



Photocatalytic ozonation: Maximization of the reaction rate and control of undesired by-products

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ABSTRACT

In the so-called photocatalytic ozonation (PO) synergistic effects between photocatalysis and ozonation enhance the rate of oxidation of organic compounds, therefore this integrated process is very promising for use in water treatment. In the present work, it is demonstrated that the improvement that can be obtained by the integrated process in comparison with the uncoupled processes depends on the relative weight between photocatalysis and ozonation. In this respect, it has been found that a relatively low rate of photocatalysis (0.3 times the rate of ozonation) is sufficient to get the highest synergy and to maximize the performances in the oxidation of formate, the adopted model organic compound. The benefits of the coupling of photocatalysis to ozonation are not limited to the increase of the oxidation rate, but include also the control of the ozonation by-product of main concern (bromate). The effect of the pH, of the presence of oxidizable organic compounds, of the presence of nitrogen on the formation or on the reduction of bromate are experimentally studied and discussed. The obtained results have relevance for the practical applications of PO, since on these bases it is possible to identify proper operating conditions.

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1. Introduction

Interest on advanced oxidation processes (AOPs) for water purification and recovery has significantly increased in the latest years. The main reason for this growing interest is the capability of AOPs to destroy recalcitrant and persistent toxic organic compounds [1–3], such as the pollutants of emerging concern [4], whose presence even at low concentration can be hazardous for human health and is not compatible with many utilizations. Ozonation (OZ) and particularly photocatalysis (PC) produce hydroxyl radicals, the strong oxidizing agent that characterizes AOPs, so they are capable of degrading organics possibly up to their complete mineralization.

However, despite the “green” features of photocatalysis [5,6], in particular if solar radiation is utilized for its activation, and the numerous and promising laboratory results [7], industrial applications of photocatalysis for water treatment are still very scarce [8]. Actually, photocatalysis is hampered by the slow kinetics, which is a consequence also of the low quantum yield [7]. Therefore, a

substantial enhancement of the rate is needed for future practical applications [8].

On the other hand, even the more established process of ozonation, which is currently used for disinfection and purification purposes in aquaculture [9,10] and in waste and drinking water treatment [11,12] is not problem-free. Actually, ozonation is negatively affected by the possible formation of undesired disinfection by-products (DBPs), such as bromate, which is a product of bromide oxidation [13,14] and is suspected to be carcinogenic.

Photocatalytic ozonation (PO), that is photocatalysis coupled with ozonation, can be a viable solution of the aforementioned problems. In fact, a synergistic effect substantially improves the oxidation rate in comparison with the rates obtained with the two processes acting in sequence [15–17] and photocatalysis may control the formation or the accumulation of bromate [18]. However, even if the synergetic effect in PO is well established and the capability of controlling the presence of bromate ions has been recently demonstrated [18], the identification of the more favourable operating conditions is still incomplete and needs further investigation.

Therefore, the aims of the present work are (i) to show that the synergy between the two processes can be maximized by tuning the relative weight between photocatalysis and ozonation, (ii) to identify the conditions (pH, presence of organic compounds, presence of oxygen, presence of nitrogen) that favour or limit the

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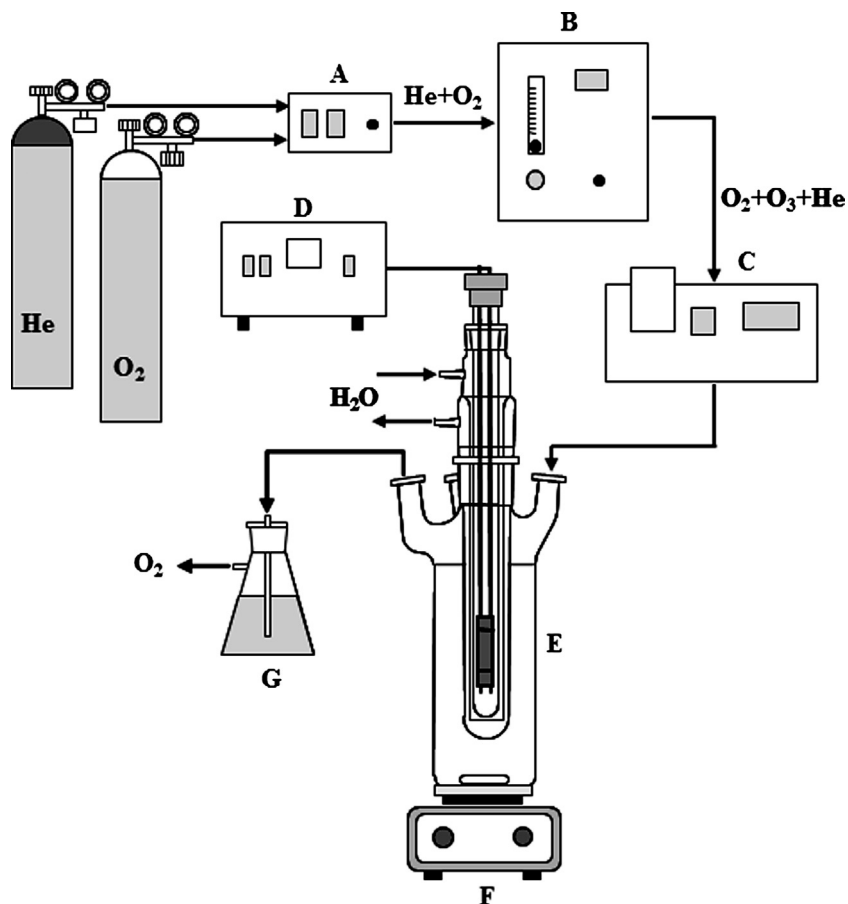


