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Photocatalytic activities of TiO_2 layers immobilized on glass substrates by dip-coating technique toward the decolorization of methyl orange as a model organic pollutant

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ABSTRACT

The aim of this article is to evaluate the photocatalytic activities of the immobilized catalyst layers of titanium dioxide for the decolorization of methyl orange aqueous solution (MO) as a model organic contaminant under UV irradiation. Three stable layers of TiO_2 powder were coated on glass substrate by facile dip-coating technique. XRD analysis showed anatase crystalline structure of catalyst films. The films crystallinity increased with the layers number. SEM analysis showed porous TiO_2 films. The multi-coating increased the coverage surface of glass support. The catalyst films showed well reproducibility and good adhesion to the support after tests. The effects of operating parameters and the number of catalyst layers on the MO decolorization were investigated. The kinetic study of the MO photo-decolorization showed a pseudo-first-order reaction. The MO color removal by the use of three coated layers of catalyst in the optimum reactor was more effective and 5 times faster than that with the use of one coated layer of catalyst at normal conditions. The immobilized layers of TiO_2 powder was found photocatalytic active for complete MO decolorization in the optimum reactor. The immobilized system may replace suspension mode and eliminate the costly separation process.

1. Introduction

The release of colored effluents in the ecosystem forms a primary source of pollution affecting all the flora and fauna in its vicinity [1]. Wastewaters from the textile industry contain large amounts of organic dyes, representing a major threat to the environment due to their toxicity and potentially carcinogenic nature [2]. Wastewater is usually treated by the technologies of ultra-filtration, biological degradation, activated carbon adsorption, nutrient removal, and chemical oxidation. The mentioned methods, however, are often ineffective to mineralize many persistent organics existed in wastewater. These organic pollutants, even in trace amount, are acutely or chronically toxic to aquatic organisms and may pose health risks to humans and animals alike owing to long-term environmental effects [3]. Face to this challenge, heterogeneous photocatalysis has proved its effectiveness and adopted as an alternative technique compared to the classical ones because of its ability to eliminate totally the organic substances without any toxic transformation or transfer to another environment and also it is mostly non-selective; thus, it can be used for a wide range of undesirable compounds which they are refractory, toxic and nonbiodegradable [4,5].

Among advanced oxidation processes (AOPs), heterogeneous photocatalysis with titanium dioxide (TiO_2) has been successfully applied to degrade organic dyes [2]. Titanium dioxide (TiO_2) is generally considered to be the best photocatalyst, and has the ability to detoxificate water from a number of organic pollutants [6]. In addition, titanium dioxide is recognized as one of the most promising photocatalysts in purification of contaminated water and solar energy harvesting, due to its long-term physicochemical stability, strong oxidizing power of its photogenerated hole, high photocatalytic activity, low cost, relative nontoxicity and excellent chemical and biological inertness [7–10].

TiO_2 photocatalyst powder in slurry mode is very useful to remove organic pollutants in water, Nevertheless, this suspension or slurry system has made the scaling-up of the photocatalysis process difficult, due to the complicated separation of suspended ultrafine solid catalysts from the reaction medium, the TiO_2 has to be removed from the decontaminated water to be reused several times [4,9,11]. Two more disadvantages are the difficulty of

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applying this method for continuous flow systems and the formation of agglomerates by TiO_2 particles, especially at high concentrations, which caused a loss of mass transfer and radiation transfer constraints [4,5,12,13]. To solve these problems, titanium dioxide in powder form can be fixed to various substrates such as glass materials (glass beads, glass plates, glass tube, reactor walls and glass rings), quartz, silica, silica gel, alumina, ceramics, stainless steel, alumina clays, activated carbon, fiberglass cloth, zeolites, polymeric material, rare earth oxides, magnesia, pumice stone, cellulose, etc. [14–24]. From the literature survey, glass is commonly used as the coating substrate due to its high transparency to the UV radiation, good adherence to support TiO_2 powder without reduction of catalyst activity, resistance to high calcination temperature; chemical inertness with both catalyst and pollutant molecules, low cost, and resistance to corrosive environments.

Many techniques have been developed to immobilize TiO_2 catalysts onto a solid support [10,25], e.g., sol–gel dip-coating or spread coating, and others like doctor blade, spray coating, spin coating, thermal treatment, chemical vapor deposition, electro-deposition, sol–spray and hydrothermal, which are reported in a recent reviews [11,12,14–16,24,26]. Among the immobilization techniques available, dip-coating technique is a very simple procedure, which offers many advantages over others, including its low cost and high film uniformity, the easy doing where the substrate is immersed in a solution or suspension catalyst and then withdrawn at well-defined speed under controlled temperature and atmospheric conditions, and also the possibility of varying the film properties by changing the solution composition [27]. In addition, the stoichiometry and the high homogeneity of the produced film can be controlled [28]. Even though the immobilization method of TiO_2 photocatalyst is more practical and economical, it would create a decrease in the photocatalytic activity due to the decrease of the catalyst surface area [9,25] and the mass transfer limitations of the pollutants to the surface of the catalyst [25], and it would also take longer time for pollutant degradation compared to the photocatalysts as suspensions [4].

