Advanced oxidation processes for the removal of dyes from synthetic industrial wastewaters

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ABSTRACT

Recent studies have demonstrated the efficiency of hydrodynamic cavitation (HC) for treating industrial wastewaters polluted by organic substances. HC provides the production of radicals OH, due to the passage of the aqueous solution through a constriction (an orifice plate or Venturi tube). The radicals react with organic pollutants to form intermediate compounds more readily degraded by the biological processes, or the degradation may lead to complete mineralization. In the present work, the HC process is applied to treat methylene blue (MB) solutions. The core of the experimental apparatus consists of a Venturi tube having an orifice of 2 mm. The effect of inlet pressure on Venturi, solution pH, and initial dye concentration is investigated on MB decolorization yield. The maximum yield is obtained at 0.55 MPa, pH = 2, and an initial dye concentration of MB of 5 ppm. The results have been compared with those obtained for another azo-dye, the methyl orange, in the same experimental conditions, showing comparable results with using HC alone, with degradation efficiencies lower than 30%; the results are unsatisfactory if the HC is used as a stand-alone technique, but can be sufficient if HC is intended as a pre-treatment step prior to a biological process.

Keywords: Dye; Hydrodynamic cavitation; Methylene blue; Wastewater treatment; Advanced oxidation processes

1. Introduction

Among the available techniques to remove micropollutants from wastewaters, advanced oxidation processes (AOPs) are processing technologies that use hydroxyl radicals to oxidize organic contaminants [1]. AOPs include heterogeneous and homogeneous photocatalysis [2,3], Fenton and Fenton-like processes [4], ozonation [5], ultrasound [6], microwaves [7], and γ-irradiation [8]. The effects of AOP treatments have been analyzed from both an experimental and theoretical viewpoint throughout the last two decades [9]; however, despite the considerable promise in wastewater treatment and recent improvements in scientific knowledge, AOPs are still only used on a small scale in pilot and industrial settings, owing to costly equipment and process costs [10]. Furthermore, the wastewater composition determines the efficacy of AOPs, and leftover streams frequently require additional treatment and management, necessitating the use of a combination of removal strategies [3,11,12]. This is the situation with Fe ions created by Fenton treatments in sludge, which require a lot of chemicals and a lot of workforce to treat [13].

In recent years, hydrodynamic cavitation (HC) has gotten much attention and interest among AOPs [14,15]. It consists of the production, expansion, and collapse of microbubbles or cavities, releasing a massive amount of energy in a short period. HC occurs when the local liquid pressure drops to the saturation pressure at a given temperature during the transition from liquid to vapor phase. Changes in flow and pressure can create HC, mainly caused
by specific constructions such as a Venturi tube or an orifice plate [16,17]. The formation of highly reactive free radicals in the aqueous environment is one of HC's key chemical impacts; these radicals can be used to speed up chemical processes like the oxidation of water contaminants [18] up to their complete mineralization. This is particularly relevant when water depuration is aimed at water reuse in a closed-loop [19,20].

Although HC technology has distinct advantages in wastewater treatment, it often may result insufficiently efficient and cost-effective to provide adequate degradation of specific chemicals [21]. By integrating HC with other AOPs, the hybrid technology's degrading efficiency can significantly improve, while decreasing processing time and oxidant use [22].

The potential of hydrodynamic cavitation for the degradation of azo-dyes from synthetic solutions is investigated in this work. Azo dyes are chemical molecules with the functional group RN-NR' (R and R' are frequently aryls) commonly used to color textiles, leather, and various foods [23]. Many azo pigments are non-toxic; others are mutagenic and carcinogenic; they are expelled in effluents after usage, and if released without treatment, they could cause environmental damage [24]. Chemical/physical techniques (floculation, coagulation, membrane filtration, and adsorption) are typically used to remove contaminants from these effluents [25], and the work by Fung et al. [26] outlined how to choose the technique based on the characteristics of dyeing wastewater. For example, ozone treatment could be used to improve the biodegradability only if major pollutants contain conjugated double bonds or aromatic groups [27]; 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 [28]; ultrafiltration processes are indicated to remove solids (1–20 nm) and dissolved organics and macromolecules with molecular weight between 300 and 300,000 g/mol [29–32]. However, the above-mentioned procedures frequently provide insufficient clearance due to some difficult-to-degrade color pigments. As a result, alternative color removal techniques such as AOPs are needed [33].

