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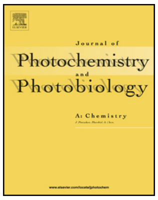

Photocatalytic degradation of the herbicide terbuthylazine: Preparation, characterization and photoactivity of the immobilized thin layer of TiO_2/chitosan

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ABSTRACT

The aim of this study was to immobilize a photocatalytic TiO_2 layer on a suitable support material for potential use in a variety of photoreactor designs. The immobilized TiO_2/chitosan thin film was used for the photocatalytic treatment of a triazine herbicide, terbuthylazine as representative agrochemical pollutant in the wastewater. The method of preparation was based on the use of a chitosan as binder and glass fiber woven roving material as a support. The employed method was found to be very simple, low cost and quite effective. Several methods of the photocatalyst characterization, such as FE-SEM/EDX, AAS, ICP-MS, TOC and nitrogen adsorption/desorption at 77 K were employed to correlate structural and morphological properties of immobilized TiO_2–chitosan/glass fiber woven roving and its photocatalytic properties under UV irradiation. Reaction was performed in a self-constructed batch mode and annular type of the photoreactor. Comparison of thermal, photolytic and photocatalytical degradation of treated terbuthylazine at different reaction conditions was performed in order to get more insight into the photocatalytic performance and reaction mechanism. It was observed that there is no decay in photocatalytic efficiency over a long period of reaction time using for the photocatalytic degradation of terbuthylazine.

1. Introduction

Photocatalytic treatment of wastewater has been recently focused on the degradation of persistent organic pollutants (POPs) which are not readily destroyed by conventional degradation methods. Among the various groups of POPs, pesticides and endocrine disrupting chemicals (EDCs) are important examples [1–6].

In the most cases the research in the TiO_2 photocatalysis is based on using suspended particles of the photocatalyst in water, due to the largest possible specific surface. The possible applications are very wide when it comes to the oxidation of organic compounds, due to the high efficiency and lack of selectivity [7–12]. The major drawback of this process is the final recovery step, which is why new separation techniques are being researched [13–16], as well as photocatalyst poisoning and regeneration [17]. Recovery is not only a problem caused by the cost of the catalyst, but also because of issues regarding the release of nanoparticles in the environment [18–21], even are more dangerous when combined with expensive metals or other potentially dangerous substances.

Immobilization of TiO_2 started in the 1980s [22] and since then a great number of supports are investigated [17] as well as a great number of immobilization procedures [23]. Since TiO_2 coatings are generally very thin, the actual surface area is very small compared to the volume of the reactor, which, along with the mass transfer limitations, can lead to 60–70% reduction in photocatalyst performance compared to the suspension form. On the other hand, the coated photocatalyst may be more easily modified by surface enhancements, new reactor design or secondary surfaces. Regeneration is often needed and also much easier, and most importantly, photocatalyst can be easily reused [17,24–29]. However, immobilization itself is not enough. In order to make photocatalysis viable on an industrial level, preparation of the photocatalyst has to be simple, safe and convenient to use. A solution where the catalyst is immobilized directly on the light source or on the reactor walls is useful in some cases [30], but during water treatment, it is hardly viable, as it would require changing big parts of the reactor systems in industrial installations.

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There is a need to develop removable, robust photocatalysts that can withstand harsh operating conditions, frequent replacement and off site regeneration in order to achieve efficient and inexpensive systems, suitable for a variety of the photoreactor design and operating conditions.

It is favorable to prepare photocatalyts from easily available and cost effective materials, without additional dangerous additives, avoiding new sources of pollution to treated water. The most common and commercially available photocatalyst is the titanium dioxide P25. Apart from price, it is known for its biological and chemical inertness and long term stability against photo and chemical corrosion [22,31–38]. In this work chitosan is used as a binder for the TiO_2 immobilization, because of its excellent film forming ability. Chitosan has excellent properties for the adsorption during photocatalytic processes, due to the presence of hydroxyl (—OH) and amino groups (—NH_2) inside its structure [39–43]. Obtained by deacetylation of chitin, it is used as a biomaterial for wounds and burns treatments or tissue engineering, as well as in pharmaceutical as a matrix in drug release systems, in the agriculture, food and cosmetic industry [44–51].

In this study a procedure for deposition of a TiO_2 coating having desirable photocatalytic properties on different support materials, such as pure cotton, a mix of cotton flax and polyester and glass fiber woven was developed. The physico-chemical properties of the immobilized photocatalysts, their activity and stability were examined using different methods. The efficiency of the immobilized TiO_2/chitosan photocatalytic layer was tested in a batch annular reactor equipped with the UV radiation source (254 nm), using a herbicide terbuthylazine (TBA) as the model component. Terbuthylazine a chloro-triazine herbicide, acts as inhibitor of photosynthesis and is widely used as an alternative for atrazine, restricted in many European countries. The aim of this work was to develop the immobilized layer of the photocatalyst and photocatalytic process for efficient removal of the *s*-triazine group of herbicides (active ingredients like simazine, atrazine, terbuthylazine, etc.) from the surface- and groundwaters.

