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Reduction of benzo[*a*]pyrene with acid-activated magnesium metal in ethanol: A possible application for environmental remediation

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ABSTRACT

Persistent organic pollutants (POPs) are a well-known threat to the environment. Substances such as polycyclic aromatic hydrocarbons (PAHs) in contaminated soils and sediments can have severe and long-term effects on human and environmental health. There is an urgent need for the development of safe technologies for their effective degradation. Here we present a new technique using ball-milled magnesium powder and ethanol solvent as a convenient electron transfer/proton source for the partial reduction of PAHs under ambient conditions. The rates of degradation were determined while evaluating the influences of acetic acid and type of ball-milled magnesium added to the reaction mixture. The results of these triplicate studies indicate that with the use of acetic acid as an activator and ball-milled magnesium carbon (Mg/C), this reducing system (Mg–EtOH) is able to achieve a 94% conversion of 250 μg/mL of toxic benzo[*a*]pyrene into a mixture of less toxic and partially hydrogenated polycyclic compounds within 24 h. This methodology can be used as a combined process involving ethanol washing followed by reduction reaction and it can also be considered as an easy handling and efficient alternative process to the catalytic hydrogenation of PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a unique class of persistent organic pollutants (POPs). Incomplete combustion or pyrolysis of organic matter and slow maturation of sedimentary organic matter, to yield petroleum, are the main known processes of PAH production. Both natural and anthropogenic sources, such as forest fires and industrial combustion of fossil fuels, are responsible for a large proportion of their formation in the environment [1–5]. Among environmental contaminants, PAHs have been of great concern because of the mutagenic and carcinogenic properties of the metabolites of several compounds. Extensive carcinogenic studies have shown that some PAHs, such as benzo[*a*]pyrene (B[*a*]P), act as potent procarcinogens once absorbed and metabolically transformed into chemically active electrophiles that form adducts within DNA. These DNA adducts can initiate further DNA damage, including strand breaks, chromosomal aberrations, mutations, and malignant cell transformation, all of which are linked to the initiation step of carcinogenesis [6,7]. PAHs are ubiquitous in their distribution, impacting on all environmental media and are considered priority pollutants [8]. As a result of their wide occurrence and toxic properties, effective techniques are required for their remediation and detoxification.

Biodegradation and phytoremediation represent environmentally-friendly and convenient in situ techniques, however, both methods have low degradation efficiencies and require long treatment times [9]. Chemical oxidation is another interesting in situ alternative, however it is an expensive technique for small or medium scale units and concerns exist that toxic by-products may form during the course of the treatment. These oxidized products may be more soluble and therefore have a higher bioavailability and toxic effect than parent PAH compounds [10]. On the other hand, chemical reduction can be considered as a more convenient method due to the fact that PAHs are quickly transformed into less toxic or detoxified compounds [11,12]. The reduction of PAHs can be achieved by catalytic hydrogenation or by the use of dissolved alkali metals. The hydrogenation reactions of PAHs, over supported noble-metal catalysts, are well known and have been shown to be efficient in reducing PAHs [13–15]. The mechanism of hydrogen addition is not well understood; but it is proposed to involve essentially concerted addition of hydrogen from the catalyst surface to the PAH molecular region having minimum bond delocalization energy [48]. Unfortunately, these catalytic reactions can prove to be a costly remediation technique due to the use of elevated temperatures or high hydrogen gas pressures in order to be active. On the other hand, alkali metal-based reductions of PAHs in liquid ammonia, are effective methods

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operating at low temperatures [16]. Metal–ammonia reductions of PAHs involve addition of electrons to generate radical anion or dianion intermediates. With ammonia serving as the proton source, protonation occurs to afford dihydroaromatic products [59]. However this technique has not seen much use due to undesirable attributes, particularly in large-scale experiments. The main factors limiting its applications are the practicality and hazardous handling of toxic liquid ammonia [17,18]. Consequently, there have been considerable efforts to design simple and economical alternatives to current reductive processes under ambient and non-toxic conditions.

For the past three decades, magnesium in an alcohol solvent has evoked considerable interest as an inexpensive and efficient reducing agent [19]. This metal reducing system has been demonstrated in the literature, as a convenient electron transfer/protic source for a number of reductive reactions such as the dehalogenation of alkyl halides [20,21] and also the reduction of conjugated double bonds tethered to aromatic ring systems, under essentially neutral conditions [22]. Phenanthrene, a priority PAH pollutant, has been shown to be partially hydrogenated to 9,10-dihydrophenathrene with magnesium in methanol [23]. The reduction process by the magnesium-alcohol system can be seen as an easy-handling alternative to transform PAHs into less toxic compounds, since the olefinic character of the aromatic bonds makes PAHs more susceptible to metabolic activation (*e.g.*, epoxide formation) [24]. So the less number of *pi* (π) bonds in the molecule, the less harmful it can be. For example, the hydrogenated derivative compound of naphthalene, tetralin (1,2,3,4-tetrahydronaphthalene) shows lower toxicity and faster biodegradation rates than its parent compound [25].

To date, the magnesium–alcohol system has been used solely for organic synthesis reactions; but can be considered as a useful chemical remediation technique due to its low-cost, easy-handling and environmental benignancy. This system is not intensively studied for degradation applications because of the fact that the alcoholysis reaction of magnesium is sluggish. Keirstead [26], examining the reduction of aromatic nitro compounds by magnesium in methanol solution, has concluded that the rate of reduction is slow due to passivation of the reactive magnesium by an unreactive oxide or hydroxide ($MgO/Mg(OH)_2$) layer, on the metal surface, which tends to block the reaction between magnesium and methanol. Nevertheless, a recent study has shown that the kinetics of alcoholysis reactions can be greatly improved by ball milling the magnesium metal [27].