Hydrodynamic cavitation has already been tested as an advanced technique for the treatment of dyeing wastewaters, and a review of the main interesting results on this topic is reported elsewhere [33]. In addition to already published papers, in a very recently published research [34], HC treatment of methylene blue (MB) was investigated by using an orifice plate, and the effects of inlet pressure, solution pH, and initial concentration on the degradation of MB dye were explored. The maximum degradation rate of MB was obtained at 0.3 MPa, pH = 2, and an initial concentration of 10 mg/L. The combination of Na2S2O8 or O3 with HC was also conducted to explore their synergistic effect. The results indicated that the degradation performance of introducing ozone is better than adding Na2S2O8.

However, the dyeing solutions used for the experiments are generally synthetic, prepared by diluting a single dye in the aqueous phase, neglecting the other substances that could be present in the textile effluents; on the contrary, textile wastewater characterization showed that this type of solutions could contain organic substances as oil, grease, surfactants, and metals. Among the few papers that try to approach the problem of treating with such techniques real waste, of particular interest are the application of hydrodynamic cavitation (HC) and its combination with other advanced processes (such as hydrogen peroxide, Fenton, photo-Fenton, photolytic and photocatalytic process) for the removal of mixed dye (Methylene blue, Methyl orange, Rhodamine B) from aqueous media [35]. From their results, the researchers concluded that the degradation of three dyes in the HC process depends on the $p_c$ at the orifice and the pH of the dye solution. The recommended optimum conditions for removal were 6 bar inlet pressure and pH 3; while the best combination for removal of ternary dye was HC + H2O2 due to its highest synergistic effect, which may lead to the complete decolorization of ternary dye.

The present work is a part of an ongoing scientific activity aimed at defining possible enhanced the hydrodynamic cavitation for the treatment of real industrial effluents. In this paper, an HC process is tested to degrade methylene blue (MB) in an aqueous solution. The research enriches the already published research on the degradation of methyl orange (MO) solutions [22,33], in which the degradation of the dye was carried out with HC alone and combined with other oxidants. The two dyes (MO and MB) are both used for the production of textiles, they are classified as azo-dye, but MB also has chloride in its chemical structure. As regards their hazards, methyl orange is “Toxic if swallowed (H301)”; MB is classified according to EC 1272/2008 as: Flammable liquid and vapor (H226); Harmful if inhaled (H332), and Causes damage to organs (H370, acute tox. 4). In addition, the solutions of MB are considered to be either persistent, bioaccumulative, and toxic (PBT) or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher. In any case, the residual solutions of MB and MO should be discharged as hazardous wastes. The previous MO degradation research showed the HC process efficiency; for that, it has been chosen to investigate the effect of HC on a more complex dye that may also be present in the textile effluents.

In this paper, experimental runs on MB pollutant degradation are presented, obtained by varying the primary process operating variables (pressure, pH, and dye initial concentration), in a lab-scale apparatus with a cavitation device (Venturi). This represents the first step for optimizing the treatment, which is to be tailored to the specific dye.

2. Materials and methods

2.1. Materials

Methylene blue (MB) (C16H18ClN3S, 1% solution, Carlo Erba, Italy) was used to prepare the dye solutions, dissolving the dye in distilled water. The initial concentration of MB has varied in the range of 2.5–10 ppm. Sulfuric acid (Carlo Erba, Italy; 96%) was used to modify the solution pH.