2. Experimental set up

2.1. Preparation of the immobilized TiO_2/chitosan layer

The TiO_2 immobilization procedure consisted of three steps: (i) preparation of suspensions, (ii) coating of a suitable substrates and (iii) drying. The photocatalyst employed was commercial powdered titanium dioxide supplied by Evonik Aeroxide (P25). According to the manufacturer's specification, P25 had an elementary particle size of 30 nm, BET surface area of ca. 58.16 $m^2 g^{-1}$ and crystalline mode based on approximately 80% anatase and 20% rutile. The photocatalyst layer was prepared using chitosan [β-(1-4)-2-amino-2-deoxy-D-glucose] (Sigma–Aldrich) as a binder to achieve immobilization/adhesion of TiO_2 on the substrate.

The photocatalyst suspension was prepared by mixing 2.5 g of chitosan in 300 ml of 0.1 mol dm^{-3} acetic acid and 40 ml of 0.2 mol dm^{-3} NaCl solution. The prepared mixed solution was stirred vigorously overnight to ensure complete dissolution of the chitosan. Subsequently, 25 g of TiO_2 and 50 ml of 0.1 mol dm^{-3} acetic acid were added and stirred for additional 24 h, until homogeneous suspension was obtained.

The substrate material was cut into rectangular parts (2 × 4 cm), after being rinsed with water and ethanol. The prepared suspension was applied on the substrate in four thin layers, using

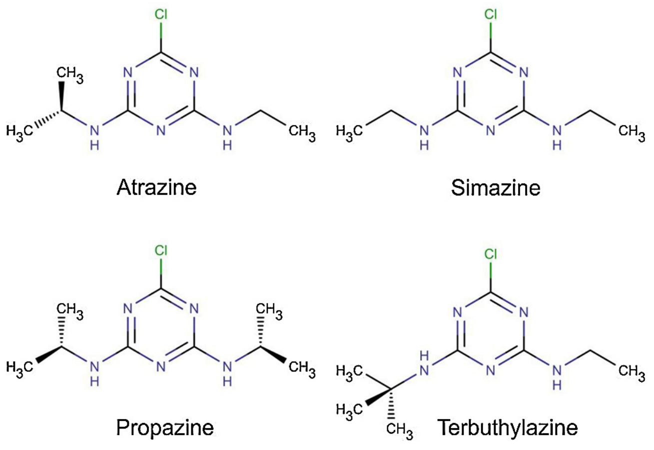

Fig. 1. Schematic representation of terbuthylazine structure (*N*-*tert*-buthyl-6-cloro-N′-ethyl-1,3,5-triazine-2,4-diamine) and other representatives of *s*-triazine herbicides.

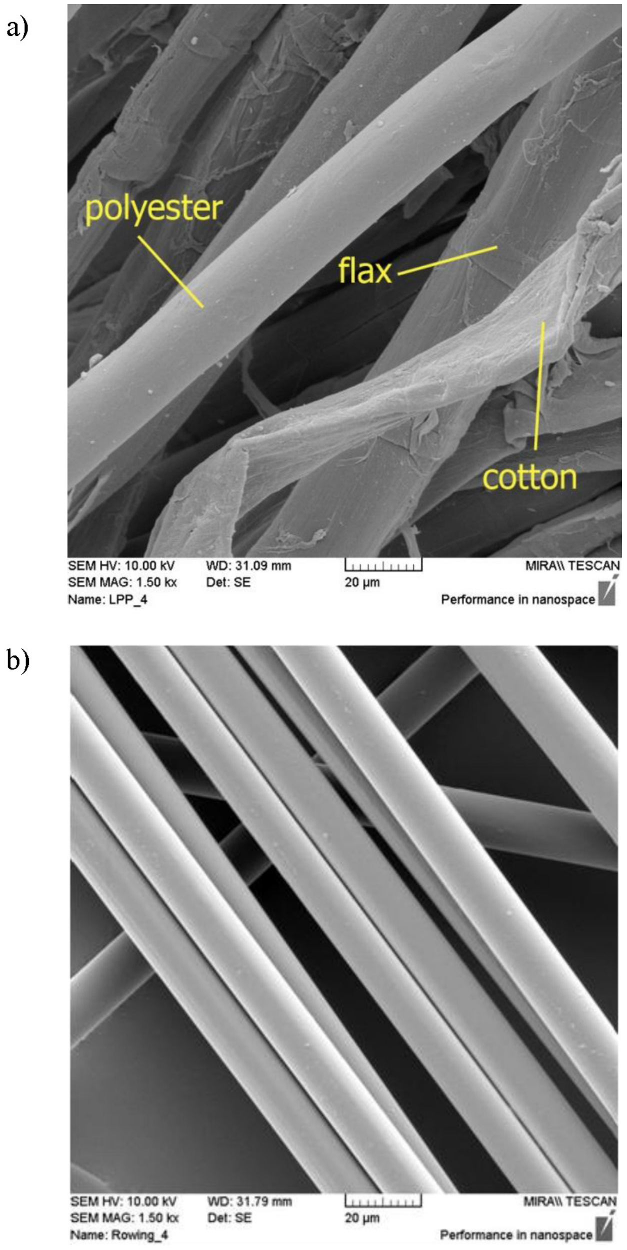

Fig. 2. SEM micrograph of support materials without photocatalyst layer. (a) cotton/flax/polyester fabric (1500×), (b) glass fiber (1500×).