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Biogenic synthesis of nano-biomaterial for toxic naphthalene photocatalytic degradation optimization and kinetics studies

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ABSTRACT

Zinc Oxide (ZnO) and Iron (Fe x)-Zn1−x O (x = 0, 0.5, 1 and 2 wt%) doped ZnO nanoparticles were synthesized using *Amaranthus dubius* aqueous leaf extract as a reducing agent. The physicochemical properties of the nanoparticles such size, shape, surface area and band energy were determined by analytical techniques. The characterization confirmed that Fe−ZnO were spherical shape with wurtzite phase structure, smaller size, and large surface with less aggregation. The photocatalytic efficiency of ZnO and Fe−ZnO were evaluated by degradation of naphthalene. The effects of various operating parameters including solution pH, photocatalyst and naphthalene concentration on the degradation efficiency and the rate of degradation were investigated. The degradation efficiency and rate of degradation of Fe−ZnO was higher than ZnO photocatalyst. The results confirmed the degradation rate of naphthalene follows the pseudo-first order kinetics. From experimental results, Fe−ZnO can be effectively used in environmental safe applications for pollutant treatment.

1. Introduction

In the current epoch, environmental issues occurred due to rapid industrialization. The effluent from various industries were enriched with organic and toxic pollutants that release into water bodies; which are potentially harmful to the biological ecosystem (Amin et al., 2014). Among the hazardous pollutants, naphthalene is a polycyclic aromatic hydrocarbon have been detected from the waste product of different process such as pyrolysis of scrap tires, blast furnace, coke oven, electric arc furnace, heavy oil plant, power plant and cement plant (Rengarajana et al., 2015; Rubio-Clementea et al., 2014). The naphthalene compound has relatively high toxicity that causes, kidney damage, congenital abnormalities, cancer and also resistant to biodegradation (Liu et al., 2016a; Griego et al., 2008). Amzad et al., reported high concentrations of naphthalene in river fishes that causes serious genetic change and carcinogenic problem to human health (Amzad et al., 2009). Chunrong and Stuart conferred OSHA's permissible exposure limit and ACGIH's threshold limit value of naphthalene was 50 mg m^{-3}, but it has encountered much higher than the threshold limit levels in the environment (Chunrong and Stuart., 2010). Therefore, the removal of naphthalene from wastewater has become an important issue of disposing effluent into the aqueous medium (Liu et al., 2016b).

Currently, most of Asian, African and Latin American people are inequity in access to clean water and proper sanitation. Hence, Innovative and non-hazardous methods/materials for water treatment are immediately required (Qu et al., 2013). Various conventional technologies such as physical, chemical, biological, and their combined have been attempted to treat the organic-contaminated water (Ferradji et al., 2014; Xuemin et al., 2015; Liu et al., 2016a). However, the processes having many disadvantages of high cost involved, time consuming and releases a large amount of secondary pollutants during the treatment. Due to most of the conventional methods were failing to apply for efficient removal of pollutants from effluent industries (Ma et al., 2016; Antoine et al., 2008; Vahid and Javad, 2014). Recently, photocatalysis is one of an emerging technology for effluent treatment (Elangovan et al., 2015). The photocatalytic degradation methods have many advantages such as inherent destructive nature, can be carried out in ambient conditions and consuming atmospheric oxygen as the oxidant, no mass transfer involved, easily recovered of photocatalyst by filtration or centrifugation, high absorption coefficients, simple equipment requirement and so on (Rajamanickam Shanthi, 2012; Dong et al., 2015).

The degradation of naphthalene was studied by various process of electron beam irradiation, electrolytic aeration, microbial and

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anaerobic degradation. The efficiency of bioremediation still remains a critical point, due to toxicity and low water solubility of naphthalene (Zhou et al., 2012; Ma et al., 2016). Behrooz Karimi et al., reported that the biodegradation of naphthalene decreased from 65.5% to 33.4% using microbes by up-flow anoxic–aerobic continuous flow combined bioreactor with increased initial concentration from 0.5 to 20 mg/L after 3 days (Behrooz et al., 2015). Vahid Mahmoodi et al., suggested that photocatalytic method can be an appropriate alternate to the conventional techniques for degradation of naphthalene (Vahid and Javad et al., 2014; Liu et al., 2016b).

The semiconductor nanoparticles (NPs) are high chemical stability, high efficiency, low production cost and high reactivity tendency surface; to convert the resistant organic materials to the inert components (Velaa et al., 2012). Among all the II-VI compounds, ZnO have numerous application from clinical to environmental. (Yin Zhang et al., 2013; Innocent et al., 2013.,) The ZnO NPs were one of the most widely used NPs, its wide band gap and toxicity makes their limited practical applications as a photocatalyst (Law,and Thong et al., 2006; Kahru Dubourguier et al., 2010). ZnO NPs enhanced photocatalytic activity in the visible region and toxicity reduction can be achieved by the strategies of doping. Ba-Abbad et al., have investigated photocatalytic activities of the ZnO and Fe–ZnO NPs for degradation 2-chlorophenol in aqueous medium under solar radiation (Ba-Abbad et al., 2013). George et al., hypothesized that a decrease in Zn^{2+} shedding could lead to a decrease in nano-ZnO cytotoxicity and confirmed its dissolution slowing by Fe doping to improve the cytotoxicity profile (George et al., 2010). Niranjan et al., described synthesis of NPs by plant extract due to its non-toxicity, biocompatible and devoid of toxic stabilizers for wide application (Niranjan et al., 2015). Harshiny et al., has also been reported that the plant extracts *Amaranthus* sp. mediated NPs was an economic and eco-friendly over benefits of chemical and physical methods for NPs synthesis (Harshiny and Matheswaran, 2015, Harshiny et al., 2015). Kaviya et al., shown that greener route synthesis was very simple and efficient method for the synthesis of metal doped ZnO used the photocatalyst was highly stable and showed the higher degradation efficiency against organic pollutant (Kaviya et al., 2015; Behera, et al., 2014).

