## Immobilized Zinc Oxide (ZnO) Photocatalysts, and Their Use in Continuous-Flow Photoreactors for Wastewater Treatment

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In spite of the progress achieved on the photo-catalysis during the last 20 years, particularly with reference to the destruction of a great variety of recalcitrant contaminants in water streams, there is still a gap of knowledge on the optimization of the performance of continuous-flow photoreactors. Zinc-oxide (ZnO) nanoparticles were immobilized on two types of substrates, (i) pretreated borosilicate glass spheres, and (ii) pre-treated Duranit (80% silica+ 20% alumina) inert balls, by immersing the substrates in aqueous solution of zinc acetate dehydrate (ZnAc) heating the solution for a couple of hours in the temperature range 80°C - 140°C to enable the growth of ZnO nanoparticles, and calcinating in an oven at 400-450 °C for 2 hrs. To assess the stability and photocatalytic capacity of immobilized ZnO, tests were performed in batch mode by using as light source either a UV-lamp 6W, or an in-house modified UV-led nail dryer 22W, both with an emission peak at 365 nm. Two types of model pollutants dissolved in deionized water were tested: methylene blue (MB), and phenol (Ph). A parametric analysis was conducted with respect to the catalyst mass to the initial mass of pollutant, and the number of photocatalysis cycles. The transient MB or Ph concentration was measured with UV-Vis spectroscopy, whereas adequate sorption surface reaction models were developed to interpret the experimental results, and estimate the kinetics of photocatalytic degradation.

Annular photoreactors were developed by inserting the 6W UV-lamp inside a glass housing placed at the middle of a cylindrical column made of PMMA or stainless steel and packing the ZnOcoated glass or Duranit beads in the annular space left between internal column walls and lamp housing. With the aid of a peristaltic pump, the MB or Ph solution recirculated continuously, at constant flow rate, between the photoreactor and a continuously-stirred vessel of variable volume. Liquid samples were collected from the vessel, at regular time intervals, to measure the MB or Ph concentration as a function of time. A parametric study was done with respect to the ratio of retention time of aqueous solution in recirculation vessel to the corresponding one in reactor, and Peclet number. A one-dimensional dynamic mathematical model was developed to describe the performance of photoreactors by coupling the sorption-surface reaction model with mass-transfer and flow processes. The model was used to: (i) estimate the kinetics of photocatalysis as a function of all pertinent parameters, by fitting its numerical solution to transient experimental measurements; (ii) design a pilot-scale photocatalytic unit for industrial applications.

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