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Solar-light-induced photocatalytic decomposition of two azo dyes on new TiO_2 photocatalyst containing nitrogen

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Abstract

The photocatalytic decolourisation of two azo dyes—Reactive Red 198 and Direct Green 99—in an aqueous solution by the artificial visible light radiation was investigated. The industrial metatitanic acid (H_2TiO_3) obtained directly from the sulphate technology installation was N-doped and used as photocatalyst. H_2TiO_3 was calcinated at different temperatures, ranging from 300 to 500 °C, for 4 or 20 h, respectively, in an ammonia atmosphere. The UV–vis/DR spectra of the modified catalysts exhibited an additional maximum in the vis region ($\lambda \approx 476.8$ nm, $E_G = 2.60$ eV for catalysts calcinated for 4 h and $\lambda \approx 479.5$ nm, $E_G = 2.59$ eV for catalysts calcinated for 20 h, which may be due to the presence of nitrogen in TiO_2 particles. The chemical structure of the modified photocatalysts was investigated using FTIR/DRS spectroscopy and the presence of nitrogen was confirmed. A photocatalytic activity of the investigated catalysts was determined on the basis of a decomposition rate of azo dyes. The decomposition of Reactive Red 99 increased with increasing the calcination temperature of photocatalysts, whereas the activity of the prepared photocatalysts towards Direct Green 198 degradation was as follows: 300–20 h < 400–20 h < 500–20 h < 300–4h < 400–4 h < 500–4 h. Both, the calcination time and temperature had no influence on the amount of nitrogen-doped into TiO_2 structure. The inversely proportional linear dependence between the decomposition rates of azo dyes and the intensity of the band attributed to the hydroxyl groups for both dissociated water and molecularly adsorbed water was observed. With increasing temperature of calcinations, the amount of the hydroxyl groups decreased, whereas the decomposition of azo dyes increased.

Keywords: Visible light active photocatalyst; The industrial precursor; Nitrogen-doped; Ammonia; Titanium dioxide; Azo dye; Reactive Red; Direct Green

1. Introduction

The wastewaters generated by the textile industry contain considerable amounts of azo dyes. The discharge of these coloured wastewaters in the ecosystem has been problematic due to their toxicity and resistance to biodegradability. Among various methods for the removal of coloured compounds, the traditional ones, such as ozonation, irradiation, H_2O_2 oxidation, ultrafiltration, extraction, activated carbon adsorption, coagulation–flocculation and combination of several techniques have been applied [1–4]. The main disadvantage of these methods is associated with the fact that they are non-destructive and their action is limited to transfer of the pollutant from one phase to another. Thus, there is a need to develop new treatment technologies that would be more effective in elimination of dyes from the waste stream at its source. Recently, new oxidation methods called advanced oxidation processes (AOPs) have been widely investigated. Among them, special attention is given to heterogeneous photocatalysis using TiO_2 as a photocatalyst. This process can be carried out under ambient conditions and may provide the ultimate solution for the destruction of commercial dyes in wastewater.

In most cases, the degradation of dissolved compound in water can be conducted with UV-illuminated titanium dioxide. The most reactive form of TiO_2 is anatase; however, it has a high-energy gap ($E_G > 3.2$ eV) and for this reason, it could be excited only by UV light ($\lambda < 380$ nm). Nowadays, the methods of moving the absorption spectrum of TiO_2 into

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the main part of solar spectrum ($\lambda > 380$ nm) are widely investigated. It has been found that the substitutional N-doping is a very effective method of preparation of vis active photocatalysts [5–10].

Over the past few years, a large amount of work has been done on the photosensitisation of semiconductors, such as TiO_2 by a variety of coloured organic compounds [11]. One reason for this interest results from the ability of them to extend the photoresponse of large bandgap semiconductors into the visible region.

The mechanism of photosensitised oxidation (photo-assisted degradation) [12] of dyes by visible radiation suggests that excitation of the adsorbed dye takes place by visible light to the appropriate singlet or triplet states, followed by electron injection from the excited dye molecule onto the conduction band of the TiO_2 particles. Simultaneously, the dye is converted to the dye radical cations that can react with the hydroxyl ions undergoing the oxidation or interact effectively with $O_2^{\bullet-}$, $HO_2^{\bullet}$ or $HO^{\bullet-}$ species to generate the intermediates that ultimately lead to CO_2. This process is termed as sensitised photocatalysis. It extends the range of excitation energies into a visible range, making the use of the solar energy more efficient.

