

EFFECT OF INCIDENT PHOTON ENERGY ON THE KINETICS AND MECHANISM OF PHOTOCATALYTIC DEGRADATION OF AZO-DYES IN AQUEOUS TiO₂ SUSPENSIONS

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EXTENDED ABSTRACT

Wastewaters generated from the textile industry contain large amounts of azo-dyes which, owing to their non-biodegradability, toxicity and potential carcinogenic nature, constitute a major threat to the surrounding ecosystem. Environmental concerns and the need of meeting the stringent international standards for rejecting wastewaters has made the development of novel, efficient and low cost methods for the purification of textile aqueous effluents an issue of major importance. TiO₂-mediated photocatalysis has been shown to be a potentially advantageous process as it may lead to complete mineralization at ambient conditions with the use of solar light as the energy source.

In the present study, the photocatalytic degradation of a model textile azo-dye (Acid Orange 7, AO7) in aqueous solution is investigated with the use of TiO₂ photocatalyst. The scope of this investigation is to compare the decolorization rate, the reaction pathways as well as the nature of intermediate and final products obtained from the photocatalytic treatment of AO7 under solar (UV/vis)- or visible (>400 nm)-light irradiation. The extent of decolorization has been determined by UV-vis spectrophotometry and the degradation of the azo-dye in solution has been followed by measurements of pH, conductivity and chemical oxygen demand (COD). The development and fate of reaction intermediates and final products with time of irradiation has been examined by GC/MS spectroscopy and ion-chromatography, while the formation of CO₂ was monitored with the use of an NDIR analyzer. *Ex situ* FTIR spectroscopy was employed to study the progress of the reaction on the TiO₂ photocatalyst surface.

It is shown that when the full solar spectrum is utilized, the dye molecules adsorbed on TiO₂ surface undergo a series of oxidation steps, which lead to rapid decolorization and formation of a number of intermediates which are produced by cleavage of the dye molecule in the vicinity of the azo-bond. These molecules are further oxidized toward compounds of progressively lower molecular weight and, eventually, to CO₂ and inorganic ions. Under these conditions, complete decolorization and mineralization of the solution is achieved with appreciable reaction rates. When the solution is irradiated with visible light ($\lambda > 400$ nm), reaction intermediates are similar to those observed under UV/vis light irradiation but decolorization takes place with much lower rates. In addition, when the solution is bleached, the COD does not further decrease with time of irradiation and reaction intermediates remain unchanged, indicating that the visible-light induced process is governed by the "photosensitization mechanism". Results obtained are used to extract information related to the mechanism of photocatalysis and the reaction pathways of photocatalytic degradation of aqueous solutions of AO7.

Key words: Acid Orange 7, photocatalysis, photosensitization, degradation pathway, titanium dioxide, solar light, visible light.