



UV–VIS photocatalytic degradation of nitrobenzene from water using heavy metal doped titania



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ABSTRACT

The photocatalytic degradation of nitrobenzene (NB) under UV–VIS irradiation with un-doped TiO₂ and various heavy metals doped TiO₂ powders were studied for aerated solutions. The dopant type (Fe, Co, Ni) and its concentration (0.5–5 wt.% TiO₂) influence on pollutant degradation efficiency were investigated. The photocatalyst with lowest Fe content (0.5 wt.%) showed a considerable better behaviour in respect to pollutant degradation than catalyst with higher Fe content and Co and Ni doped titania catalysts. The experiments were carried out for solutions with $(0.37\text{--}8.45) \times 10^{-4}$ M NB initial content, using 50–250 mg/L catalyst dose, at various pHs (4–10) and irradiation time between 30 and 240 min. The kinetics of NB degradation and organic nitrogen mineralization was assessed and pseudo-first order rate constants were calculated. For optimum working conditions (0.5 wt.% Fe doped-TiO₂ loading of 250 mg/L, 2.52×10^{-4} M pollutant initial concentration, pH = 7 and 240 min irradiation time) NB removal and organic nitrogen mineralization efficiencies were 99% and 85%, respectively. It was also demonstrated that degradation process occurs on catalyst surface, so experimental results are in accordance with Langmuir–Hinshelwood model.

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1. Introduction

Nitrobenzene (NB) is one of hazardous organic compounds, which is frequently found in petroleum industry discharged effluents. Due to its bio-refractory character and high chemical stability, this pollutant cannot be efficiently removed by classical biological or physical–chemical treatment processes. In the past decades, semiconductor photocatalysis has been frequently applied for the advanced degradation of toxic pollutants [1–3]. Among various semiconductors titania was a widely studied photocatalyst, due to the strong oxidation power of photo-generated holes, its chemical inertness, low cost, photostability and nontoxicity [4]. Because of the high energy band gap (3.2 eV), titania can be activated only by ultraviolet (UV) light [5]. In addition, low photo quantum efficiency and high recombination of

electron–hole pairs restrict the titania application. In order to improve optical absorption and photocatalytic activity of TiO₂ many attempts have been made [6]. One feasible approach consists of doping oxide semiconductor with metal or non-metal [7–9]. Impregnation, co-precipitation and sol–gel methods are used to introduce dopants in semiconductor matrix [10]. Nikam et al. [11] pointed out that 5 wt.% Mn–TiO₂ catalyst proved to be 50% more efficient than un-doped TiO₂ for methylene blue dye oxidation, under visible light irradiation. Tayade et al. [12] studied the effect of Li, Mg, Pd and Sr doping and observed that 0.5 wt.% Li impregnated TiO₂ photocatalyst presents the highest initial nitrobenzene degradation rate (8×10^{-6} M min⁻¹). The same behaviour was also reported in the case of Cr and Ce dopants (concentration ratio $M^{n+}:Ti^{4+} = 5:100$), which are photocatalytic inactive to phenol degradation compared with Li dopant [13]. The authors concluded that various dopant types induced different changes on catalyst photoactivity according to ionic radii and redox potential of $M^{n+}/M^{(n-1)+}$ couple of dopants. Beside dopant type, its concentration can modify the adsorption property of

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