

On the Comparison and the Synergistic Effect of Chemical AOP and Hydrodynamic Cavitation

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The recent regulation policies and an increasing public concern are focusing on the presence of priority and emerging pollutant in water. In order to obtain high efficiencies on their abatement in the prevention and remediation of water sources, the Advanced Oxidation Processes (AOP) are among the most interesting and reliable opportunities. Although they have shown a great potential, their employment in waste water treatment plants is still unsatisfactory mainly because of the elevated treatment cost. A great opportunity is given by hybrid cavitation techniques offering low energy consumption. When applied individually hydrodynamic cavitation (HC), often gives insufficient removal percentage degradation, but its efficacy can be significantly enhanced by combining it with other advanced oxidation processes such as Fenton-like treatments. The research study presents the preliminary results of an experimental campaign with the aim of optimizing the process of hybrid HC oxidation and individuating its feasibility in removing emerging pollutants. This paper focuses on the parallel and combined treatment of HC/Fenton and HC/Activated Persulfate, by evaluating the synergistic index and the energy consumption in the p-nitrophenol (pNP) degradation.

1. Introduction

The removal of priority pollutants from wastewater is receiving an increasing attention for the unsuitability of conventional biological treatment in removing such compounds (Rodriguez et al., 2011). In order to match the future stringent regulations, it is necessary to develop innovative separation (Erto et al., 2010) and purification techniques (Capocelli et al., 2012). Among the techniques aimed at the pollutant destruction, Advanced Oxidation Processes embrace the most studied and promising group.

Some example of AOPs are cavitation (ultrasonic and hydrodynamic), photo-catalytic oxidation and Fenton chemistry through Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like processes. Recently, oxidation based on persulfate has drawn increasing attention as an alternative low-cost oxidant in the chemical oxidation of contaminants at mild conditions; its activation via electron transfer from transition metals generates sulphate radicals, extremely reactive species (Rodriguez et al., 2012). These "chemical" AOP can achieve the mineralization of the organic substances as compared to separation and concentration of toxic chemicals by physical and mechanical methods which usually generate secondary pollution (Bagal and Gogate, 2014).

Cavitation techniques are considered a promising "chemical-free" application in the AOP field, for the capability of generating hot spots conditions: cleavage of water molecules (and contaminants) with the formation of reactive species such as hydroxyl radical ($\cdot\text{OH}$) and the initiation of oxidation reactions (Capocelli et al., 2012). In the hydrodynamic cavitation (HC) the hot spots are generated by forcing the water to pass through an orifice or a properly designed constriction. Although HC has shown promising results, its full theoretical comprehension (Capocelli et al., 2014) and high-scale implementation for water

treatment are still at early phase of development (Capocelli et al., 2013a). An effective way in HC research and development is to combine it with chemical oxidation giving benefits of possibly lower energy requirements and lower chemical use (Bagal and Gogate, 2013).

Each AOP alone has shown some limitation to the large scale implementation. The rates of mineralization in HC is lower than other AOP and its applicability to actual effluent streams is hardly explored (all the studies are mostly with the simulated single pollutant solutions, the results of which may not be applicable for a complex effluent stream with large COD values) (Bagal and Gogate, 2014). On the other hand "chemical" AOPs do not represent an universal solution because of some disadvantages; for example Fenton processes are effective in the range of pH 2–4, need additional treatment of the generated iron sludge, has the risk related to the storage and transportation of hydrogen peroxide, require the neutralization of the treated solution before disposal and, most important, the degree of oxidation is limited by the oxidant dose (Bagal and Gogate, 2014).

Thereby, it is widely recognized that a combination of different AOPs is more efficient for wastewater treatment as compared to individual oxidation process due to the high degree of energy efficiency and generation of higher quantum of free radicals: the similarity between the mechanisms of destruction and the overcome of individual drawbacks, points towards the efficacy of the combined process for the degradation of recalcitrant organic pollutants (Bagal and Gogate, 2014).

Objective of the present work is to investigate the application of cavitation in combination with chemical oxidation for pNP degradation. The process analysis and optimization is realized firstly by considering the separate treatment unit: HC and chemical oxidation (through Fenton and activated persulfate). Successively, the hybrid method is evaluated together with the individuation of possible benefits and synergistic features. The principal aim is to understanding possible synergistic effects and finding optimal conditions of the coexistence of different degradation mechanisms and optimize a process and a technology suitable for the industrial treatment of waste waters.