In this present work, we report the influence of high-energy ball milling on the passivation behavior of magnesium in alcoholic solutions and we also present an investigation on the potential of this system to reduce selected PAH compounds under ambient and optimum conditions.

2. Materials and methods

2.1. Chemicals

B[*a*]P was purchased from Accustandard Co. (New Haven, CT). Nitrobenzene (internal standard), toluene and absolute ethanol solvents were obtained from Fisher-Scientific (Ottawa, ON.). Unmilled magnesium powder (nearly spherical particles, 4–11 μm particle size distribution) 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

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. Mg powder (85 g) was 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.

2.3. Experimental procedure

The alcoholysis reactions for milled and unmilled magnesium powders were carried out in 20 mL vials with PTFE lined caps. A 2-mL aliquot of 250 μg/mL B[*a*]P in absolute ethanol was added to react with 0.1 g of magnesium powder (ball-milled or unmilled). Then 20 μL of glacial acetic acid (1 vol.%) was added before capping the vial. The vial was then placed on a lab bench at room temperature (~27 °C) for a selected amount of time. At designated time points, extraction of B[*a*]P and derived products was performed by adding 2 mL of toluene to the vials and sonicating for 10 min. This 4-mL miscible solution was drawn into a filtered syringe (nylon filter/0.45 μm pore size) and then transferred into a 20-mL centrifuge tube. Next, 4 mL of deionized water was added to facilitate separation of the ethanol/toluene mixture. The sample was then centrifuged for 20 min to allow complete separation, partition of analytes in the toluene layer and removal of any residual Mg particles. The toluene layer was then extracted for analysis. All of the experiments were conducted in triplicates. The toluene extracts were analyzed, by GC–MS in triplicate, for the residual concentrations of the parent B[*a*]P compound, and concentrations of newly formed hydrogenated derivatives. By using the 250 μg/mL B[*a*]P stock solution as the reference control, and comparing its response factor to that of the toluene extract of the reaction mixture (B[*a*]P and Mg), in the absence of acetic acid, it was determined that the extraction efficiency of the experiments was approximately 93%.

2.4. Sample characterization method

GC–MS analyses were performed on an Agilent 6850 series II gas chromatograph fitted with an autosampler and Agilent 5975 MS detector. A DB-5 capillary column (DB-5MS 30 m × 0.25 mm i.d.; 0.25 μm film thickness) was used with flow rate (helium) of 1 mL/min. The analysis program was: after an initial temperature of 80 °C held for 3 min, the column was ramped at 25 °C/min to 320 °C and held for 5 min prior to cool down. The temperatures of injector and detector were maintained at 280 and 250 °C respectively. Injection volumes were 1 μL and were performed in splitless mode using helium as carrier gas (gas velocity 38 cm/s). Purge time and flow rate were set at 0.5 min and 100 mL/min. A calibration plot for B[*a*]P was prepared in the concentration range of interest and was found to be linear with R^2 values >0.98. Eluted compounds were identified by comparing sample mass spectra to reference spectra catalogued in the National Institute of Standards and Technology (NIST). Due to commercial unavailability of hydrogenated B[*a*]P standards, a response factor equal to the parent compound was presumed. Nitrobenzene was used as an internal standard for the analyses.

Morphology and elementary composition of the powder samples were examined by a scanning electron microscope (SEM) LEO 1455VP (20 kV). The samples were prepared by dispersing the powders onto a conductive carbon adhesive attached to the sample stub before insertion into the microscope.

3. Results and discussion

3.1. Rationale for experimental approach

The aim of this research is to develop a combined process involving ethanol washing followed by reduction with magnesium metal as a means to remediate soils heavily contaminated with PAHs. Extraction of PAHs with ethanol and their subsequent transformation into less toxic compounds could be an attractive process. Past experiments have shown that with three or four successive ethanol washings, greater than 90% removal efficiency was obtained for PAH-contaminated soils [28,29]. Lundstedt et al. [30] found that treating aged soils with ethanol prior to Fenton oxidation, actually enhanced the depletion of strongly-adsorbed PAHs by improving their desorption from the soil matrix. Lee et al. [31] have also demonstrated that ethanol is an effective solvent in extracting high-molecular-weight (HMW) PAH compounds from coal-tar contaminated soils and improving the availability of such PAHs to microorganisms in soil slurry biodegradation studies. The ethanol pre-treatment of soils resulted in a higher degradation rate, with approximately 90% of the total PAHs removed within 17 days while it required 35 days for biodegradation of soil without ethanol pre-treatment.

