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Relationship between Structure of Some Nitroaromatic Pollutants and Their Degradation Kinetic Parameters in UV-VIS/TIO2 System

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Abstract : Hazardous organic compounds like nitroaromatics are frequently found in chemical and petroleum industries discharged effluents. Due to their bio-refractory character and high chemical stability 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. Among various semiconductors titania was a widely studied photocatalyst, due to its chemical inertness, low cost, photostability and nontoxicity. In order to improve optical absorption and photocatalytic activity of TiO2 many attempts have been made, one feasible approach consists of doping oxide semiconductor with metal. The degradation of dinitrobenzene (DNB) and dinitrotoluene (DNT) from aqueous solution under UVA-VIS irradiation using heavy metal (0.5% Fe, 1%Co, 1%Ni) doped titania was investigated. The photodegradation experiments were carried out using a Heraeus laboratory scale UV-VIS reactor equipped with a medium-pressure mercury lamp which emits in the range: 320-500 nm. Solutions with (0.34-3.14) x 10-4 M pollutant content were photo-oxidized in the following working conditions: pH = 5-9; photocatalyst dose = 200 mg/L; irradiation time = 30 – 240 minutes. Prior to irradiation, the photocatalyst powder was added to the samples, and solutions were bubbled with air (50 L/hour), in the dark, for 30 min. Dopant type, pH, structure and initial pollutant concentration influence on the degradation efficiency were evaluated in order to set up the optimal working conditions which assure substrate advanced degradation. The kinetics of nitroaromatics degradation and organic nitrogen mineralization was assessed and pseudo-first order rate constants were calculated. Fe doped photocatalyst with lowest metal content (0.5 wt.%) showed a considerable better behaviour in respect to pollutant degradation than Co and Ni (1wt.%) doped titania catalysts. For the same working conditions, degradation efficiency was higher for DNT than DNB in accordance with their calculated adsobance constants (Kad), taking into account that degradation process occurs on catalyst surface following a Langmuir-Hinshalwood model. The presence of methyl group in the structure of DNT allows its degradation by oxidative and reductive pathways, while DNB is converted only by reductive route, which also explain the highest DNT degradation efficiency. For highest pollutant concentration tested (3 x 10-4 M), optimum working conditions (0.5 wt.% Fe doped –TiO2 loading of 200 mg/L, pH=7 and 240 min. irradiation time) assures advanced nitroaromatics degradation (ηDNB=89%, ηDNT=94%) and organic nitrogen mineralization (ηDNB=44%, ηDNT=47%).

Keywords : hazardous organic compounds, irradiation, nitroaromatics, photocatalysis
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