Chemosphere 91 (2013) 1273–1280

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Reductive degradation of oxygenated polycyclic aromatic hydrocarbons using an activated magnesium/co-solvent system

Marc R. Elie, Christian A. Clausen, Cherie L. Yestrebsky *

Environmental Chemistry Laboratory, University of Central Florida, 4000 Central Florida Blvd., Orlando, FL 32816, United States

HIGHLIGHTS

- ▶ The use of Mg–cosolvent system for the simultaneous degradation of OPAHs at room temperature.
- ▶ Reductive degradation of the selected OPAHs occurred, after the activation of Mg with acetic acid.
- ▶ This system degraded the selected OPAHs (>86%) and produced several derivatives within 24 h.
- ▶ Degradation products may be less toxic than OPAHs.
- ▶ This is the first report on OPAH remediation and may lead to the development of an actual field application.

ARTICLE INFO

Article history:
Received 11 September 2012
Received in revised form 21 February 2013
Accepted 22 February 2013
Available online 26 March 2013

Keywords:
Magnesium
Degradation
Oxygenated polycyclic aromatic hydrocarbons
Chemical reduction

ABSTRACT

This study evaluates the capability of zero-valent magnesium and a protic co-solvent to promote the degradation of oxygenated polycyclic aromatic hydrocarbons compounds, specifically 9-fluorenone, 9,10-anthraquinone, 7,12-benz(a)anthraquionone, and 7H-benz(de)anthracene-7-one. At room temperature conditions, greater than 86% degradation efficiency is observed after 24 h of reaction time for a mixture containing 0.05 g of magnesium and four selected oxygenated aromatic hydrocarbons with 250 mg L^{-1} concentrations. It is noted that glacial acetic acid is needed as an activator for the degradation reaction to proceed. It is also presumed that the acid removes oxide and hydroxide species from the magnesium surface. With the GC–MS analysis of the reaction products, possible reductive pathways are suggested. Furthermore, this study is the first report on the degradation of these emerging contaminants and it is proposed that the magnesium-powder/protic-solvent system is a promising low-cost reagent and may allow for the future development of an economic and environmentally-friendly remediation application.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely occurring in natural media such as soil, sediment, water, air and plants as a result of both natural and anthropogenic processes. Volcano eruptions, forest fires, car exhaust and combustion of fossil fuels create the majority of PAHs in the environment (Gan et al., 2009). These widespread organic compounds are considered as priority pollutants due to the mutagenic and carcinogenic properties of several PAHs and their metabolites. As a result of their wide occurrence and toxic properties, effective techniques are required for their degradation and detoxification.

PAHs have been extensively investigated throughout the literature, but their oxygenated derivatives may have increased human and environmental risks. Reports on the toxicological importance of oxygenated polycyclic aromatic hydrocarbons (OPAHs) have resulted in a growing interest in the environmental occurrence and fate of these contaminants. Moreover, recent studies have shown that the concentrations of OPAHs are significant and even higher than those of the parent PAH concentrations (Layshock et al., 2010; Musa Bandowe et al., 2010). OPAHs are transformation products of PAHs containing one or more carbonylic oxygen(s) attached to the aromatic ring structure and consist of ketones and quinones (Lundstedt et al., 2007). These oxidized derivatives can be produced during incomplete combustion or pyrolysis of organic material and emitted alongside PAHs. Subsequent research has shown that OPAHs result from the photochemical oxidation of PAHs in the atmosphere (Vione et al., 2006) and the microbial degradation of PAH-contaminated soils (Andersson et al., 2003). These polar compounds are ubiquitous, potentially more soluble than parent PAH compounds and consequently may have a higher bioavailability (Lundstedt et al., 2007). This is a cause of concern, due to the fact that there is growing evidence that OPAHs are direct-acting mutagens and carcinogens (Durant et al., 1996). OPAH quinones can act as generators of reactive oxygen species (ROS) in biological

---

* Corresponding author. Tel.: +1 407 823 2135; fax: +1 407 823 2252.
E-mail address: cherie.yestrebsky@ucf.edu (C.L. Yestrebsky).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.02.031

systems leading to gene mutations. In addition, OPAHs can undergo enzymatic and non-enzymatic redox cycling; forming DNA adducts which can ultimately induce carcinogenesis (Bolton et al., 2000). Bioassay of solid environmental samples, containing OPAHs, have demonstrated to be more toxic to human and bacteria cells, compared to PAH-containing fractions (Xia et al., 2004; Lemieux et al., 2008). Thus contaminated sites with OPAHs require immediate remedial action to protect human and ecosystem health. To the best of our knowledge, no investigations on OPAH-remediation methods have been reported in the literature.

In our previous work (Elie et al., 2012), it was demonstrated that the developed reducing-system was able to degrade and convert 94% of toxic benzo[a]pyrene (initial concentration of 250 mg L^{-1}) into a mixture of less toxic and partially-hydrogenated derivatives. The objective of this study is to investigate the potential of this system for the reduction of selected OPAH compounds under ambient conditions. The experimental results may provide a better understanding of the efficiency and necessary optimization of this system for future research on the simultaneous degradation of PAHs and OPAHs in solid environmental matrices.