2. Materials and Methods

Oxidation experiments with Fenton and Activated Persulfate as the oxidants were carried out in a batch reactor at 20 °C. The reaction volume were of 0.5 L, initial pNP concentration was 20 mg/L. The amount of reactants were varied as reported in Table 1, where the experimental runs are summarized. The concentration of pNP was analysed in time by using HPLC in order to evaluate the conversion of reagents. As preliminary tests, the conversion of additive chemicals, TOC and toxicity have been evaluated for some of the runs. On the basis of the first test, hybrid tests have been performed, by combining chemical oxidation and hydrodynamic cavitation. The experimental device, shown in Figure 1, is detailed described in a previous paper (Capocelli et al., 2013b) and consists of closed loop circuit with a Venturi reactor. Figure 2 shows the geometrical characteristics of the constriction. 4-nitrophenol, hydrogen peroxide (30 %w/v), Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) were obtained from Sigma Aldrich.

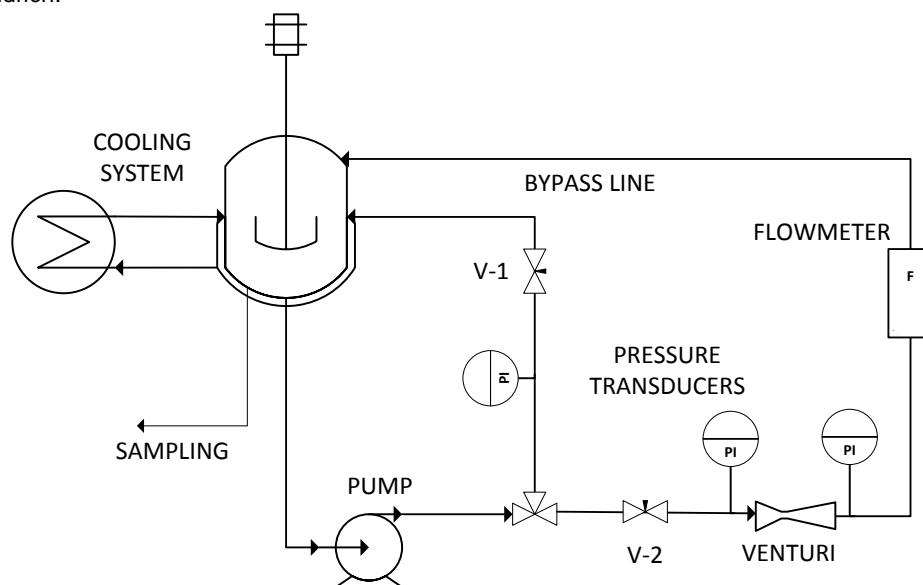


Figure 1: Sketch of the experimental apparatus

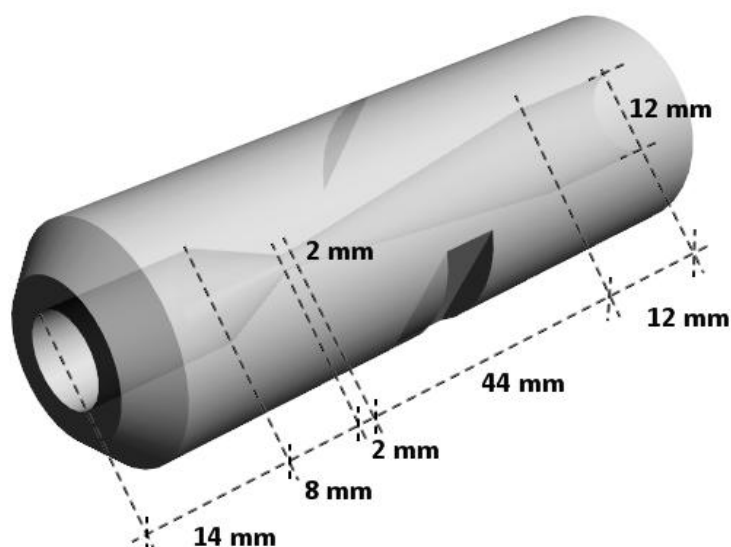
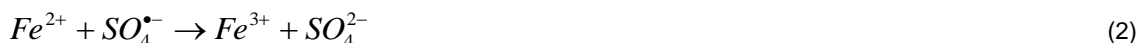
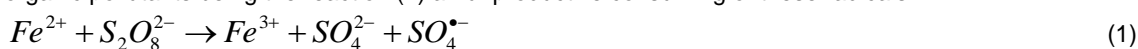


Figure 2: Geometry of the Venturi constriction

3. Results and discussion

For the discussion of preliminary tests, the results focused on the pNP conversion (X). The experimental conditions are reported in Table 1. Figure 3a reports X during the reaction with activated persulphate. The sulphate radicals are formed by reaction among Fe^{2+} and persulphate (Eq. 1). These radicals attack the organic pollutants being the reaction (2) an unproductive consuming of these radicals



Activated Persulfate experiments show a maximum final conversion at higher Fe^{2+} initial loading. Besides, Fe^{3+} is very slowly reduced to Fe^{2+} by some organic intermediates. Therefore, it is noticed a quick rise in pNP conversion at initial stages (when sulfate radicals are formed). The mineralization is not satisfactory (circa 10 %). Afterwards, a second stage of low oxidation rate is observed. The extrapolation of a first-order kinetic constant is reported in Table 1 for the initial stage of reaction.

