Journal of Environmental Chemical Engineering 2 (2014) 759–764

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

An energy efficient photocatalytic reduction of 4-nitrophenol

Kalyani Urkude [a], Sanjay R. Thakare [a,b,*], Sandeep Gawande [a]

[a] Department of Chemistry, Govt. Institute of Science, Civil Lines, Nagpur 440001, India
[b] Nanotech Lab, Department of Chemistry, Science College, Congress Nagar, Nagpur 440012, India

ARTICLE INFO

Article history:
Received 5 August 2013
Accepted 21 November 2013

Keywords:
TiO_2-PANI composite
4-NP
Energy efficiency
Photocatalysis

ABSTRACT

An energy efficient (E_{EO} value 80 kWh/m^3) method for photocatalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by using TiO_2-Polyaniline (TiO_2-PANI) composite in presence of visible light is presented in this article. Reduction of 4-NP in presence of a well known reducing agent $NaBH_4$ is inert in aqueous suspensions. Here we observed the high adsorptive and electron conducting capacity of TiO_2-PANI favors the reduction of 4-NP to 4-AP. Steady drop off in the absorbance at 400 nm monitored over UV–vis spectrophotometer confirms the decrease in the concentration of 4-NP. Prepared catalyst found to be highly efficient in the reduction of 4-NP under visible light irradiation.

Introduction

As per the environmental agencies reports over environmental pollutants, aromatic organic pollutants had been major concerns since these pollutants have harmful effects on living systems. Phenol and its derivatives had been listed by EPA as priority pollutants [1]. 4-Nitrophenol (4-NP) is one of the most common organic pollutants in agricultural and industrial wastewater [2]. Several attempts had been made to remove these kinds of organic pollutants from the waste water because the release of these pollutants into the environment causes harmful effects on living systems due to their toxicity. Accordingly, many methods such as photocatalytic degradation [3], microbial degradation [4], and catalytic degradation [5] had been developed to remove the hazardous 4-NP.

In these reported techniques microbial treatments of pollutant provides safer and effective methods compared to the chemical treatment techniques. Nevertheless, these methods have some drawbacks like slow reaction rates and unavailability of suitable microorganisms. Chemical treatment of 4-NP involves degradation or the reduction to 4-aminophenol (4-AP) with the help of suitable chemicals. The 4-AP is one of the vital intermediate in the pharmaceutical products. Reduction of 4-NP to 4-AP requires relatively high reaction temperature and hydrogen pressure. The evaluation of treatment cost is, at the moment, one of the major aspects that need more attention. There are number of important factors in selecting a waste water treatment technology, including economics, economy of scale, regulations, effluent quality goals, operation (maintenance, control and safety), and robustness [6]. Although all these factors are important, economics is often dominant. In fact the production of 4-AP from 4-NP, therefore becomes less preferable. Recently, Y. Zhang reported Au-Graphene oxide photocatalyst for the effective reduction of 4-NP [7]. On the other hand when the reaction is catalyzed by gold and silver, the conversion of 4-NP to 4-AP in an aqueous solution can be achieved under mild reaction condition, but these catalysts are economically not favorable. Recently, Gazi et al. reported that the photocatalytic reduction of 4-nitrophenol (4-NP) has been carried out using the visible irradiation under a metal-free (eco-friendly) condition [8]. The main limitation which they faced in this method is the stability of the catalyst in the reaction medium under a strong reducing atmosphere. The reuse of the catalyst in such a condition fastening the intense red color of the catalyst, by fading, which may be due to the reduction of the dye present on the resin surface and hence it is suspected that the catalyst is slowly losing its efficiency after every use. Along with the stability factor the efficiency is also quite low with reference to the application point of view. Now a days, many attempts have been made to increase the efficiency of the existing catalyst by increasing the recombination time of the excited electrons, increasing stability and widening their activity in the visible region by combining with graphene, C_3N_4, Polyaniline (PANI), etc. [9–13].

In this communication our aim is to introduce cost and energy efficient TiO_2-PANI composite photocatalyst for the reduction of 4-NP to 4-AP having a stability under strong reducing conditions. The efficiency of photocatalytic process is expressed in terms of electrical energy per order and quantum yield for photocatalytic conversion.

* Corresponding author at: Department of Chemistry, Govt. Institute of Science, Civil Lines, Nagpur 440001, India. Tel.: +91 9011097694.
E-mail address: sanjaythakare@yahoo.co.uk (S.R. Thakare).

2213-3437/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jece.2013.11.019

Experimental

All chemicals used in our experiments were reagent grade and used without further purification. The morphology and structure of catalyst were determined by transmission electron microscopy (TEM) (Philips-CM200 TEM), X-ray diffraction (XRD) (XPERTPRO) with Cu Kα radiation and PNMR (Varian). The reactions were monitored by UV–vis spectroscopy (SHIMADZU-1800) and products were characterized by FT-IR (BRUKER Alpha model).

Synthesis of composite materials

TiO_2-PANI composite synthesized by simple sol–gel method reported by H. Zhang et al. [14] The solution of 0.008 g L^{-1} concentration was obtained by dissolving about 0.005 g PANI in 100 ml tetrahydrofuran (THF); to this solution a 5 g of TiO_2 was added. The suspension was ultrasonicated for 1 h, and stirred for 6 h, and then filtered. The prepared precipitate was washed with water several times and then dried at 60 °C for 6 h.

