



Evaluation of a modified TiO₂ (GO–B–TiO₂) photo catalyst for degradation of 4-nitrophenol in petrochemical wastewater by response surface methodology based on the central composite design



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ABSTRACT

In this study, a novel boron–graphene oxide–TiO₂ (B–GO–TiO₂) was synthesized by sol–gel method. The structure and properties of nano particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. The analysis of the process was performed by varying four significant independent variables, including four numerical factors (concentration of 4-NP, dosage of photo catalyst, initial pH and reaction time). The experiments were conducted based on a central composite design (CCD) and analyzed using response surface methodology (RSM). The photo catalytic activity of samples was monitored by UV–vis absorption measurements and chemical oxygen demand (COD) test. The results showed that degradation of 4-NP in acidic pH is more favored than in neutral and basic pH. The modified modes reduced recombination of photo generated electron and holes, and extended the absorption of TiO₂ into the visible light. The photo catalytic properties of B–GO–TiO₂ are more effective than those of pure TiO₂ and other modified TiO₂. The removal efficiency of 4-NP for B–GO–TiO₂, B–TiO₂ and GO–TiO₂ was about 100, 85 and 80%, respectively, and also removal efficiency of COD was about 85, 70 and 65%, respectively, under visible light irradiation and optimum condition (4-NP concentration = 25 mg/l, concentration of photo catalyst = 1 g/l, amounts of COD = 300 mg/l and pH of 3 after 180 min).

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1. Introduction

4-Nitrophenol (4-NP) is a toxic and bio-refractory pollutant in petrochemical wastewater which can cause considerable damage to the ecosystem and human health. It can damage the central nervous system, kidney, liver, and blood of humans and animals. 4-NP and its derivatives are used in the production of pesticides, and as insecticides and herbicides [1,2]. Nitro aromatic is employed in the production of explosives and many synthetic dyes [3]. Therefore, 4-NP and its derivatives are common pollutants in many natural waters and industrial wastewater [3]. Nitro phenols are stable and soluble in water. The presence of the Nitro group in the phenolic ring makes it more resistant to chemical and biological decomposition [4]. Economical and effective degradation of toxic compounds from wastewaters is one of the most urging recent challenges in environmental chemistry and engineering. Conventional wastewater treatment systems (physical, chemical or biological) are non-destructive, since they only convey

the pollutant to another phase or location and produce a potentially dangerous and toxic secondary effluent which will leave its own disposal requirement [5].

Heterogeneous photo catalysis techniques are generally applied for treatment of wastewater containing refractory organic contaminants with the purpose of reuse due to its ability to achieve complete mineralization of the compounds under mild conditions such as ambient temperature and pressure [6]. Various solid semiconductors such as oxides (TiO₂, CeO₂, ZnO, ZrO₂, V₂O₅, WO₃, Fe₂O₃ and etc.) and sulfides (CdS, ZnS, etc.) have been used [7,8]. Among the photo catalysts examined, titanium dioxide (TiO₂) has been found to be the most influential because of its photo stability, availability, non-toxic nature, low operating temperature, low energy consumption, high photo catalytic activity, relatively high chemical stability, appropriate flat band potential, water insolubility under most environmental conditions and preventing the formation of undesirable by-products [9–11].

In fact, TiO₂ has two major drawbacks, consisting in its relatively large energy band gap (3.2 eV for the anatase phase, 3.0 eV for the rutile phase), which hampers the exploitation of solar light in photo catalytic reactions and in the low quantum efficiency

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of photo catalyzed reactions, because of the high recombination probability of the photo generated electron–hole pairs [12–15].

Several modifications were employed for improving the efficiency of TiO_2 , including doping (metal and nonmetal) of TiO_2 [16], sensitization of TiO_2 with inorganic or organic compounds [17] and incorporation of electron-accepting materials such as carbon source materials [5,17].

Doping TiO_2 by nonmetal or metal ions has been considered as one of the most promising ways to develop TiO_2 -based photo catalysts for reducing the recombination of photo generated electron and holes, and to extend its light absorption into the visible region [18–20].

Nonmetal doping also induces oxygen vacancies which have a significant influence on catalytic activity [21–23]. Boron atoms can substitute oxygen atoms in the TiO_2 lattice and the p orbital of B is mixed with $\text{O}2p$ orbital, which causes the band-gap narrowing [23] and it also increases in the quantity and separation photo generated charge carriers which lead to an increase in the lifetime of the charge carriers and holes [24,25].

A highly appealing approach toward the development of nano composite photo catalysts relies on the combination of TiO_2 with carbonaceous materials, including mesoporous carbon and carbon nanotubes, and more recently graphene based materials, the substrate of choice being graphene oxide (GO) [26].

