Journal of Industrial and Engineering Chemistry 26 (2015) 1–36

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Review

Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: A comparative review

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ARTICLE INFO

Article history:
Received 9 May 2014
Received in revised form 27 August 2014
Accepted 28 October 2014
Available online 4 December 2014

Keywords:
Photocatalytic oxidation
Xenobiotic organic compounds
Modified titanium dioxide (TiO_2)
Industrial wastewater treatment
Visible and solar photoactivity

ABSTRACT

This article compares the effectiveness of pure and modified TiO_2 for photocatalytic degradation of different organic matters and clarifies the advantages of the modified TiO_2 with photoactivity under visible light. Photocatalytic degradation technique with titanium dioxide is generally applied for treating wastewater containing refractory organic contaminants with the purpose of reuse due to its ability to achieve complete mineralization of the compounds under mild conditions such as ambient temperature and pressure. Performance of different types of photocatalytic reactors, effects of important parameters on the reactors performance, effect of various methods used to enhance the photocatalytic activity of TiO_2 including doping, sensitization of TiO_2 and surface modification are discussed in details. So far, a few review papers have been published and extensive information have been reported on the structure and electronic properties of TiO_2, difference between TiO_2 with other common semiconductors used for photocatalytic applications, various methods used to enhance the photocatalytic characteristics of TiO_2 including dye sensitization, doping, coupling, the effects of various operating parameters on the photocatalytic degradation of phenols and dyes and types of reactors, comparison between effective modes of TiO_2 application as immobilized on surface or as suspension, and photocatalytic hybrid membrane system are presented. However, in the published review papers, performance of the different modified photocatalysts is rarely compared quantitatively. Therefore, in order to provide an inclusive and effective comparison among the studies, specific removal rate (SRR) (mg compound$_{removed}$/g cat. h) was calculated as a response.

Contents

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http://dx.doi.org/10.1016/j.jiec.2014.10.043
1226-086X/

Introduction

Industry development is pervasively connected with the disposal of a large number of various toxic pollutants, which are harmful to the environment, hazardous to human health, and difficult to degrade by natural means [1]. Phenols and phenolic compounds are some of the major organic contaminants in industrial wastewater. Sources of phenol include discharges of chemical process industries such as pulp and paper, dyestuff, pharmaceutical agrochemical, petrochemical, food-processing, petroleum refining, steel, tanning, fiber wood, preservatives of food stuffs, coal gasification, polymeric resin production, oil refining, coking plants, and paper mills as well as, herbicides and fungicides production. When phenol-containing water is chlorinated, toxic polychlorinated phenols can be formed. Hence, such effluents require proper treatment before being discharged into the environment. Since they are stable and soluble in water, their removal to reach safety levels in the range 0.1–1.0 mg/L is not easy [2–4]. Removal of color from wastes is often more important than the other organic substances because even the presence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably [5–7]. Henry Perkin accidentally discovered the World's first commercially successful synthetic dye Mauevin in 1856. Since then about 10,000 different dyes and pigments have been produced and used in various industries. Over 7×10^5 tons of dyes are produced annually worldwide. More than half of all dyes used in various industries are azo dyes; which are characterized by one or more azo bonds (–N=N–). It is estimated that about 15% of worldwide produced dyes are lost with wastewater during synthesis and processing [8–10]. The entering of those colored wastewaters in the environment is a major source of non-esthetic pollution and eutrophication that can produce dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater or receiving water bodies [11]. Sources of dye include discharges of chemical process industries such as textile, paper, plastic, leather, ceramic, cosmetics, ink, and food processing [6–9,12–14]. Oxidation processes (biological, chemical or physical) are some of the major steps in water treatment. Biological oxidation is thought to be economically feasible and widely applicable. However, biodegradation is very sensitive to numerous environmental factors. It is slow and often produces unpredictable results. Moreover it is not sufficient for COD and TOC removal in the wastes water with a high fraction of organic compounds. Thus biodegradation is uneconomical for highly concentrated waste effluents and the presence of toxic pollutants in treated water might make this method inapplicable [12–14]. For the removal of such recalcitrant pollutants, traditional physical techniques (such as adsorption on activated carbon, ultra filtration and reverse osmosis, and incineration) can generally be used efficiently. Nevertheless, they are non-destructive, since they merely transfer the contaminant to another phase or location and produce a potentially dangerous and toxic secondary effluent which will leave its own disposal requirement. Consequently, regeneration of the adsorbent materials and post-treatment of solid wastes, which are expensive operations, are needed [8,9,12–15]. Chemical methods have been proved to be expensive as they require high dosage of chemicals and produce large quantity of sludge [16–18]. However, sometimes decomposition by conventional treatments may be difficult. For these situations, it is necessary to develop more effective processes for destruction of such contaminants. Among them, some systems based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have experienced an increasing interest due to their high oxidant power. These systems are commonly named advanced oxidation processes (AOPs) [19,20]. Among the possible technologies to accomplish this task, novel and economical advanced oxidation techniques based on catalytic or chemical photooxidation are emerging as a promising alternative. Semiconductor mediated photocatalytic oxidation has been accepted as a promising alternative to the conventional methods because most of the pollutants can be completely mineralized to CO_2 and H_2O with suitable catalysts [21,22].

Photocatalysis versus conventional technologies

Advanced oxidation process (AOP) has become an attractive choice for degradation of organic compounds from wastewater by employing hydroxyl radicals. There are several methods for generating hydroxyl radicals, e.g. Fenton-based processes [23–31], UV-based processes [32–35], ozone based processes [36–41] and photocatalytic processes [6–8,22,42]. Photocatalytic process as an environmentally friendly process has considerable advantages over some existing technologies; it destroys pollutants rather than merely transferring them to another phase (e.g. activation carbon adsorption, gas sparging) without the use of potentially hazardous oxidants (e.g. ozone, chlorination) [43]. This process can be carried out under ambient conditions (atmospheric oxygen is used as oxidant and solar light can be used as light source) and usually leads to complete mineralization of organic pollutants into CO_2 and H_2O [44,45]. In spite of the advantages of AOPs, there are several limitations in their use: (a) costs may be higher than competing technologies because of energy requirements, (b) harmful intermediates may be formed, (c) pretreatment of the wastewater may be required to minimize cleaning and maintenance of UV reactor and quartz sleeves, (d) handling and storage of ozone and hydrogen peroxide require special safety precautions and (e) major challenges for the photocatalytic process are catalyst deactivation, slow kinetics, low photoefficiency, and unpredictable mechanism [45]. However AOPs are still more effective than the other techniques for wastewater treatment containing toxic and