Materials Science and Engineering C 70 (2017) 178–183

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Iron doped SnO_2/Co_3O_4 nanocomposites synthesized by sol-gel and precipitation method for metronidazole antibiotic degradation

Shilpi Agarwal [a], Inderjeet Tyagi [b], Vinod Kumar Gupta [a,*], Maryam Sohrabi [c], Sanaz Mohammadi [c], Ahmad Nozad Golikand [c,d,**], Ali Fakhri [e,*]

[a] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
[b] Department of Chemistry, Indian Institute of Technology Roorkee, 247667, India
[c] Department of Chemistry, Shahr-e-Qods Branch, Islamic Azad University, Tehran, Iran
[d] Jaber Research Laboratory, NSTRI, P.O. Box: 14395-836, Tehran, Iran
[e] Young Researchers and Elites Club, Science and Research Branch, Islamic Azad University, Tehran, Iran

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 12 July 2016
Accepted 24 August 2016
Available online 26 August 2016

Keywords:
Nanocomposites
Fe doped
Photocatalytic property
Antibiotic

ABSTRACT

Sol-gel and precipitation reaction methods were used to synthesize Un-doped and Fe-doped SnO_2/Co_3O_4 nanocomposites under UV light; the synthesized nanocomposites were applied for the photocatalytic degradation of metronidazole antibiotic. The developed photo catalyst was well characterized using energy dispersive X-ray spectrometer (EDX), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), field emission scanning electron microscopy (FE-SEM), UV–Visible and photoluminescence (PL) spectroscopy. Effective parameters such as pH, photocatalyst dose and contact time was optimized and well investigated. From the obtained facts it is clear that the 98.3% of MTZ was degraded with in 15 min, pH 6 and 0.1 g catalyst when the Fe molar ratio was 1:1 at %. As compared to results obtained from un-doped SnO_2/Co_3O_4 nanocomposites Fe doped SnO_2/Co_3O_4 nanocomposites possess greater photocatalytic efficiency.

1. Introduction

Increasing demand of clean water sources due to the rapid population growth, development of industrialization, and long-term droughts have become a burning pollution issue worldwide. With this growing demand, several practical strategies and solutions have been adopted to yield more viable water resources [1]. Antibiotics are bothersome emerging pollutants due to the risk of aquatic toxicity and the development of persistent bacterial strains [2–5].

Metronidazole (2-(2-methyl-5-nitro-1H-imidazol-1-yl)etha- nol, $C_6H_9N_3O_3$) is an antibiotic broadly used as medicine for curing bacterial and protozoal infections including trichomoniasis, amoebiasis, vaginosis and gingivitis. Furthermore, it has been extensively used as an additive in poultry and fish feed to promote weight production and eliminate parasites [6]. Due to its usage in the fishery and poultry industries, MTZ gets accumulated in aquatic food chain as well as terrestrial food chain. MTZ possess severe detrimental and noxious effect on the human health as well as prevailing flora and fauna of the particular ecosystem. MTZ proves to be genetically toxic to humans [7], toxic to aquatic organisms [8] and potentially carcinogenic and mutagenic. Since MTZ is highly soluble in water i.e. 9.5 g dm^{-3} and it also possesses very low biodegradability hence get accumulated in the aquatic food chain, due to low biodegradability and high solubility in water it is very difficult to remove MTZ from wastewater treatment plants and MTZ has been found in surface waters and ground waters at contents from ng dm^{-3} to mg dm^{-3} [9–10]. In order to shun the undesirable effects of this antibiotic to humans and ecological environment, research efforts are necessary to build up effective methods for its removal from wastewaters. In order to meet the above requirement the most appearing interdisciplinary technology called nanotechnology has progressed in many field such as mechanics, aerospace, electronics, and materials science in ten years ago.