2. Materials and methods

2.1. Chemicals

9-Fluorenone (9-FLUO), 9,10-anthraquinone (9,10-ANTQ), 7H-benz(de)anthracene-7-one (BEZO), 7,12-Benz[a]anthracenequinone (7,12-BaAQ) and 9-fluorenol (9-FLUOL) were purchased from TCI America (Portland, OR). Anthracene (ANT), fluorene (FLU), Benz[a]anthracene (BaA) were purchased from Accustandard Co. (New Haven, CT). Nitrobenzene (internal standard), ethyl lactate, toluene and absolute ethanol solvents were obtained from Fisher-Scientific (Ottawa, ON.). Spherical magnesium (Mg) powder (with a particle diameter distribution of 20–100 μm) was obtained from Hart Metals, Inc. (Tamaqua, PA). Helium gas, for GC/MS analysis, was purchased from Air Gas (Atlanta, GA). All chemicals were received in high purity (⩾98%) and ACS reagent, analytical grade.

2.2. Ball milling procedure and Mg powder characterization

Red Devil 5400 series paint shaker, fitted with custom plates to hold milling canisters, provided vibratory energy (670 rpm) for ball milling of the metal. The canister and balls are made of stainless steel. The canister has an internal diameter of 5.5 cm and a length of 17 cm corresponding to a capacity of about 250 mL. 76 g of Mg powder and 9 g of graphite (C) were introduced into the canister with 16 steel balls (1.5 cm diameter), corresponding to a ball-to-powder mass ratio of 3:1. The canister was sealed under nitrogen atmosphere. The milling duration was varied from 30 min to 1 h.

Morphology and elementary composition of the ball-milled powder was examined by a scanning electron microscope (SEM) LEO 1455VP (20 kV) equipped with an Oxford Inca energy-dispersive X-ray spectrometer (EDS). The analysis of the sample was facilitated by dispersing the powder onto a conductive carbon

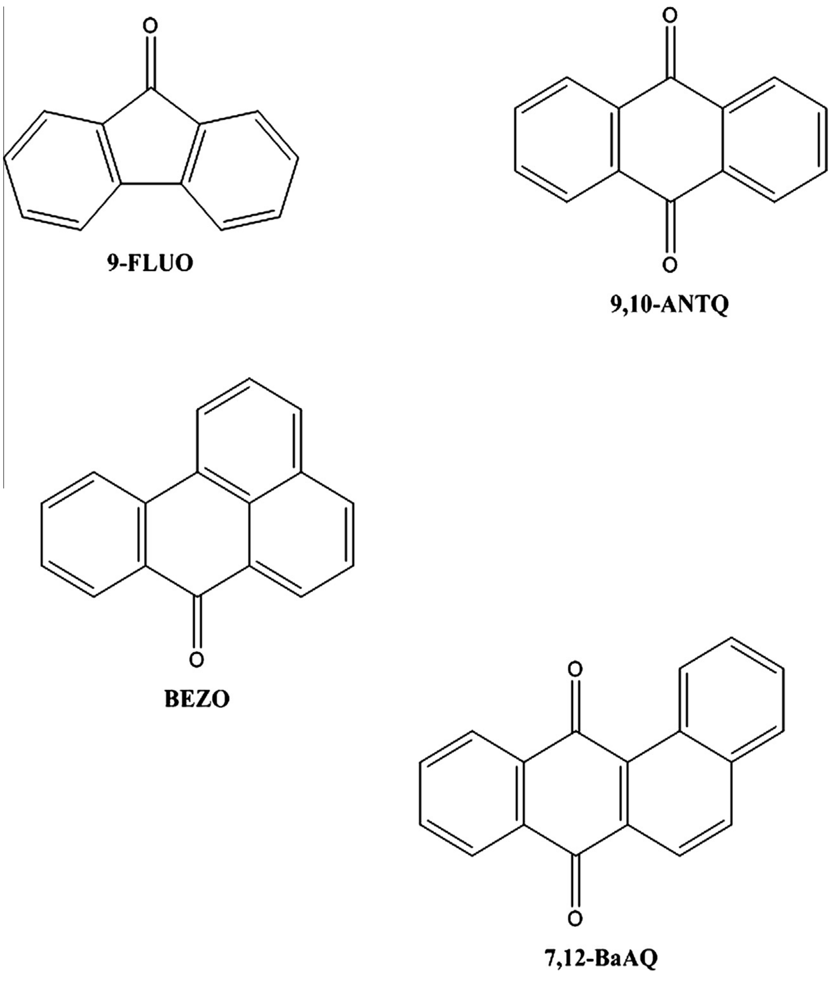

Fig. 1. Chemical structures of the selected OPAHs.