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N-doped TiO_2 nanosheets for photocatalytic degradation and mineralization of diazinon under simulated solar irradiation: Optimization and modeling using a response surface methodology

Amir-Ahmad Salarian [a], Zahra Hami [a], Nezam Mirzaie [b], Seyed Mohsen Mohseni [c], Anvar Asadi [d,e,*], Hamide Bahrami [d], Mehdi Vosoughi [f], Abdolazim Alinejad [g], Mohammad-Reza Zare [h]

[a] *Department of Toxicology, Faculty of Medicine, Aja University of Medical Sciences, Tehran, Iran*
[b] *Social Determinants in Health Promotion Research Center, Hormozgan University of Medical Sciences, Bandar Abbas, Iran*
[c] *Department of Environmental Health Engineering, School of Public Health, Qom University of Medical Sciences, Qom, Iran*
[d] *Department of Environmental Health Engineering, School of Health, Student Research Office, Shahid Beheshti University of Medical Sciences, Tehran, Iran*
[e] *Department of Environmental Health Engineering, Faculty of Health and Research Center for Health Sciences, Hamedan University of Medical Sciences, Hamedan, Iran*
[f] *Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran*
[g] *Student Research Committee, School of Medicine, Shahroud University of Medical Sciences, Shahroud, Iran*
[h] *Lar School of Medical Sciences, Shiraz University of Medical Sciences, Shiraz, Iran*

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ABSTRACT

The nitrogen doped TiO_2 (N-TiO_2) was synthesized via a facile hydrothermal method using titanium (IV) butoxide as a titanium precursor and urea as a dopant source. The catalyst was characterized by transmission electron microscopy (TEM), X-ray diffractometry (XRD), surface area (BET method) and band gap energy by diffuse reflectance spectroscopy (DRS). N-TiO_2 is a mesoporous nanocrystal sheet with the mean pore diameter of 14.9 nm, specific surface area of 66.3 m^2/g, crystallite size of 27 nm, and band gap energy of 2.83 eV. Response surface methodology (RSM) with central composite design (CCD) was utilized for the modeling and optimization of the operational photodegradation variables such as pH, catalyst loading, initial diazinon concentration, and irradiation time. Under the optimum conditions established, the performance of 85% and 63% for degradation and mineralization of diazinon were experimentally reached, respectively. Moreover, the obtained quadratic model showed high correlation ($R^2 = 0.95$ (degradation) and $R^2 = 0.928$ (mineralization)) between the predicted and experimental values. It was found that all the selected variables had an important effect on diazinon removal.

1. Introduction

Diazinon (O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl phosphorothionate) is a nonspecific and highly toxic thionophosphorous organophosphate (OP) pesticide which has low persistence in the environment [1]. It is extensively used to control insects and, just in the USA, 6 million pounds of diazinon are annually used on farming sites [2]. Diazinon is categorized as moderately hazardous of class II by the World Health Organization (WHO), which has log K_{ow}, vapor pressure, and Henry's law constant of 3.3, 1.4×10^{-4} mm Hg at 20 °C and 1.4×10^{-6} mm^3/mol, respectively [3,4]. It is non-polar and moderately mobile which is a concern for groundwater and surface derived drinking water [5]. Several techniques have been tested for the removal of diazinon from contaminated solutions such as adsorption [6], conventional and advanced oxidation processes [7], coagulation/flocculation/sedimentation [8], biodegradation [9] and photocatalyst [10]. However, photocatalytic processes offer many advantages for the removal of micropollutants including complete oxidation, no formation of polycyclised products, availability of highly active and cheap catalysts, and oxidation of pollutants in the ppb range [11].

