ABSTRACT

The development of porous catalysts

for the degradation of organic dyes in wastewater based on advanced oxidation processes

Industrial wastewaters containing organic pollutants pose a very serious environmental problem. Advanced oxidation processes (AOP) offer a possible solution for cleaning such wastewaters. The main requirements for utilizing AOP are a catalyst and an oxidant or, in the case of photocatalysis, a photocatalyst and a source of ultraviolet (UV) light. The main disadvantage of AOP is the high cost of catalysts. In my doctoral thesis, I tried to overcome this problem by synthesizing/developing new, environment-friendly, cost-efficient (photo)catalysts for the (photo)catalytic degradation of dyes in industrial wastewaters in pH neutral conditions. The thesis has two parts; the first deals with Fenton-type catalysts, and the second with TiO_2 and ZnO photocatalysts. In both cases, catalysts were immobilized onto porous silicate support in order to ease their removal from the system. Porous silicates were chosen for their high specific surface areas and inertness.

Firstly, I focused on Fenton-type catalysts, which usually comprise iron as the catalyst and hydrogen peroxide as the oxidant and work at pH≈3. I replaced iron with manganese catalyst because it is relatively cheap and can work in neutral pH conditions. By means of direct synthesis, I incorporated manganese into a porous silica support, thus producing manganese-functionalized silica nanoparticles. These nanoparticles proved to be effective catalysts for the Fenton-type process of degrading cationic model dye methylene blue in the presence of hydrogen peroxide as an oxidant. I achieved 80% degradation in 30 minutes at neutral pH conditions at room temperature. By using X-ray Absorption Spectroscopy (XAS) it was shown that manganese incorporated into silica support is catalytically active, while Mn_2O_3 nanoparticles cause a simultaneous degradation of hydrogen peroxide.

Secondly, I investigated photocatalytic AOP, where TiO_2 and ZnO nanoparticles are usually used as photocatalysts. I researched the photocatalytic efficiency of such nanoparticles at neutral pH conditions and by incorporating them into porous silica support, I managed to improve their recyclability. By post-synthetic modification, I incorporated TiO_2 and ZnO nanoparticles into two types of porous silicates: SBA15 with well-defined hexagonal array of pores, and KIL2 with disordered pores. The fotocatalytic efficiency of these composites was tested on anionic model dye Reactive blue 19 (RB19) at neutral pH conditions, at room temperature and under UV light. Although the surface of composites is negatively charged at neutral pH conditions, I measured a significant adsorption of anionic dye onto the surface of the ZnO-SiO_2 composite. I proved that the high dye adsorption is the result of strong positive charges on the surface of ZnO nanoparticles, which on the surface of silica support are present in the form of mixed oxides. On the contrary, the surface of TiO_2 nanoparticles is negatively charged, and form only a physical mixture of oxides on the surface of the silica support. In the case of TiO_2-SiO_2 composites, I measured faster dye degradation when nanoparticles were incorporated into ordered silicate SBA15, while in the case of ZnO-SiO_2 composites, the opposite was true; degradation was faster when nanoparticles were incorporated into the disordered KIL2 support. Depending on the desired ratio of the adsorption/decomposition, a suitable composite as a photocatalyst may be selected for photocatalytic wastewater treatment containing lower concentrations of pollutants.

KEYWORDS: degradation of dyes in wastewater, advanced oxidation processes (AOP), Fenton-type catalytic oxidation, manganese functionalized silicate nanoparticles, photocatalytic oxidation, TiO_2 and ZnO nanoparticles immobilized onto porous silicate support.