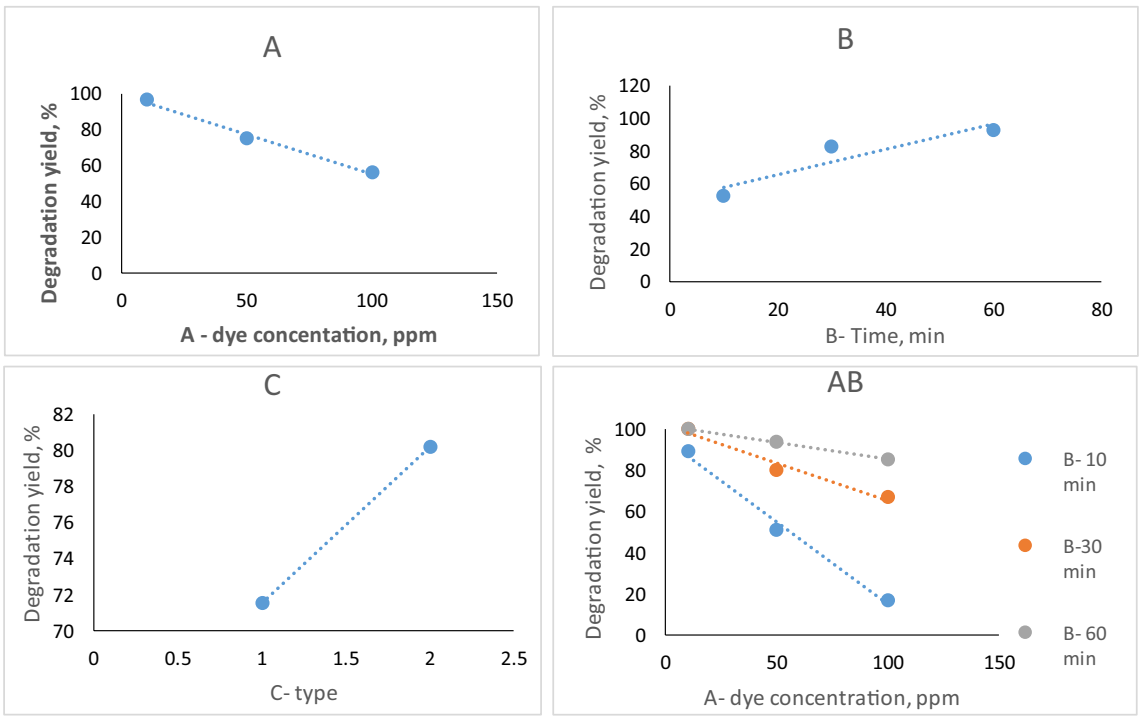

Fig. 10 Main effect and interaction

costs (Gore et al. 2014). Moreover, the secondary pollution problem is prevented by decomposing the residual ozone into oxygen (Malik et al. 2018). As a result, the generation of more hydroxyl radicals (·OH) and the enhancement of ozone dissolution in the effluent (Olson and Barbier 1994) is achieved. Results obtained from O_3 treatment combined with HC are presented below (Fig. 11). The combined process results in a 30-min degradation of 2–4% more than O_3 alone and substantially better than HC alone. This can be explained by the increased synergistic effect that results from the interaction of HC and O_3. The HC improves the gas–liquid mass transport, which supports ozone's oxidation potential. As a result, MB achieves its maximum oxidation capacity (Ku et al. 1997; Bhat and Gogate 2021). The optimization of HC in terms of inlet pressure and cavitation number and the combination with ozone could be an effective solution to reduce the treatment time on the one hand and save energy on the other hand. The degradation rate reaches 99% under the hybrid process.

The result obtained in Fig. 11 can be explained by the fact that the degradation rate constantly rose noticeably when HC and O_3 interacted as the amount of O_3 increased, indicating good synergy between O_3 and HC. There are two primary causes. On the one hand, HC may promote gas–liquid mass transfer, bringing ozone into direct contact with organic contaminants. Ozone may efficiently oxidize MB contaminants due to its high oxidation potential of 2.08 V. On the other hand, the oxidative capacity of MB molecules is further increased by the decomposing of ozone into a more reactive form of ·OH when HC is present.

The synergist effect for the experiment HC and ozone for the experiment with 20 ppm of dye was 1.6. For other test experiments conducted for an initial solution concentration greater than 10 ppm, the degradation yields are near zero, so the effect was not calculated. A value greater than 1 confirms the positive impact of the combined process.