3.2. Use of acetic acid as activator

The reaction between magnesium powder and an alcohol is characterized by the production of a magnesium alkoxide and hydrogen gas [32]. The direct synthesis of magnesium ethoxide (Eq. (1)), from metallic magnesium and ethanol, has been known for a considerable time [33].

$$Mg + 2CH_3CH_2OH \rightarrow Mg(OCH_2CH_3)_2 + H_2 \quad (1)$$

In our experiments dealing with magnesium in PAH–ethanol solutions at room temperature, no hydrogen release is observed and no degradation of the PAH standard occurred. The lack of reaction may be due to the presence of a passivating oxide or hydroxide ($MgO/Mg(OH)_2$) layer, on the metal surface, which hinders the contact between magnesium and ethanol. This is also in accordance with corrosion studies indicating that ethanol and higher alcohols cannot attack the magnesium surface at ambient temperatures [34]. This result can be explained by the inductive effect of the alkyl group, creating a stronger O—H bonding of the alcohol group and ultimately making ethanol less acidic to attack the oxide layer in order to react with the magnesium surface. To initiate and accelerate a reaction with magnesium, the oxide/hydroxide layer must be removed in order to increase the active magnesium surface [35,36]. To activate a magnesium-induced reaction, compounds may be added to the reaction mixture. Catalysts such as mercuric chloride are often used [37] as well as mineral acids or organic acids. For our experiments, glacial acetic acid was selected as the activator due to its numerous benefits.

Contrary to toxic mercuric chloride and strong mineral acids, weak organic acids such as acetic acid can effectively remove the oxide layer without much damage to the base metal; they are safe and easy to handle [38]. Chavez and Hess [39] have shown that glacial acetic acid removes cupric oxide (CuO) and cupric hydroxide ($Cu(OH)_2$) from the surface of a copper film. After 10 min of immersion, acetic acid removes the copper oxide/hydroxide layer, at room temperature, without attacking the copper surface. Another reason for choosing glacial acetic acid is because of its water-free content. Studies have shown that the presence of water [26] or the addition of water (0.3 vol.%) to an alcohol solution [34,40] can drastically impede the alcoholysis reaction of magnesium. It is believed that acetic acid reacts with magnesium oxide (MgO) or magnesium hydroxide ($Mg(OH)_2$) at the surface of the metal, forming more soluble products (Eqs. (2) and (3)), thereby causing channels in the oxide/hydroxide layer through which ethanol can reach the magnesium.

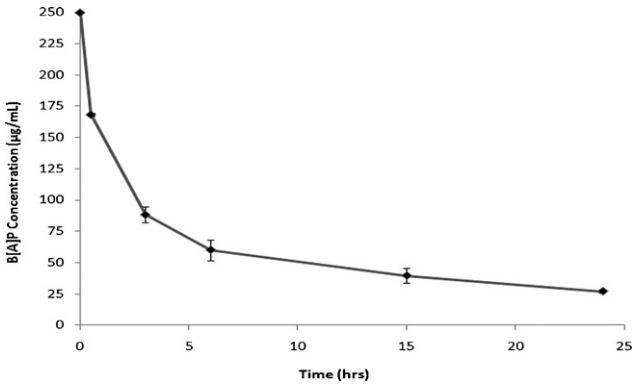

Fig. 1. B[*a*]P degradation in 24 h. Reaction conditions: at room temperature, 250 μg/mL of B[*a*]P in 2 mL of ethanol mixed with 0.1 g of ball-milled magnesium powder and acetic acid added (1 vol.%).

$$MgO + 2CH_3COOH \rightarrow Mg(CH_3COO)_2 + H_2O \quad (2)$$

$$Mg(OH)_2 + 2CH_3COOH \rightarrow Mg(CH_3COO)_2 + 2H_2O \quad (3)$$

3.3. Degradation of benzo[a]pyrene with ball-milled magnesium metal

According to the procedures described in Section 2.3, the influence of reaction time was evaluated for the chemical reduction of 250 μg/mL B[*a*]P with 0.1 g of ball-milled magnesium powder. The time points used in this study are 0 h, 0.5 h, 3 h, 6 h, 15 h and 24 h. Time points between 6 and 15 h and between 15 and 24 h were omitted due to the fact that extensive preliminary studies indicated that no significant change in concentration occurred during these time intervals. The reduction of B[*a*]P yielded 4,5,11,12-tetrahydrobenzo[*a*]pyrene (4,5,11,12-H_4B[*a*]P) and 7,8,910-tetrahydrobenzo[*a*]pyrene (7,8,9,10-H_4B[*a*]P) as the main products and 4,5-dihydrobenzo[*a*]pyrene (4,5-H_2B[*a*]P) being a consumed intermediate. Fig. 1 shows the degradation of B[*a*]P over time. After 30 min of reaction, around 32% of B[*a*]P was transformed and at 24 h 89% of the initial concentration was degraded. Table 1 and Fig. 2 summarize the product distribution analysis of the chemical reduction of B[*a*]P with magnesium/ethanol

Table 1
Product distributions (mol% ± standard deviation of triplicate vials) that resulted from the reaction conditions as in Fig. 1.

Products	0.5 h	3 h	6 h	15 h	24 h
Benzo[*a*]pyrene	67.3 ± 0.5	35.31 ± 2.5	24.05 ± 3.3	15.8 ± 2.4	10.8 ± 0.5
4,5,11,12-TetrahydroB[*a*]P	8.61 ± 0.1	23.26 ± 0.8	30.46 ± 0.34	33.7 ± 1.03	38.46 ± 1.8
7,8,9,10-TetrahydroB[*a*]P	8.94 ± 0.7	26.2 ± 1.15	29.5 ± 1.9	31.42 ± 1.6	33.4 ± 0.8
4,5-DihydroB[*a*]P	14.9 ± 0.16	12.31 ± 0.68	9.2 ± 0.84	9.0 ± 0.87	8.37 ± 0.37
Recovery (%)	99.5	97.08	93.21	89.4	91.03

Table 2
Product distributions (mol% ± standard deviation of triplicate vials) that resulted from the reaction condition as in Fig. 3.

