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Combination of ozonation and photocatalysis for purification of aqueous effluents containing formic acid as probe pollutant and bromide ion

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ARTICLE INFO

Article history:

Received 6 August 2013

Received in revised form

29 November 2013

Accepted 3 December 2013

Available online 13 December 2013

Keywords:

Ozonation

Photocatalysis

Bromate

Water purification

Photocatalytic ozonation

Advanced oxidation processes

ABSTRACT

The treatment by advanced oxidation processes (AOPs) of waters contaminated by organic pollutants and containing also innocuous bromide ions may generate bromate ions as a co-product. In the present work heterogeneous photocatalysis and ozonation have individually been applied and in combination (integrated process) to degrade the organic compounds in water containing also bromide anions. The results show that: i) the sole photocatalysis does not produce bromate ions and in the case of its presence, it is able to reduce bromate to innocuous bromide ions; ii) the integration of photocatalysis and ozonation synergistically enhances the oxidation capabilities; and iii) in the integrated process bromate ions are not produced as long as some oxidizable organics are present.

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1. Introduction

Water detoxification can provide a substantial contribution to water conservation, which is one of the primary objectives of sustainability. In fact, organic polluted and contaminated waters can be recovered and utilized (or reutilized in a closed system) with vital savings of water resources. Some Advanced Oxidation Processes (AOPs), such as ozonation and photocatalysis, have been demonstrated to be able to accomplish

this task (Hoigné, 1998; Beltran, 2003; Chong et al., 2010; Pichat, 2013; Augustina et al., 2005) and to get rid of the organics which are recalcitrant to biological degradation. Therefore, research on these technologies is continuously growing in the recent years. However, the possible formation of undesired oxidation by-products must be taken into account since they may negatively affect the quality of the water. For instance, it is known that bromide ions can be oxidized to bromate ions, which are of major concern for human health (WHO, 1993) and aquatic life (Hutchinson et al.,

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1997; Buttler et al., 2005). On the other hand, bromide ions are almost always present in aqueous systems albeit at various concentrations. Indeed, the Br^- concentrations are relatively low in rainwater, ranging from 0 to $110 \mu\text{g L}^{-1}$ (Neal et al., 2007), but may increase in groundwater where the normal values are between 10 and $2 \times 10^3 \mu\text{g L}^{-1}$ (Flury and Papritz, 1993), to reach a much higher content in seawater (typically about $67 \times 10^3 \mu\text{g L}^{-1}$). Areas close to the sea usually show larger Br^- contents in water and soils than inland areas (Yuita, 1983). The three major manmade releases of bromine into the environment are from mining, from emission of 1,2-dibromoethane, which is used as scavenger in leaded fuel (Kittel, 1983), and from the use of fertilizers and pesticides in agriculture (Bowen, 1979) causing a considerable increase of concentration.

Furthermore, bromide is found in nearly every drinking water source at concentrations ranging from less than 10 to nearly $3 \times 10^3 \mu\text{g L}^{-1}$ (Krasner et al., 1989). In a study on the drinking water sources in USA, Amy et al. (1994) reported an average bromide level ranging between 80 and $100 \mu\text{g L}^{-1}$.

The choice of the AOP for treating wastewater containing bromide is very critical; ozonation of natural waters in the presence of organic compounds and significant bromide levels can cause the harmful formation of brominated organics (Cavanagh et al., 1992; Richardson et al., 1999) and bromate ions (Siddiqui et al., 1995). Since the 90s, the International Agency for the Research on Cancer (IARC) has classified bromate as a potentially carcinogenic species. The WHO (1993) guidelines calculated that a concentration of bromate of $3 \mu\text{g L}^{-1}$ is associated with an upper-bound excess lifetime cancer risk of 10^{-5} . However, due to limitations in available analytical and treatment methods, WHO recommended a provisional guideline value of $25 \mu\text{g L}^{-1}$, for which the risk increases to 7×10^{-5} . The United States Environmental Protection Agency (USEPA) adopted a minimal lethal concentration (MLC) for bromate of $10 \mu\text{g L}^{-1}$ based on the considerations about the minimal health risk, the current available treatment technologies, and the limits of experimental analysis. The same value was proposed by the Drinking Water Commission of the European Union (Council Directive 98/93/EC, 1998). Therefore, these limitations must be considered in any kind of proposed water treatment and guidelines must be drawn to avoid or to control the increase of bromate, which accumulation can be harmful in particular in closed, recirculation systems.

