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Photocatalytic degradation of roxarsone by using synthesized ZnO nanoplates

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ABSTRACT

An efficient photodegradation of roxarsone (ROX) was achieved by using synthesized zinc oxide (ZnO) nanoplates under UV light irradiation. ZnO nanoplates were synthesized by facile wet chemical method. Characterization of ZnO nanoparticles was done by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, diffuse reflectance (DRS) UV–Visible absorption spectroscopy, BET analyzer, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The obtained results reveal that the synthesized sample is ZnO which has hexagonal structure and plate-like morphology. The band gap and specific surface area of ZnO was found to be 3.02 eV and 7 $m^2 g^{-1}$ respectively. ROX's degradation by-products such as As(III), As(V) were analyzed by high performance liquid chromatography-hydride generation coupled with atomic absorption spectrometry (HPLC-HG-AAS). The photogenerated hydroxyl (•OH) and carbon-centered radicals were detected by electron paramagnetic resonance (EPR) spectroscopy. According to experimental evidences a possible photocatalytic mechanism has also been proposed. Photocatalytic degradation of ROX leads to mineralization as CO_2 and As(V). This can be considered as a promising method for removing ROX from contaminated waters.

1. Introduction

In industries, inorganic arsenic compounds are used in steel production, paints, glass, enamel, ceramic, leather, etc., (Lshiguro, 1992). In addition, some organoarsenical compounds have been used as drugs to treat serious diseases, such as acute promyelocytic leukemia, multiple myeloma, chronic myeloid leukemia and acute myeloid leukemia (Chen et al., 2015; Iland and Seymour, 2013). Organo arsenic compounds have also been used in the agricultural sector as pesticides, herbicides, fungicides and insecticides (monosodium methanearsonate (MSMA), disodium methanearsonate (DSMA), calcium acid methanearsonate (CAMA) and cacodylic acid and its sodium salt) (Qia and Donahoe, 2008; Matschullat, 2000).

Especially in poultry industry, roxarsone (3-nitro-4-hydroxyphenylarsonic acid), an organo arsenic compound has been used as an antiparasitic additive and animal feed additive (Nachman et al., 2013). Bednar et al. (2003) was found that the ROX was excreted with manure. ROX contaminated manure may be used as a fertilizer in agricultural land and thus it may reached into water ecosystem by leaching and surface runoff process. Therefore ROX can pollute surface water and ground water and subsequently enter into the food chain (Mafla et al., 2015). Recently, Nigra et al. (2016) have reported that the use of arsenic-based poultry drugs contributed to arsenic exposure in the U.S. population. It was found that depending on the oxidation state (III or V) and chemical form, arsenic has adverse effects such as skin lesions, severe gastrointestinal, circulatory and nervous system problems on human health (Tyler and Allan, 2014). Arsenic has also been recognized as a carcinogen, as it can cause skin and lung cancer in chronic intake (Pershagen, 1981). Therefore, it is very important to study the removal of ROX from the contaminated water.

So far different treatment methods such as electrocoagulation (Amrose et al., 2013), adsorption (Mandal et al., 2013), photolysis (Kim et al., 2014), and photocatalysis (Lu et al., 2014) for removal

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of ROX have been studied. Among them, photocatalysis has much attention by the researchers. Due to inertness, low toxicity, stability, and photoactivity, ZnO nanoparticles have huge consideration as photocatalyst. ZnO is an n-type semiconductor with band gap of 3.2 eV. It was used as photocatalyst for the degradation of many organic dyes (Lee et al., 2016). However, for the best of our knowledge, ZnO was not used as photocatalyst for the degradation of ROX.

In this work, photodegradation of ROX in presence of UV active ZnO nanoplates was assessed.

2. Experimental section

2.1. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), sodium hydroxide (NaOH) and ethanol (C_2H_5OH) were received from Merck, Germany. Roxarsone ($C_6AsNH_6O_6$) was obtained from Sigma-Aldrich, USA. All reagents were analytical grade and were used as received. Distilled water was produced in Millipore Direct-Q® purifier 3 UV (Merck, Germany) being 18 MΩ cm, which was used to prepare all ROX solutions.

2.2. Synthesis of ZnO nanoplates

Wet chemical method was used for the synthesis of ZnO nanoplates with minor modifications (Kolodziejczak-Radzimska and Jesionowski, 2014). About 2 g of zinc acetate dihydrate was dissolved in 200 mL of ethanol (0.5 M). In another flask, 0.8 g of sodium hydroxide was dissolved in 200 mL of ethanol (1 M). Both solutions were placed in a bath sonicator for 1 h (Ultrasonic cleaner, CD-4820, China). After that, NaOH solution was slowly added into zinc acetate dihydrate solution. The resulting mixture was ultrasonically treated for an hour and allowed to stand for overnight. The as formed precipitate was filtered, washed with deionized water and dried in an oven at 100 °C for 3 h. Finally the dried solid was calcined at 500 °C for 8 h (Muffle furnace, Thermo Scientific).