Products	0.5 h	3 h	6 h	15 h	24 h
Benzo[*a*]pyrene	57.5 ± 5.5	22.0 ± 3.6	6.7 ± 0.53	5.99 ± 0.07	5.7 ± 0.76
4,5,11,12-TetrahydroB[*a*]P	24.05 ± 5.7	47.8 ± 1.5	55.4 ± 1.3	62.5 ± 0.78	66.4 ± 2.04
7,8,9,10-TetrahydroB[*a*]P	13.1 ± 3.74	24.3 ± 2.27	27.3 ± 2.97	28.4 ± 0.04	30.7 ± 0.14
4,5-DihydroB[*a*]P	3.5 ± 0.51	3.9 ± 0.19	4.3 ± 0.05	4.8 ± 0.02	5.1 ± 0.65
4,5,7,8,9,10,11,12-OctahydroB[*a*]P	0.32 ± 0.04	1.3 ± 0.09	2.25 ± 0.89	2.6 ± 0.10	3.9 ± 0.02
4,5,7,8,9,10-HexahydroB[*a*]P	0.44 ± 0.01	1.1 ± 0.05	1.4 ± 0.03	1.98 ± 0.01	2.25 ± 0.09
7,8,9,10,11,12-HexahydroB[*a*]P	0.16 ± 0.04	0.56 ± 0.04	0.68 ± 0.5	1.1 ± 0.007	0.8 ± 0.05
Recovery (%)	99.07	100.9	98.03	107.4	114.8

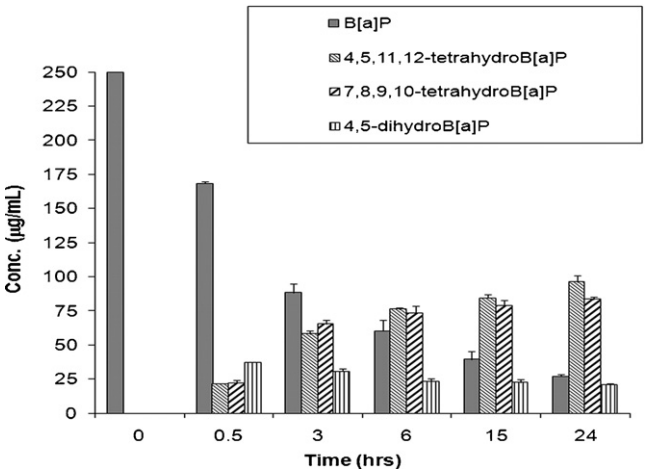

Fig. 2. Distribution of products resulting from chemical reduction of B[*a*]P by activated magnesium–ethanol system. Reaction conditions as in Fig. 1.

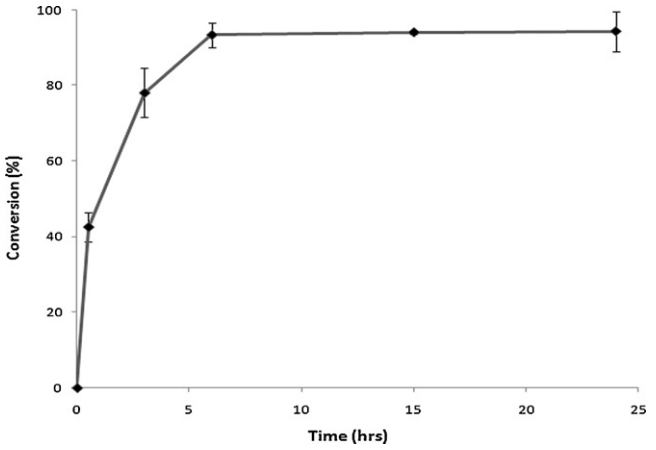

Fig. 3. B[*a*]P conversion in 24 h. Reaction conditions: at room temperature, 250 μg/mL of B[*a*]P in 2 mL of ethanol mixed with 0.1 g of ball-milled magnesium/carbon (Mg/C) powder and acetic acid added (1 vol.%).

system. The quantitation of the recovery products was calculated from the GC/MS response to the parent compound, due to the fact that standards of the hydrogenated products are not commercially available.

3.4. Degradation of benzo[a]pyrene with ball-milled magnesium/carbon (Mg/C)

Using the same procedures described in Sections 2.2 and 2.3, the influence of reaction time was evaluated for the chemical reduction of 250 μg/mL B[*a*]P with 0.1 g of magnesium powder, previously

