

Catalytic system based on recyclable Fe⁰ and ZnS semiconductor for UV-promoted degradation of chlorinated organic compounds

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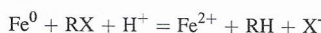
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ABSTRACT

Fe⁰ (ZVI) is one of the most effective reactants for treatment of water contaminated with chlorinated hydrocarbons, pollutants recalcitrant to degradation. Unfortunately, ZVI use is limited by corrosion and loss of reactivity over time. In order to suppress oxidation and passivation phenomena of iron, in this study ZVI was coupled to a suitable semiconductor (ZnS). Under UV light, electrons in the valence band of ZnS are promoted in the conducting band (E_{CB} = -1.04 eV vs NHE) and are able to reduce Fe²⁺ to Fe⁰ (E₀ = -0.44 eV vs NHE). The ZnS_ZVI composite was simply prepared by coating commercial ZnS with Fe⁰ obtained by reducing Fe (II) salt with sodium borohydride. The achieved ZnS_ZVI catalytic system was characterized by FESEM, WAXD, Raman and N₂ adsorption at -196 °C, with the aim to analyze morphology and crystalline structure of both components of the ZnS_ZVI system. Catalytic activity tests showed that ZnS_ZVI is effective in degrading probe molecules, eriochrome black T dye (EBT) and chlorobenzene (PhCl), from aqueous solutions under UV light irradiation. The experimental results show that in both cases the reductive action of Fe⁰ on the N = N bond of EBT and C-Cl of PhCl is synergistically coupled to the oxidative action of ZnS towards by-products. OH radicals, generated by the reaction between the electron holes in the valence band of ZnS and H₂O (OH⁻), were indeed confirmed by photoluminescence analysis. Recyclability tests indicate that ZnS_ZVI is highly stable since its catalytic activity, on both probe molecules, remains unchanged even after several cycles of reuse under UV irradiation. ZnS_ZVI catalytic behavior towards EBT has been carefully analyzed and a possible mechanism of EBT degradation has been proposed, which involves the formation of a Fe²⁺-EBT complex whose structure has also been suggested.

1. Introduction

The increasing accumulation of toxic organic/inorganic pollutants in water streams and groundwater natural reservoirs represents a pressing worldwide problem [1]. Particularly relevant is the concern for pollutants recalcitrant to degradation. Among them, chlorinated hydrocarbons are typically treated in aqueous media with Fe⁰ (ZVI) which reacts with halogenated pollutants (RX) and H⁺ according to the following general reaction [2–5]:



The above reaction involves the ZVI oxidation and the pH increase, which in turn promotes the formation of iron hydroxides, which are deposited on the ZVI surface by passivating it and reducing its reactivity

[2]. Corrosion and loss of reactivity limit ZVI use in long-term engineering processes for the remediation of groundwater, such as in permeable reactive barriers. To overcome corrosion phenomena, recently, the ZVI surface modification by deposition of small amounts of a second metal with high positive redox potential (such as Pd, Pt, Ag, Ni and Cu) led to an increase of ZVI performances [6–8]. However, a loss of activity over time was observed, due to accumulation of metal oxides or chemisorption of other compounds onto active sites or loss of the weakly bound second metal particles, making the benefit of bimetals only short-lived [6,9]. In order to enhance the ZVI performances, some authors recently proposed to add TiO₂ or ZnO semiconductor photocatalysts to ZVI with the aim of coupling the photocatalytic degradation action of semiconductors together with the reductive action of ZVI [10–13]. Furthermore, ZVI was also recently added to g-C₃N₄ and g-C₃N₄/MoS₂ with the aim to promote the photogenerated electron – hole pairs

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