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Alternative support materials for titania photocatalyst towards degradation of organic pollutants

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ABSTRACT

Stainless steel mesh and hemmed knitted fiber glass strips were coated with TiO_2 sol to study the possibilities of the two materials as alternative supports for TiO_2 in photocatalytic wastewater treatment process. Commercially available P25, P90 and PC500 powder catalysts were successfully immobilized on stainless steel mesh and fiber glass strips. The prepared photocatalysts were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The retention (stability) of as-prepared layers of photocatalyst on fiber glass strips was tested by sonication test. Best adhesion levels were achieved with P90; with only 17% of photocatalyst loss during the harsh sonication test. The photocatalytic activity was tested with degradation of phenol and commercial textile dye Reactive Blue 19 in flow-through photoreactor. After 240 min of irradiation, mineralization degree of pollutants ranged from 72 to 99% for RB-19 and 38 to 94% for phenol.

1. Introduction

Advanced oxidation processes (AOP) were developed in search of low-cost and efficient methods for degradation of persistent organic pollutants (POPs) in wastewaters [1]. Phenol, a highly volatile aromatic compound in form of white or transparent crystals, is one of the most common POPs found in wastewaters [1]. It is considered carcinogenic, genotoxic and causes weight reduction and infertility to exposed organisms [2]. Because of its harmful properties, it is recognized as potentially hazardous to environment and human, so it needs to be removed from wastewaters before they are released in the environment.

Reactive Blue 19 (RB-19), known as Remazol Brilliant Blue R, is a commercial dye, used in textile industry. It is also categorized as POP. Due to aromatic anthraquinone structure it is very resistant to chemical oxidation [3,4]. Moreover, high dye concentration in surface waters can block photosynthesis [4]. When degrading RB-19 by photocatalysis, one of the AOPs, discoloration occurs much sooner than complete mineralization. TOC analysis is an important technique to observe this discrepancy and signals possible formation of stable reaction intermediates that may be even more toxic than the parent compound.

Photocatalysis aims at degradation of POPs to carbon dioxide, water, mineral salts and acids [5,6]. In this regard TiO_2, the most common photocatalyst, can be used as suspension or immobilized on different supports. The main advantage of suspended photocatalysts is a high contact surface area, which contributes to higher degradation rate of pollutants.

Slurry reactors that utilize suspended photocatalysts are mostly used in pilot laboratory experiments. However, for industrial large-scale applications immobilized photocatalysts are much more desired, since there is no need for filtration unit at the end of the process [7]. This reduces initial and also operational costs, making the method more economically acceptable for large scale industrial usage. Like suspended photocatalysts, immobilized photocatalysts also have its downsides, the main being lower efficiency due to reduced reaction surface, decreasing the degradation rate [7,8]. Because of that the time of photocatalytic treatment has to be prolonged, lowering the daily capacity of substrate treated. Second limitation is that efficient methods for immobilization still need to be developed. Our objective here was to develop industrially viable methods for photocatalyst application together with economically effective supports. For that reason immobilized photocatalyst was used.

For immobilization, different types of supports can be used (glass, aluminum, stainless steel, ceramics, quartz sand, etc.) [9–18]. Due to low costs, good flexibility and efficiency showed in several publications [13–17], fiber glass strips (FGS) have become increasingly popular as support for immobilization of photocatalysts. TiO_2 immobilization on FGSs can be fast and simple, as presented also in this work. A modified dip-coating technique used for FGSs, however, was not appropriate for

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immobilization of TiO_2 on stainless steel mesh (SSM). Therefore, TiO_2 was immobilized on SS mesh by adapting method of electrophoretic immobilization [23]. Dip-coating technique was not found appropriate for SSM support due to two main reasons. In the case of too dense sol, the resulting photocatalyst layer was too thick, for which clear openings were also filled with the sol, which severely decreased retention (stability) as sol in the openings is less stable and was damaged by water flow. In the case of too thin sol, immobilization was impossible since it was running off too quickly to successfully immobilize it.

Research conducted by Dougna et al. [12] reported that stainless steel is a preferable option for immobilization of TiO_2 photocatalyst, compared to Ahlstrom paper with TiO_2 photocatalyst immobilized. El-Kalliny et al. [13] showed that for degradation of sodium hydroxide, stainless steel woven wire mesh is a good photocatalyst substrate due to its large surface area and the possibility of light to be effectively distributed through it. Mozia et al. [14] tested stainless steel mesh and fiberglass strips as substrates for TiO_2 photocatalyst in degradation of phenol. Chen and Chen [15] found that TiO_2 immobilized on fiberglass strip is up to 68% more efficient than TiO_2 suspended in solution. Li et al. [16] obtained similar results while comparing efficiency of TiO_2 immobilized on fiberglass strip and TiO_2 applied on glass as thin film. TiO_2 immobilized on fiberglass strip was up to 40% more efficient degrading methylene blue dye. Erjavec et al. [17] have successfully prepared glass fiber supported TiO_2 photocatalysts for degradation of bisphenolic components in both batch and mixed flow reactor. TiO_2 was immobilized by impregnating the non-wovenglass fiber cloth [17]. A supported catalyst composed of a nanostructured TiO_2 film deposited on a stainless steel mesh using the metal organic chemical vapour deposition technique was prepared by Murgolo et al. [18]. The as-prepared supported photocatalysts demonstrate higher efficiency for degradation of a mixture of contaminants of emerging concern in real groundwater than observed under direct photolysis and photocatalysis using only TiO_2 (Degussa P25) at the same amount of photocatalyst [18].

