



Gas-liquid effluents treatment in a semi-batch bubbling reactor using Fenton's reagent

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1. Introduction

In the last years, the application of multiphase reactors for environmental processes has increased significantly as an alternative for more conventional ones. Among them stands out the bubbling reactors (BRs), which enable the effective transfer of the pollutant(s) from the gas to a liquid phase [1] for further treatment. The use of BRs and their integration with other processes increased considerably in recent years; a particular example are the advanced oxidation processes (AOPs), like the Fenton process, which are based in the production of a highly oxidizing species, i.e., the hydroxyl radical (HO[•]), able to oxidize most organic pollutants present in wastewaters. The Fenton process main reaction ($\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^\bullet$) results from the catalytic decomposition of hydrogen peroxide (H_2O_2) using an iron salt (usually ferrous ion – Fe^{2+}) for the formation of HO[•] species in liquid phase [2], under acid conditions and moderate conditions of temperature and pressure. Such AOP has been widely studied for liquid effluents treatment.

In this work, it was aimed to evaluate the possibility of using a BR for the treatment of a gas stream containing a model compound, i.e., toluene, using Fenton's process in liquid phase. This way, after absorption of toluene by the liquid where the Fenton's reagents (H_2O_2 and Fe^{2+}) are present, generated hydroxyl radicals oxidize the dissolved toluene, increasing the driving force for further pollutant absorption. The process parameters optimization was carried out, and after the gas treatment stage, a sequential gas-liquid treatment process was proposed for the first time to decrease the organic load generated in the liquid phase. After proving the concept at lab-scale, process scale-up was carried out using a column bubble reactor.

2. Methods

A lab-scale bubbling reactor (0.9 L-capacity) equipped with a water recirculation jacket connected to a temperature control system (Polystat CC1 from Huber), operated under semi-batch mode (with continuous gas supply), was used to perform the toluene treatment. For the gas treatment experiments, the BR was initially filled with 0.5 L of distilled water (pH = 3.0), where a predetermined mass of catalyst ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 99%, Panreac) was added. Toluene (C_7H_8 99 %, JMGS) continuous bubbling was initiated, using a cylindrical gas diffuser (2.5x1.4 cm, HxD, respectively) placed axially centered inside the BR, at the same time that the oxidant (H_2O_2 30 % w/v, VWR) was introduced through a liquid port in the bottom of the BR. The toluene stream was bubbled at 1.0 L/min (at room temperature and atmospheric pressure) with a feed concentration of 0.08 g/L (determined using gas chromatography with flame ionization detection – GC-FID, from Agilent). For the liquid treatment stage, the toluene bubbling was replaced by air bubbling at the same flow rate. During all experiments, gas and liquid samples were periodically collected to measure the evolution of the toluene removal from the gas (using GC-FID) and the dissolved organic carbon (DOC) concentration (using a TOC-L analyzer from Shimadzu) in the liquid.

3. Results and discussion

Firstly, the usability of the BR to perform the toluene treatment using the homogenous Fenton's process was evaluated. The amount of toluene transferred increased when bubbling was coupled with the treatment process using Fenton's reagent (as compared with bubbling in water without Fenton's reagents) because oxidation of the dissolved toluene by the generated HO[•] species increases the driving force for further pollutant absorption.

The effects of temperature (25-40 °C), and H₂O₂ (5 to 20 mM) and Fe²⁺ (0 to 5 mM) dosing in the amount of toluene transferred from the gas to the liquid phase were assessed, reaching a maximum toluene removal of 3.9 g after 120 min of treatment under optimized conditions (T = 25 °C, H₂O₂ = 20 mM, and Fe²⁺ = 2.5 mM). The amount of toluene absorbed by the liquid is obtained from the typical curves as shown in Fig. 1 for the gas treatment step (stage 1). However, for all experiments, a simultaneous increase in the amount of organic species generated in the liquid (as inferred from the DOC concentration) due to the partial pollutant oxidation was observed (see stage 1 in Fig. 1). So, a sequential gas-liquid treatment (including intermediate stages of liquid oxidation) was implemented.

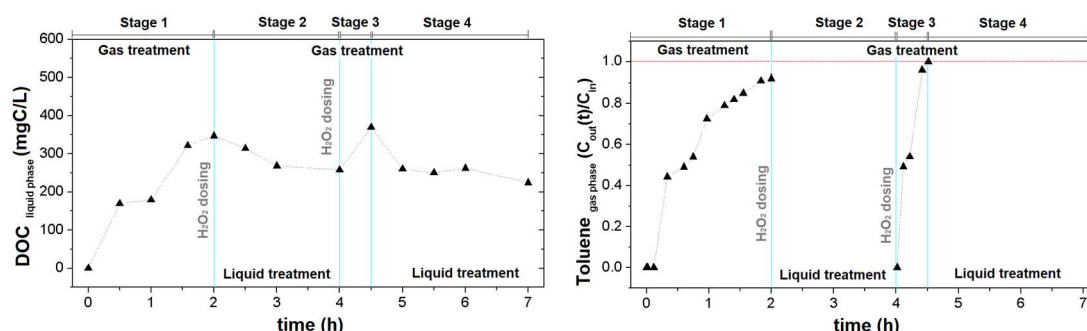


Figure 1. Sequential gas-liquid treatment using Fenton's reagent in a bubbling reactor. Experimental conditions: V = 0.5 L, pH₀ = 3.0, T = 25 °C, [Fe²⁺]₀ = 2.5 mM, [H₂O₂]₀ = 20 mM, and [H₂O₂]_{beginning of stages 2 and 3} = 58 mM.

For the sequential gas-liquid treatment, before the new gas treatment stage (stage 3), more oxidant was added at the beginning of stage 2, which decreased DOC content. Then, a new gas absorption + oxidation was implemented, until the liquid saturation (stage 3) – i.e., until outlet toluene concentration approaches the feed one. This strategy increased the toluene removal, so that after the full sequential gas-liquid treatment, more than 5.0 g of toluene had been transferred.

A scale-up of the process using a bubbling column reactor - BCR (with a 10 times higher volumetric capacity) was also performed, increasing the number of gas treatment stages during the process that was successfully extended to 20 h (data not shown).

4. Conclusions

- The BR proved to be an excellent device for gas treatment using the Fenton's process in the liquid phase;
- The optimization of the reaction parameters provided the transfer of 3.9 g of toluene per cycle;
- The gas treatment increases the DOC in the liquid phase; however, the sequential treatment proved to be an alternative for the reduction of DOC, besides enabling a new gas treatment stage;
- The scale-up of the process to a BCR was successfully performed.

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References

- [1] V.N. Lima, C.S.D. Rodrigues, R.A.C. Borges, L.M. Madeira, Crit. Rev. Environ. Sci. Technol. 48 (2018) 1–48.
- [2] C. Walling, Acc. Chem. Res. 8 (4) (1975) 125–131.