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Energy consumption of three different advanced oxidation methods for water treatment: a cost-effectiveness study

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ABSTRACT

The present work provides an economic comparative study of three TiO_2-based advanced oxidation technologies for removing two well known contaminants from water. The relative costs and outcomes of catalytic ozonation (TiO_2/O_3 in dark), photocatalytic oxidation ($TiO_2/UVA/O_2$), and photocatalytic ozonation ($TiO_2/UVA/O_3$) were compared with regard to the degradation of oxalic acid and dichloroacetic acid as model compounds. The combination of TiO_2, UVA, and O_3 showed the highest cost-effectiveness among the assessed methods. In the case of oxalic acid decomposition, the cost-effectiveness of catalytic ozonation and photocatalytic oxidation was about two and nine times less than that of photocatalytic ozonation. For the degradation of dichloroacetic acid, catalytic ozonation and photocatalytic oxidation were two and 15 times more expensive than photocatalytic ozonation systems with regard to their output. These results were explained well by the synergistic effects on the generation of hydroxyl radicals using photocatalytic ozonation systems.

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1. Introduction

In recent years, the application of advanced oxidation technologies (AOTs) to environmental issues has attracted considerable attention. Many works in the literature have reported on the ability of these technologies to oxidise and remove various organic and inorganic compounds from air, water and, wastewater (Agustina et al., 2005; Sekiguchi et al., 2010; Beltran et al., 2008; Chatzisymeon et al., 2013). In particular, recalcitrant substances and microorganisms which show high persistence against biological and conventional treatments are mainly considered as good targets for advanced oxidation processes (Robertson et al., 2012; Kasprzyk-Hordern et al., 2004).

Oxygen, ozone, and hydrogen peroxide are three significantly important reagents involved in AOTs. Other oxidising reagents such as: persulfate ($S_2O_8^{2-}$), chlorine (Cl_2), etc. may also be used in this way. These are used either combined with each other or applied with different sorts of catalysts and photocatalysts homogeneously (Pillai et al., 2009; Sauleda and Brillas, 2001) and heterogeneously (Giri et al., 2008; Khataee and Kasiri, 2010; Robert and Weber, 1998) and/or in the presence of a wide spectrum of types of irradiation (Nienow et al., 2009; Puma et al., 2010). Therefore, a wide range of

possible combinations could be introduced and evaluated for the oxidation of target pollutant molecules. The purpose of such combinations is the effective generation of hydroxyl radicals as non-selective oxidants which can highly oxidise almost all categories of chemical compounds. The mechanisms of OH radical generation in different AOT systems have been sufficiently described in many works (Chong et al., 2010; Agustina et al., 2005).

Due to the high energy costs involved in handling AOTs (ozone generation, light sources, pumps, etc.), they are still categorised as expensive processes in practice. Therefore, besides investigating the technical feasibility of these technologies in solving environmental problems (Chong et al., 2012), an economic feasibility study must be involved in each treatment case. This important aspect which can promote the commercialisation of AOTs is often neglected.

In this paper, the aim was to provide a methodology for determining the optimum operational conditions of three different advanced oxidation methods and to evaluate comparatively their cost-effectiveness with respect to energy consumption for the removal of organic compounds from aqueous solutions. Other expenses such as maintenance, personnel costs, materials, and so on have not been included in this investigation. Catalytic ozonation (TiO_2/O_3), photocatalytic oxidation ($TiO_2/UVA/O_2$), and photocatalytic ozonation ($TiO_2/UVA/O_3$) were used as oxidation systems. Moreover, based on our experiences in dealing with oxalic acid (OXA) and dichloroacetic acid (DCA) as refractory contaminants in

water, these compounds were chosen as model substances for the present study. The treatments were carried out using a laboratory-scale falling film reactor.

2. Experimental

2.1. Materials and analysis methods

Oxalic acid and dichloroacetic acid of analytical grade (Merck, Germany) were used in preparing the aqueous solutions for the present assessment. An initial concentration of 1 mM was chosen for model compounds in the aqueous solutions. The concentration measurements of oxalic acid and dichloroacetic acid were performed by ionic chromatography using a Dionex DX 500 with conductivity detection connected to an Ion Pac AG4A (guard column) and an AS14 anion exchange column with a 4 mm format (Dionex). The flow rate of the mobile phase, $NaHCO_3$ (1.7 mM)/Na_2CO_3 (1.8 mM), was fixed at 1.2 mL/min.

All runs were carried out under ambient temperature conditions. The treatments were performed at the original acidic pH value of the aqueous solutions of model compounds (pH ≈ 3). A minor decrease in the solution pH was determined over the treatment durations (maximum: 0.2 pH units).

An ozone generator (model OZ 502/10 provided by Fischer, Germany) produced ozone on demand. Pure and dry oxygen (Air Liquide, >99.5 vol.%, H_2O < 200 ppmv) was used as the source of ozone generation as well as for the oxidation process using photocatalytic oxidation systems. By changing the power of the ozone generator from 6 W to 30 W, the ozone concentration in the gas phase was varied from 25 ± 5 mg/L to 135 ± 5 mg/L. An ozone analyser (Ozomat GM model RT1, produced by Anseros, Germany) measured the ozone concentration in the gas phase. Proportionally to the ozone concentration in the gas phase, the ozone concentration in the liquid phase was determined to vary between 10 ± 2 and 36 ± 2 mg/L. The indigo method (Bader and Hoigne, 1981) was used for this measurement.

