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VUV/TiO_2 photocatalytic oxidation process of methyl orange and simultaneous utilization of the lamp-generated ozone

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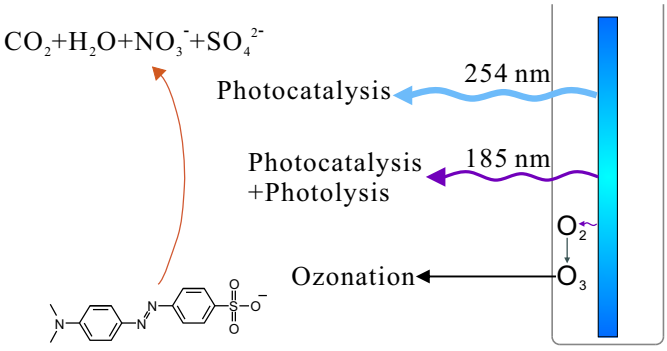
HIGHLIGHTS

- Utilization of lamp-generated ozone in photolytic and photocatalytic degradation.
- Mechanistic study by an innovative cross analysis of COD and UV–visible absorbance.
- Photolytic and photocatalytic oxidation assisted by ozone in a microbubbling reactor.
- Photocatalytic ozonation adopting UV lamp with 185 nm vacuum-UV output.

GRAPHICAL ABSTRACT



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ABSTRACT

A photocatalytic reactor using an ozone-generating mercury vapor lamp with the capability to simultaneously utilize the ozone internally generated from the lamp was fabricated. The reactor included a microbubble-generating mechanism to facilitate the dissolution of ozone and oxygen in the reaction liquid. Photocatalytic and photolytic degradation were investigated using two types of mercury vapor lamps: an ozone-generating lamp emitting at both 254 nm and 185 nm as well as a germicidal lamp emitting only at 254 nm. The roles of ozone, 254 nm light and 185 nm light under the degradation of methyl orange were investigated.

In particular, the mineralization of methyl orange in different processes, namely pure ozonation, photolysis under an ozone-generating lamp with or without the assistance of ozone, photolysis under a germicidal lamp, TiO_2 photocatalysis under an ozone-generating lamp with or without the assistance of ozone and TiO_2 photocatalysis under a germicidal lamp, were analyzed with the chemical oxygen demand and UV–visible absorption measurements.

1. Introduction

In the past decade, heterogeneous photocatalytic oxidation utilizing semiconductor catalysts, mostly TiO_2, assisted by ozone (O_3), an allotrope of oxygen that is much more reactive than the common diatomic O_2, has already attracted much attention (Agustina et al., 2005). Now, many researchers have adopted the term photocatalytic ozonation, to describe this sort of advanced oxidation process (AOP) (Mehrjouei et al., 2015; Xiao et al., 2015). Ozone is referred to as a strong oxidizing agent. Nevertheless, numerous publications have already reported the inability of ozonation alone

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to treat organic chemical solutions constituted in a laboratory (Giri et al., 2007, 2008b; Kopf et al., 2000; Ye et al., 2009) or industrial wastewater (Gimeno et al., 2007). The ozonation alone is characterized by slow oxidation rates and incompetence in reaching high degrees of mineralization (Gilbert, 1987; Giri et al., 2007; Liakou et al., 1997a). Photocatalytic oxidation using air or oxygen is the forerunner of photocatalytic ozonation and has already drawn widespread attention before the booming interest of the photocatalytic ozonation (Hoffmann et al., 1995; Linsebigler et al., 1995). TiO_2 is the most influential photocatalyst in this field owing to its low cost, low toxicity, high stability and impressive ability to decompose organic pollutants (Konstantinou and Albanis, 2004).

Generally speaking, ozonation may be quite efficient and effective in destroying the original organic molecules (Destaillats et al., 2000; Koch et al., 2002; Wang et al., 2003), yet a good extend of mineralization is more likely to be observed in a photocatalytic oxidation (Beltran et al., 2008; Dombi et al., 2002; Giri et al., 2007; Jing et al., 2011; Lachheb et al., 2002; Liu et al., 2005; Mozia et al., 2005; Rey et al., 2012).

