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Preparation of N doped TiO_2 via microwave-assisted method and its photocatalytic activity for degradation of Malathion

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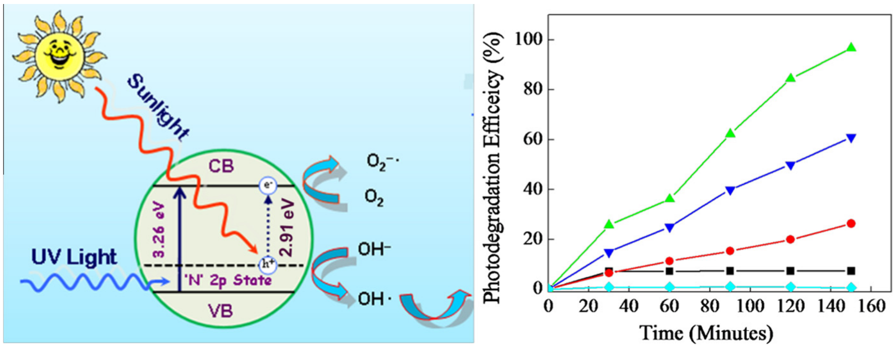
HIGHLIGHTS

- N-doped TiO_2 having anatase phase with 10 nm particle size.
- Optical absorption measurement indicated the red shift in the absorption band edge upon N-doping.
- A 97% and 60% photocatalytic degradation of Malathion were achieved under UV and sunlight, respectively.
- The degraded products were less toxic as compared to Malathion confirmed by cytotoxicological study.

GRAPHICAL ABSTRACT



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ABSTRACT

We report herein, nitrogen doped TiO_2 nanostructure synthesized by simple microwave assisted method, where ammonia was used as hydrolyzing agent. The synthesized nanomaterials were characterized by means of X-ray diffraction (XRD) which demonstrated that N-doped TiO_2 is in anatase phase with average crystallite size of 10 nm. Doping of N into the lattice of TiO_2 was supported by X-ray photoelectron spectroscopy (XPS), Fourier transform-infrared spectroscopy (FT-IR), CHNS analysis, energy dispersive spectroscopy (EDS). The diffuse reflectance spectroscopy (DRS) showed shifting of absorption edge toward the visible region. Thermogravimetric–differential thermal analysis (TGA–DTA) points out N-doped TiO_2 nanoparticles are thermally stable. In order to achieve maximum degradation efficiency, the effect of catalyst loading, pH and light sources (UV and sunlight) were studied. A maximum 97% degradation efficiency was achieved under optimized conditions. A 80% reduction in the chemical oxygen demand (COD) was observed after 150 min that indicated mineralization of Malathion. The cytotoxicological studies indicate that photocatalytically degraded products were less toxic as compared to Malathion.

Introduction

In the recent years, intense efforts have been made for the preparation of low dimensional nanomaterials of metal oxides, because of remarkably different physical and chemical properties as compared to bulk [1]. Among all the metal oxides, titanium dioxide has been reported as one of the most promising material due to its wide range of technological applications in various fields such as photocatalysis [2], dye sensitized solar cells [3], hydrogen generation [4], antibacterial activity [5], UV blocker [6], self cleaning [7] and gas sensors [8]. TiO_2 is an important photocatalyst for the degradation of organic pollutant from wastewater because of low cost, non toxic and photostability [9]. TiO_2 having anatase phase is desirable for photocatalytic activity because of its electron mobility is larger than that of the rutile phase [10]. TiO_2 has

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drawbacks which include higher recombination rate, low quantum yield and wide band gap (3.2 eV) [11]. Due to these, only ultraviolet light can initiate the photocatalysis process. Consequently, this limits the practical use of TiO_2 under natural sunlight, since entire solar spectrum consist of only 5% UV light. There are only a few reports are available on the degradation of organic moiety from wastewater under natural sunlight using TiO_2 as a photocatalyst. In order to utilize whole solar spectrum (5% UV, 46% Visible light), it is essential to develop new catalyst which is efficient in visible region, therefore the tuning of TiO_2 band gap into visible region has gained much interest. There are several approaches are used to modify TiO_2 by suitable doping like metal [12], nonmetal [13] and coupling with semiconductors [14]. Among all these nitrogen doped TiO_2 has been most extensively studied, which shows outstanding photodegradation performance under visible light. The origin of this photo response is at higher wavelength due to the mixing of the 2p nitrogen level with the oxygen 2p orbital to form the valence band, which results in a narrow band gap [15]. A 1% nitrogen doping resulted into ten-fold increment of photodegradation efficiency under visible light as compared to pristine TiO_2 [16]. Nowadays, preparation of N-doped TiO_2 with anatase phase has been of great interest for photocatalytic applications. Although, there are several methods are available for the preparation of metal oxide nanomaterials but the microwave assisted technique has potential advantages over the conventional methods such as the growth rate of product is very high for small particle size and always the product exhibits a narrow size distribution as a consequence of fast homogenous nucleation, molecular homogeneity and selective heating rate [17].