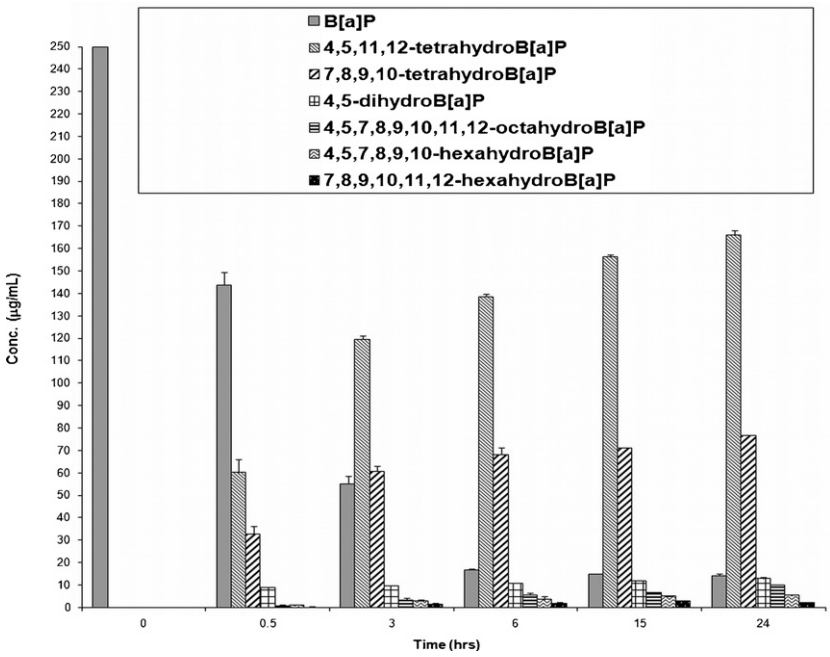

Fig. 4. Distribution of products resulting from chemical reduction of B[*a*]P by activated Mg/C–ethanol system. Reaction conditions as in Fig. 3.

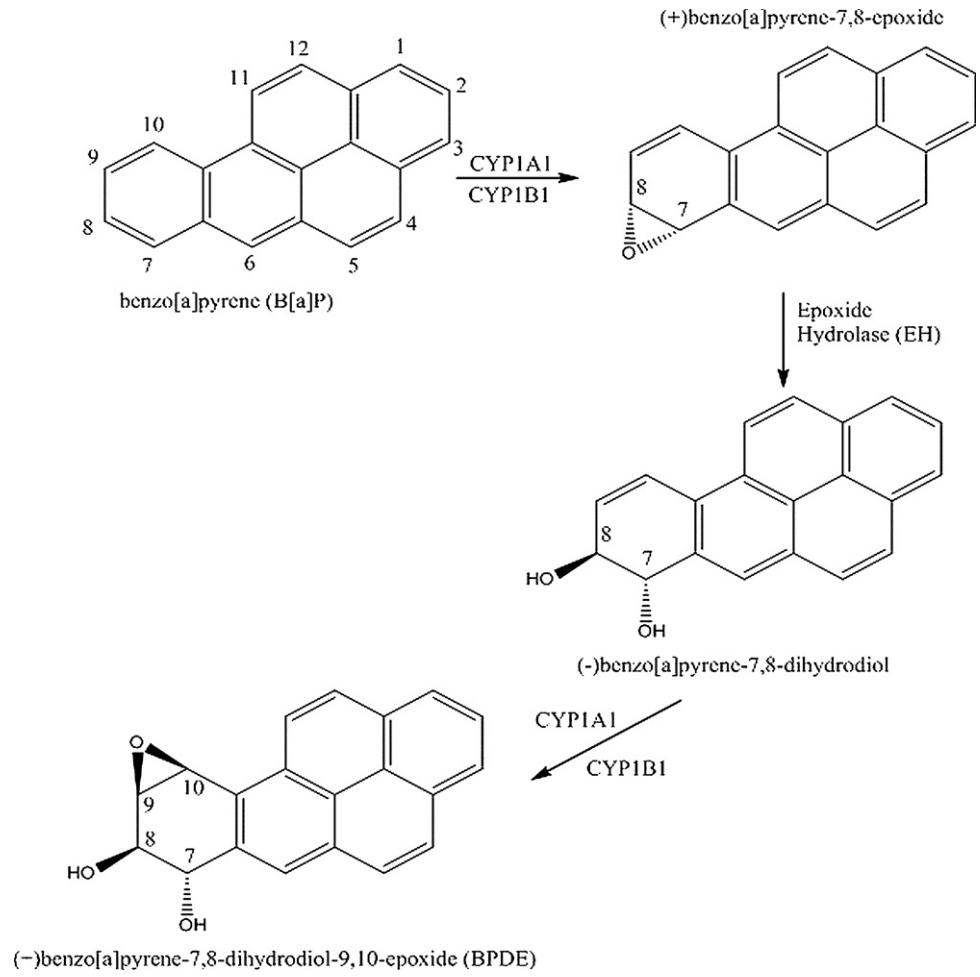

Fig. 5. Metabolism of benzo[*a*]pyrene yielding the carcinogenic benzo[*a*]pyrene-7,8-dihydrodiol-9,10-epoxide (BPDE). Adapted from reference [47].

ball-milled with 10 wt.% graphite (76 g of Mg/9 g of C). The time points used in this study are 0 h, 0.5 h, 3 h, 6 h, 15 h and 24 h. The reason for using Mg/C powder, for this experiment, was based off observations that graphite carbon can facilitate the activation process and improve the reaction kinetics of Mg [41,42].