2.2. Reactor and setups

A falling film reactor was utilised for handling the oxidation systems in this study. A rectangular frame with a special structure made of aluminium was enclosed on both sides by two sheets of self-cleaning glass provided by Pilkington Activ™ as reactor walls. This kind of glass is coated with a thin, colourless, and invisible layer of TiO_2 presenting photoinduced superhydrophilic activity and photocatalytic properties (Mills et al., 2003; Chin and Ollis, 2007; Mehrjouei et al., 2011, 2012). The photoactive surface area of Pilkington Activ™ glasses under the operational conditions of the falling film reactor was about 0.5 m^2 1 L of aqueous solution was injected into the reactor through the top cap so that it would fall over the surface of the glass sheets, forming liquid falling films. The solution recirculation through the reactor was performed using a gear pump at a rate of 1 L/min. A gas stream of ozone and/or oxygen simultaneously flowed at a rate of 10 L/h from the bottom input points into the reactor and left the reactor from the top outlet.

Seven UVA lamps (KG, LT 15 W/009 UV, produced by Narva Lichtquellen GmbH & Co., Germany) were fixed inside the reactor to illuminate the surface of the Pilkington Activ™ glasses. The effect of the number of UVA lamps on the oxidation efficiencies was evaluated by using seven switched-on UVA lamps or by switching off three lamps and using just four switched-on UVA lamps for treatments.

The internal volume of the falling film reactor is 0.01 m^3. This design incorporates three different phases (immobilised photocatalyst as solid phase, aqueous solutions as liquid phase, and ozone/oxygen as gas phase) in an effective oxidative complex with a high surface to volume ratio (10^4 m^2/m^3). The latter is an important factor in fixed-photocatalyst setups for improving the mass transfer properties of oxidation systems. Details of the experimental setup and the reactor design are shown in Fig. 1.

3. Results and discussion

3.1. Oxidation of model compounds

To better understand the oxidation behaviour of the model compounds under the conditions of the falling film reactor, treatment of their solutions was performed initially. Fig. 2 shows the removal trends of oxalic acid and dichloroacetic acid using the three advanced oxidation methods chosen.

Oxalic acid and dichloroacetic acid have already been reported to have low reactivity with ozone alone; however the ozonation processes could be improved by applying different types of catalysts (Wang et al., 2009; Beltran et al., 2005). Under the conditions of the present study, it was observed that existing TiO_2 as a heterogeneous catalyst in the ozonation medium (catalytic ozonation) caused decreases in the initial concentrations of dichloroacetic acid and oxalic acid of about 10% and 25%, respectively, after 1 h of treatment time (Fig. 2). The degradation efficiencies of catalytic ozonation were less than the efficiencies achieved by other oxidation methods, indicating that the presence of catalyst in the dark could not greatly enhance the performance of the ozonation systems.

However, adding illumination to the abovementioned system, that is, irradiating the surface of TiO_2 by UVA lamps in the presence of ozone (photocatalytic ozonation), greatly increased the oxidation rates and the degradation efficiencies of both compounds. An almost complete removal of oxalic acid and ca. 65% efficiency in the removal of dichloroacetic acid were observed after 20 min when using the photocatalytic ozonation technique (Fig. 2). These significantly improved oxidation outputs could be explained by the synergistic effects of the TiO_2/UVA/O_3 combination on the generation of hydroxyl radicals (Mehrjouei et al., 2011, 2012). The OH radicals can oxidise our model compounds more rapidly and non-selectively in comparison with ozone molecules.

The application of photocatalytic oxidation (TiO_2/UVA/O_2) systems showed different results in the degradation of the chosen model substances. While more than 95% of the initial concentration of oxalic acid was decomposed after 1 h, only about 30% of the dichloroacetic acid was oxidised in this period (Fig. 2). This difference in efficiencies can be attributed to the difference in molecular size between these two carboxylic acids. Compared to oxalic acid, the space occupied by the bigger molecules of dichloroacetic acid could hinder the adsorption of more molecules on the surface of the photocatalyst, and as a consequence it negatively influences the oxidation rate of dichloroacetic acid in the presence of photoinduced hydroxyl radicals. Unpublished results of our group concerning the adsorption tests of these two model compounds indicate that the adsorption level of oxalic acid is about two times more than that of dichloroacetic acid on an immobilised TiO_2 sample (6.19 μg/cm^2 for oxalic acid vs. 3.49 μg/cm^2 for dichloroacetic acid). These adsorption results are in a good agreement with those observed in the photocatalysis of model compounds in the presence of ozone and oxygen.

According to the results shown in Fig. 2, the initial removal rates of oxalic acid using catalytic ozonation, photocatalytic oxidation, and photocatalytic ozonation are 6 μM/min, 28 μM/min, and 141 μM/min respectively. Likewise, considering the results presented in Fig. 2, the removal rates of dichloroacetic acid using catalytic ozonation, photocatalytic oxidation, and photocatalytic