Basically, large surface area is favorable to improve the photocatalytic activity of the photocatalyst system. The large surface area often results from the small particle size or porous structure, which usually corresponds to better anatase crystallinity. Thus, it is expected that retaining a large surface area in the immobilized form of photocatalyst may improve its photocatalytic activity [26].

To overcome the weakness of the immobilization limitation, we can take advantage of the multi-coating technique, which have been recently invoked as a useful method for many purposes, such as waste water treatment especially the elimination or mineralization of organic pollutants [29]. The immobilization of a high amount of catalyst via multi-layer system offers the advantage to increase the photocatalyst surface area and thus increase its photocatalytic activity.

Another issue that needs to be solved is the catalyst activity during its recycled use is the reduce of the activity of the immobilized catalyst with reuse. The decrease of activity is considered to be caused by the elimination of some particles from the catalyst surface during use and also by fouling of catalyst surface by the formation of by-products during the course of the degradation process [26]. So, to succeed the challenge of a total elimination of toxic organic matter present in the aqueous medium, the choice interest of immobilized catalyst layers would be not limited to the conservation of catalyst activity during their re-use, but also to ensure both of catalyst stability and capacity to defend the interactions produced by the reaction medium. For this reason, stability and reproducibility of photocatalyst are important in the immobilized system.

In fact, high active photocatalyst with stable, repeatable form plays the mainly important factor to eliminate organic pollutants from water. However, this latter is not enough to ensure a high efficient photocatalytic application. In practice, the optimum operating factors such as dye initial concentration, solution pH, light intensity, etc., existed and may lead to the maximum efficiency of the photocatalytic process.

In the literature, many researches were interested to study the effect of operating factors on the photocatatytic degradation efficiency of organic pollutants. However, little attention has been diverted to study the effect of coated catalyst layers on the dyes photodegradation when the whole optimum conditions are met together, especially the use of loaded layers of catalyst powder at high light intensity.

This work used immobilized catalyst layers of TiO_2 powder in the optimum reactor, in order to improve the performance of photocatalytic decolorization of methyl orange (MO) as a model organic molecule.

This paper reported, in the first time, the immobilization of catalyst layers on glass substrates by easy dip-coating technique, examined their photocatalytic activities, stability and reproducibility in the

dye decolorization process. In this work, we investigated the effect of operating parameters (dye initial concentration, solution pH, stirring speed and light intensity) on the photocatalytic decolorization of MO. This research was more focused on the effect of coated catalyst layers on the performance of the dye photo-decolorization process at optimum operating conditions. In addition, the paper studied the kinetic of the dye decolorization reaction in the UV/TiO_2 system.

2. Materials and methods

2.1. Materials

Methyl Orange powder ($C_{14}H_{14}N_3NaO_3S$, molecular weight 327.34 g mol^{-1}) was purchased from Fluka and used as the model of organic pollutants. Degussa P25 titanium dioxide powder (mainly anatase with a specific surface area of 50 $m^2\,g^{-1}$ and a mean particle size of 30 nm) from Sigma-Aldrich, ethanol (C_2H_5OH, 96 vol.%) and nitric acid (HNO_3), were supplied by Sigma-Aldrich. The nitric acid was used to adjust the pH of the deposition suspension. Acetone (C_3H_6O, 99.5%) was obtained from Cheminova Internacional.

2.2. Elaboration and characterization of films

The glass slides made from Citoglas England with a surface of 7.5 cm^2 (25 mm × 30 mm) were sonicated for 15 min, with successively distilled water, acetone and ethanol, to remove impurities from substrates. Then they were dried at 80 °C and weighed before any coating by using digital balance to determine the initial weight of the substrate.

The film was prepared by suspending 3 g of TiO_2 powder in 60 mL of 30/70% (w/w) methanol/water mixture, which was sonicated for 15 min to obtain a better dispersion of TiO_2 particles in the suspension. This was followed by adding dilute nitric acid (0.1 N) to adjust the pH of the suspension at pH 3 (Hanna pH-meter) in order to obtain strong adhesion between TiO_2 and the support [17]. Therefore, it is expected that there is an electrostatic attraction between the two surfaces that will enhance the adhesion [17,30]. The whole suspension was vigorously stirred for 1 h to prevent the particles aggregate of TiO_2 and ensure its full dispersion [31]. As precaution, the vigorous stirring of the suspension was maintained until the deposition step to avoid the reproduction of the sedimentation.