Environmental Nanotechnology, Monitoring & Management 6 (2016) 134–138

Contents lists available at ScienceDirect

Environmental Nanotechnology, Monitoring & Management

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

Green mediated synthesis of zinc oxide nanoparticles for the photocatalytic degradation of Rose Bengal dye

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ARTICLE INFO

Article history:
Received 25 July 2016
Received in revised form
23 September 2016
Accepted 26 September 2016

Keywords:
ZnO nanoparticles
Green synthesis
Artocarpus heterophyllus
Photodegradation
Rose Bengal dye
UV light

ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesised by a simple method using leaf extract of jackfruit (*Artocarpus heterophyllus*). The phytochemicals present in the leaf act as stabilising agents. The green synthesised ZnO nanoparticles were characterized by X-ray diffraction (PXRD), Scanning Electron microscopy (FESEM), Energy dispersive spectroscopy (EDS) and Transmission electron microscopy (TEM). XRD pattern confirmed the formation of crystalline ZnO nanoparticles. The SEM images showed porous, sponge-like agglomerated structures. TEM analysis showed the ZnO nanoparticles formed to have hexagonal wurtzite structure and the particles ranging between 15 and 25 nm. The green synthesised ZnO nanoparticles exhibited excellent photodegradation efficiency (>80%, 0.24 g/L, 1 h) against Rose Bengal dye, a main water-pollutant released by the textile industries. The characterisation results confirmed that the ZnO nanoparticles can be efficiently synthesised using jackfruit leaf extract as stabiliser and the photodegradation results proved the efficiency of the green synthesised ZnO nanoparticles for the degradation of Rose Bengal dye.

1. Introduction

Dyes are colored organic compounds which impart color to the substrates like textile materials, paper, leather and plastics. Most of these dyes are released into the effluents and the dyes in the effluents are to be degraded prior to their release into water bodies. Degradation of most of the dye molecules yield non-colored dye fragments leaving behind the effluent decolored satisfying the requirement of decolorization. But these non-colored fragments such as aromatic amines are even more toxic than the original dye (Liakou et al., 1997). The physical and physicochemical treatment methods like adsorption, coagulation, flocculation, reverse osmosis techniques are being widely used to decolorise the effluents (Rauf and Ashraf, 2009). But these methods remove the color physically giving rise to problem of solid disposal. Chemical techniques like oxidation/reduction and ozonolysis, can alter the chemical structure of the dye thereby decolorising the effluent but giving rise to other products which accumulate in the water streams (Akpan and Hameed, 2009). Biological techniques like aerobic/anaerobic digestion and Electrochemical techniques like ion-oxidation result in the formation of sludge which increases the cost of solid disposal. However these techniques are used in combination depending on the characteristics of the effluent (Joshi et al., 2004; Kuo and Ho, 2001; Lopez et al., 2004; Lall et al., 2003; Lv et al., 2005; Salker and Gokakakar, 2009). Researchers are now trying out Advanced oxidation processes for degradation of dyes in which the dyes can be completely degraded to carbodioxide, water and some inorganic ions. Several metal oxides like TiO_2, SnO, NiO, Cu_2O, Fe_3O_4, and also CdS have been utilized as photocatalyst in the catalytic oxidation of dyes. These are nontoxic, highly photosensitive, have wide band gap and stability (Muhd Julkapli et al., 2014). The metal oxides are usually activated to enhance the photo degradation of dyes under solar light (Giwa et al., 2012). This work is on the photocatalytic degradation of Rose Bengal dye (Color Index International generic name: Acid Red 94) using ZnO a photosensitive metal oxide. The chemical structure of the dye molecule is shown in Fig. 1. Based on the nature of the chromophore, Rose Bengal falls under the class of xanthene derivatives of dyes (Geofrey, 2016). It is an organic anionic, water soluble and a photosensitive dye widely used in textile and photochemical industries The degradation of Rose Bengal present in textile effluent are tried using bacteria (Khan and Mathur, 2015), Cr substituted MnFe2O4 ferrospine (Hankarea et al., 2012), zinc sulphide (Sharma et al., 2013).

Many metaloxide nanoparticles can be synthesised using available physical and chemical methods in less time. Most of these methods involve harmful chemicals in the process which may get

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http://dx.doi.org/10.1016/j.enmm.2016.09.004
2215-1532/

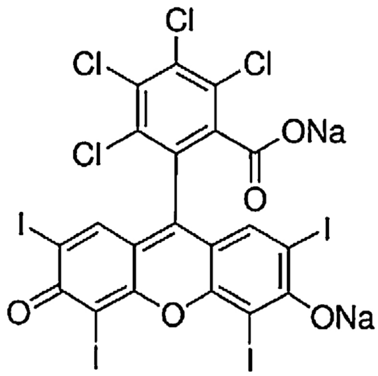

Fig. 1. Structure of Rose Bengal Dye.

