



Research article

p-Nitrophenol degradation by Fenton's oxidation in a bubble column reactor



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ABSTRACT

This paper reports on a study of the oxidation of *p*-nitrophenol (PNP) in a bubble column reactor (BCR). The use of the air stream aimed to provide perfect mixing in the liquid phase, which was successfully achieved and checked experimentally; there were no concentration gradients along the column, even at the lowest air flow rate used ($Q = 1$ mL/min at room temperature and atmospheric pressure). The effect of the operating variables was assessed, and a total reduction of PNP was reached, as well as mineralization of 49.2%, oxidant consumption of 90.3%, and with an efficiency of use - $\eta_{H_2O_2}$ - of 0.09 mg C/mg H_2O_2 , under the best operating conditions found - $Q = 1$ mL/min, $[H_2O_2] = 1.6$ g/L, $[Fe^{2+}] = 80$ mg/L, $pH = 3.0$ and $T = 22-24$ °C - (after 120 min of reaction). Following this, various strategies were developed for improving the mineralization rate; it was found that the addition of H_2O_2 every 5 min and readjusting the pH after 30 min of reaction allow the attainment of a much higher TOC removal (75.1%) and efficiency of oxidant use ($\eta_{H_2O_2} = 0.17$ mg C/mg H_2O_2) with less oxidant. A reaction mechanism was proposed, based on intermediates identified that include *p*-nitrocatechol - PNC, *p*-benzoquinone - PB, hydroquinone - HQ - and carboxylic acids (oxalic, maleic and fumaric). Since the performance achieved in the BCR was good, and very similar to that obtained in a conventional batch reactor, it was possible to verify the efficacy of carrying out the Fenton process in this reactor configuration, which in our future work will focus on the treatability of industrial effluents.

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1. Introduction

Nitroaromatic compounds are widely employed in the manufacture of pharmaceuticals, pigments, dyes, plastics, pesticides and fungicidal agents, explosives and industrial solvents (Spain, 1995). *p*-Nitrophenol (PNP) is toxic to many living organisms, it may accumulate in the food chain (Donlon et al., 1996), and it has been classified as a priority pollutant by the EPA of the United States of America, which restricts its maximum concentration, in industrial wastewater, to between 1 and 20 mg/L (Khatamian et al., 2012; Patterson, 1985). PNP is stable in the environment and non-biodegradable (Kavitha and Palanivelu, 2005; Trapido and Kallas, 2000). Thus, removing PNP prior to discharge of industrial wastewater into water bodies will minimize the environmental impacts and safeguard human health.

Wastewaters containing PNP have been treated by biological

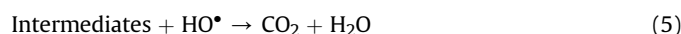
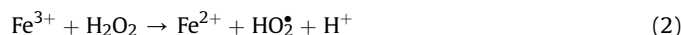
(Bhatti et al., 2002; Gemini et al., 2005; Kulkarni and Chaudhari, 2006; Sponza and Kuşçu, 2005), physical (Bielska and Szymanowski, 2004; Haydar et al., 2003; Li et al., 2009; Zhou et al., 2008a, 2008b) and chemical (Bo et al., 2006; Dai et al., 2008; Sun and Lemley, 2011; Zhang et al., 2012, 2007, 2003) processes. The biological degradation is often inefficient because PNP is toxic. The physical treatment techniques merely transfer the pollutant to another phase; thus, new waste disposal problems are generated. Through chemical processes, high degradation rates can be reached, and almost total mineralization is possible if the reaction conditions and reactor are adequately designed.

Among chemical processes it is worth stressing the advanced oxidation processes (AOP) that take advantage of the strong oxidative capability of the generated hydroxyl radical, which, after fluoride, is the species with the highest oxidation potential (2.8 eV (Papadopoulos et al., 2007)). These radicals are highly reactive, non-selective, and attack most organic molecules, hopefully producing CO_2 , H_2O and inorganic ions, or at least intermediate compounds with less toxicity (Rosenfeldt et al., 2007; Skoumal et al., 2006). One important AOP is the Fenton reaction that generates

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hydroxyl radicals by the decomposition of hydrogen peroxide catalysed by the ferrous ion in an acid medium (eq. (1)), the catalyst being regenerated by the reaction between Fe^{3+} and H_2O_2 (eq. (2)) or HO_2^\bullet (eq. (3)). The complex mechanism is briefly summarized in the following reactions (Walling, 1975):



Equations (4) and (5) show, respectively, the oxidation of organics (RH) by hydroxyl radicals and the mineralization of intermediates. Other relevant reactions occur simultaneously in the Fenton process, namely the ones associated with the scavenging of the hydroxyl radicals in the presence of an excess of either oxidant (eq. (6)) or ferrous iron (eq. (7)) (Walling, 1975):



The Fenton process has several advantages: it is considered a “green technology” because it makes use of environmentally friendly reagents, is highly efficient, incurs low capital cost, can be simply applied, and operation can be carried out at room temperature and atmospheric pressure. The oxidation agents have non-selectivity characteristics, i.e. ability to oxidize various pollutants at the same time, and the process still has instantaneous startup time with toxicity reduction and biodegradability improvement of wastewater, allowing for combination with biological processes (Arslan et al., 1999; Bigda, 1995; Flaherty and Huang, 1992).

