



Pollutant degradation over dye sensitized nitrogen doped titania substances in different configurations of visible light helical flow photoreactor



Zohreh Mesgari, Javad Saien*

Department of Applied Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran

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ABSTRACT

Different nitrogen doped titania (N-TiO₂) substances were synthesized, sensitized with hematoporphyrin (HP) and their thin films were fabricated on supporting structures. Two kinds of supporting, wire gauze structured packing and quartz Raschig ring random packing were utilized in a visible light, helical flow photoreactor. The HP/N-TiO₂ nanohybrid powders, suspended in the solutions, were also prepared to compare their photocatalytic activity. Different techniques of SEM, TG–DTA, XRD, FT-IR, UV–Vis spectroscopy and elemental analysis were used to characterize the products. Methyl orange (MO) substrate was used as a model dye pollutant in aqueous solutions with measuring the level of degradation and TOC. The influencing parameters like the amount of sensitizing HP, nanohybrid dosage, film thickness and repetitive operating capability were investigated and optimum mild conditions were obtained. The process kinetic was well fitted by pseudo first order kinetic model and the electrical energy was drastically less than those reported for other similar processes. Among the employed configurations, the random packing showed the highest efficiency and the lowest energy consumption. Meanwhile, the HP/N-TiO₂ with 3 mM initial concentration of HP represents a potential alternative for the treatment. Comparison with similar processes represents the superior performance of the process.

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1. Introduction

Today, presence of recalcitrant organic pollutants in wastewaters has caused serious environmental problems and thereupon purification of water is a fascinating challenge [1]. Nevertheless, water pollution caused by injurious organic pollutants, such as organic dyes, pesticides and antibiotics, affects seriously the quality of water resources and human health. To challenge these problems, use of solar light is an optimal way to treat wastewaters due to its availability, its cleanliness, continuous energy, free of charge and easy operations. Utilizing efficient and selective metal oxide semiconductors in the process of the photocatalytic degradation of recalcitrant organic pollutants is another matter of interest [2–4]. Titania has been commonly used as the main substance because of its many useful properties under light irradiation and in aqueous media. However, due to a wide band gap ($E_g = 3.0\text{--}3.2\text{ eV}$), this semiconductor can only be activated upon irradiation with energetic photons of more than corresponding E_g for which only less than 5% of solar spectrum is corresponding [2].

The utilization of solar light to supply energy is an already well-established idea [3]. To extend the light absorption of TiO₂ into the visible light region and hindering the recombination of excited electrons and holes for highly active photocatalysts, different preparation methods and various dopants have been utilized in many efforts [4]. Accordingly, band-gap energy can be shifted by doping TiO₂ with nonmetal elements such as N, C, S and P [5]. Incorporation of N atom, for instance, produces a localized energy state above the valence band of TiO₂ and thus when N doped TiO₂ is exposed to visible light, electrons are transferred from the localized states to the conduction band [6]. Compared to the other elements, N-TiO₂ composites represent a considerable photocatalytic activity and strong absorption under visible light irradiation [7,8].

Meanwhile, dye sensitization has long been an efficient way to extend the absorption spectra of wide band gap TiO₂ from ultraviolet into visible region. Some common sensitizers include ruthenium polypyridyl complexes [9], squaraines [10], porphyrins [11], and natural dyes [12]. Natural dyes have been the popular subjects of many researches due to their non-toxicity and complete biodegradation. Light absorption is performed by a layer of dye that is chemically attached to the surface of TiO₂. A corresponding compound, hematoporphyrin (HP), is a biological compound with

* Corresponding author.

E-mail address: saien@basu.ac.ir (J. Saien).

excellent properties [13]. This dye absorbs visible light leading to the excitation by triggering a photoelectron and simultaneously transferring it to the conduction band of TiO_2 . This feature therefore illustrates a promising method, if nitrogen doped TiO_2 precursors being sensitized with natural dyes to improve the photocatalytic activity under visible-light [11].

Another important field is the utilized photoreactors which include two major types: slurry reactors (photocatalyst powders being suspended in the aqueous phase) [7] and immobilized reactors (photocatalyst being fixed to a support) [14]. Photocatalytic reactors based on the slurry suspension systems need simple reactor configuration design and possess high surface area for adsorption and reaction. However, their application is limited with respect to stirring during reaction and difficulties in separation and recovery of photocatalyst powders after each run [15]. On the other hand, release of photocatalyst powders into the environment leads to potential adverse impact on human and ecological health [16]. In this case, the alternative is to immobilize photocatalysts on a support or within the photoreactor body to overcome these problems. It also extends the application of photocatalysts towards purification of wastewater containing different pollutants [17]. Photoreactors using TiO_2 coated support can prevent the tedious post separation process but require special design to overcome mass transfer limitation, increase illuminated surface area and enhance light utilization efficiency.