Fig. 1. Scheme of the experimental system. Mass controller (A); ozonator (B); UV-vis spectrophotometer (C); ballast of the lamp (D); reactor (E); magnetic stirrer (F); ozone trap (G).

formation of bromate, and (iii) to establish the operating conditions that improve the removal of bromate, in the case it is produced.

2. Experimental

The experimental set up is almost the same utilized in a previous study [18]. A description containing the essential information is reported below, but additional details can be found in [18].

The scheme of the experimental system is shown in Fig. 1. An annular slurry batch reactor (volume 500 cm³) was utilized for all the OZ, PC and PO experiments. The collection of the samples of the reacting solution and the measurements of the pH took place at regular time intervals. The lamp, which is positioned on the axis of the reactor, emits a narrow spectrum of UVA radiation with a maximum at 365 nm. Borosilicate glass for the walls of the reactor minimizes the absorption of this radiation.

Ozone was produced by a corona discharge ozonator (Microlab) which was fed with 900 cm³ min⁻¹ of pure oxygen or alternatively with a He–O₂ mixture (80% He, 20% O₂). The resulting ozone concentrations are 4.9 × 10⁻⁴ M with pure oxygen and 0.55 × 10⁻⁴ M with the He–O₂ mixture. According to the Henry's constant in [19] the corresponding concentrations of ozone in the liquid phase are 1.05 × 10⁻⁴ M and 0.58 × 10⁻⁴ M, respectively. In a few experiments, the ozonator was fed with technical grade air. The measured concentrations of oxygen in the reacting solution were very close to equilibrium (1.3 × 10⁻³ M for pure O₂ and 2.6 × 10⁻⁴ M for the He–O₂) and were almost unchanged by the possible presence of ozone.

Formate and formic acid were utilized as model compounds for the oxidation experiments in the reactor. These compounds have relatively simple pathways of mineralization, so that the analysis of the kinetic data is simplified. Furthermore, formic acid and formate are short chain organic molecules, which are representative of some chemical species, which are commonly formed during the oxidation of more complex organic compounds. Moreover, the rate of direct attack of ozone to these organic compounds is sufficiently low to take advantage of the synergism between ozone and photocatalysis [17].

4-Nitrophenol (4-NP) was utilized in some experiments as a model organic compound containing nitrogen. All the chemicals (Sigma–Aldrich) were of laboratory grade and were used without further purification. The aqueous solutions were prepared with de-ionized water.

The photocatalyst is commercial TiO₂ Degussa Aeroxide P25. A weighted amount of the photocatalytic powder was vigorously dispersed for 15 min in a given volume of the solution to obtain a uniform suspension. The photocatalyst concentration was 0.2 g L⁻¹ unless otherwise indicated. This value is sufficiently high to permit an almost complete absorption of the photons in the reactor.

The temperature was maintained constant at about 300 K during all the experiments. Before any experiment, the reactor was maintained without illumination for 30 min in order to permit “dark” adsorption of the chemicals and to reach steady concentrations in the suspensions.

The volume of the samples withdrawn for the chemical analysis was 3 cm³. The collected samples were immediately filtered in a PTFE filter (Millipore) with 0.2 μm pores to separate the TiO₂ powders.

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