Time points between 6 and 15 h and between 15 and 24 h were omitted due to the fact that extensive preliminary studies indicated that no significant change in concentration occurred during these time intervals. The reaction of Mg/C and B[*a*]P yielded more byproducts and slightly faster kinetics than the reaction with ball-milled Mg. Compounds such as 4,5,11,12-H_4B[*a*]P and 7,8,9,10-H_4B[*a*]P were obtained as the main products, while 4,5-H_2B[*a*]P, 4,5,7,8,9,10,11,12-octahydobenzo[*a*]pyrene (4,5,7,8,9,10,11,12-H_8B[*a*]P), 4,5,7,8,9,10-hexahydrobenzo[*a*]pyrene (4,5,7,8,9,10-H_6B[*a*]P) and 7,8,9,10,11,12-hexahydrobenzo[*a*]pyrene (7,8,9,10,11,12-H_6B[*a*]P) are obtained as minor products. Fig. 3 shows the conversion of B[*a*]P over time. After 30 min of reaction, approximately 42% of B[*a*]P was transformed and 94% of the initial concentration was degraded at the 24-h mark. Table 2 and Fig. 4 summarize the product distribution analysis of the chemical reduction of B[*a*]P with magnesium/ethanol system. It is thought that the slow degradation past the 6-h mark and the incomplete conversion of B[*a*]P is related to the observed precipitation/accumulation of $Mg(OCH_2CH_3)_2$ onto the powder's surface, preventing further access of ethanol to unreacted Mg sites. This is in accordance with the preparation of magnesium ethoxide (white precipitate) in ethanol solution [43].

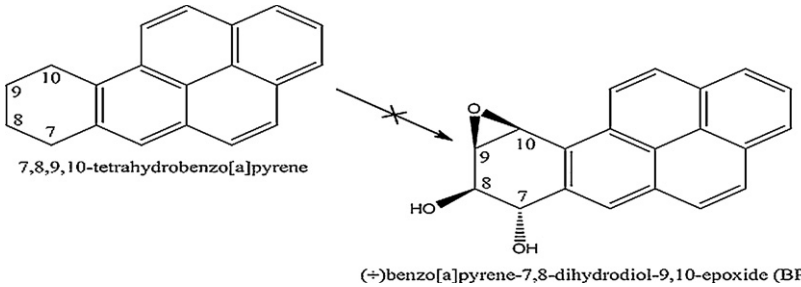

Fig. 6. With the reduction of B[*a*]P into 7,8,9,10-H_4B[*a*]P, the sterically hindered diol-epoxide formation is avoided at the 7,8,9,10 carbon positions (no double bonds present for oxidation). Therefore BPDE or similar carcinogenic metabolite is not formed.

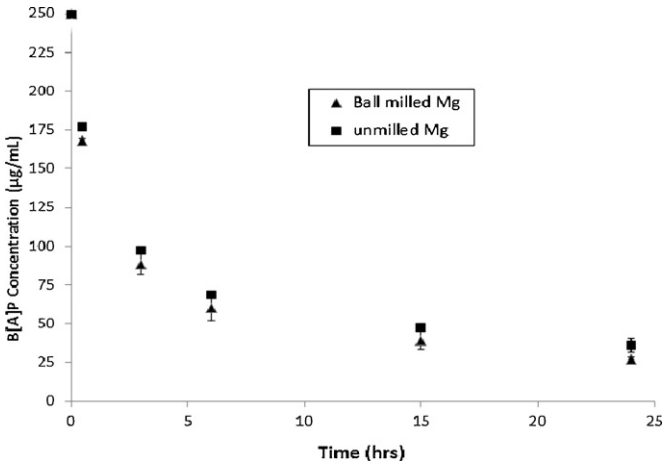

Fig. 7. Comparison studies of B[*a*]P degradation using ball-milled Mg powder vs. unmilled Mg powder (as received). Reaction conditions: at room temperature, 250 µg/mL of B[*a*]P in 2 mL of ethanol mixed with either 0.1 g of ball-milled or unmilled magnesium powder and acetic acid added (1 vol.%).

3.5. Reduction of B[a]P and its possible detoxification

The carcinogenic activity of PAHs is expressed through their biotransformation, by microsomal enzymes, into reactive epoxide and diol epoxide intermediates capable of covalently binding with DNA to induce strand breaks and DNA damage, leading to mutation and ultimately cancer [44–46]. Yuan et al. [12] has demonstrated that products of partial hydrogenation of B[*a*]P were devoid of mutagenic and genotoxic activity toward any of the *Salmonella* and *Escherichia coli* strains used in the study. From these results, it can be implied that the less number of *pi* (π) bonds in the PAH molecule, the less harmful it can be and also complete hydrogenation is not necessary to detoxify B[*a*]P. With our experimental results, we have shown that B[*a*]P can be reduced with the Mg/ethanol system and two tetrahydrogenated isomers, 4,5,11,12-H_4B[*a*]P and 7,8,9,10-H_4B[*a*]P, are the main by-products. Even though, no toxicity information is known for these hydrogenated products, correlating our results with the aforementioned findings of Yuan et al. [12], it may be argued that 7,8,9,10-H_4B[*a*]P and 4,5,11,12-H_4B[*a*]P hydrogenated product may not show any appreciable genotoxic activity and is probably less toxic compared to its parent B[*a*]P compound.

By comparing the metabolism of B[*a*]P to the possible metabolism of its hydrogenated derivatives, another reasoning can be made to support the argument that the magnesium/ethanol system is a convenient method to transform PAHs into less harmful compounds. The metabolic activation of B[*a*]P, by cytochrome P450s (CYPs) mono-oxygenase enzymes, is one of the most widely investigated study cases. In this metabolism reaction, B[*a*]P is oxidized at the 7, 8, 9, 10 positions to form B[*a*]P-7,8-dihydrodiol-9,