A broad range of nanomaterials applications has made these novel materials a top most priority in almost every field of technology and science. Metal oxide nano-materials are a kind of nanomaterials and represent one of the main important classes of nanopowders due to their physical stability, non-toxicity and high chemical, environment friendly, efficient biological properties, etc. Among these materials, the best interest in the synthesis of semiconductor oxides, such as TiO_2 [11–13], CeO_2 [14], MoO_3 [15,16], and WO_3 [17,18], these materials are used in many applications, such as catalysis [11,12], gas and humidity sensing

* Corresponding authors.
** Correspondence to: A. N. Golikand, Jaber Research Laboratory, NSTRI, P.O. Box: 14395-836, Tehran, Iran.
E-mail addresses: vinodg@uj.ac.za, vinodfcy@gmail.com (V.K. Gupta), anozad@aeoi.org.ir, anozad01@gmail.com (A.N. Golikand), ali.fakhri88@yahoo.com (A. Fakhri).

http://dx.doi.org/10.1016/j.msec.2016.08.062
0928-4931/

[13,14], and photo chromic devices [16,18]. But all the previously developed metal oxides are either costly enough or possess very low degradation ability for the antibiotic.

In order to meet the low cost and high degradation capacity requirement, in the present work SnO_2/Co_3O_4 nanocomposites which are further modified through Fe doping which directly increases its photocatalytic ability are synthesized and applied as a photocatalytic agent for the degradation of the MTZ antibiotic from the wastewater. The synthesized photo catalyst shows an excellent degradation ability for MTZ antibiotic. It almost shows 98.3% degradation within 15 min of contact time.

2. Materials and methods

2.1. Materials

All the chemicals were obtained from Merck Ltd., USA. All the chemicals used for the study were of analytical grade.

2.2. Synthesis of nanocomposites

2.2.1. Synthesis of Co_3O_4 nanoparticles

In a typical reaction process for the growth of Co_3O_4 nanocomposite, 0.1 g cobalt nitrate solution was prepared using 50 mL of distilled water as solvent and stirred continuously at room temperature for 30 min, which was later treated with 5 drops of 0.2 M sodium hydroxide under continuous stirring for another 30 min, which was later followed by heating at 70 °C for 30 min [19,20]. After heating a gel was formed, which was then centrifuged with the help of distilled water and then filtered, the resultant product was dried in the oven at 100 °C for 3 h, which was followed by the calcination at 600 °C for 3 h in order to obtain the cobalt oxide nanoparticles.

2.2.2. Synthesis of SnO_2 nanoparticles

In a typical reaction process for the growth of SnO_2 nanocomposite, 0.9 g of $SnCl_4 \cdot 5H_2O$ was introduced into 40 mL of distilled water to form a transparent tin solution, followed by the addition of 1 mL of $NH_3 \cdot H_2O$ (28 wt%) under stirring to promote the process. Continuous stirring for about 30 min, and later on heating at 100 °C for 1 h results in the conversion of the white precipitated precursor sol to gel [21], which was then centrifuged and washed using distilled water and ethanol, then dried in an oven at 100 °C. Finally, SnO_2 nanoparticles were obtained by annealing the precipitated precursor in a muffle furnace at 300 °C for 2 h.

2.2.3. Synthesis of un-doped and Fe-doped SnO_2/Co_3O_4 nanocomposites

The pure SnO_2/Co_3O_4 nanocomposites were synthesized according to the procedure mentioned in Sections 2.2.1 and 2.2.2. The tin and ammonia solution was added to cobalt nitrate solution and stirred under magnetic stirrer for 1 h. Then 5 drops of 0.5 M NaOH was added into this solution and then stirred continuously stirring for 60 min. The resultant product dried in at 120 °C for 2 h and it was calcined at 600 °C for 3 h.

In a typical synthesis for Fe-doped SnO_2/Co_3O_4 nanocomposites, the $FeSO_4 \cdot 7H_2O$ was added drop-wise to 50 mL tin and ammonia solution under continuous stirring. 0.06 mol of thiourea was added drop by drop to mixture at 30 min. The solution was then heated at 100 °C for 1 h. The suspension was added to cobalt nitrate solution and stirred under magnetic stirrer for 30 min. Then 5 drops of 0.5 M NaOH was added into this solution and then stirred continuously stirring for 60 min. The resultant product dried in at 120 °C for 2 h and it was calcined at 600 °C for 3 h. The different molar ratios of Fe doped samples to SnO_2/Co_3O_4 nanocomposites are (1:1), (1:2) and (2:1) at % level.

