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Enhancement of nano titanium dioxide coatings by fullerene and polyhydroxy fullerene in the photocatalytic degradation of the herbicide mesotrione

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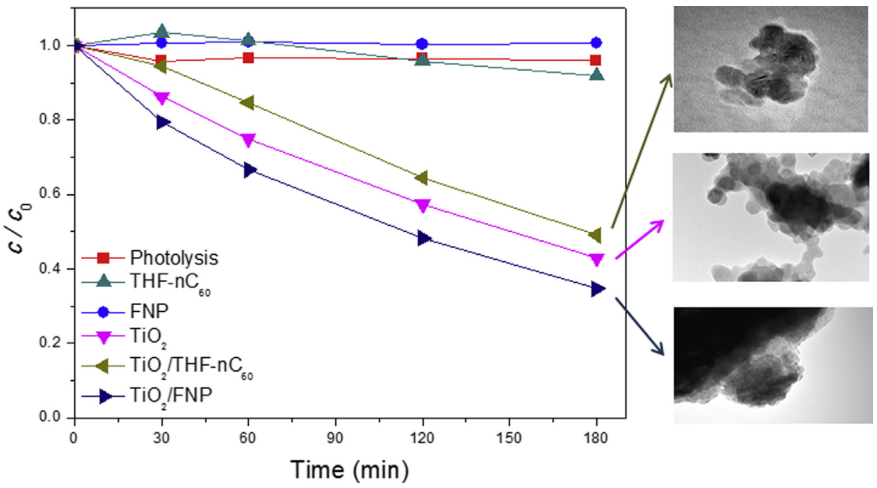
HIGHLIGHTS

- The surface modification of TiO_2 Hombikat with THF-nC_{60} and FNP were done.
- FNP increased negatively charge and catalytic surface of TiO_2 Hombikat.
- Removal of mesotrione using TiO_2/THF-nC_{60} and TiO_2/FNP were examined.
- FNP and electron acceptors enhanced photocatalytic efficiency of mesotrione removal.
- Percentage of mineralization was the highest in the case of TiO_2/$KBrO_3$/FNP system.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface modification of commercial TiO_2 Hombikat (TiO_2) using nanoparticles of fullerene C_{60} with tetrahydrofuran (THF-nC_{60}), as well as fullerenol $C_{60}(OH)_{24}$ nanoparticles (FNP) was investigated in this study. Characterization of THF-nC_{60}, FNP, TiO_2, TiO_2/THF-nC_{60}, and TiO_2/FNP was studied by using DES, ELS, TEM, SEM, DRS and BET measurements and their photoactivity has been examined on the mesotrione degradation under simulated sunlight. It was found that FNP in self-assembled nanocomposite TiO_2/FNP increased negatively charge, as well as catalytic surface of TiO_2. In addition, TiO_2/FNP exhibits a shift of band gap energy to lower values compared to TiO_2 and TiO_2/THF-nC_{60}. BET surface area has not showed significant differences among catalysts. Furthermore, it was found that the highest photoactivity

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was obtained for TiO_2/FNP system. Besides, influence of different concentrations of electron acceptors (H_2O_2 and $KBrO_3$), as well as scavengers on the kinetics of mesotrione removal in aqueous solution with/without TiO_2 and FNP under simulated sunlight was investigated. Namely, addition of mentioned electron acceptors has resulted in higher mesotrione degradation efficiency compared to O_2 alone. Besides, in the first period substrate degradation probably takes place via hydroxyl radicals and after 60 min of irradiation the reaction mechanism proceeds mainly via holes. The most efficient system for mesotrione degradation and mineralization were TiO_2/7 mM $KBrO_3$ and TiO_2/7 mM $KBrO_3$/40 μl FNP, respectively.

1. Introduction

Herbicides are widely used in management of different weeds for obtaining higher yields of cultivated crops. One of the disadvantages of herbicides using, because of their extensive use, is that together with their metabolites through spray drift, soil leaching, or runoff, can reach aquatic ecosystems (Bonnet et al., 2008). These compounds have high water solubility, chemical stability, persistence, and even at low concentrations may cause toxic or carcinogenic effects in the environment. Moreover, herbicides and their metabolites have become a severe environmental problem due to stability to natural decomposition, persistence and toxicity (Abdessalem et al., 2010; Oturan et al., 2010).

Mesotrione [2-(4-methylsulfonyl-2-nitrobenzoyl)-1,3-cyclohexanedione] is a pre- and post-emergent herbicide from the family of benzoyl-cyclohexanedione, to control of wide spectrum of broad-leaved and grass weeds, especially in corn farming. It was developed at Zeneca's Richmond, CA, research facility as one of a novel triketone compounds and registered in Europe in 2000 and in the U.S. in 2001 (Alferness and Wiebe, 2002). Mesotrione is a relatively new substance on the market, which is still insufficiently investigated and for this reason scientists pay great attention to its research. This herbicide is stable in water for about 90 days (DT_{50}) in the presence of light according to the European Commission report (2003). Joly et al. (2013) in their study have proven that mesotrione appeared to be highly toxic herbicide to *Vibrio fischery* than other investigated active ingredients. This herbicide is classified by the GHS hazard statement as very toxic to aquatic life (H400) and very toxic to aquatic life with long lasting effects (H410) in the environmental hazards index (Joly et al., 2013).

