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$TiO_2/BaTiO_3$-assisted photocatalytic mineralization of diclofop-methyl on UV-light irradiation in the presence of oxidizing agents

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ABSTRACT

Gas chromatograph–mass spectroscopic identification of intermediate products in the degradation of diclofop-methyl and the kinetics of the reaction has been investigated. Formation of 4-[(2,4-dichlorophenoxy) phenoxy] ethane and (2,4-dichlorophenoxy) phenol was investigated. The other intermediate products are 2,4-dichlorophenol, 2,4-dichlorobenzene, phenol and acetic acid have been ascertained. The decrease in the concentration of the parent/intermediate compounds is followed by UV–vis spectral study and the supportive information on the functional groups in the intermediates has been obtained from IR-spectroscopy. Degradation process proceeds with oxidation–reduction reaction by the attack of $OH^{\bullet}$, $H^{\bullet}$, $O_2^{\bullet-}$ free radicals, which are photogenerated on the UV-light illuminated $TiO_2/BaTiO_3$ photocatalysts particles in aqueous medium. In this presentation another wide band gap semiconductor $BaTiO_3$ is shown to have comparable photocatalytic efficiency. The oxidizing agents are added to accelerate the rate of the reaction by enhancing the formation of free radicals. Based on the intermediates formed in the process of degradation, a suitable mechanism has been proposed.

1. Introduction

The contamination of surface water with herbicides results primarily from surface run off from agricultural activities. Pesticides constitute the large group of polluting chemicals. The industrial waste is another major source for pesticide contamination. Post application and seasonal concentrations of different herbicides have been reported to exceed the maximum contaminant level permitted for surface waters [1,2]. In this regard diclofop-methyl (DCM) is a post emergence herbicide used to control wild oats and annual grassy weeds brassicas, carrots, peas, potatoes, field beans, French beans, broad beans, barley, wheat, parsnip, soya beans, oilseed rape, onions, sugar beet, lettuce, linseed oil and lucerne [3]. It has been reported that diclofop-methyl is one of the most commonly detected herbicide in many countries [2], with concentrations frequently reaching the milligrams per liter level due to its properties of persistence and mobility. This herbicide is toxic to many organisms and has low solubility in water. As a result, conventional biological remediation processes are not suitable to remove this pesticide from contaminated water and therefore alternative treatment methods are required. There are several treatment processes available for the destruction or detoxification of hazardous organic wastes because of the growing restrictions placed on waste discharges and land disposal. Amongst these methods the advanced oxidation process (AOP) are the most promising alternative to treat herbicide wastes [4,5] because, they involve the generation of hydroxyl radicals ($HO^{\bullet}$) that are species non-selective and highly reactive oxidants. The photocatalytic oxidation (PCO) of organic pollutants is based on the photochemical production of electron–hole pair in a solid semiconductor under irradiation by light of energy greater than its optical band. Photocatalytic oxidation involves two important aspects. First the adsorption of the pollutant on the surface of the photocatalyst takes place which is followed by oxidation with positively charged holes by direct abstraction of the pollutants electron. Second aspect is oxidation at the catalyst surface or in its vicinity with hydroxyl radicals.

Photocatalytic studies have usually employed titanium dioxide as the photocatalyst. The role of photocatalyst in general is to promote the reaction by lowering the activation energy. In this process it is essential to suppress the recombination process and to increase the life time of separated electron–hole pairs for the achievement of high photocatalytic activity, so that fast electron transfer occur from the surface of the catalyst to adsorbed intermediates. TiO_2 is the most commonly used photocatalyst in photocatalytic treatment of water and waste water because of its superior photo activity and low toxicity. In this presentation another wide band gap semiconducting particles $BaTiO_3$ is shown to have comparable photocatalytic efficiency. Photochemical activity of $BaTiO_3$ in aqueous

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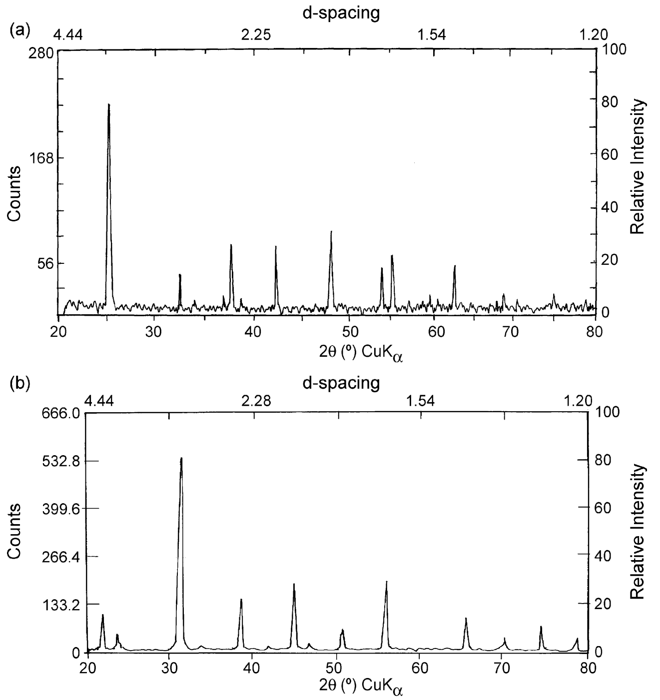


Fig. 1. (a) XRD pattern for TiO_2 photocatalyst and (b) XRD pattern for $BaTiO_3$ photocatalyst.