The work involves enhancing experimental technical factors such as inlet pressure, beginning concentration, pH, and combinations of HC with ozone, as well as exploring MB degradation at high concentrations. The following are the appropriate process parameters: 4.5 bar inlet pressure, initial pH 2.0, and initial solution concentration = 10 mg/L (Fig. 12). Table 3 also provides a comparison of various studies relating to dye degradation employing HC in hybrid configuration, showing the specifics of the cavitation devices and the significant outcomes.

Energy and cost estimation for MB degradation

From an industrial point of view, it is crucial to consider the costs of the process. The following compares different methods for treating solutions with varying concentrations of dyes (Ku et al. 1997). More in detail, only the operative cost related to the energy consumption for the degradation of the 95% dye has been included. The time was calculated by using the following Eq. 6:

$$t_{95\%} = 2.996 \times k \tag{6}$$

where k is the kinetic constant of the degradation.

The energy consumption (kWh) was estimated by equation Eq. 7:

$$E = \frac{P_E(kW) \times t_{95\%}\,(h)}{\text{treatment volume}\,(m3)} \tag{7}$$

P_E is the power csumed for the treatment.

Where P_E for the HC experiments is equal to electrical consumption of the pump as in Eq. 8:

$$P_E = \frac{\Delta P(\text{Pa}) \cdot Q(\frac{\text{m3}}{\text{s}})}{\eta} \tag{8}$$

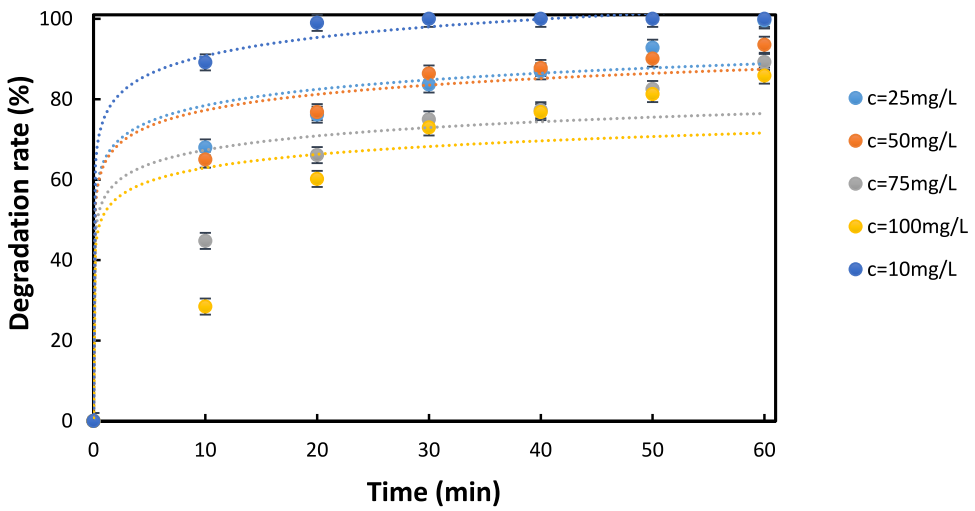

Fig. 11 Effect of HC combined with O_3 on the degradation of MB. (P_{in} = 4.5 bar; O_3 = 8 LPM; V = 1L; pH 2; T = 20 ± 2 ℃)

Table 3 Comparison with other studies of MB Degradation using hydrodynamic cavitation

Sr. No.	References	Degradation method	Optimum conditions and operating parameter	Results
1	Wang et al. 2022)	HC (orifice plate.) Ozone, $Na_2S_2O_8$	1. Pressure = 3 bar 2. pH 2 3. Oxidant: O_3 = 012 g/h 4. $Na_2S_2O_8$ = 0.05 g/l	decolorization in 60 min 1. O_3 (0.12 g/h) = 92.55% 2. HC + O_3 = (0.12 g/h) 99.3% 3. HC alone = 21.8%
2	Kumar et al. 2017)	HC (circular venturi), hydrogen peroxide, photocatalysis (TiO_2)	1. Pressure = 5 bar 2. pH 2 3. Oxidant: H_2O_2 = 1:20 4. TiO_2 = 200 mg/l	1. decolorization in 60 min HC = 15.32%, H_2O_2 = 23.58%, HC + H_2O_2 = 99.64%,HC = 9.46%, HC + H_2O_2 = 18.41%, HC + TiO_2 = 12.68% 2. decolorization in 120 min HC = 32.32%, TiO_2 = 26.52%, HC + TiO_2 = 64.58%