When it comes to photocatalytic oxidation, nevertheless, there is still a lot of room for improvement. For example, the fast recombination rate of the photo-generated holes and electrons that severely reduce quantum yield (Linsebigler et al., 1995) is an issue that must be addressed. Both O_2 and O_3 are able to be adsorbed onto the surface of a photocatalyst, react with the photo-generated electrons and suppress the recombination. O_3 is a much more powerful oxidant as compared to O_2; thus it can be more effective to prevent the recombination of holes and electrons and eventually improve the rate of photocatalytic oxidation if O_3 exists (Li et al., 2016; Lian et al., 2015; Mehrjouei et al., 2015; Sun et al., 2013). Currently, most of the researchers conducted their aqueous state UV + TiO_2 + O_3 photocatalytic ozonation studies with either UVA lamps (Aguinaco et al., 2012; Beltran et al., 2008; Černigoj et al., 2007; De Moraes et al., 2000; Farré et al., 2007; García-Araya et al., 2010; Gilbert, 2002; Gimeno et al., 2007; Jing et al., 2011; Kopf et al., 2000; Mehrjouei et al., 2014; Oyama et al., 2009; Rajeswari and Kanmani, 2009; Rodríguez et al., 2012; Wang et al., 2002; Wu et al., 2008) or germicidal UVC lamps (254 nm) (Giri et al., 2010, 2008a, 2007, 2008b; Hsing et al., 2007; Hur et al., 2005; Li et al., 2005, 2003, 2006; Prados et al., 1995; Tanaka et al., 1996; Tong et al., 2005; Ye et al., 2009; Zou and Zhu, 2008) and a separate O_3 generator. Although one of them (Wang et al., 2002) attempted to use low-concentration ozone at about 200 ppm from an ozone-generating low pressure mercury vapor lamp, most of the researchers adopted an electrical O_3 generator capable of generating O_3 with hundred times higher concentration.

Germicidal UVC light (254 nm, hereafter named as 'UVC') is more efficient in the mineralization of organic molecules in photocatalytic oxidation as compared to UVA (Li Puma and Yue, 1999). Thus, more attention should be placed on UVC light sources. Low pressure mercury vapor lamps are the most common UVC light source. Constructed with high purity quartz, the lamps that also can produce a non-negligible vacuum-UV emission at 185 nm are capable of generating ozone in air and hydroxyl radical (**.**OH) in water (Gonzalez et al., 2004). This type of lamp is essentially a dichromatic light source with emissions at both 254 nm and 185 nm and hereafter named as "VUV lamps." The dichromatic light from VUV lamps is hereafter referred to as "VUV." The presence of vacuum-UV light could be very much conducive to the destruction of organic pollutants as vacuum-UV light photolysis alone without photocatalyst is already found to be quite efficient in the mineralization of organic matters (Szeto et al., 2015). Nevertheless, to the best of our knowledge, no research group has reported on the use of a VUV emitting mercury vapor lamp in photocatalytic ozonation studies.

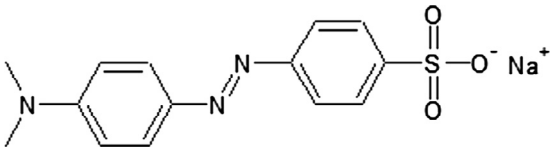

Fig. 1. Methyl orange.

AOP simultaneously utilizing both the light and the ozone internally generated by the VUV lamp has been frequently reported by the studies investigating the photocatalyst free UV + O_3 systems (Zoschke et al., 2014). The use of ozone-generating mercury vapor lamps and simultaneously utilizing lamp-generated ozone is also not uncommon in the research concerning gaseous state photocatalytic ozonation (Fu et al., 2011, 2012), but the same is seldom found in the aqueous state.

Ozone has a high optical absorption at 254 nm (Zoschke et al., 2014) and accumulated ozone around the lamp can absorb UVC light. Pumping the lamp-generated ozone away can improve UVC output and can also create an extra opportunity for oxidation if the ozone is applied to the contaminated water under treatment. These lead to improved energy efficiency. Nevertheless, as far as we know, no publication has been found to feature aqueous state VUV + TiO_2 + O_3 photocatalytic ozonation utilizing the aforementioned internally generated ozone. Therefore, exploring the aqueous state VUV photocatalytic oxidation assisted by ozone originated from the VUV lamp is worthwhile. In this study, a classical mercury vapor lamp with VUV output was adopted as the primary light source and methyl orange (in other words, azobenzene carrying a sulfonic and a dimentylamino substitution on each side, Fig. 1), a common model for AOP studies, was adopted as the organic degradation target owing to its rich UV–visible light absorption properties.

Apart from the VUV + TiO_2 + O_3, experiments on VUV + TiO_2, VUV + O_3, VUV only, UVC + TiO_2, UVC only and O_3 only were also performed for the purpose of comparison.

In order to further clarify the role of ozone and 185 nm light in each condition, a certain extent of mechanistic study was carried out by obtaining the UV–visible absorption spectrum of degradation product samples, and the data were compared with the chemical oxygen demand (COD) results, which was the primary means for evaluating the extent of mineralization.

For the sake of the effective mass transfer of ozone from the gaseous to the aqueous phase, the photocatalytic reactor used in this study had a specially designed microbubble generating mechanism.

2. Experimental

2.1. Reagents

Commercial TiO_2 Degussa P25 was used as photocatalyst throughout the study. Methyl orange ACS grade indicator (MO) was purchased from AJAX chemicals. All reagents were used as received without further purification. Thermo nanopure UV water was used for solution preparation.

2.2. Structure of the photocatalytic reactor

A cylindrical glass photocatalytic reactor shown in Fig. 2 with height of 320 mm, inner diameter of 42 mm and maximum working volume of 320 ml was used in the experiments.

The reactor (b), with an inner diameter of 42 mm and a height of 320 mm, had 2 side ports facing each other near the bottom for aeration and water circulation. A lamp (h) within a waterproof