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Photocatalytic activity of ZnO impregnated Hβ and mechanical mix of ZnO/Hβ in the degradation of monocrotophos in aqueous solution

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Abstract

Adsorption experiments were carried out with monocrotophos (MCP) over supports (Hβ, HY and HZSM-5), ZnO, supported ZnO (ZnO/Hβ(I), ZnO/Hβ(M), ZnO/HY(I), ZnO/HZSM-5(I)) and TiO_2/Hβ. The results revealed that Hβ has better adsorption than HY and HZSM-5. Among the supported catalysts, ZnO/Hβ(I) showed higher percentage of adsorption than others. A series of supported catalysts (impregnation and mechanical mix) were prepared with different ZnO loadings and characterised by X-ray diffraction (XRD), SEM and BET surface area analysis. The photocatalytic degradation of monocrotophos in aqueous solution was carried out by using ZnO, supports and supported ZnO with low pressure mercury lamps. The influence of various parameters such as initial concentration of MCP, pH, catalyst loading and light intensity on the degradation was optimised. It was found that degradation of MCP followed first order kinetics. The experimental results demonstrated that the presence of zeolite in ZnO could enhance adsorption as well as degradation of MCP in aqueous suspension. The optimum loading for impregnated catalysts is 5 wt% whereas 1 wt% for mechanical mix catalyst. The time required for complete mineralisation of MCP under optimal experimental conditions over ZnO, 1 wt% ZnO/Hβ(M) and 5 wt% ZnO/Hβ(I) was 600, 360 and 240 min, respectively. The higher activity of ZnO/Hβ(I) is mainly due to fine dispersion of ZnO and hydrophobicity of the support.

Keywords: Monocrotophos; Supported ZnO; Relative photonic efficiency; Photocatalytic mineralisation

1. Introduction

The photocatalytic degradation of organic pollutants in water, using semiconductors such as TiO_2 and ZnO, has attracted extensive attention during the last two decades [1].

Previous studies have proved that such semiconductors can degrade persistent organic pollutants such as pesticides, detergents, dyes and volatile organic compounds under UV light irradiation, leading to total mineralisation of these pollutants into CO_2 and water [2–5]. However, the fast recombination rate of photogenerated electron/hole pair hinders the commercialisation of this technique [4]. This has led to great interest in improving the photocatalytic activity by suitable modification of semiconductors for the degradation of organic compounds in water. There are a number of studies related to ZnO coupled with metal oxides such as SnO_2, WO_3, Fe_2O_3 [6,7] and a few rare earth oxides [8] for the purpose of improving photocatalytic activity of ZnO. It is reported that coupled semiconductors increase the photocatalytic efficiency. Similarly supported semiconductors are also found to increase the photocatalytic efficiency [9,10].

ZnO, as a photocatalyst, has received much attention due to its low cost and high photo-activity in several photochemical and photo-electro-chemical processes [11–13]. ZnO is a II–IV compound semiconductor with a wide and direct band gap of 3.37 eV and a large excitation binding energy of 60 meV [14]. The salient advantage with ZnO is its large absorption of solar spectrum [15]. Akyol et al. [16] studied the photocatalytic decolorisation of Ramazol Red RR in aqueous ZnO suspension reporting that ZnO exhibited higher photocatalytic activity. Photocatalytic degradation of Reactive Blue 4 over ZnO in a slurry reactor was reported by Neppolian et al. [17]. The degradation of the dye was facilitated by alkaline pH, and the presence of persulfate and carbonate ions. Sakthivel et al. [18] reported photocatalytic degradation of Acid Green 16 using ZnO irradiated with sunlight. Poulios and Tsachpinis [19] investigated the photocatalytic degradation of Reactive Black

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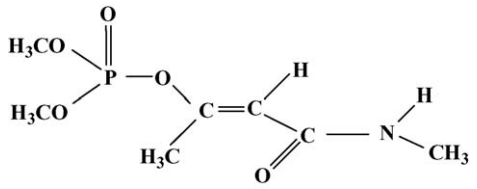

Fig. 1. Structure of monocrotophos.

5 using different semiconducting oxides viz., TiO_2 (Degussa P-25), UV-100 TiO_2, ZnO and TiO_2/WO_3 and observed that the decolorisation process was fastest with ZnO. Poulios et al. [20] conducted photocatalytic degradation of Auramine O in aqueous suspension using ZnO and TiO_2 separately in a batch reactor. They found that the rate of degradation of pollutants is faster with ZnO than with TiO_2 (Degussa P-25) [19,20]. Hoffman et al. [1] have also shown that ZnO produces H_2O_2 more efficiently than TiO_2. Thus, ZnO photo-assisted degradation may proceed in three different ways viz., photocatalytic oxidation or oxidation with photocatalytically generated H_2O_2, or simultaneous operation of both ways [21].