2.3. Adsorbent characterization

A scanning electron microscopy (SEM); TESCAN MIRA 3 LMU Digital Scanning Electron Microscope, and X-ray diffractometer (XRD) Philips X'Pert were used to characterize the adsorbent in order to evaluate the surface morphological and anatomical property. UV–Vis and photoluminescence studies were performed using TEC Avaspec 2048 Spectrophotometer (excitation source = Xenon arc lamp 450 W). The magnetization measurements of all synthesized samples were carried out using vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Company). The catalyst compositions were analyzed with an energy dispersive X-ray spectrometer (EDX-700HS, SHIMADZU).

2.4. Evaluation of photocatalytic property

Photocatalytic activities of the synthesized photocatalysts were tested under UV light irradiation. The photocatalytic degradation was evaluated using the mixture of photocatalysts and MTZ solution in an open cylindrical stainless glass vessel with a volume of 200 mL covered with transparent plastic sheet to avoid evaporation of Metronidazole solution. The UV light was generated from a 125 W UV lamp at 365 nm irradiation. In each experiment, 200 mg photocatalyst was suspended in 100 mL model Metronidazole aqueous solution with a concentration of 30 mg/L. At given time intervals after initiation of UV light irradiation, 3 mL of samples were collected into centrifuge tubes, centrifuged at 8000 rpm for 10 min and passed through 0.22 μm Millipore membrane. Then, the concentration of MTZ in solution was analyzed using a UV–Vis spectroscopy (SHIMADZU 1800) at its maximum absorbance wavelength of $\lambda = 319$ nm.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 1 indicates XRD patterns of Co_3O_4 and its supported SnO_2 catalysts. The diffraction pattern for SnO_2 demonstrates several peaks at $2\theta = 27.2, 34.4, 52.2$ Fig. 1A that referred to cassiterite tetragonal structure (JCPDS card No. 41-1445). Fig. 1B shows peak positions ($2\theta =$ 19.02, 31.3, 36.88, 38.59, 44.85, 59.41 and 65.30) and relative intensities obtained for the Co_3O_4 has cubic phase structure (JCPDS card No: 073-

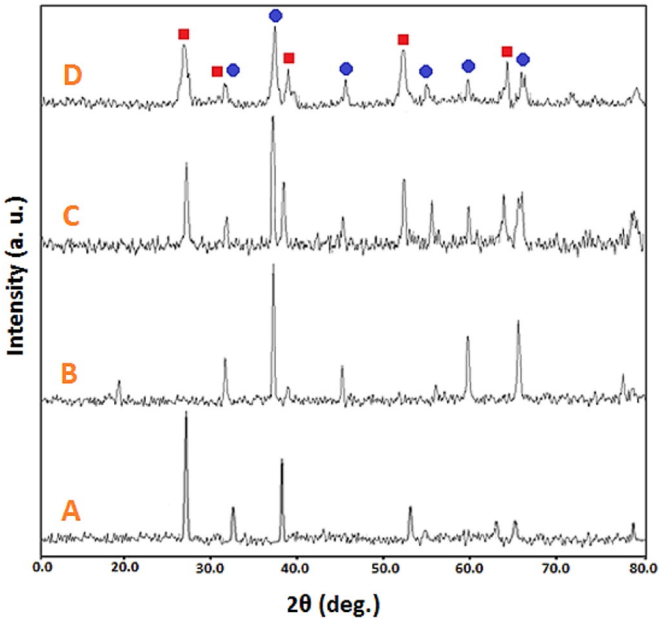

Fig. 1. X-ray diffraction analysis of SnO_2 (A), Co_3O_4 (B), un-doped (C) and Fe-doped SnO_2/Co_3O_4 nanocomposites (1:1) (D).