Stylidi et al. [13] proposed a TiO_2-mediated photodegradation mechanism for Acid Orange 7, what led to the decolourisation or to complete mineralisation of the dye solution. Initially, the interaction with solar light resulted in cleavage of the dye molecule in the vicinity of the azo bond and the formation of molecules containing naphthalene- and benzene-type rings. The primary reaction intermadiates underwent a series of successive oxidation steps, which led to the formation of aromatic acids and then to aliphatic acids of progressively lower molecular weight. Eventually, the complete mineralisation of carbon, nitrogen and sulfur heteroatoms into CO_2, NH_4^+, NO_3^- and SO_4^{2-} ions was achieved. The same authors [14] stated that when the solution of azo dye, such as AO 7 was bleached, the formation of active oxidative species did not take place, the oxidation reactions ceased and the concentrations of the dye intermediates remained practically stable upon a further exposure to visible light irradiation.

There are several studies related to the application of visible light active photocatalyst for the mineralisation of dyes [13–16]. The photobleaching rates of dyes with varying chemical structures in an aqueous dispersion utilizing a visible light differed significantly from families of dyes and were dependent on the light source and crystalline form of TiO_2 used [15].

Liu et al. [15] conducted, such as Acid Orange 7 (AO7), Procion Red MX-5B (MX-5B) and Reactive Black 5 (RB5) using the nitrogen-doped TiO_2 nanocatalysts and commercially available TiO_2–P25 (Degussa) under both UV illumination and solar light. The nitrogen-doped TiO_2 had the highest photocatalytic activity among all catalysts tested, with 95% of AO7 decolourised during the first hour under UV illumination and 70% under direct sunlight irradiation. A complete decolourisation of dye was obtained after 3 h of the process. During the experiment conducted with TiO_2–P25 (Degussa), no detectable decolourisation of azo dyes under solar light was observed.

Kuo and Ho [16] studied the photocatalytic decolourisation of an organic dye methylene blue. The authors observed that solution of methylene blue could be almost completely decolourised by the solar light/TiO_2 film process, while there was about 50% colour remaining with solar irradiation only. The colour removal rate with solar light irradiation was almost two times higher than that of artificial UV light irradiation.

In our earlier research [17,18], we found that incorporation of nitrogen into titanium dioxide by calcination for 4 h in NH_3 atmosphere creates a possibility to obtain visible light active photocatalysts. The aim of the presented work was the investigation of the effect of extending of the calcination time up to 20 h on the photocatalytic properties of N-doped TiO_2. The industrial metatitanic acid (H_2TiO_3) obtained directly from the sulphate technology installation was applied for preparation of N-doped TiO_2. The photocatalytic activity of the modified TiO_2 was evaluated on the basis of decomposition of two model azo dyes—Reactive Red 198 and Direct Green 99.

On the basis of our earlier investigations, the catalysts calcinated at the temperatures of 300–500 °C were selected for further experiments, due to their high photoactivity towards decolourisation of the dyes.

2. Experimental procedures

2.1. Materials

The azo dyes Reactive Red 198 (RR198) and Direct Green 99 (DG99) were the commercial products supplied by the company ‘‘Boruta Colour’’ (Poland). The dyes were used in the experiment without further purification. The molecular structure of the model compounds and UV–vis spectra are presented in Fig. 1a and b.

The industrial metatitanic acid (asssigned later as a ‘‘base’’) obtained directly from the sulphate technology installation was applied as a precursor for catalyst preparation. Before use, metatitanic acid was washed off three times with ammonia water and then with distilled water in order to remove the residual sulfate ions and then dried at 100 °C. N-doped TiO_2 catalysts were obtained by calcination at temperatures of 300, 400 and 500 °C in the gaseous NH_3 atmosphere for 4 and 20 h, respectively. The modification of catalysts was performed in the pipe furnace model R40/250/12-C40 (Nabertherm, Germany). A detailed description of the preparation procedure can be found in [17,18].

The obtained photocatalysts were ground in agate mortar before use. All experiments were carried out with use of double distilled water.