Figure 3b reports the results of Fenton treatment at two initial concentration: at higher Fe loading, a fast conversion of pNP is noticed. This is accompanied by a fast H_2O_2 consumption and low mineralization: final TOC reduction is observed at 42 % and 25 %, respectively for Fenton 1 and 2. Due to H_2O_2 remaining for a longer time in the media, a higher mineralization is achieved with 5 ppm (40 %), if compared with that obtained using 20 ppm (30 %). Intermediates detected are hydroquinone, benzoquinone and nitrocathecol. The HC alone treatment results are given in Figure 4a at different inlet pressure, P_{in} . The highest removal rate is observed at 0.45 MPa. The existence of an optimal pressure value is visible in different research paper and can be explained by the coexistence of two competing mechanisms (Capocelli et al., 2013a-b): the intensity of bubble collapse and number of bubble generated in dependence to P_{in} . Moreover, the increasing of cavity cloud at higher inlet pressure reduces the cavitation intensity (Pradhan and Gogate 2010).

Therefore, the experiments were repeated at three pressure levels with the addition of Fenton and activated persulfate: the preliminary test suggested the inefficacy of increasing the pressure above the limit of 0.45 MPa for the used Venturi device. The pNP conversion is reported in Figure 4b, an overall improvement has been observed with the highest conversion for the HC/Fenton at 0.45 MPa. In order to quantify the improvement obtained in the hybrid technique, two parameters are calculated: the synergistic effect f (Eq.3) and the cavitation yield (Eq.4).

$$f = \frac{k_{HC/APS}}{k_{HC} + k_{APS}} \quad (3)$$

$$Y = \frac{(pNP_0 - pNP_t) \cdot V}{P \cdot t} \quad (4)$$

where k is the (initial) pseudo-first order constants calculated for each experimental run, V is the solution volume, t the treatment time, pNP_0 and pNP_t the concentration of p-nitrophenol at time 0 and t , respectively.

From Table 1, it is possible to observe an elevated increasing of the energy efficiency (as cavitation yield) in the hybrid techniques. The HC/APS increases Y for more than two times, while the HC/Fenton as even a greater improvement with a maximum at 0.2 MPa (more than eight times).

The synergistic effect indicates if the hybrid techniques is the mere sum of two separated phenomena. For the observed experiments, a synergy is very visible for the implementation of HC/APS. If HC is used combined with PS it is possible to reduce the Fe^{3+} to Fe^{2+} , as noticed by Pradham and Gogate (2010). Similar consideration can be found in the work of Raut-Jadhav et al. (2013) for the degradation of imacloprid and Bagal and Gogate (2013) for the degradation of 2,4-dinitrophenol. A higher value of f has been found in the HC/APS runs, suggesting the idea that the Persulfate can be activated through the implementation of HC; further experiment without the introduction of Fe^{2+} will confirm the hypothesis.

Table 1: Characterization and results of the experimental runs.

Experiment	P_{in} [MPa]	Fe^{2+} [mg/L]	PS [mg/L]	H_2O_2 [mg/L]	PNP_0 [mg/L]	pH	k [min ⁻¹]	f	Y [mg/J 10 ⁵]
HC	2						0.0010		6.7
	3.5	-	-	-	20	3.5	0.0072	-	8.6
	4.5						0.0098		7.8
	5						0.0059		4.4
Fenton 1	-	5	-	40	20	3.5	0.0224	-	-
Fenton 2	-	20	-	40	20	3.5	0.0283	-	-
APS 1	-	5	280	-	20	3.5	0.0055	-	-
APS 1	-	20	280	-	20	3.5	0.0116	-	-
HC/Fe	2						0.0282	1.2	55
	3.5	5	-	40	20	3.5	0.0299	1.0	33
	4.5						0.0452	1.4	24
HC/APS	2						0.0121	1.9	27
	3.5	5	280	-	20	3.5	0.0169	1.3	24
	4.5						0.0390	2.5	23