Despite the positive attributes of ZnO, poor adsorption properties lead to great limitation in exploiting this photocatalyst for its maximum efficiency. To circumvent this limitation, several attempts have been made to improve the efficiency of ZnO by using suitable supports such as glass, polymers, stainless steel, quartz, pyrex, paper, fabric, monoliths and zeolites [22–25]. Among the supports, zeolites have more advantageous owing to their special features such as high surface area, hydrophobic and hydrophilic properties, tunable chemical properties, high thermal stability and eco-friendly nature [26]. Reddy et al. [27] reported the photocatalytic degradation of salicylic acid using TiO_2/Hβ zeolite. They found that zeolite β increased the adsorption of pollutants as well as generation of large amount of hydroxyl ($^{\bullet}OH$) and peroxide radicals ($HO_2^{\bullet}$), which are the critical species in the photocatalytic degradation process. If the advantages of ZnO over TiO_2 are held, it is presumed that ZnO supported zeolite also exhibits better photocatalytic activity than TiO_2 supported zeolite. Further there is only limited literature available for the photocatalytic degradation of organic pollutants using ZnO supported zeolite. This prompted us to undertake an investigation featuring the preparation of ZnO supported catalysts by impregnation and mechanical mixing methods, and their photocatalytic activity towards degradation of monocrotophos (MCP) (Fig. 1), which is known as an insecticide. The influence of various parameters such as initial concentration of MCP, pH, amount of catalyst and light intensity on the degradation has been studied to achieve complete mineralisation of MCP. Finally, the relative photonic efficiency of ZnO supported catalysts and pure ZnO is compared and the results are presented in this manuscript.

2. Experimental

2.1. Materials

The technical grade sample of monocrotophos was received from Sree Ramcides Chemicals, India. Sodium form of zeolites Y, β and ZSM-5 with Si/Al ratios 3, 15 and 53, respectively, was obtained from Sued-Chemie India Pvt. Ltd., India. Zinc oxide was obtained from Merck, India. HPLC grade acetonitrile was purchased from Merck, Darmstadt, Germany. All the chemicals were used without any further purification. Reaction mixtures and HPLC mobile phase were prepared in doubly distilled water.

2.2. Preparation of photocatalysts

The sodium form of zeolites Y, β and ZSM-5 was converted into the H-form by repeated ion exchange with 1 M ammonium nitrate solution at 80 °C, and subsequent calcination at 550 °C in air. The resultant H-form of zeolites was abbreviated as HY, Hβ and HZSM-5. ZnO supported catalyst was prepared by the impregnation method. HY, Hβ and HZSM-5 were used as the host material. The requisite volume of zinc nitrate solution was added into zeolite powder with continuous stirring. This mixture was kept in an oven at 120 °C overnight and then calcined at 550 °C for 5 h. Thus, ZnO impregnated catalysts were obtained and referred to as ZnO/Hβ(I). Different ZnO loadings (0.5, 1, 3, 5 and 7 wt%) were obtained by varying the concentration of zinc nitrate solution. The mechanical mixing method involved grinding of appropriate quantities of ZnO and Hβ in a pestle and mortar. The catalyst with ZnO of 0.5, 1, 3 and 5 wt% were prepared by the mechanical mixing method and referred to as ZnO/Hβ(M).

2.3. Characterisation of photocatalysts

X-ray diffraction patterns of Hβ, ZnO, ZnO impregnated Hβ catalysts were recorded by employing a PANalytical X-ray diffractometer with monochromated high intensity Cu Kα radiation in the scan range of 2θ between 5° and 70°. BET surface area analysis of Hβ, HY, HZSM-5, ZnO/Hβ(I) and ZnO/Hβ(M) was carried out using a Quantochrome Autosorb 1 sorption analyser. SEM analysis was performed using a Leo-Stereoscan 440 microscope.

2.4. Photocatalytic reactor set-up

Photocatalytic degradation was performed in a slurry batch reactor. The cylindrical photochemical reactor, measuring 30 cm × 3 cm (height × diameter) provided with a water circulation arrangement, was used in all the experiments. The irradiation was carried out using 8 × 8 W low pressure mercury lamps built into a lamp housing with polished anodised aluminium reflectors and placed 6.5 cm away from the reactor. The lamps emit predominantly UV radiation at a wavelength of 254 nm. The reactor set-up was covered with aluminium foil followed by a black cloth to prevent UV light leakage.

2.5. Adsorption studies

Prior to photocatalytic experiments, adsorption study of MCP on ZnO, support (Hβ, HY and HZSM-5) and ZnO supported catalysts was carried out by mixing 100 ml of aqueous solution of MCP with 100 mg of the catalyst. This slurry was equili-