In this work, ZnO and Fe–ZnO NPs were synthesized using *Amaranthus dubius* extract as reducing agent. The physico-chemical characterizations of NPs such as size, shape, surface area and band energy were analyzed using analytical instruments. The photocatalytic efficiency of *A. dubius* mediated ZnO and Fe–ZnO NPs has been studied for degradation of naphthalene under UV irradiation. The effect of different operating conditions such as photocatalyst loading, initial pH, and initial concentration of naphthalene were studied on degradation efficiency. The degradation kinetics of naphthalene were also investigated.

2. Materials and method

2.1. Synthesis of ZnO NPs

The *A. dubius* extract mediated ZnO NPs were synthesized using equal volumes of 1.0 M znic nitrate [$Zn(NO_3)_2$] solutions and prepared leaf extract (pH 9). The Leaf extracts were prepared as reported by (Harshiny et al., 2015). The pH of solutions was adjusted using 0.1 N HCl and 0.1 N NaOH. For synthesis of Nps, the extract was added drop-wise into Zn $(NO_3)_2$ solution with continuously stirring using a magnetic stirrer at 37 ± 1 °C for 30 min. The pale yellowish white precipitates were formed and filtered with Whatmann filter paper. The filtrate was washed with Milli-Q water and dried in oven at 90 °C for 5 h. The synthesized ZnO NPs were stored in desiccators.

2.2. Synthesis of Fe-doped ZnO NPs

For synthesis of *A. dubius* extract mediated Fe–ZnO NPs, Zn $(NO_3)_2$ and ferric chloride were used as the precursor of Zinc and Iron respectively, The Zn and Fe precursor solutions were mixed in the stoichiometries proportion $(ZnO)_{1-x}(Fe)_x \leq 0.01$. The leaf extract (pH 9) was added drop-wise into precursor solution with continuous stirring at 37 ± 1 °C for 30 min. The reddish yellow precipitates were formed and filtered with Whatmann filter paper. The filtrate was thoroughly washed with Milli-Q water to remove the unreacted ions from the precipitates and dried in oven at 90 °C for 5 h.

2.3. Characterization

The optical properties of the samples were measured using a Shimadzu UV -1800 spectrophotometer and UV 2600 Shimadzu diffuse reflectance spectroscopy (DRS). The X-ray diffraction (XRD) datas were obtained by Rigaku Ultima III by step scan technique with Cu-Kα radiation (1.500 A, 40 kV, 30 mA). The particle size distribution (PSD) and zeta potential were measured by Hiroba SZ-100 nanopartica. Fourier transform infrared (FTIR) spectra of the sample were recorded between 4000 and 400 cm^{-1} using Jasco FTIR- 4200. The Morphologies were analyzed using Tecson, Scanning Electron Microscope (SEM) and elemental compositions were determined using EDAX″TSL AMETEK, Energy-dispersive X-ray spectroscopy (EDS). The surface area analysis (SAA) was done by N_2 adsorption isotherm using a Micromertics ASAP 2020 V3.04 H. Prior to the analysis the samples were degassed with nitrogen at 300 °C for an hour. The magnetic properties of NPs were investigated using VSM (Lake shore model 7404). The Electron Paramagnetic Resonance (EPR)/electron spin resonance (ESR) Spectra was recorded at room temperature on BRUKER BIOSPIN, Model: EMX. XPS technique was carried out on a K-Alpha instrument supplied by Thermoscientific, USA.

2.4. Photocatalytic experiments

The photocatalytic activity of synthesized NPs have tested by degradation of naphthalene solution under UV irradiation. The experiments were carried out in a cylindrical double jacket container with cooling water circulation for maintaining the constant temperature. The reactor was placed on a magnetic stirrer for continuous stirring under UV light of 16 W. The naphthalene solution of 500 mL was filled in the reactor and required amount of NPs were added. The solution was continuously exposed to UV light maintained at 37 ± 1 °C for 4 h. The samples were collected at a regular interval of time and filtered to remove the photocatalyst before analysis. The degradation of naphthalene was assessed using UV–visible spectrophotometer with a wavelength range of 200–700 nm. The photocatalytic degradation efficiency for naphthalene was calculated using the following equation:

$$\text{Percentage of degradation} \frac{A_o - A_t}{A_o} \times 100 \quad (1)$$

where A_o and A_t is the absorbance of the initial concentration and after time 't' of naphthalene solution.

The kinetic of naphthalene degradation was tested using pseudo-first order kinetics equation

$$-r = kC \quad (2)$$

where, C is the concentration of naphthalane, k represent the rate constant.

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