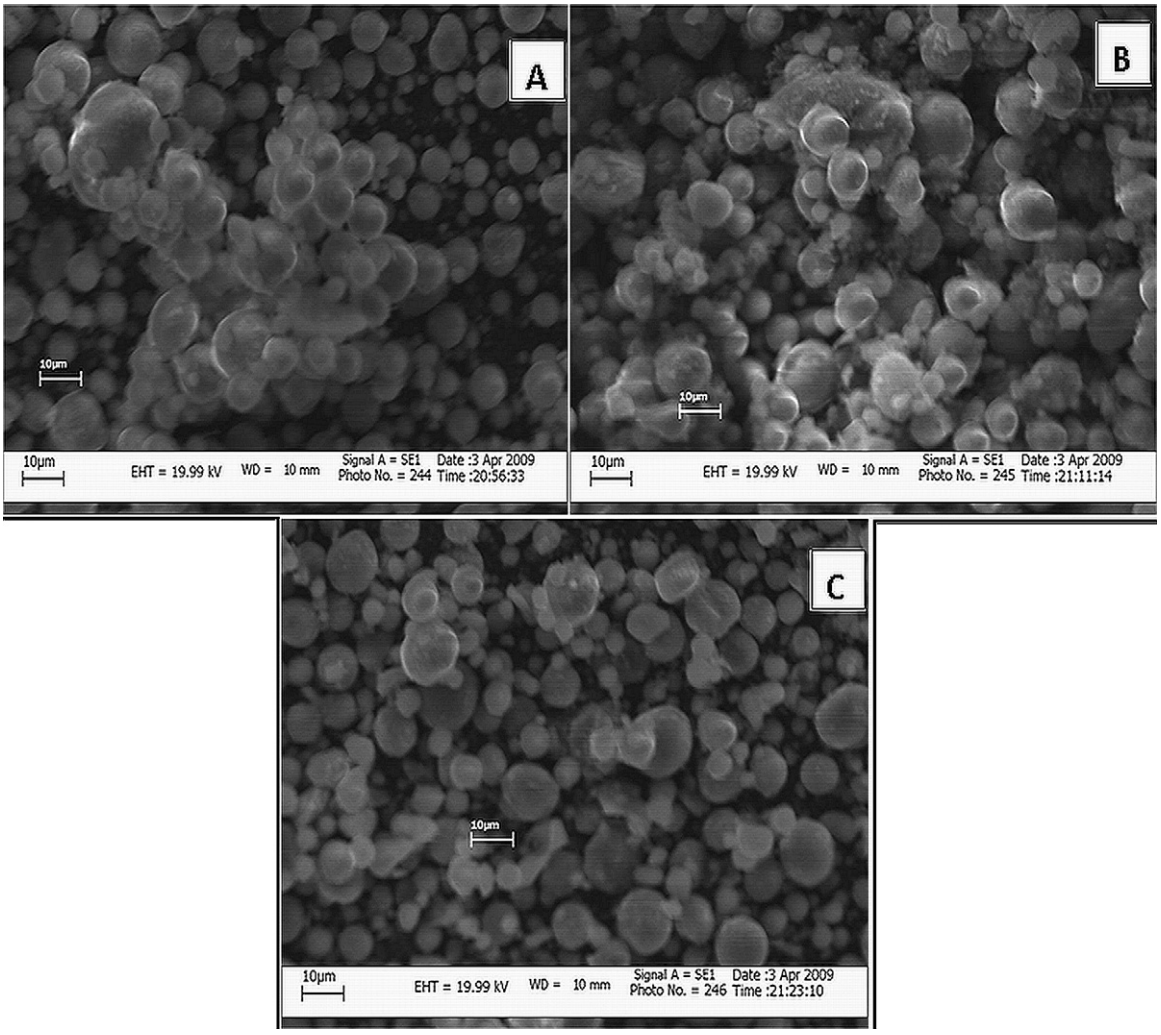

Fig. 8. SEM micrographs of (A) unmilled Mg powder (B) ball-milled Mg powder and (C) ball-milled Mg/C powder.