Photocatalytic degradation in the last few years has attracted increasing attention because its effectiveness in rapidly degrading and mineralizing organic pollutants (Chong et al., 2010; Dong et al., 2015; Miranda-García et al., 2011; Reddy and Kim, 2015). Various photocatalysts were being studied but nano-TiO_2 is the most used semiconducting photocatalyst in comparison to all others because of high efficiency, low cost, physical and chemical stability, widespread availability and non corrosive property. The main disadvantage of TiO_2 using as a catalyst is wide band gap (anatase, ~3.2 eV) which requires a quite expensive ultraviolet irradiation for formation of electron–hole pairs which participate in reductive and oxidative reactions that can lead to the decomposition of organic pollutants (Carp et al., 2004; Herrmann et al., 2007). Therefore many efforts have been made to improve the photocatalytic degradation under visible light irradiation. A large number of different carbon nanomaterials such as carbon nano-tubes, graphene, fullerenes and their derivatives, activated carbon, soot etc. were used to cover the surface of TiO_2 (Puma et al., 2008). Due to its unique properties, such as an electron donor-acceptor assembly, fullerene C_{60} occupies an important place in the research field concerning photooxidation processes, photochemical solar cells, and TiO_2 photocatalysis (Guldi and Prato, 2000; Long et al., 2009; Orfanopoulos and Kambourakis, 1994; Po et al., 2010). Fullerene C_{60} moderately absorbs light in the visible and UV range by crossing into the unstable singlet excited state ($^1C^*_{60}$), and then, after a rapid intersystem crossing, into a stable lower triplet state ($^3C^*_{60}$) (Kajii et al., 1991). In the excited state, fullerene C_{60} has excellent electron acceptor-donor properties, much better than in the ground state and can be easily reduced to the anion C_{60}^{6-} (Ohsawa and Saji, 1992). The fullerene radical anion $C_{60}^{\bullet-}$, formed by the reduction of C_{60}, can transfer an electron to the surface on which it is adsorbed, such as TiO_2 (Kamat et al., 1994). Photocatalytic properties of C_{60}/TiO_2, Pt-C_{60}/TiO_2, CdS-C_{60}/TiO_2, V-C_{60}/TiO_2, WO_3-C_{60}/TiO_2, β-cylcodextrin-C_{60}/TiO_2 nanocomposites are better compared with TiO_2 (Ali and Sandhya, 2014; Lin et al., 2009; Meng et al., 2012a,b, 2014; Oh and Ko, 2009; Oh et al., 2009, 2010). Fullerene functionalization with polar OH groups in polyhydroxylated fullerene $C_{60}(OH)_{24}$ can influence and contribute to better adsorption and increased water solubility of TiO_2 (Krishna et al., 2006, 2008). The enhancement of the TiO_2 photocatalytic properties was successfully achieved with polyhydroxylated fullerene in many chemical and biological model systems (Kamat et al., 1994; Krishna et al., 2006, 2008; Makarov et al., 2002). Furthermore, Park et al. (2009) have reported that unlike fullerene, adsorbed fullerenol activates TiO_2 under visible-light irradiation through the surface complex (SC) mechanism. Fullerol/Nb-TiO_2 showed better photocatalytic properties as compared with the Nb/TiO_2 irradiated with wavelengths of the visible part of the spectrum (higher than 420 nm) on the model of reduction of chromate (Cr^{6+}), the oxidation of iodide, and the degradation of 4-chlorophenol (Lim et al., 2014).

Besides the disadvantage of ultraviolet irradiation application and low efficiency in utilizing solar light, the recombination of photogenerated electrons and holes is another drawback in semiconductor photocatalysis because greatly restricts the photocatalytic activities of TiO_2. One of the possible manners to reduce the effect of charges recombination is adding of appropriate electron acceptor to system. Molecular oxygen can act as very efficient electron acceptor, but additional oxidants, such as H_2O_2 and $KBrO_3$ were also often used to propose enhancement of the photodegradation efficiency (Abramović et al., 2013; Ahmed et al., 2011; Armaković et al., 2015; Muneer and Bahnemann, 2002; Qamar and Muneer, 2005; Rahman and Muneer, 2005; Singh et al., 2007; Šojić et al., 2009).

The aim of this work was the surface modification of commercial TiO_2 Hombikat (TiO_2) using nanoparticles of fullerene C_{60} with tetrahydrofuran (THF-nC_{60}), as well as fullerenol $C_{60}(OH)_{24}$ nanoparticles (FNP). Characterization of THF-nC_{60}, FNP, TiO_2, TiO_2/THF-nC_{60}, and TiO_2/FNP was studied in detail. Besides, their effects on the photocatalytic degradation of mesotrione in aqueous suspension were examined using simulated sunlight. To prevent charges recombination, we tested introducing of H_2O_2 and $KBrO_3$ as