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Photocatalytic degradation of a model textile dye using Carbon-doped titanium dioxide and visible light

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ABSTRACT

Rhodamine B (RhB), a dye widely used in the textile manufacturing, contributes with other dyes to harm the environment. Here, with the final goal to provide new tools for the removal of dyes from water, visible light activated carbon-doped titanium dioxide was used to investigate on the decolourization and the photocatalytic degradation of RhB dye from water solutions. The photodegradation activity was tested varying the initial concentration of RhB and the amount of carbon-doped titanium dioxide, taking into account the ratio between the amount of catalyst and the amount of RhB (TiO_2/RhB), thus obtaining a parameter that allows the method to be scaled up without losing its effectiveness. Values of k_2 and $t_{0.5}$ were obtained by fitting kinetics data to a second-order kinetic adsorption model. The important role played by doped TiO_2 particles is demonstrated by the highly efficient color removal obtained during the visible light-induced photocatalysis. The presence of different degradation intermediates was demonstrated by means of UV–vis Absorption and Fluorescence spectroscopy. Such results underline that the whole photodegradation process does not end with the decolourization occurrence.

1. Introduction

Dye pollutants produced from the textile manufacturing are becoming a serious source of environmental contamination [1,2]. It is estimated that thousands of different dyes and pigments are used industrially and an enormous number of synthetic dyes are yearly produced worldwide. Textile factories are second only to agriculture in the amount of pollution they create and the large amounts of water they use. Pollutants released by the global textile industry are continuously doing incredible harm to the environment, polluting lands and making them useless and unproductive [3].

Dyes are substances widely used in textile, as well as in pharmaceutical, food, plastics, paper manufacturing [4–8]. The chromophores, responsible for the specific dye color, are classified according to their chemical structure and their application field. The chromophore-containing centers are based on various functional groups, among these the main are azo, anthraquinone, methine, nitro, arylmethane, carbonyl groups. Donating substituents able to generate color amplification of the chromophores are denominated auxochromes (amine, carboxyl, sulfonate and hydroxyl).

Among these molecules Rhodamine B (RhB) is a fluorescent cationic dye widely used in textile dyeing because of its more rigid structure than other organic dyes, and is also a well-known fluorescent water tracer [9]. Due to its cationic structure, it can be used for anionic fabrics that contain negative charges such as polyester fibers. RhB results harmful to human and animals: it causes irritation of the skin, eyes and respiratory tract. Also, Rhodamine dyes are highly toxic to reproductive and nervous systems and it has been proven that drinking water contaminated with Rhodamine could lead to subcutaneous tissue borne sarcoma [10].

Worldwide regulations for industrial wastewater require significant elimination of the dyestuff amount from the effluent [11]. Nevertheless, it has been evaluated that a considerable part of the dyestuff is still being released to the ecosystem. Several approaches have been developed for the effluent treatment but none of them is still sufficiently effective and a combination approach seems to be so far the most

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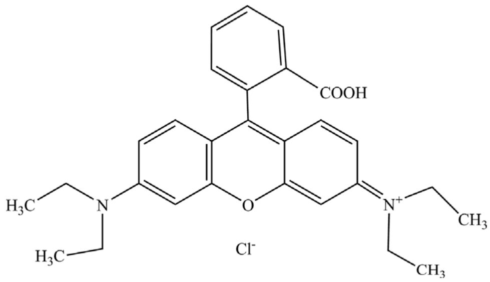

Fig. 1. Rhodamine B chemical structure.

efficient.

Generally, dyestuff is faced with chemical and physical methods, such as adsorption and bio-treatment, co-precipitation, coagulation, filtration, activated carbon, ozonation, and photochemical decolourization [12,13]. These methods frequently share the inconvenience of incomplete degradation of the dye molecule, which leads to the formation of toxic by-products. These limits of conventional water treatment methods can be overcome by the use of advanced oxidation processes, which have the ability to completely mineralize the dyes, including the opening of the aryl ring. Usually, advanced oxidation processes consist of procedures in which active hydroxyl radicals act as strong oxidants for degradation of polluting materials. Most of these processes are based on the high oxidation capacity of hydroxyl radicals (2.8 V). One of the most effective methods among the advanced oxidation route is the use of UV rays combined with oxidant such as titanium dioxide.