This study aimed to find an efficient visible light photocatalyst of titania, nitrogen and HP nanohybrid to use in a developed photoreactor. Different thin film layers of N- TiO_2 , sensitized with different HP dosages, were synthesized to evaluate their efficiency. An efficient helical flow photoreactor for treatment of polluted aqueous solutions with a low light energy consumption and a satisfactory mass transfer level was employed. Two immobilized HP/N- TiO_2 nanohybrid configurations were developed: wire gauze structured packing and quartz Raschig ring random packing. Their performance was compared with the HP/N- TiO_2 nanohybrid powders in suspended solutions and also with bare TiO_2 operations, all examined for degradation of methyl orange (MO) as a model dye pollutant.

2. Experimental

2.1. Chemicals

Sigma Aldrich HP ($\geq 45\%$) was used without further purification. The titanium isopropoxide ($\geq 98\%$), urea ($\geq 99.5\%$), ethanol ($\geq 99.9\%$), acetyl acetone ($\geq 99.0\%$), HCl (37%), NaOH ($\geq 99\%$) and MO (C.I. 13025) were purchased from Merck and used as received without further purification. Fresh deionized water was prepared from a deionizer apparatus (Hastaran Co.) and used in the preparation of solutions.

2.2. Analysis and instruments

The morphology of samples was determined using JEOL-JSM 840 scanning electron microscopy (SEM). Cross section observations by scanning electron microscopy enabled the thickness of the formed thin films to be estimated. SEM samples were prepared according to a known procedure where films were cut into pieces and immobilized in different epoxy resin samples in a vertical orientation and then were polished in order to allow cross section observation. The powder samples were thermally analyzed in air by a Perkin Elmer Pyris Diamond TGA (STA 6000) at a scanning rate of $5^\circ\text{C}/\text{min}$. The crystal structure of the samples were also analyzed by Structure-APD 2000 X-ray powder diffraction (XRD), recorded with Cu $K\alpha$ radiation ($\lambda = 0.15406\text{ nm}$) radiation in the

2 θ range of $20\text{--}80^\circ$. The Fourier transform infrared spectra (FT-IR) were recorded on a Perkin-Elmer 65 spectrophotometer. The UV-Vis spectra of MO solution samples and TiO_2 samples were recorded by a UV-Vis spectrophotometer (Jasco-V630). Percentage of nitrogen in the calcinated nanoparticles was measured through an elemental analyzer (NC 2500 Thermo Quest). The particle size distribution are verified using Zeiss-Sigma field emission scanning electron microscopy. The particle distribution was conducted by measuring the average diameter of approximately more than 1040 particles using the Image J software. Total organic carbon was measured by the TOC analyzer (Shimadzu, V_{CSH} model).

2.3. The helical flow photoreactor and its configurations

The photocatalytic experiments were carried out in a developed helical flow photoreactor as schematized in Fig. 1. The annular photoreactor operates in a closed circuit, recirculating content at 45 mL/s of flow rate. A 150 W visible Osram metal halide lamp (black UV light, the emission spectrum of lamp [18] presented as Fig. S1 in supplementary material) was placed in the axis of the annulus to irradiate the reactor. The tangential inclined inlet of the solution provides a precise upward helical flow around the light source and reaches the top tangential downward outlet point. The HP/N- TiO_2 nanohybrids were tested in three different reactor configurations:

- (i) Slurry reactor, in which different concentrations of HP/N- TiO_2 nanohybrid powders were suspended in the photoreactor.
- (ii) Wire gauze structured packing reactor, in which a wire gauze structured packing, coated with HP/N- TiO_2 nanohybrids, was immobilized in the space between tubes of the photoreactor.
- (iii) Random packing reactor in which quartz Raschig rings, coated with the HP/N- TiO_2 nanohybrids, were filled in the photoreactor active zone.

2.4. Preparation of N- TiO_2 precursor

The N- TiO_2 sol was prepared according to a reported procedure [19]. Briefly, titanium isopropoxide, anhydrous ethanol and acetyl acetone were first mixed at room temperature. After stirring with magnetic force for at least 60 min, the clear and yellow solution was obtained. Deionized water was then added and the mixture was stirred for 30 min. After that few drops of concentrated HCl solution were added to the sol to adjust the pH at about 1.7. At the next step, the solution of urea in ethanol was added dropwise to the mixture (6.0 M ratio of nitrogen to titanium). Urea was used as a source of nitrogen that can transfer the photocatalytic activity of TiO_2 to the visible light region. Transparent yellow solution was obtained after stirring for 180 min. The bare TiO_2 was also prepared using a similar method unless urea addition.

2.5. Deposition of HP/N- TiO_2 thin films

Among different thin film deposition techniques, the sol-gel dip coating is the simplest, cheapest, most convenient and has advantages such that TiO_2 is easily anchored on the substrates bearing the large area products and not requiring complicate equipment [4]. Here, the N- TiO_2 precursor was first coated on two kinds of supports: wire gauze structured packing and quartz Raschig rings. The constructed packing was a steel type structured packing made of wire gauze sheets. The specific surface area and the void fraction of this packing were $2100\text{ m}^2/\text{m}^3$ and $0.91\text{ m}^3/\text{m}^3$, respectively. The dimensions of each quartz Raschig ring were 0.7 cm outer diameter and 1.3 cm length. Before deposition of photocatalyst substrate,

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