**Hydrodynamic cavitation as a treatment for the removal of methylene blue from synthetic textile wastewaters**

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**1. Introduction**

Azo dyes are recalcitrant pollutants that constitute a significant burden to the environment; they 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. 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 [1]. These effluents are usually treated to remove pollutants by means of chemical/physical processes (flocculation, coagulation, membrane filtration, and adsorption). But the above mentioned treatments often offer unsatisfactory removal for the presence of some types of color pigments, hard to degrade. Hence alternative processes to remove dyes become necessary, as advanced oxidation processes (AOPs). Among AOPs, hydrodynamic cavitation (HC) has been receiving increasing attention and interest in recent years; 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 occurs at the transition from the liquid phase to the vapor phase when the local liquid pressure drops to the saturation pressure at a given temperature. HC can be generated by alterations in the flow and pressure, which are usually caused by specific constructions like a Venturi tube or an orifice plate [2, 3]. 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 [4]. 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 [5]. By combining HC with other AOPS, the efficiency of degradation of the hybrid technology can be considerably promoted and the processing time and the amount of oxidant can be also reduced [6].

In the present study, the potentiality of hydrodynamic cavitation is analyzed for the degradation of an azo –dye, the methylene blue (MB) from synthetic solutions, mimicking textile effluent wastewaters.

**2. Methods**

Hydrodynamic cavitation experiments have been performed by using the lab-scale experimental apparatus showed in detail elsewhere [6]. The reactor has a volume capacity of 1 L and it has a thermostatic system to keep constant the temperature. The pump withdraws the liquid from the reactor and sends it into the main pipe and through the cavitation device (Venturi tube), where cavitation occurs, therefore it is reinjected in the tank. The liquid flowrate through a by–pass line is checked by a regulating valve.The diameter of the lines is equal to 12 mm. 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 and two manometers (PI, Barksdale Control Products, UPA2 KF16809D). The cavitation device is a Venturi tube with maximum diameter of 12 mm as piping diameter, while the minimum one is 2 mm. The length of the converging and diverging section is 32 mm and 46 mm, respectively. The divergence angle value is 5.74°.

Methylene blue 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. 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. Three series of experiments have been performed in order to study the effect of initial inlet pressure to Venturi that has been varied up to 5.5 bar, the effect of initial pH of solutions (2, 4, 6, 8) and finally the effect of the addition of hydrogen peroxide (molar ratio dye/hydrogen peroxide = 01/30; 1/42; 1/85). The last two series of experiments have been conducted considering an inlet pressure of 5.5 bar (optimal condition found in the first series of test). The reaction time has been set to 60 min, and the samples were collected at regular intervals of 10 min and the analyzed to quantify the extent of MB degradation. The collected samples were analyzed using UV-Spectrophotometer (Cary 1E, UV Visible spectrophotometer Varian) in order to observe a change in the absorbance of MB 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 Eq. [(1)](https://www.sciencedirect.com/science/article/pii/S2213343718306572%22%20%5Cl%20%22eq0005):

** $decolourization efficiency= \frac{\left[MB\right]\_{0}-\left[MB\right]\_{t}}{\left[MB\right]\_{0}} x 100$ (1)

Where *[MB]t* and *[MB]0* were the concentrations of methylene blue in ppm at a generic time (t) and at the initial time.

**3. Results and discussion**

*3.1 Effect of the initial pressure on the HC process*

The effect of the inlet pressure on MB decolourization was studied at different inlet pressures ranging from 2 – 5.5 bar. Fig.1 shows the results of this first series of experiments.

**Figure 1.** Degradation of MB as a function of inlet pressure; pH = 2 and MB initial concentration = 5 ppm

As reported in the scientific literature, the dye degradation increased with increasing the inlet pressure to the Venturi tube, except for the test carried out at 3 bar where a slight reduction in yield was measured. As a consequence of an increase in inlet pressure, a higher number of cavities formed, therefore more collapsing occurred generating additional OH radicals that react with dye. In this case, no reduction in yield was recorded and no higher pressure values were tested for system limits on a laboratory scale, and therefore the choked cavitation phenomenon could not be observed. The lowest and highest values of HC efficiency on the studied process after 1 h, were 7.63% and 24.91% at 3 bar and 5.5 bar, respectively.

*3.2 Effect of the initial solution pH on the HC process*

Fig. 2 shows the results of the second series of experiments. The tests have been performed varying the initial pH solution (2, 4, 6, 8) at the initial pressure of 5.5 bar (optimal pressure, Fig.2).

**Figure 2.** Degradation of MB as a function of inlet solution pH; inlet pressure =5.5 bar and MB initial concentration = 5 ppm

It was observed that the decolourization yield of MB increased with a reduction of the pH value of solutions. A maximum yield near to 25% has been observed at pH of 2, the minimum efficiency has been measured at the pH 8 (8.24%). As demonstrated by scientific literature the acidic pH favors the process, due to the increased production of OH-radicals necessary for the degradation reaction

*3.3 Effect of the addition of hydrogen peroxide on the HC process*

In a second series of experimental tests, the decolourization of MB solution (5 ppm) has been investigated by combining HC with different concentrations of hydrogen peroxide. The presence of this oxidant increases the free radical formation and consequently more OH˙ are available for the degradation of dye. A blank test of MB decolourization was also performed with hydrogen peroxide in the absence of HC under the operative conditions just described (5 ppm of dye, 20 °C, 60 min). After that, a synergism between H2O2 and HC was studied using a mixture of 5 ppm MB and oxidant in the following molar ratio dye/hydrogen peroxide: 1:30; 1:42; 1:85. The results of this third series of experiments are shown in Fig. 3. The degradation in the blanket test was negligible, the highest values of HC efficiency on dye decolourization (95.96%) has been obtained adding H2O2 at the molar ratio dye/hydrogen peroxide of 01/42. It can be seen the positive effect of oxidant combined with HC. A peak efficiency was also recorded during this test, beyond this concentration of hydrogen peroxide the yields decreased until 87.82% using a molar ratio of 01/85. This phenomenon is due to the recombination of radicals. Therefore, the use of oxidant increased the performance of the HC just in the optimum concentrations function of the concentration and type of the substances to degrade and also function of the cavitation intensity existing in the device which decides the capacity for the dissociation of hydrogen peroxide.

**Figure 3.** Degradation of MB as a function of molar ratio dye/hydrogen peroxide; inlet pressure =5.5 bar, solution pH= 2, and MB initial concentration = 5 ppm

**4. Conclusions**

In the present work, the efficiency of the hydrodynamic cavitation for the decolourization of methylene blue has been studied by using a Venturi device. The effect of inlet pressure, solution pH and hydrogen peroxide concentration on dye degradation (5 ppm of MB) has been investigated. The efficiency of the process was significantly influenced by the inlet pressure and by pH of the solutions. More in details, an increase in pressure has a positive effect, while an increase in the pH of the solution has a negative effect. The maximum decolourization yield (24.91%) has been obtained in the following conditions: inlet pressure of 5.5 bar and pH of 2. Subsequently, the experiments were performed with adding hydrogen peroxide in the dye solutions and the efficiency of the combination HC-H2O2 was studied. The combined treatment showed an enhancement of the yields (until to 95.96%) using a molar ratio dye/hydrogen peroxide of 01/42, pH = 2, 5.5 bar after 60 min of treatment. It is clear that the use of the combined process has positive effects on the energy consumption of the HC process. Future research activities will be aimed to test the efficiency of a combined treatment with adding other oxidants, varying the dye concentration and adding more pollutants in order to simulate a textile industrial effluent closer to the real one.

**References**

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