2.2. Hydrodynamic cavitation apparatus

HC experiments were carried out using the apparatus reported in Fig. 1. The setup consists of a holding jacket...
tank of 1 L volume, a centrifugal pump (1,100–3,500 rpm, maximum 375 W, Fluid-o-Tech TSFR series), a pressure meter (Barksdale Control Products, UPA2 KF16809D), a control valves, Venturi tube, flanges, and fittings to accommodate the HC device, the mainline and the bypass line. A thermostatic bath keeps the temperature in the jacketed tank constant at 20°C. A Venturi tube is placed on the mainline; the bypass line is provided to control the flow of the liquid and hence the inlet pressure to the HC device by the control valve (V-1). The inside diameter of the lines and Venturi is 12 mm. All piping components are in Rilsan®, except for valves and the pump, which are in stainless steel to avoid corrosion.

The Venturi is in Plexiglas®; the length of the convergent and divergent is 32 and 46 mm, respectively, the orifice is 2 mm, and the divergence angle is 5.74°. The setup is a closed system; the dye solution is fed into the tank and flushed to avoid corrosion. The Venturi is in Plexiglas®; the length of the convergent and divergent is 32 and 46 mm, respectively, the orifice is 2 mm, and the divergence angle is 5.74°.

2.3. Methods

For each experiment, one liter of MB solution at different concentrations was prepared by mixing dye solution with distilled water. This solution was fed into a jacketed tank. The temperature was kept constant at 20°C. During the test, V-2 was kept fully open, while the valve opening of V-1 depended on the desired inlet pressure to the Venturi device for the specific experiment. The treatment time was set to 1 h, and the samples were collected every 10 min. Three series of experiments have been performed: the effect of inlet pressure on MB decolorization (range: 0.2–0.55 MPa), the impact of the initial pH of the solution (pH range: 2–8) and the effect of the dye concentration $c$ MB (2.5 < $c$ MB < 10 ppm) have been investigated, respectively. The concentration of MB for the collected samples was evaluated by a change in the absorbance of MB with time at a specific wavelength (A) that depended on pH value. After constructing the calibration line, the absorbance was measured using UV-Spectrophotometer (Cary 1E, UV/Visible Spectrophotometer Varian). The MB decolorization efficiency $\eta$ was determined according to Eq. (1):

$$\eta = \frac{[MB]_0 - [MB]_t}{[MB]_0} \times 100$$

where $[MB]_0$ and $[MB]_t$ 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 inlet pressure

In this first series of experiments, the effect of the different Venturi initial pressures on dye decolorization was investigated over the range of 0.20–0.55 MPa. The results are shown in Fig. 2.

The positive effect of the inlet pressure can be seen since the increase in pressure leads to an increase in the degree of decolorization of MB. The efficiency of degradation was near 10% for pressures of 0.2, 0.3, and 0.4 MPa; instead, it was 20% and 25% for an inlet pressure of 0.5 and 0.55 MPa, respectively. This trend is similar to that already found in the literature for other dyes [22,33,36], and the increase of HC efficiency on MB decolorization can be attributed to the enhanced radicals OH production as a result of the intensification of the cavitation activity at the higher pressures [37,38]. To clarify this point, the effect of pressure on MB degradation has been reported in Fig. 3 also in terms of cavitation number, defined as in Eq. (2):

$$C_v = \frac{P_s - P_v}{0.5 \nu v}$$

where $P_s$ and $P_v$ are the pressure downstream of the Venturi device and the vapor pressure of the liquid, respectively; $\nu$ is the fluid velocity at the convergent. The cavitation number is a dimensionless parameter, extensively used in the literature to characterize this kind of device; as the inlet pressure increases, the flow rate increases and the cavitation number decreases because of the higher kinetic energy of the liquid flow. As $C_v$ becomes less than one, the fluid velocity grows, resulting in increased turbulence and, therefore, cavitation occurs with the formation and subsequent implosion of the cavitation bubbles.

From the graph in Fig. 3 it can be seen that for an increase in the pressure upstream of the Venturi, the cavitation number decreases due to the greater kinetic energy of the circulating liquid, falling below the unity for an inlet pressure above 0.2 MPa. Therefore, to be sure to work in cavitating conditions, experiments are conducted for an inlet pressure well above 0.2 MPa. Similar behavior was found for MO and in that case, the phenomenon of choked cavitation condition was observed for pressure above 0.55 MPa ($C_v = 0.37$), characterized by many cavities that merged to form vapor bubbles without collapse to produce radicals useful for the solution decolorization, that produced an inversion in the curve.