The main focus of this research is (i) to find chemically inert and economically efficient support materials for the immobilization of TiO_2 that can be used in photocatalytic wastewater treatment and (ii) to develop a user-friendly method for the immobilization of TiO_2 on the support materials. P25, PC500 and P90 were used as titania source. The titania were immobilized on fiber glass strips (FGSs) and stainless steel mesh (SSM) by modified dip-coating and electrochemical deposition technique, respectively. The photocatalytic activity of as-prepared samples was investigated in the treatment of model wastewaters containing phenol and RB-19 as aqueous pollutants. The degradation process was followed by different techniques, e.g. high performance liquid chromatography (HPLC), total organic carbon (TOC) analysis, and UV–vis spectrophotometry.

2. Experimental procedure

2.1. Chemicals and materials

All the chemicals in this study were used as purchased: dye Reactive Blue 19 (RB-19) from Bezema (≥98%), phenol (≥99.5%) from Fluka, tetraethyl orthosilicate (TEOS, ≥98%) from Acros Organics, ethanol (absolute, ≥99.9%) from Carlo Erba, isopropyl alcohol (≥99.9%) from Carlo Erba, hydrochloric acid (≥37%) from J.T. Baker, Levasil 200/30% from H.C. Stark, oxygen – O_2 (≥99.9) from Merck, ammonium acetate (≥96%) from Merck, acetonitrile (≥99.9%) from J.T. Baker. Commercial TiO_2 nanopowders were obtained from Evonik Degussa (Aeroxide® P25 and P90) and Cristal Global (Millenium/CristalACiV™ PC500). All aqueous solutions were prepared using double deionized water from the NANOpure system (Barnstead). Hemmed knitted fiber glass strip (5 cm × 230 cm) was acquired from Toolcraft, while stainless steel mesh (d = 1.4 mm, w = 0.315 mm, AISI 304) and stainless steel net (d = 1.6 mm, w = 11.2 mm, AISI 304) from Fipis d.o.o.

2.2. Preparation of titania/binder sol suspension

Immobilization of different commercial TiO_2 nanoparticles on fiber glass strips (FGSs) and stainless steel mesh (SSM) was conducted using the sol suspension procedure [9,19,20]. For titania sol preparation, 30 mL titanium tetraisopropoxide (TTIP) diluted in 5 mL ethanol was hydrolyzed in an aqueous solution (90 mL) of $HClO_4$ (70%), where acid stabilized the sol. During hydrolysis and condensation reaction of TTIP, a white precipitate of hydrated amorphous TiO_2 was formed, which was then refluxed for 48 h, causing the crystallization and deaggregation of TiO_2, resulting in a stable nanocrystalline titania sol.

In another part, a homogeneous silica sol was prepared from TEOS (3.72 mL), deionized water (2 mL) and HCl (37–38%) (15.5 μL), to hydrolyze silica precursor for later condensation reaction. Afterwards, 4.2 mL titania sol, 600 μL silica sol, 1 mL Levasil 200/30% and 4 mL ethanol were gradually mixed together to give a binder sol. Finally, 1.6 g of titania nanopowders (PC500, P25 or P90) were suspended in the binder sol. The titania/binder sol was then placed in a cold ultrasonic bath for 10 min to obtain the final sol suspension that contained 17.8 wt.% total TiO_2.

Titania-silica sol that was prepared as described above was used for fiber glass strips coating. However, for stainless steel mesh, diluted sol was applied, containing 32 mL of total amount of ethanol and selected P90 titania nanopowder. It is important to mention that the amount of titania from TTIP in the titania/binder sol suspension is very low compared with commercial titania (0.0081 mol vs. 0.05 mol), therefore the effect of titania sol from TTIP precursor in the titania/binder sol suspension is negligible regarding its activity contribution, however it acts beneficially as a binder component [19].

2.3. Immobilization of titania/binder sol suspension

Hemmed knitted fiber glass strips (FGSs) and stainless steel mesh (SSM) were used as photocatalyst substrates.

Immobilization on FGSs was done by dip-coating technique using a home-made device, which allowed constant and steady TiO_2 sol immobilization. Before immobilization, the FGSs were washed with ethanol and deionized water. After drying, the clean FGSs were slowly dipped in titania/binder sol horizontally and then dried. The pulling speed of strip was 1 cm s^{-1}. Amount of deposited catalyst after first immobilization was 3.9 mg cm^{-2}, which is sufficient for effective absorption or UV-irradiation. The photocatalysts immobilized on FGSs were placed in an oven at 150 °C for 1 h. P25, PC500 and P90 have already crystalline structure and the heat treatment is needed just to immobilize the titania/binder sol suspension on fiber glass or SSM effectively. It does not have any important effect on the crystallinity of the photocatalyst [22]. Afterwards, the immobilized photocatalysts were cooled to room temperature and then placed under UV light to degrade any organic matter which was not eliminated during the drying procedure.

Electrophoretic method of TiO_2 immobilization on SSM was applied which was adopted from Yanagida et al. [23] and slightly modified. The electrochemical deposition system consisted of a laboratory power supply (Voltcraft PS 405 PRO), a polished aluminum plate, and a Plexiglas container. The Plexiglas container was filled with the titania-binder sol, in which the aluminum plate (used as the anode) and SSM (used as the cathode) were submerged. Prior to the immobilization process, the SSM was cut into hexagonal shape (side = 8 cm) and rinsed with ethanol. After applying the electric power of 200 W (40 V, 5 A) for 20 s, the SSM was taken out from the container and the excess sol suspension was removed by an air compressor. Afterwards, the mesh was dried and put in an oven at 150 °C for 1 h and then placed under UV light for 1 h to remove any organic residues. Only two layers could be deposited on one piece of support because of electric current limitations. With a stronger power supply, more layers can be immobilized. If immobilization time was longer than 20 s, the layer was too thick,