COMPARISON OF DIFFERENT TiO_2 SAMPLES AS PHOTOCATALYST FOR THE DEGRADATION OF CARBARYL IN A PILOT PLANT REACTOR

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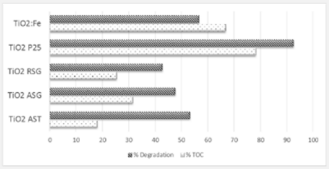

"Graphical Abstract"

Different iron-doped and undoped TiO_2 powdered samples, synthesized by the sol-gel method and a commercial TiO_2 (Degussa P-25) which was used as reference, were characterized and evaluated by means of the oxidation and mineralization percentages of aqueous Carbaryl solutions in a 1 sun solar CPC collector. All catalyst samples were characterized using SEM, UV Vis DRS, XRD and N_2 adsorption-desorption isotherms.
The results showed that titania (anatase) with solvothermal treatment exhibited the highest BET area (55 m^2 g^{-1}), even higher than Degussa P25 (50 m^2 g^{-1}). All synthesized catalysts were capable to partially oxidize Carbaryl, but total mineralization was not achieved. The highest Carbaryl mineralization rate (66.8%) was attained by the TiO_2:Fe catalyst, after 180 min of solar exposition time (47.86 KJ/L). This value was close to the Degussa P25 result (78.2 %) at similar experimental conditions.

Introduction

Due to the high capacity of titania for mineralizing very efficiently many organic compounds in aqueous media, a great interest in using titanium dioxide as photocatalyst for environmental remediation has arisen [1].
On the other hand, Carbaryl (1-naphtyl N-methylcarbamate) is a white crystalline solid that belongs to the carbamate pesticides family, and it is mainly used as insecticide. Carbaryl is toxic to humans and it is classified as a likely human carcinogen by the EPA. The elimination of residual Carbaryl from contaminated surface water is an issue of environmental concern [2].
Therefore, the goal of this study was to compare the photocatalytic activity of three different iron doped and undoped TiO_2 catalysts, prepared using the sol-gel method combined with two different drying treatments for solvent extraction and iron doped sample.

Material and Methods

Iron-doped and undoped TiO_2 powdered samples were synthesized by the sol-gel method and two different drying treatments (rotary evaporator and solvothermal), were characterized and evaluated in photo catalytic solar activity tests. The tested photocatalysts were: 1) anatase with rotavapor treatment (ASG), 2) rutile with rotavapor treatment (RSG), 3) anatase with solvothermal treatment (AST), 4) iron (0.2% at) doped titania (TiO_2:Fe) with rotavapor treatment, and a commercial TiO_2 (Degussa P-25) which was used as reference. All catalyst samples were characterized using Scanning Electron Microscopy (FE-SEM), UV Vis Diffuse Reflectance Spectroscopy, X-Ray Diffraction (XRD) and N_2 adsorption-desorption isotherms (BET area). The photocatalytic activity of these TiO_2-based materials was evaluated by means of the oxidation and mineralization percentages of aqueous carbaryl solutions at mild alkaline media in a 1 sun solar CPC collector (3L of total volume and 0.29 m^2 of solar irradiation area) under solar-light irradiation during 180 min.

Results and Discussion

The AST sample exhibited the highest BET area (55 m2/g) from all the synthesized titania samples, and slightly higher than the Degussa P25 sample (50 m2/g). The same phase (anatase) but dried using the rotary evaporator treatment showed a BET area 62% lower than the AST value, but when iron was incorporated to this phase, the specific surface area increased 24.4% (respect to ASG) due to the produced porosity (Table 1).
The band gap value obtained for solvothermal sample (AST) was close to Degussa P25, but the lowest values were obtained for rutile (RSG) and TiO_2:Fe samples (Table 1). Also, it was observed that absorption was significantly enhanced with the incorporation of Fe as dopant. These results are similar to values reported by Sood *et al* [3]. These results indicate that the sol-gel method caused a band gap decrease therefore these samples can absorb more photons in the visible region than AST and Degussa P25.

Table 1. Physical and optical properties of different powdered TiO_2 samples

Samples	Crystal size (nm)	Specific surface area (m^2/g) n=2	Vp (cm^3/g) n=2	Band gap value (eV)
ASG	27.4	21.1 ± 0.6	0.05	2.95
RSG	61	0.1 ± 0.0	0.01	2.92
AST	16.8	55.1 ± 0.8	0.14	3.12
Degussa P25	22.7	50.1 ± 0.8	0.12	3.2
TiO_2:Fe	27.9	26.2 ± 0.3	0.05	2.93

On the other hand, the percentages of degradation and mineralization of carbaryl obtained during the photocatalytic solar reaction after 180 min are shown in the Graphical Illustration. It is worth to notice that all synthesized TiO_2 catalysts were capable to partially oxidate Carbaryl, although total mineralization was not achieved. This suggests that all semiconductor powders exhibit high photocatalytic activity.

The highest Carbaryl degradation (92.7%) and mineralization percentage (78.2 %) were achieved using Degussa P25, it is important to mention that these values were in accordance with those obtained by [4]. The efficient photocatalytic performance of Degussa P25 is due to the mixed phases into the lattice of TiO_2, which contains atypically small rutile crystallites interwoven with anatase crystallites. The intersection points between these two phases allow a rapid electron transfer from rutile to anatase. Thus, rutile acts as an antena to extend the photoactivity into visible wavelengths and the similary sized structural arrangement of TiO_2 particles creates catalytic "hot spots" at the rutile-anatase interface [5].

In opposite, the worst photocatalytic performance was obtained using rutile phase (RSG), despite it showed the lowest band gap value (2.92 eV) and thus photons of lower energy could be used to generate more electron-holes pairs. However, its recombination process rates are fast [5], additionally particle size is very large then charge carriers cannot be employed in the photocalytic reaction.

The anatase phase (TiO_2-ASG) syntetized by the same sol-gel process than RSG, allowed to achieved higher Carbaryl degradation and mineralization percentages than rutile phase. Nevertheless, the solvothermal method (AST) enhanced the anatase phase catalytic activity, since it generates smaller spherical partices then charge carriers can easily arrived to the surface of TiO_2, in spite of this total mineralization was not achieved.

Finally, iron doped titanium dioxide increased significantly the mineralization percentage, because these metal ions inhibit the recombination process of electron-hole pair [3], thereby it improves the charge carriers separation (e- / h+). Additionally, the anatase phase band gap decreased, thus more photons can be employed to generate electron-hole pair, consequently its photocatalytic behavior enhance and it is close to Degussa P25.

The accumulated energy QUV (KJ/L) by sun concentrators calculated by methodology described by [6] was 47.86 KJ/L.

Conclusions

The results showed that all TiO_2 samples, synthesized by the sol-gel method and alternatively two drying treatments, were capable to partially oxidate Carbaryl, but not total mineralization was achieved.

The anatase sample produced using the solvothermal treatment for drying or extracting the solvent (AST) exhibited the highest BET area ($55 m^2/g$), even higher than Degussa P25 ($50 m^2/g$).

The highest Carbaryl mineralization was achieved using TiO_2:Fe (66.8%), after 180 min of solar exposition time (47.86 KJ / L); this efficiency mineralization value was close to the result obtained with Degussa P25 (78.2 %) at similar experimental conditions.

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