adsorbed on the product formed making it not suitable for medical applications. These methods are also very expensive. Several metal oxide nanopartcles are synthesised using different parts of plants and microbes like algae, yeast, fungi etc. (Karnani and Chowdhary, 2013). The ecofriendly materials like plant extracts (Jain et al., 2009), bacteria (Saifuddin et al., 2009), fungi (Verma et al., 2010) & enzymes (Willner et al., 2007) used for the synthesis of metaloxide nano particles makes it suitable for Pharmaceutical and many other medical applications. ZnO nanoparticles are synthesised using different parts of plants like Calotropis Procera (Singh et al., 2011), Aloevera (Sangeetha et al., 2011), Cassia auriculata (Ramesh et al., 2014), grape fruit (Kumar et al., 2014), Hibiscus (Devi and Gayathri, 2014), Moringa Oleifera (Elumalai et al., 2015), Azadirachta Indica (Bhuyan et al., 2015), Cassia Fistula (Suresh et al., 2015). The present work depicts the synthesis of nanoparticles using jackfruit (*Artocarpus heterophyllus*) leaf extract. Jackfruit is an evergreen tree grown in several tropical and subtropical regions. The jackfruit leaves are found to be rich in Terpenoids, Flavonoids, phenols, steroids, glycosides, carbohydrates and saponins (Raaman and Sivaraj, 2014). These phytochemicals present act as fuel in oxidative combustion of Zinc nitrate hexahydrate. The synthesised nanoparticles were used for photocatalytic degradation of Rose Bengal dye.

Notations

C_O	Initial concentration of the reactant at time mg/L t = 0
C	Concentration of the reactant at any time t, mg/L
CB	Conduction band
ISC	Intersystem crossing
K_1	Surface reaction rate constant, mg/(L min)
K_2	Langmuir Hinshel wood adsorption equilibrium constant, L/mg
K_{app}	Apparent first-order rate constant, min^{-1}
MO	Metal oxide
r	Rate of disappearance of dye, mg/(L min)
RB_o	Rose Bengal molecule
RB_1	Excited singlet state of Rose Bengal molecule
RB_2	Excited triplet state
CB	Conduction band
t	Time
VB	Valence band

2. Materials and methods

Zinc nitrate hexahydrate (AR) was purchased from Merck Chemical Reagent Co. Ltd. India. Rose Bengal (RB) was purchased from Rolex Chemical Industries.

2.1. Synthesis of ZnO nanoparticles

Jackfruit leaves were collected from RVCE campus, washed and cut into pieces. It was boiled in distilled water for around an hour to get wine colored leaf extract. The extract was filtered and preserved in the refrigerator. A known amount of zinc nitrate hexahydrate ($Zn(NO)_3{\cdot}6(H_2O)$) was added to the leaf extract and heated for about an hour to get a thick dark brown colored liquid. This liquid was taken in a crucible and calcined at 600 °C for one hour. Whitish powder of ZnO nanoparticles formed in the crucible was removed from the furnace and crushed into a fine powder by using pestle and mortar.

2.2. Characterisation techniques

The phase purity and crystalline nature was examined using PXRD: JDX 8030, JEOL. Surface Morphology was studied using Carl Ziess Model: Neon-40, EDS was taken using Tecnai T 20 with W filament and TEM was done using JEOL 2000 FX-II. The optical properties were studied using Systronics double beam UV–vis Spectrophotometer.

2.3. Photocatalytic degradation of Rose Bengal dye

For photocatalytic degradation studies, dye solution of different concentration was made using double distilled water. 250 mL of dye solution and the known amount of synthesised zinc oxide nanoparticles were taken in a glass vessel with diameter 18 cm and placed on an orbital shaker which was kept under 30 W Philips Mercury vapour lamp. The reaction mixture was irradiated by focusing the light directly onto the reaction mixture at a distance of 18 cm. At specific intervals the slurry was withdrawn, centrifuged to separate the nanoparticles and the absorbance was found using spectrophotometer. The percentage of dye degraded can be determined as

$$\%\text{Degradation} = \frac{C_o - C}{C_o} \times 100 \qquad (1)$$

where C_o is the initial concentration of dye at time t = 0 and C is the dye concentrations at any time t, respectively. The experiment was repeated by varying the parameters such as dye concentration, catalytic load, irradiation time and pH.

3. Results and discussion

3.1. Green mediated synthesis and characterisation of ZnO nanoparticles

In green mediated synthesis of ZnO nanoparticles, Zinc nitrate hexa hydrate is an oxidant and the phytochemicals present in the leaf are the stabilisers. The phytochemicals like Terpenoids, Flavonoids, phenols, steroids, glycosides, carbohydrates and saponins present in the jackfruit leaf act as strong stabilising agents. The characterisation results of the synthesised ZnO nanoparticles conclude that the jackfruit leaf extract can be used as effective reducing and stabilising agents for synthesising polycrystalline zinc oxide nanoparticles. The strong and narrow diffraction peaks indicate the crystalline nature of nanoparticles synthesised and all the peaks are similar to the available standard diffraction data. XRD peaks of the synthesised ZnO nanoparticles are shown in Fig. 2. All diffraction peaks positioned at 31.74, 34.38, 36.30, 47.51, 56.61, 62.81, 66.36, 68.98, 69.10, can be indexed to the (100), (002), (101), (102), (110) (103) (200) (112) and (201) planes of ZnO. The surface morphology of green synthesised ZnO nanoparticles stud-