Among the used photocatalysts, TiO_2 is one of the most popular and promising materials, but is has large band gap (3.0–3.2 eV) which is inactive under visible light illumination [11,12]. Therefore, pure TiO_2 has been modified by various ways such as impurity doping [13–18] and dye sensitization [19] to obtain visible light reactivity. Nonmetal doping of TiO_2 by the incorporation of nonmetals (N, S, F, C) has been considered as an effective method for extending the absorption band-edge of TiO_2 to the visible-light region [20]. Sakthivel et al. [21] prepared nitrogen-doped TiO_2 using tetraisopropoxide or titanium tetrachloride as a precursor of titania and thiourea as a dopant source. They used N-TiO_2 for photocatalyze mineralization of 4-chlorophenol by visible light ($\lambda \geq 455$ nm) and observed 30% mineralization of 4-chlorophenol in the presence of TiO_2-N/3 after irradiation for 3 h.

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* Corresponding author at: Department of Environmental Health Engineering, School of Health, Student Research Office, Shahid Beheshti University of Medical Sciences, Tehran, Iran.

E-mail address: anvarasadi@sbmu.ac.ir (A. Asadi).

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Kisch et al. [22] used nitrogen-modified titania under visible-light (λ ≥ 455 nm) for the photocatalytic degradation of formic acid and found that the obtained TiO_2-N_1 and TiO_2-N_2 had intense band absorption, resulting in the corresponding band gap of 2.46 and 2.20 eV.

The aim of this work is to prepare N-doped TiO_2 nanosheets facets through the facile hydrothermal method. Urea was used as the source of nitrogen. The photocatalyst samples were characterized by TEM, XRD, DRS, and BET. The photocatalytic activity of the N-TiO_2 sample was examined via the degradation and mineralization of diazinon as a model pollutant irradiated by simulated solar light. Moreover, response surface methodology (RSM) was applied for the optimization of photocatalytic degradation and mineralization of diazinon. The effect of pH, catalyst dose, initial diazinon concentration and reaction time were investigated and optimized values were obtained.

2. Materials and method

2.1. Materials

Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) and urea (CH_4N_2O) were used as obtained from Merck (Germany). Commercial powder of Degussa P-25 (70% anatase, 30% rutile and 98.9% purity) was used as obtained from Degussa AG. Hydrofluoric acid was purchased from Loba Chemie (India). Ethanol (96%) was obtained from Razi Co. (Iran).

2.2. Catalyst preparation

Nitrogen doped TiO_2 nanosheet was prepared by hydrothermal method [23,24] with some modification. In a typical preparation 15 mL of Titanium isopropoxide with 2 mL of hydrofluoric acid solution (ca. 40 wt%) were mixed in a dried Teflon-lined autoclave and then kept at 180 °C for 24 h. The atomic ratio of F^- to Ti was 1. After hydrothermal reaction, the precipitate was separated by centrifuge and filtration, washed with ethanol, deionized water and 0.02 N NaOH (each one three times) and then dried at 80 °C for 8 h. The obtained powder was mixed mechanically with a proper amount of urea (1:3 W/W) for 1 h and then calcined at 450 °C for 2 h. Bare TiO_2 nanosheet was obtained at the same way without adding urea.

2.3. Catalyst characterization

TEM micrograph was performed using an EM10C (Germany) microscope operating at accelerating voltage of 80 kV. The photocatalyst for electron microscopy was dispersed in ethanol and sonicated at 20 kHz for 15 min and then applied a drop of very dilute suspension on Formvar carbon coated grid Cu Mesh 300.X-ray diffraction patterns of the samples were carried out at room temperature by STOE (Darmstadt, Germany) diffractometer using a Cu Kα radiation (λ = 1.54060 Å). Generator settings were 40 kV, 40 mA. Data were obtained in the 2θ range of 10–80°, with a scanning step of 0.06° and 1 s/step. The average dimension (D) of particles was estimated by the Debye-Sherrer's formula [25] based on widening of the anatase (101) peak as:

$$D_{(h\,k\,l)} = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where k is the shape factor (normally equal to 0.9), λ the wavelength of X-ray of Cu Kα radiation, β the full width at half maximum (FWHM) of the (h k l) peak, and θ is the diffraction angle. Diffuse reflectance spectra (DRS) of the samples were measured on an Avantes spectrophotometer (Avaspec-2048-TEC) with a $BaSO_4$ as a reference material. A given amount of TiO_2 powder was uniformly pressed in the tablet and placed in the sample holder on integrated sphere for the reflectance measurements. Specific surface area (SSA) was measured based on nitrogen adsorption–desorption at 77 K via a Belsorp mini II (Japan) and calculated according to the BET and BJH isotherm models. The pore volume and the average pore size of the doped TiO_2were determined at a relative pressure (P/P_0) of 0.986 based on volume of adsorbed nitrogen. The elemental analysis (CHN analyses) of the N-TiO_2 photocatalyst was conducted by Thermo Finnigan Flash-1112 EA, microanalyzer. Batch equilibration technique was utilized to determine the pH at the point of zero charge (pH_{pzc}). In a typical experiment, 50 mL of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask at room temperature and then for stabilization of pH and preventing of CO_2 dissolution, N_2 gas was bubbled through the solution. Initial pH values ($pH_{initial}$) of NaCl solutions were adjusted to a value between 2 and 12 by adding 0.1 M HCl or 0.1 M NaOH solutions. The N-TiO_2 photocatalyst (0.15 g) was added to the solution and after 24 h shaking at 250 rpm the pH_{final} was measured and plotted against $pH_{initial}$. The pH_{pzc} is the point where the curve crossed the line $pH_{initial} = pH_{final}$.

2.4. Experimental procedure

Photodegradation of diazinon were carried out in home-made tubular cylindrical Pyrex under visible light at ambient temperature. In each run, 20 ml of solution containing known concentration of diazinon and photocatalyst was prepared, sonicated for 6 min and then allowed to equilibrate for 20 min in the darkness. Irradiation was performed with a 350 W (simulated solar light) xenon (Xe) lamp (XBO), which was positioned 25 cm above the solution. The integrated lamp intensity measured with a LUX-UV-IR meter (LEYBOLD, Germany) was 95 mW/cm^2 with the wavelength range of 380–900 nm. At a given time interval, 1 mL aliquots of the aqueous suspension was withdrawn, centrifuged, and filtered through syringe filters (Ø = 0.22 μm) to remove the remaining particles. The diazinon concentration was determined using a Knauer HPLC (C18 ODS reverse phase column, 250 × 4.6 × 5) with a UV-PDA detector at a wavelength of 247 nm. The mobile phase consisted of 60% acetonitrile (HPLC Grade, Merck) and 40% ultra-pure water. The flow rate was 1 mL/min and the sample volume was 20 μL. The degree of degradation was calculated as:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \tag{2}$$

where C_0 and C_e stand for the diazinon concentrations before and after reaction, respectively.

2.5. Experimental design and optimization by response surface methodology

Response surface methodology (RSM) is a collection of statistical and mathematical techniques invented to find the optimal response within the specified ranges of the factors. Design-Expert 7.0.0 and Minitab 16 software were used for the analysis of the obtained experimental data. Central composite experimental design (CCD) which is the widely used form of RSM was applied for the optimization of photocatalytic degradation and mineralization of diazinon. Four experimental factors at three levels (−1, 0, 1) were taken into consideration as follows: pH (x_1), catalyst dose (g/L) (x_2), initial diazinon concentration (mg/L) (x_3), and irradiation time (min) (x_4). The operating ranges and levels of the independent variables investigated in this study are given

Table 1
Predictor variables and their coded levels and actual values used for experimental design.

Variable	Real values of coded levels				
	$-\alpha$	-1	0	1	$+\alpha$
pH (x_1)	3	5	7	9	11
C. Dose (x_2)	0.5	1.5	2.5	3.5	4.5
Diazinon concentration (x_3)	1	4	7	10	13
Time (x_4)	15	40	65	90	115