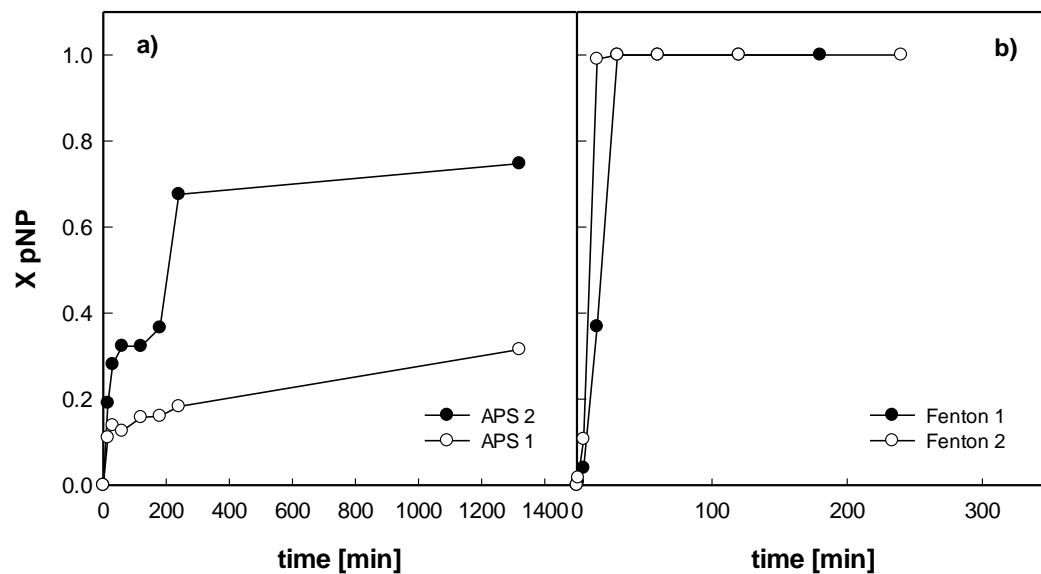


Figure 3: pNP degradation in APS (a) and Fenton (b) experiments

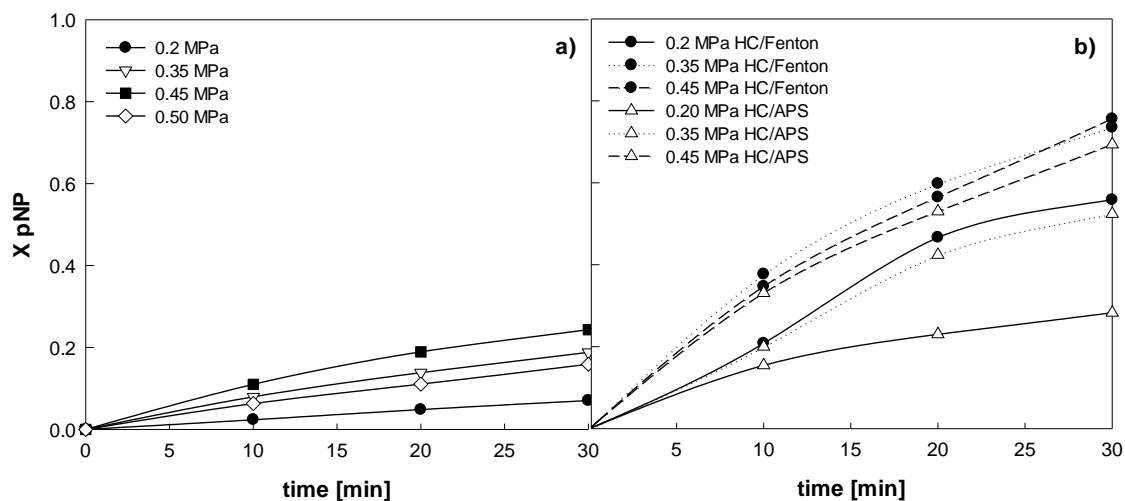


Figure 4: pNP degradation in HC (a) and hybrid experiments (b)

4. Conclusions

The proposed combined treatment strategy is energy efficient and economical as compared to individual processes of cavitation and Fenton or APS. The optimization of the system should include the addition of chemicals as well as the investigation of intermediates. A preliminary analysis individuates that toxic intermediates remain in the media for some experimental runs. Mineralization and H_2O_2 consume will be investigated as fundamental in making the HC hybrid technique more feasible for full scale treatment. The

optimization of reagent loading will be studied with different concentration and sequential addition of reactive in the combined process.

Arise consideration for further analysis are:

- The possibility of treatment at natural pH should be performed in order to balance the degradation results with the need of chemicals required for pH adjustment
- Multipollutant experiments and toxicity analysis are mandatory in order to definitely confirm the possibility of full scale employment
- Mathematical modelling and CFD analysis should be performed in order to evaluate the controlling mechanisms and address the synergistic effect

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