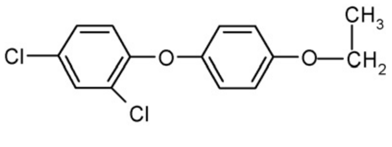
solution under UV-light has been studied. This includes kinetic parameters like rate, rate constant, order and process efficiency. This work opens the possibility to develop more efficient photocatalysts for detoxification process. The aim of the present study is to investigate the prime mechanisms involved in the photocatalytic degradation of diclofop-methyl and to examine the effect of oxidizing agent and characterizing the intermediate products which are produced during the photo transformation process.

2. Experimental

2.1. Materials

2.1.1. Pesticide

The Pesticide sample of 96.6% pure was obtained from Rallis India Limited, an Agrochemical Research Center, Bangalore, India. The pesticide sample was used as such obtained from the industry. The pesticide diclofop-methyl: methyl 2-[4-(2,4-dichlorophenoxy) phenoxy] propionate is also called by the trade names Illoxan, Hoelon, Hoe-Gross, etc. It is a colorless, odorless crystals having molecular formula: $C_{16}H_{14}Cl_2O_4$; molecular weight: 341.20; melting point: 39–41 °C; boiling point: 173–175 °C at 0.1 mbar; vapor pressure: 3.4×10^{-7} mbar at 20 °C and 1.5×10^{-5} mbar at 30 °C. It is readily soluble in common organic solvents, e.g. acetone-40, xylene-50, methanol-40 (all in g/100 ml), etc., least soluble in water, i.e. only about 50 mg/l at 22 °C [3]. The structural formula of the herbicide is shown in Scheme 1.



Scheme 1. Structure of diclofop-methyl.

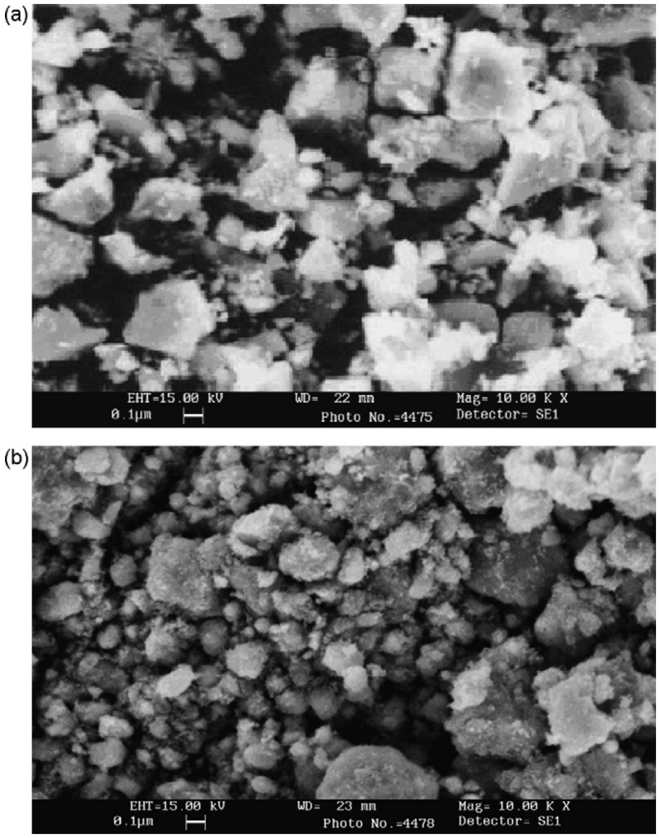


Fig. 2. (a) SEM picture for TiO_2 powder and (b) SEM picture for $BaTiO_3$ powder.

2.1.2. TiO_2 and $BaTiO_3$

Titanium tetrachloride, ammonium hydroxide, Sulphuric acid and barium hydroxide, ammonium persulphate, hydrogen peroxide, nitric acid and sodium hydroxide all obtained from E-Merck chemicals. The solutions are prepared using double distilled water. The photocatalysts used are fine grained powders of anatase form of TiO_2 prepared by gel to crystalline conversion method to yield nanoparticles as reported earlier [6]. $BaTiO_3$ is also obtained by reaction of gels of hydrated titania with barium hydroxide as reported by Kutty and coworker [7]. The recovered solids from both the process were oven dried at 105–120 °C. $BaTiO_3$ is further annealed at 450 °C for 4 h and TiO_2 is annealed at 600 °C for 4 h.

2.2. Characterization of TiO_2 and $BaTiO_3$

The X-ray diffractograms for the finely ground TiO_2/$BaTiO_3$ photocatalyst powders are obtained using Phillips PW 1050/70/76 X-ray diffractometer which is operated at 30 kV and 20 mA. Cu Kα radiation was used with nickel filter. The scanning range employed was $2\theta = 5–85°$. The normal scanning speed was 2°/min and the check speed being 2 mm/min. The crystallite size measured from Scherrer's equation [8] relating the pure diffraction breadth (half-band width) to crystallite size normal to plane *hkl* as

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D_{hkl} is mean dimension in Å, λ is the wave length, β is the pure diffraction line broadening, θ is the Bragg's angle of the reflection *h,k,l* and *K* is the constant approximately equal to unity. Half bandwidth depends on crystallite size and microstrain in the lattice [9]. The calculated crystallite size of anatase TiO_2 is 17.93 nm and that of $BaTiO_3$ is 19.24 nm (Fig. 1a and b). The particle size