2.3. Characterization

XRD analysis was performed by using a diffractometer (D4 Endeavor, Bruker AXS, Germany) with Cu K_α radiation. The morphology and size of the ZnO was analyzed by scanning electron microscope (JSM-6380 LV, JEOL, Germany) and a transmission electron microscope (JEM 1200EX II, JEOL, Germany) with F82 (Gatan, USA) camera. The IR spectrum was recorded by Fourier transform infrared (FTIR) spectroscopy (Nexus 470 FTIR, Thermo Scientific, USA). To determine the absorption spectrum, diffuse reflectance (DRS) spectrophotometer (UV UV–Vis was used −2700, Shimadzu, Japan) with integrating sphere (ISR-2600 Plus) was used. The specific surface area was measured by BET analyzer (Tristar II 3020, Micromeritics, USA) with nitrogen as adsorbate at −196 °C (77 K).

2.4. Photocatalytic experiment

All the photocatalytic experiments were conducted in a borosilicate reactor with an effective volume of 150 mL, equipped with inlet and outlet gases to modify the reaction conditions. The concentration of ROX and ZnO was 15 mg L^{-1} and 2.5 g L^{-1} respectively. The pH of the solution was adjusted to 7 with phosphate buffer (0.01 M) (Merck, Germany). Photodegradation experiment was performed at constant UV-A light (365 nm) irradiation with a maximum intensity of 2.16 mW/cm^2 (Phillips HB311/A, equipped with 620W UV lamps), under continuous stirring condition (MMS-3000 magnetic stirrer, Boeco, Germany). To monitor the reaction, samples were taken periodically using syringes and subsequently subjected to filtration using a nitrocellulose membrane filter with a pore diameter of 0.22 μm (Merck, Germany). The filtrate was analyzed by high performance liquid chromatography (Merck-L-7100 Hitachi®, Japan) with UV–Vis (L-7420, Merck-Hitachi®, Japan) detector. Chromatographic separation was performed on a Hibar (250 – Purospher Star 4.6mm RP_18, Merck, Germany) column. A mixture of 1% acetic acid and 8% methanol was used as a mobile phase. The UV detector (243 nm) with the injection volume of 50 μL and flow rate of 1.0 mL min^{-1} was used. Inorganic compounds such as As(III) and As(V) were determined by a HPLC coupled to an hydride generator and atomic absorption spectrometer (HPLC-HG-AAS), (HPLC pump Flexar and AAnalyst 200 spectrometer, both Perkin Elmer, USA). Chromatographic separation was performed on a Chromolith (100–4.6 mm RP-18e, Merck, Germany) column by using 0.5 mM tetrabutylammonium hydrogen sulphate (100 mM acetic acid/sodium acetate buffer solution, pH = 4.8) as a mobile phase (Yañez et al., 2015). Online hydride generation was achieved by using 10 v/v% hydrochloric acid together with 1.5% potassium iodide, and 1.5 mL min^{-1} of 1.5 m/V% $NaBH_4$ (flow rate = 1.5 mL min^{-1}). Atomic absorption spectroscopic analysis of arsenic was performed at λ = 193.7 nm with a quartz cell. The temperature of the cell and argon flow rate was 900 °C (electrically heated) and 100 mL min^{-1} respectively. The data analysis was performed on OriginPro 8.0 (origin Lab®). Spin trap experiments were performed using an EMX micro 6/1 Bruker ESR spectrometer working at X–band equipped with a Bruker SuperHigh QE cavity resonator. To detect the photogenerated free radicals during photocatalytic reaction, DMPO (5,5-Dimethyl-1-pyrroline N-oxide) was used as a spin trap.

3. Results and discussion

3.1. Characterization

The chemical composition of the synthesized ZnO was analyzed by EDS during TEM measurements. Fig. 1a shows strong peaks at 1.05, 8.63 and 9.53 keV which is due to L_α, K_α and K_β line of Zn respectively. A peak corresponds to oxygen (O) was found at 0.53 keV (K_α). A peak at 8.04 keV is due to K_α line of Cu that arises due to backscattering of the incident electrons from the TEM copper grid. This result clearly indicated that the sample was composed by Zn and O. Similar observations have been reported by Maleh et al. (2016). In order to find the molecular formula, the weight percentage of each elements acquired from EDS coupled with SEM have been used. The mole ratio of Zn and O was found to be 1:4. The inconsistency of EDS data with ZnO may be due to presence of surface functional groups.

XRD (Fig. 1b) pattern of the prepared sample shows the peaks (2θ=) at 31.36°, 34.03°, 35.8°, 47.16°, 56.26°, 62.54°, 67.64°, 68.79°, 69.45°, 72.82° and 77.33° attributed to wurtzite ZnO crystal planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) respectively (JCP2 01-079-0206). The observed lattice parameters are, a = 3.24992 Å, b = 3.24992 Å, and c = 5.20658 Å with $p6_3mc$ space group. The high intense peak (2θ = 35.8°) reveals that the synthesized ZnO crystal preferably grows along the (1 0 1) plane which is well consistent with those reported in literature (He et al., 2016). High intensity with sharpness of diffraction peaks indicates that the ZnO has good crystallinity. Besides, no impurity diffraction peaks were detected which indicates the proper purity of the synthesized ZnO sample. By using (Scherrer, 1918) Scherrer equation (Eq. (1)), the average crystallite size of ZnO was found to be 25 nm.