Titanium dioxide (TiO_2) is well recognized as a low cost and efficient catalyst for degradation of organic matters [14]. The application of titanium dioxide as heterogeneous photocatalyst is well established for the remediation of water and air purification [15,16]. For instance, the photocatalytic degradation of azo dyes in aqueous solution is based on photo activation of TiO_2 with UV light, which leads to a sequence of reactions resulting in the production of oxidants. The so formed compounds (hydroxyl radicals) can easily react with organic compounds on the TiO_2 surface [17]. However, since titanium dioxide has a band gap of 3.2 eV, which can be activated only under UV-light irradiation, efforts have been made to discover methods providing the photoactivation of this photocatalyst under visible light. Doping of TiO_2 represents a widely used approach for developing TiO_2 based materials useful for environmental applications [18]. Different methods for the synthesis of carbon doped TiO_2 particles have been proposed to improve the photocatalytic activity [16,19]. Recently different research groups highlighted the efficiency of a visible-light-active TiO_2 photocatalyst prepared through carbon doping using glucose as the carbon source towards organic compounds [20–22].

RhB is largely used to prove the efficiency of catalysts in general and for TiO_2 in particular, towards organic matter [23–27]. Nevertheless, as stated above due to the possibility of incomplete degradation of the dye molecule it would be useful to clarify the difference between decolourization and degradation. In fact, a decolourization process does not necessarily correspond to a complete degradation of the dye [28]. Furthermore, the presence of different photocatalytic degradation processes, such as chromophore cleavage, opening-ring, N-de-ethylation, and mineralization have also to be taken into account [29,30].

The aim of this investigation is the study of the photodegradation process of the dye, RhB, induced by a carbon doped visible light-active TiO_2 photocatalyst. Furthermore, an accurate investigation of the decolourization and the photocatalytic activity of carbon doped TiO_2 toward RhB was accomplished. The final goal is to provide new tools for the challenging removal of dyes from water.

2. Materials and methods

2.1. Materials

Glucose, titanium isopropoxide (97%), ethanol, potassium chloride, sodium carbonate and Rhodamine B (RhB) were purchased from Sigma-Aldrich.

2.2. Carbon-doped titanium

Carbon-doped TiO_2 (CDT) was synthesized following the method reported by Ren et al. [21]. TiO_2 particles were prepared by the hydrolysis of titanium isopropoxide in ethanol performed in the presence of potassium chloride. The sample was continuously stirred to produce

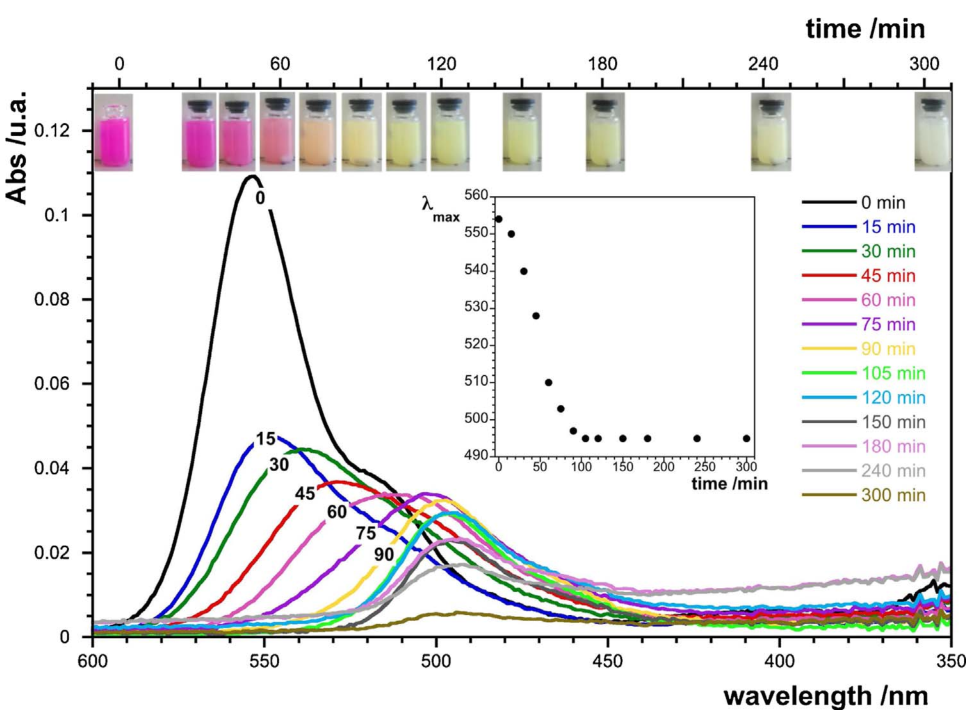

Fig. 2. RhB UV–visible adsorption spectra and sample decolourization pictures as a function of time exposure to visible light irradiation. Inset λ_{max} shift. Ti/RhB: 150.