In the literature, numerous studies report on the use of closed (batch) reactors to degrade model compounds or treat real wastewater by the Fenton process, which brings disadvantages in terms of industrial applicability because they operate discontinuously. Another configuration is the continuous stirred tank reactor, but these reactors need somewhat complex mechanical agitation. The utilization of bubble column reactors (BCRs) overcomes the problems of these previous configurations. This reactor is a cylinder vessel with a gas distributor at the bottom (Kantarci et al., 2005; Shaikh and Al-Dahhan, 2013) that can be operated in semi-batch (the gas stream is fed continuously and the liquid phase discontinuously) or continuous (the gas and liquid are fed continuously e.g. in counter-current) mode. This reactor configuration has numerous advantages such as good heat and mass transfer, no moving parts, ease of operation, and low operating and maintenance costs (Kantarci et al., 2005; Shaikh and Al-Dahhan, 2013); moreover, the agitation in the reaction medium is provided by the gas bubbles rising through the liquid phase (De Vreede et al., 2006).

The BCRs are utilized as multiphase contactors and reactors in chemical, petrochemical, biochemical and metallurgical industries (Degaleesan et al., 2001). In environmental applications the BCRs are extensively applied in the effluent's treatment by ozonation (Gogate and Pandit, 2004), but only a very reduced number of studies are reported in literature using this reactor configuration for reduction of Hg^0 , NO and SO_2 from gas streams by Fenton (Guo et al., 2011; Liu et al., 2015; Zhan et al., 2013; Zhou et al., 2015) or UV/ H_2O_2 (Liu et al., 2010b) processes; the use of the photo-Fenton process has been described for the removal of volatile organic

compounds from gas waste (Handa et al., 2012; Tokumura et al., 2008, 2013, 2012).

The main goal of this work was to study the degradation of PNP in a bubble column reactor using the Fenton process. To our knowledge, there are no previous studies on the use of bubble columns for the degradation of organic compounds in the liquid phase by this oxidation process. We therefore conducted a parametric study to evaluate the effect of the operating conditions in PNP removal, mineralization, and oxidant consumption. In addition, it was objective of the study: i) to test different approaches that would enhance the efficiency of the process in terms of TOC removal, ii) to propose a mechanism for PNP degradation, and iii) to compare the performance achieved in the BCR with a reactor more commonly used (batch reactor).

2. Materials and methods

2.1. Fenton's experiments

The Fenton reaction was carried out in an acrylic bubble column reactor, which was operated with 7 L of PNP solution; the PNP concentration used (500 mg/L) is typical of industrial effluents (Bhatti et al., 2002; Ji et al., 2017). The internal diameter of the column is 0.098 m and its height 1.40 m; at the bottom of the column there is a gas dispenser that consists of an acrylic dish with 9 orifices, each one with a diameter of 0.5 mm. The column also has three samples collection points located at 0.5, 0.7 and 0.9 m measured from the base of the column (Fig. 1).

First, the air was fed through the base of the column making use of an air pump (Aqua Medic Mistral 2000); a flowmeter (Ohmega FL-2015) allows measuring/control the flow rate of supplied air. Next, the PNP solution was fed into the column and the pH adjusted to the desired value using 1 M H_2SO_4 (Panreac). Following this, the required amount of ferrous sulfate heptahydrate (Panreac®) and H_2O_2 30% (w/v, from Fisher Chemical®) was added, this corresponding to the initial time of reaction. The column was operated at room temperature (22–24 °C).

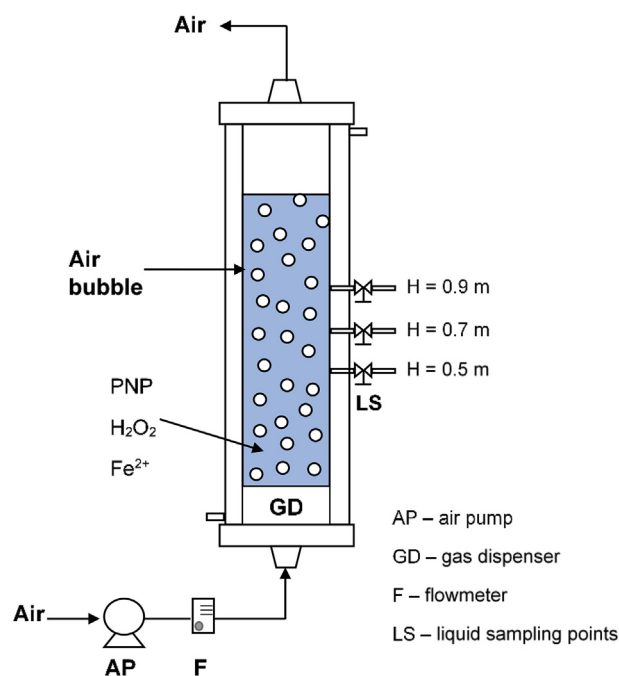


Fig. 1. Scheme of the bubble column reaction set-up.

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