Ozonation (see e.g. Von Gunten, 2003) and photocatalysis (see e.g. Ravelli et al., 2009) are promising AOPs for water treatment. During ozonation of water containing bromide, the formation of bromate occurs. In particular, oxidation by ozone and by the induced oxidizing agents (e.g., the hydroxyl radical, $\cdot\text{OH}$) results in the formation of different intermediate brominated species (hypobromous acid, hypobromite ions, bromite, bromide radicals, and hypobromite radicals) and eventually bromate (BrO_3^-) (Siddiqui et al., 1995).

Heterogeneous photocatalysis is one of the most studied AOPs in the last two decades (Herrmann, 2005; Augugliaro et al., 2010; Akpan and Hameed, 2011a, 2011b; Ibhaddon and Fitzpatrick, 2013; Pichat, 2013). This catalytic process uses semiconductor oxides irradiated by UV light in presence of oxygen at room temperature. The light activates the

photocatalyst and generates on its surface electron–hole pairs, which cause the occurrence of redox reactions of the adsorbed species. This method has been successfully used for wastewater treatment and it is suitable to perform the complete degradation of organic and inorganic pollutants, the reduction of metal ions and the inactivation of many bacteria (Augugliaro et al., 2004; Akpan and Hameed, 2010; Ali et al., 2011; Sunada et al., 2003). Heterogeneous photocatalysis has been also used for purification of indoor air and gaseous effluents contaminated by organics (Pichat et al., 2000; Taranto et al., 2007).

Ozone in combination with heterogeneous photocatalysis, also called “photocatalytic ozonation” (Tanaka et al., 1996; Klare et al., 1999; Piera et al., 2000), has been studied in liquid phase to treat aniline (Sanchez et al., 1998), phenol (Villaseñor et al., 2002), formic acid (Wang et al., 2002), cyanide ions (Hernandez-Alonso et al., 2002), oxalic acid (Addamo et al., 2005) and monochloroacetic acid (Mas et al., 2005). In this “integrated process” a significant improvement of the oxidation performances has been reported since the rate of mineralization of organic substances is greatly enhanced. Likely explanation of the onset of this effect (Tanaka et al., 1996; Klare et al., 1999; Piera et al., 2000; Sanchez et al., 1998) is that ozone is able to generate $\cdot\text{OH}$ radicals on the TiO_2 surface through the formation of an O_3^- ozonide radical ion. Therefore, the production of $\cdot\text{OH}$ radicals on the irradiated surface of photocatalyst would be more effective in the presence of ozone than with oxygen.

In the present work heterogeneous photocatalysis and ozonation have been applied individually or in combination (integrated process) to degrade the organic compounds in water containing bromide anions. Particular attention has been given to the strategies that allow a control of the formation of bromate. In order to represent the organics which are present in wastewaters, formate ions and/or formic acid were adopted since they are small molecules whose degradation pathway is simple so that a more direct analysis is possible of the fundamental phenomena which take place in the system. 4-nitrophenol was also utilized in selected runs as probe molecule to check the effect of the chemical nature of the contaminant on the oxidation process. Photocatalysis, ozonation and the integrated process were studied in order to determine the kinetics of: i) degradation of the organic compound in the presence of bromide ions and ii) formation of bromate ions.

2. Material and methods

The reactions were carried out in an annular batch photoreactor with Pyrex walls which do not absorb UV-A light. The set up of the reacting system is schematically shown in Fig. 1. The 500 cm^3 photoreactor was equipped with ports in the upper part in order to feed gases, to measure pH and temperature and to withdraw samples of the reacting suspension. A medium pressure Hg lamp (Helios Italquartz, Italy, nominal power 125 W) was positioned on the axis of the photoreactor. The lamp was cooled by a Pyrex water-cooling thimble constituting the inner part of the annulus. The emission spectrum of the lamp presents a maximum at 365 nm. The

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