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Review

Organic pollutants removal in wastewater by heterogeneous photocatalytic ozonation

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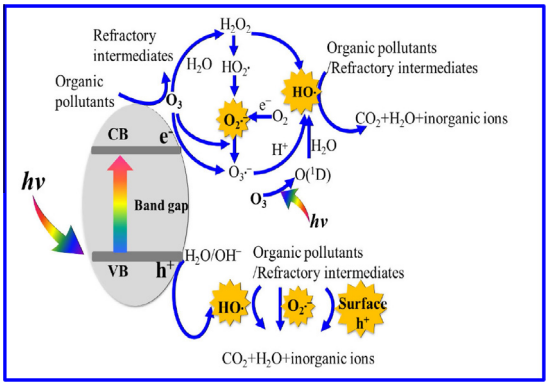
HIGHLIGHTS

- Current catalysts in photocatalytic ozonation are dissected.
- Strategies for fabricating novel TiO_2-based photocatalysts are summarized.
- The operation parameters in photocatalytic ozonation are reviewed.
- Reaction mechanism and generation paths of hydroxyl radicals are discussed.
- Future developing trends are proposed for photocatalytic ozonation.

GRAPHICAL ABSTRACT

Organics oxidation mechanism and the generation pathways of hydroxyl radicals in heterogeneous photocatalytic ozonation.



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ABSTRACT

Heterogeneous photocatalysis and ozonation are robust advanced oxidation processes for eliminating organic contaminants in wastewater. The combination of these two methods is carried out in order to enhance the overall mineralization of refractory organics. An apparent synergism between heterogeneous photocatalysis and ozonation has been demonstrated in many literatures, which gives rise to an improvement of total organic carbon removal. The present overview dissects the heterogeneous catalysts and the influences of different operational parameters, followed by the discussion on the kinetics, mechanism, economic feasibility and future trends of this integrated technology. The enhanced oxidation rate mainly results from a large amount of hydroxyl radicals generated from a synergistically induced decomposition of dissolved ozone, besides superoxide ion radicals and the photo-induced holes. Six reaction pathways possibly exist for the generation of hydroxyl radicals in the reaction mechanism of heterogeneous photocatalytic ozonation.

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Contents

1. Introduction

Industrial activity releases about 300–400 million tons of heavy metals, solvents, toxic sludge and other waste into the global waters each year, posing a great threat to human beings (Palaniappan et al., 2010). Owing to an increasing concern about the refractory organics in wastewater, water quality control and regulations against hazardous pollutants has become more and more stringent in many countries (Pera-Titus et al., 2004). Moreover, new recalcitrant organic pollutants are continuously emerging and discharged into environment (Thomas, 2002), and some burgeoning organics have been found in drinking water (Benotti et al., 2009). As a result, the development of new eco-friendly methods to obliterate these contaminants becomes an imperative task.

Advanced oxidation processes (AOPs), arising in 1970s, are highly competitive technologies for the destruction of a wide range of recalcitrant organic pollutants resistant to conventional approaches. They successfully function in the advanced treatment of low concentrated effluents, and can also be used as pretreatment to enhance the biodegradability of wastewater. Organic contaminants are mainly decomposed by hydroxyl radicals ($HO^{\cdot}$) in the AOPs, a highly reactive agent that non-selectively destroy almost all organics in water (Staehelin and Hoigné, 1982; Glaze and Kang, 1989; Oyama, 2000; Kasprzyk-Hordern et al., 2003; Pera-Titus et al., 2004; Wang and Xu, 2012). The in situ generation of $HO^{\cdot}$ can be facilitated by using luminous, chemical and other form of energy (Augugliaro et al., 2006). To enhance the overall performance, various AOPs are combined in the wastewater treatment, which usually cause interesting synergies (Augugliaro et al., 2006; Shemer et al., 2006; Huang et al., 2008; Oller et al., 2011; Wei et al., 2011; Zeng et al., 2013).

Heterogeneous photocatalysis and ozonation have proved to be efficient tools for eliminating organic contaminants in wastewater (Gaya and Abdullah, 2008; Nawrocki and Kasprzyk-Hordern, 2010). Photocatalysis has shown to be adequate for the destruction of a wide variety of compounds, but the mineralization is slowly attained due to its low oxidation rate and the process is advantageous only for very dilute solutions (Hoffmann et al., 1995; Augugliaro et al., 2006). Ozone is a robust oxidizing agent ($E^0 = 2.08$ eV) compared with other agents, such as H_2O_2 ($E^0 = 1.78$ eV), and can react with several classes of organic compounds through direct or indirect reactions (Oyama, 2000; Zhao et al., 2008, 2009; Cao et al., 2014; Xing et al., 2014a; Huang et al., 2015). Ozonation is more powerful than photocatalysis in organics degradation and more ascendant in treating highly concentrated samples (Agustina et al., 2005; Augugliaro et al., 2006). However, the main drawback of these routes is that they lead to a very limited mineralization of organic pollutants, therefore it is necessary to modified the approach when the complete removal of the compounds and their degradation intermediates is required. To further enhance the mineralization, a combination of heterogeneous photocatalysis with ozone is expected to decompose organic substances more quickly and thoroughly, as shown in Fig. 1. This combination has revealed dramatically synergistic effect that can increase the treating efficiency and shorten the reaction time, as well as the overall costs (Kopf et al., 2000; Wang et al., 2002b; Augugliaro et al., 2006; Wang and Xu, 2012). Consequently, the simultaneous application of heterogeneous photocatalysis and ozonation has great potential in pollutant abatement and wastewater treatment.

Though homogeneous photocatalytic ozonation can also enhance the efficiency in reducing chemical oxidation demand (COD), biochemical oxidation demand (BOD) and total kjeldahl nitrogen (TKN) in effluents (Kern et al., 2013), metal ions would also stay in the solution and thereby giving rise to a second pollution. An additional removal of homogeneous catalyst is then required, which makes the process more complex and expensive. Hence, only heterogeneous photocatalytic ozonation will be discussed in this paper, which is more promising and robust as a new water treatment technology.

In the last decade, photocatalytic ozonation has drawn accelerated attention since its first appearance. The citation in the related area keeps constant growing, as elucidated in Fig. 2. However, to the best of our knowledge, very few reviews on this issue were devoted over all journals, except for the only one published in 2005 (Agustina et al., 2005). The scope of the present paper is to comprehensively address the heterogeneous photocatalytic ozonation of wastewater based on the recently published work. Table 1 summarizes the target pollutants, light sources, catalysts, reaction intermediates, reaction dynamics and main results in these papers. On this basis, the authors shed light on the heterogeneous catalysts and the influences of various operational parameters, further with intensive investigation on the kinetics, reaction mechanism and