To complete the comparison between MB and MO, Fig. 4 has been realized: it shows the Venturi degradation...
efficiency of MO and MB as a function of time for different pressures under the same operative conditions. As can be seen, the orange curves, relative to MO, are almost always above the corresponding MB blue curves; this is probably due to the most complex nature of methylene blue, which is hard to degrade with respect to methyl orange and confirms the need of using a combined treatment to increase the number of hydroxyl radicals OH able to successfully attack the MB molecule. Only for the lower pressure level (0.4 MPa), MB degradation efficiencies are higher than the corresponding MO values, however less than 10%.

3.2. Effect of solution pH and MO initial concentration

The second series of experiments have been performed to investigate the effect of the initial pH of the solutions. All tests have been carried out at the initial pressure of 0.55 MPa, which is the optimal pressure value found in the first series. Fig. 5 reports the degradation yield as the initial pH solution function.

The decoloration yield decreases as the pH of the solution increases; the minimum value has been recorded at pH = 8 (around 8%). Instead, the maximum value was obtained at pH = 2. This trend confirms state-of-the-art for the hydrodynamic cavitation process applied to treat pollutants as dye [22,33,39,40]. Acid conditions favor the HC because if the presence of H+ ions decreases, OH radicals are recombined: in this condition, the radicals cannot react with organic substances. The positive effect of acidic conditions are particularly relevant at high pressure, and it can be explained by considering the phenomenon of cavitation: at higher pressures, there is an intensification of the cavitation activity, leading to increased production of OH radicals, and the presence of H+ ions disadvantages their recombination. Comparing this result with the one previously obtained with MO, it is particularly interesting what happens at different pH values: while for MO in basic conditions the degradation yields were near zero, for MB when pH > 6, removal efficiencies in the range 5%–15% have been obtained. This can be a useful finding for all these processes that need basic conditions to occur, for which to change the solution pH from basic to acidic would need a huge chemical requirement.

In the third series of experiments, the MB concentration was varied, and the solutions were prepared to contain $c_{MB} = 2.5, 5, \text{ and } 10 \text{ ppm. All tests have been carried out at the initial pressure of 0.55 MPa, and pH } = 2$ (an optimal condition found in the previous experiments). After 1 h of reaction, the degradation yields were 26%, 24%, and
less than 2% for 2.5, 5, and 10 ppm of MB. This trend is easily explained, considering that as the initial dye concentration increased, the total molecules of MB increased. In contrast, the total amount of radicals OH remained unchanged (at the same inlet pressure), thus reducing the process efficiency. Therefore, to efficiently treat solutions with higher dye concentrations, a magnifier of OH radical activity would be needed, as the addition of another oxidant with a synergistic effect.

4. Conclusions

This work concerns the study of the cavitation process to degrade methylene blue. The study comprises optimizing the experimental parameters: the inlet pressure to the Venturi device, the initial pH solution, and the initial dye concentration. The main conclusions are summarized below. Inlet pressure has a relevant positive effect: as the pressure increases, the efficiency of the dye decolorization process increases, and an acidic medium favors the HC process. The optimal conditions among those investigated to degrade MB are 0.55 MPa, initial pH 2, and an initial solution concentration of 5 ppm. The maximum efficiency for MB decolorization was around 25%. As regards the effect of the initial concentration of dye on HC efficiency, the results showed that there were no significant differences, in terms of yields, between 2.5 and 5 ppm, while the yield decreased sensibly by up to 1.5% for concentrations of 10 ppm.

The research has shown that hydrodynamic cavitation could be used to treat aqueous solutions containing methylene blue. To increase yields and thus broaden the scope of the process, oxidants could be added that increase the production of radicals useful for the degradation reaction. However, if the HC process is intended as a pre-treatment to a biological step, a partial degradation would be of help to the demolition of organic content.

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References