At the present, environmental problems owing to pesticide in the field of agriculture concerning with wastewaters are becoming much more serious problem in developing countries [18]. In particular Malathion (S-1,2-bis(ethoxicarbonyl)ethyl 0,0-dimethyl-phosphorodithioate), is relatively water soluble organophosphorous pesticides. It is suspected to cause childhoodleukemia, anemia, and kidney failure [19]. As far as fish tissues concerned, the damage of DNA occurs due to exposer of Malathion and confirmed to be genotoxic [20]. Malathion is highly toxic to bees and other beneficial insects, some fish and other aquatic life [21]. Malathion has been still widely used in agricultural applications with a broad range of target pests [22]. In order to remove all these pollutants from wastewater, the use of heterogeneous photocatalysis has emerged as a promising method to degrade a large variety of pesticide due to its simplicity, low cost, and reusability [23]. Therefore, it is vital need to study the toxicity of pesticides and its post-degradation products, for this purpose plant genotoxicity assays are exploited owing to its relatively inexpensiveness, fast and gives reliable results for the chemicals which cause chromosomal aberration in plant cells [24].

The present study is mainly focused on the development of solar light driven N-doped TiO_2 photocatalyst with controlled size by microwave assisted method. In order to achieve the maximum photocatalytic activity, a series of experiments were carried out such as, the effect of pH, irradiation sources (Natural sunlight and UV light) and photocatalyst loading. The effect of Malathion and its degraded products were also studied for cytotoxicity in meristematic root tip cells of *Allium cepa*.

Materials and methods

Materials

Titanium tetra-isopropoxide (TTIP, 98%), cetyl trimethyl ammonium bromide (CTAB, 99%) were purchased from Spectrochem Pvt. Ltd., Mumbai (India). 25% ammonia was purchased from Loba Chemie Pvt. Ltd., Mumbai (India). Absolute ethanol (99.9%) was purchased from Changshu Yangquan Chemicals, China and sodium dodecyl sulfate (SDS, extrapure) was purchased from Thomas Baker Pvt. Ltd., Mumbai. All chemicals used for preparation of solutions were of analytical grade and used as received. All solutions were prepared in millipore water obtained from millipore water system (Millipore Corp. Bangalore, India).

Synthesis of microwave assisted N-doped TiO_2 nanoparticles

N-doped TiO_2 nanocrystalline powder was prepared by controlled addition of 0.1 M TTIP in 100 mL of absolute ethanol with constant stirring to get clear solution. Then sufficient amount of surfactant solution (1% CTAB + 1% SDS) was added with constant stirring followed by dropwise addition of aqueous ammonia at room temperature until solution reached to pH = 8. After complete precipitation, the precipitate was washed with millipore water and acetone several times to ensure complete removal of impurities. The precipitate was subjected to microwave irradiation for 20 min in domestic microwave oven (Input 900 W, 250 MHz, LG Make,) with on–off cycle (20 on −40 s off). The dried precipitate was grounded by using agate mortar pestle and calcined at different temperatures for 2 h in temperature controlled muffle furnace. The phase purity and the degree of crystallinity of the N-doped TiO_2 nanomaterials were monitored by XRD technique.

Characterization of synthesized N-doped TiO_2

XRD of as-synthesized N-dopedTiO_2 was recorded on a Panalytical diffractometer with Cu Kα radiation (λ = 1.5406 Å) in the range of 2θ, 10–90°. The average crystallite size of anatase N-doped TiO_2 was calculated by using Scherrer's formula. X-ray photoelectron spectra were recorded using an ESCA-3000 (VG Scientific Ltd. England) using Al Kα radiation (1486.6 eV) and constant pass energy of 50 eV. Fourier transform infrared spectrum (FT-IR) of N-doped TiO_2 was recorded on Spectrum-one (Perkin Elmer) in the range of 4000–400 cm^{-1} using KBr pellet. The diffuse reflectance recorded on Varian cary-5000 UV–Vis.–NIR spectrophotometer. Thermal stability of N-dopedTiO_2 was tested by using TGA–DTA instrument, SDT Q600V20.9 Build 20 (TA Instruments, USA) under N_2 atmosphere. The surface morphology of N-dopedTiO_2 nanoparticles was scanned by scanning electron microscope (SEM) (JEOL, JSM-6360) at various magnifications. The transmission electron microscopy (TEM) images were scanned using JEOL JEM 2100 TEM equipped with high resolution gatan CCD camera. To know the elemental composition of the N-doped TiO_2 nanocrystalline powder, the EDS was recorded using SEM Model JEOL 6360 connected with EDS. Nitrogen, Carbon, Hydrogen content of TiO_2 were estimated by CHNS Analyzer using Thermo Finnegan Flash EA 1112 CHNS elemental analyzer, surface area of the anatase N-doped TiO_2 was measured by BET surface area at 77 K performed on Autoabsorb 3100.

Photocatalytic activity of N-doped TiO_2

The photocatalytic activity of N-doped TiO_2 was evaluated for the degradation of Malathion by both natural sunlight and UV light (365 nm). To evaluate optimal photocatalytic activity of N-doped TiO_2, its amount was varied from 0.5 to 2 g/dm^3 in Malathion solution (15 ppm). The effect of pH on the photocatalytic activity was studied by adjusting pH of solution from 4 to 8 using HCl and NaOH (1 M) each. The photoreactor was kept open to air to get sufficient oxygen for photochemical reaction. Typically, in this experiment photocatalyst was added in photoreactor containing 100 mL of 15 ppm Malathion. Before irradiation to light, the solution was stirred for 30 min in dark to ensure an adsorption–desorption equilibrium, then exposed to light. The numbers of