Photoreduction of 4-nitrophenol under the visible irradiation

The relative photocatalytic activity of 4-NP reduction was evaluated at different catalytic conditions. The TiO_2-PANI composite was dispersed in the 4-NP solution (1×10^{-5} M) to achieve a concentration of 1 g L^{-1} (the amount of the overall photocatalyst is same in every photo-reduction experiment). The mixed suspension was first stirred in dark for 1 h to reach the adsorption–desorption equilibrium of 4-NP. A Philips lamp (40 W/230 V) was placed 10 cm away from the reaction vessel, which was used to provide a full-spectrum emission without any filter to simulate the sunlight source. The photocatalytic reaction was started by turning on the Philips lamp. 4 mL of the aliquot was extracted at various irradiation times and centrifugated to remove the photocatalyst. The concentration of residual 4-NP in the upper clear layer was determined by recording the maximum absorbance of 4-NP at 400 nm with the UV–vis spectrophotometer.

The reduction product was verified by FT-IR and P-NMR spectroscopic analysis (ESI).

Results and discussion

The product TiO_2-PANI composite synthesize by H. Zhang et al. method was verified by XRD, TEM, DRS spectroscopic methods and results are comparable to the reports (ESI).

The reduction of 4-NP by $NaBH_4$ in the presence of noble metal nanoparticles as catalysts has been intensively investigated for the efficient production of 4-AP. Therefore, the reduction of 4-NP to 4-AP with an excess amount of $NaBH_4$ was used as a model system to quantitatively evaluate the catalytic activities of the resultant TiO_2-PANI composite. To evaluate the comparative photoreduction activity, the three systems such as system-1 ($NaBH_4$-4-NP-visible light), system-2 (TiO_2-PANI-4-NP-visible light) and system-3 (TiO_2-PANI-$NaBH_4$-4-NP-visible light) were used.

Effect of addition of $NaBH_4$ on photocatalytic reduction of 4-NP

It is observed that after the addition of $NaBH_4$ in 4-NP solution the absorption peak shifts to the 400 nm corresponding to the nitrophenolate ions formation [8]. When TiO_2-PANI composite was added into the reaction system, the strong absorption peak 400 nm starts decreasing after elimination with visible light system-3. This decrease in of strong peak at 400 nm indicates reduction of 4-NP to 4-AP, the reduction process was monitored by measuring the time-dependent absorption spectra of the reaction mixture solution. As shown in Fig. 1, the absorption intensity of 4-NP at 400 nm decreases quickly with time, accompanied by the appearance of the new peaks of 4-AP at 230 nm and 300 nm, indicating conversion of 4-NP to 4-AP [11].

It should be noted that the reduction of 4-NP by $NaBH_4$ was completed within 11 min with system-3, the temporal changes during the conversion are shown in UV–visible spectrum (Fig. 1a), with the observation of a fading and ultimate bleaching of the yellow color of the reaction mixture in aqueous solution. However, in case of system-1 and system-2 didnot shows any conversion as shown in Fig. 1b, since these reaction required high temperature and pressure, and UV light illumination respectively. Due to the presence of excess of $NaBH_4$ compared to 4-NP, the rate of reduction is independent of the concentration of $NaBH_4$, and the reaction could be considered pseudo first order with respect to the concentration of 4-NP [11]. Hence, $\ln(C_t/C_0)$ versus time can be obtained based on the absorbance as the function of time, and good linear correlations are observed, as shown in Fig. 1b, suggesting that the reactions follow pseudo first order kinetics. The kinetic reaction rate constant (defined as k) are estimated from the slopes of the linear relationship to be 3.76×10^{-2} min^{-1}.

In chemical industries these kinds of hydrogenation reactions are of common processes, which are usually monitored by chromatographic methods such as Gas chromatography (GC) and high performance liquid chromatography (HPLC). However these methods are not suited for inline applications and exhibits relatively long measurement times. Here we have exemplarily investigated the catalytic reduction of 4-NP by applying in situ measurement of Infra-red (IR) spectra over attenuated total reflectance IR (ATR-IR). IR spectra are taken over a very short time scale and the results are shown in the Fig. 2. Fig. 2(a) shows

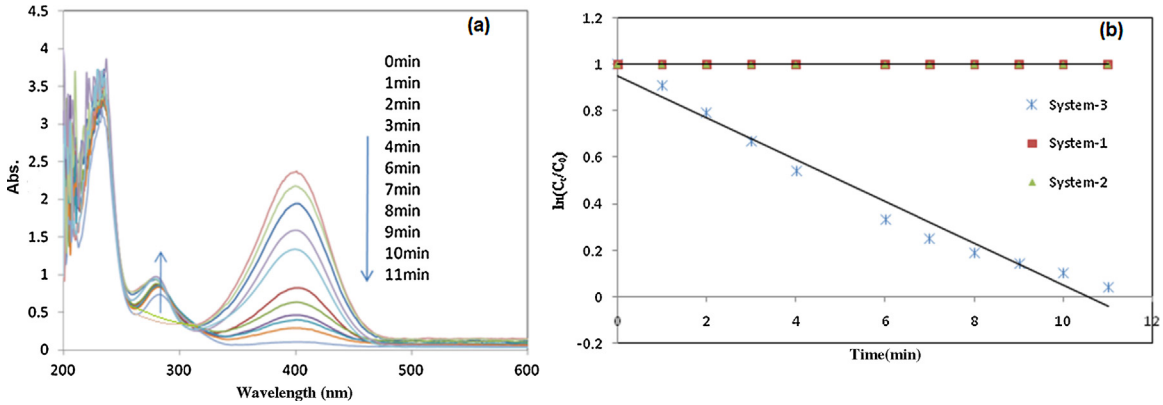

Fig. 1. (a) Absorption spectra showing the temporal changes occurred during the reduction process. (b) Plot of $\ln(C_t/C_0)$ versus time (min) of the photo reduction of 4-NP with different systems keeping concentration of 4-NP 1×10^{-5} M constant and with excess of $NaBH_4$