Graphene, a two-dimensional (2D) carbon material, is a very attractive material for fabricating graphene containing inorganic composites because of its singular electronic characteristic, high clarity, pliable structure and large theoretical specific surface area, excellent mobility of charge carriers and good electrical and thermal conduction [27–29]. One of its many utilizations is the use of graphene in the preparation of highly photo active composite materials based on titanium oxides. Graphene is the ideal nano structural product to be paired with titanium dioxide, growing its ability to absorb as well as its photo catalytic activity. The electrons freed after the titanium dioxide activation are easily transported to the graphene nano sheets and recombination of e^- and h^+ is strongly reduced, which enhances the process efficiency [30].

Most recently, the delocalized conjugated graphene have been expected to tailor the electronic properties in order to open the possibilities of new chemistry and the new physics on graphene. Heteroatoms (e.g., nitrogen, boron) doped or co-doped graphene can enhance its electronic and catalytic properties [31]. Application of hetero atom dopants into the carbon materials can vary the spin density and charge distribution of carbon atoms resulting in new catalytic activity [19–22]. Boron-doped GR (BGR) also exhibited better electrochemical performance in the oxygen reduction reaction and super capacitor than the undoped graphene [32,33].

In the present work, boron was used for doping graphene/ TiO_2 composites, which utilized solar light and conductivity of graphene concurrently and promote the electron transfer from photo catalyst surfaces to reactants. Prepared photo catalyst was used for the degradation and mineralization of 4-nitrophenol (4-NP) under visible light irradiation. The effects of initial concentration of 4-NP, concentration of photo catalyst, reaction time and initial pH on the removal efficiency of 4-NP were determined.

2. Material and methods

2.1. Precursor preparation

2.1.1. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized using the Hummers method. The graphene oxide (GO) was made from natural graphite by the Hummers method as reported in the literatures [33–35].

2.1.2. Synthesis of boron doped TiO_2

All chemicals were of reagent-grade without further purification. At room temperature, a desired amount of boric acid was dissolved in 60 ml of anhydrous ethanol and 3 ml water in an ultrasonic bath for 60 min (Solution A). Solution B was prepared by dissolving 12 ml of tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) into 33 ml of anhydrous ethanol. Subsequently, 1 ml of HCl (12M) was added drop wise into solution B. Then solution A was added into solution B very slowly. A white precipitate was observed immediately. After aging for 24 h at room temperature, the white precipitate was filtered and dried at 100°C for 10 h, then it was calcined at 450°C for 2.5 h.

2.1.3. Synthesis of TiO_2/GO and $\text{B-TiO}_2/\text{GO}$

A suspension containing 100 ml of ethanol and 70 mg of pure TiO_2 (or B-TiO_2) nano particles were mixed with 30 mg of GO and after ultra-sonication for about an hour, it was transferred to a rotary evaporator under vacuum for 45 min. After rotating in the evaporator, the ethanol was evaporated out and TiO_2/GO and $\text{B-TiO}_2/\text{GO}$ dried.

2.2. Instrumental characterization methods

XRD patterns were obtained with a diffract meter on Rigaku, Japan, RINT 2500 V using Cu K α radiation. Fourier transform infrared (FT-IR) spectra were recorded in KBr wafers with Bruker FT-IR. SEM analysis is used to determine morphology, aggregate particle size, grain boundaries and defects. The surface morphologies were observed and estimated by means of a Philips XL30 microscope at an accelerating voltage of 10 kV. UV–vis diffuse reflectance absorption spectra (DRS) were recorded by a Cary 5000 UV–vis–NIR spectrophotometer equipped with an integrating sphere using BaSO_4 as a reference.

2.3. Experimental design

The effects of four independent numerical factors, concentration of 4-NP, dosage of photo catalyst (B-GO-TiO_2), pH and reaction time were investigated. Experimental range and levels of the independent variables are shown in Table 1. The concentration of 4-NP varied from 25 to 75 mg/l at 3 levels (25, 50 and 75 mg/l), photo catalyst concentration from 0.5 to 1.5 g/l at 3 levels (0.5, 1 and 1.5 g/l) and pH at 3 levels (3, 7 and 11). The photo catalytic performance was evaluated based on the full face-centered CCD experimental plan (Table 2). The removal efficiency of 4NP was dependent response. The results were completely analyzed using analysis of variance (ANOVA) automatically performed by Design Expert software (Stat-Ease Inc., version 7.0). The Design Expert software is windows-compatible software which provides efficient design of experiments for the identification of vital factors that affect the process and uses response surface methodology (RSM) to determine optimal operational conditions. The results can be obtained as 3D presentations for visualization and also as contours to study the effect of system variables on responses. From these

Table 1
Experimental range and levels of the independent variables.

Type of numerical variables	Variables	Range and levels		
		–1	0	1
	A-Initial concentration of 4NP	25	50	75
	B-Concentration of catalyst	0.5	1	1.5
	C-Initial pH	3	7	11
	D-Reaction time	30	105	180

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