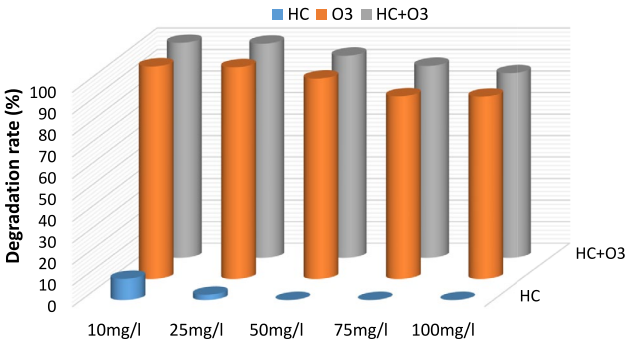

Fig. 12 Comparison of MB degradation efficiency in HC, O_3, and HC + O_3 processes. (P_{in} = 4.5 bar; O_3 = 8 LPM; V = 1L; pH 2; T = 20 ± 2 °C)

ΔP is the pressure drop, Q is the volumetric flow and η is the efficiency (for hypothesis of 50%).

For ozone experiments, the energy consumption was fixed to 105 Watts, as reported in the technical manual of the ozonizer. Table 4 reports the results of this analysis. The energy cost has been estimated multiplied by the PE by the actual price in Italy (0.35 €/kWh). The highest cost is for the single process of hydrodynamic cavitation, which has long treatment times to reach 95% degradation. For example, treating 10 ppm of dye by cavitation alone takes nearly 28 h of treatment time. The time and cost are greatly reduced by using ozone alone or the combined process.

In most cases, the cost for the hybrid process is more expensive (for the same degradation) because in this case, there are two energy cost items, the one related to ozonator consumption and the one related to pump consumption. As regards the cavitation yields, the hybrid process appears to have a higher yield only when working with low concentrations of dye. As the MB concentration increases under the conditions investigated, there is no obvious benefit in using the combined process, the most significant positive effect indeed being attributable to the presence of ozone.

Table 4 Energy consumption for the degradation of 95% of dye solutions

Dye concentration	HC	Ozone (8 L/min)	HC and ozone	Cost for energy (€)	Cavitation yield (mg of dye degraded/J)*
10 ppm	Yes	No	No	620	9.57E–06
10 ppm	No	Yes	No	6	1.75E–05
10 ppm	Yes	Yes	Yes	20	1.90E–05
25 ppm	–	Yes	No	50	1.04E–04
25 ppm	–	No	Yes	50	6.63E–05
50 ppm	–	Yes	No	49	1.15E–04
50 ppm	–	No	Yes	87	8.34E–05
75 ppm	–	Yes	No	69	8.92E–05
75 ppm	–	No	Yes	105	7.49E–05
100 ppm	–	Yes	No	68	1.00E–04
100 ppm	–	No	Yes	110	7.47E–05

(*Calculated at 30 min)

Conclusions

The research paper highlights the importance of the AOP's process in dye treatment. The main objective of this study is to explore the effect of ozone in dye decolorization when it was acting with HC. In the first series of experiments, the optimum operating condition was defined as $P_{in} = 4.5$ bar, pH 2, O_3 dosage = 7.5 mg/L; with the strong oxidation potential, the ozone can promote the efficiency of the process. Thus, the degradation yield increased to greater than 95% when the treatment was carried out with O_3 and $HC + O_3$. Moreover, the combined approach can be more effective in a wide range of concentrations (10–100 mg/l). The ozone and integrated processes allow for lower treatment costs as the time for dye degradation is reduced. Although the combined methods record shorter times for 95% dye reduction, compared to the ozone-only process, the costs turn out to be slightly higher than in the ozone-only case, as there are more energy costs in the hybrid process than in the single treatments. Further investigation should be carried out to investigate the effect of other oxidants as the initial solution concentration varies since, in this study, it was shown that hydrodynamic cavitation alone is effective only for low concentrations of the pollutant; as this concentration increases, a hybrid process should be opted for by going to optimize the concentrations of the reagents according to those of the dye.

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Data availability All other relevant data generated and analyzed during this study, which include experimental, graphic and computational data, are included in this article.

Declarations

Conflict of interest The authors declare no conflict of interest.

Institutional Review Board Not applicable.

Informed consent Not applicable.

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