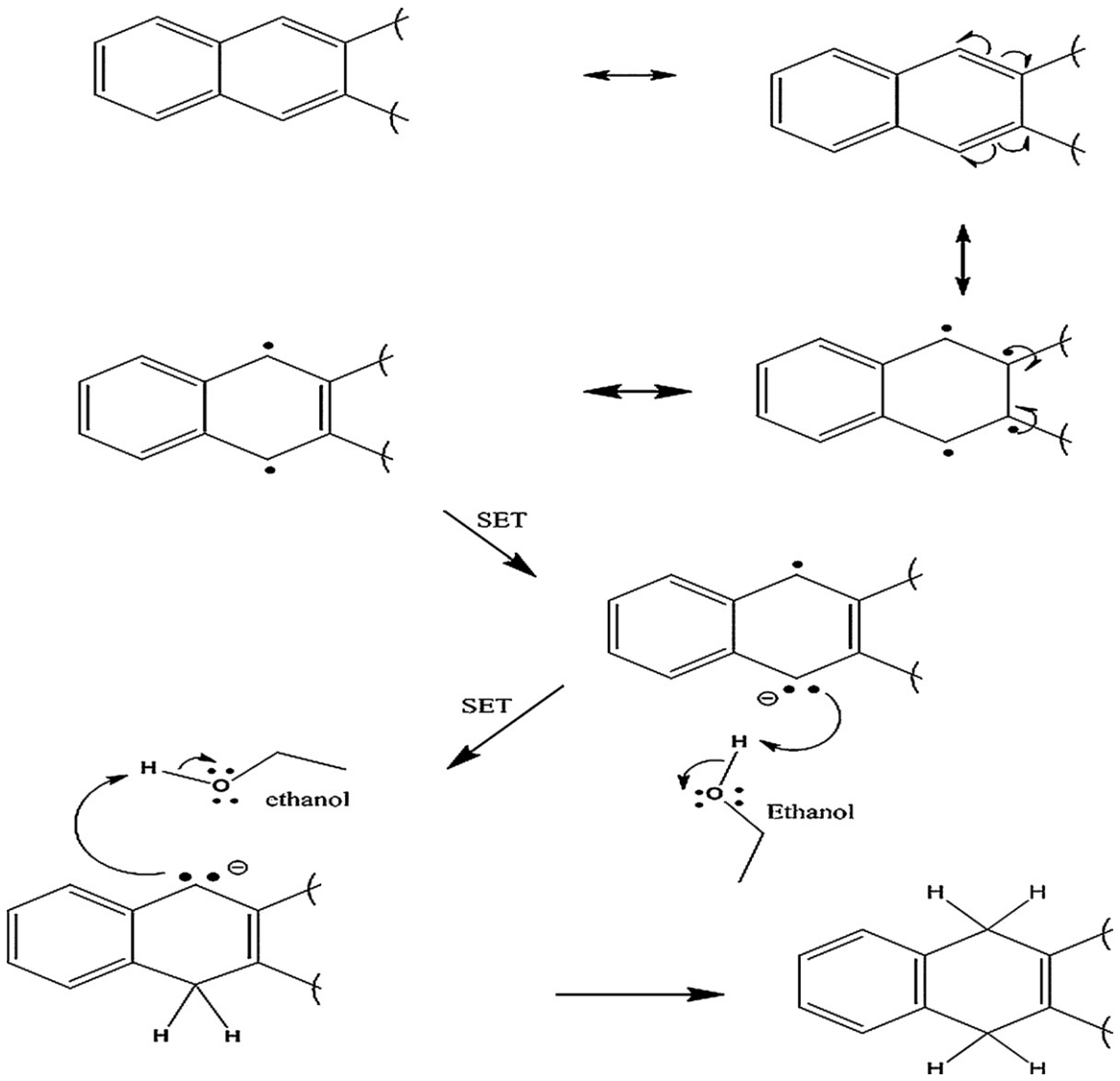

Fig. 9. Proposed reduction mechanism for the reaction of PAHs with magnesium–ethanol system.

10-epoxide (BPDE) (Fig. 4), which is characterized as the "ultimate carcinogenic" metabolite [47]. Due to the sterically hindered diol-epoxide (at 7, 8, 9, 10 carbon positions), BDPE is an electrophilic intermediate that bind to nucleophilic DNA bases, eliciting adverse biological activity [45]. According to mechanistic studies of B[*a*]P metabolism done by Sims et al. [44] and Baird et al. [47], the 9,10 epoxide formed, on the 7,8-diol derivative of B[*a*]P, is protected by vicinal hydroxyl substituents that sterically hinder interaction with enzymes (Fig. 5). Therefore only sterically hindered 9, 10 epoxide derivatives of B[*a*]P, also known as bay region epoxides, resist detoxification from epoxide hydrolase enzymes and have the potential to bind to DNA; while all other arene epoxides catalyzed by CYPs will be rapidly converted by epoxide hydrolase (detoxication enzymes) to corresponding dihydrodiols, which are easily excreted from the body. From the conclusions of these studies, it may be argued that for the possible metabolism of 7,8,9,10-H_4B[*a*]P, carcinogenic metabolites like BDPE cannot form due to the fact that enzymatic oxidation by CYPs (epoxide formation) may not occur at the 7, 8, 9, 10 carbon positions in the absence of double bonds (Fig. 6). Also it can be hypothesized that any electrophilic epoxides eventually formed, from the benzene rings present in 7,8,9,10-H_4B[*a*]P, will be rendered less reactive and easier to excrete by detoxication enzymes.

Another advantage of this experimental study is the fact that reduction of PAHs can be done at ambient temperature and produce several hydrogenated products; while higher temperatures and hydrogen pressures are needed for the costly catalytic hydrogenation method of PAHs to achieve near perhydrogenation [14]. Fu et al. [48] have shown that palladium-catalyzed hydrogenation of B[*a*]P, at room temperature, only yields 4,5-H_2B[*a*]P in 24 h.

3.6. Influence of ball milling on Mg properties

Comparing the results between the reactions of unmilled Mg and milled Mg (Fig. 7), no significant improvement is induced by the ball milling treatment. In both cases, during 24 h, the initial B[*a*]P concentration decreased by approximately 80% and yielded two main products (4,5,11,12-H_4B[*a*]P and 7,8,9,10-H_4B[*a*]P) and a consumed intermediate (4,5-H_2B[*a*]P). Zidoune et al. [49] and Grosjean et al. [50] have shown that the ball milling (a low cost technique) does remove the oxide layer and create new Mg surfaces; but such reactive surfaces readily oxidize when exposed to the atmosphere. They have also reported that ball-milled Mg exhibits a thinner oxide-hydroxide film and better corrosion resistance than their unmilled counterparts. Korshunov et al. [51] and Unwin et al. [52,53] have demonstrated that neighboring metal particles unite

as agglomerates due to the increasing formation of an amorphous and superficial oxide layer. This suggests that the lower the thickness of the passivating layer, the less particle aggregation there is. SEM observations, in our study (Fig. 8A and B), confirms this by showing that milled Mg continually exposed to air has less agglomerated micron-sized particles than unmilled magnesium powder.

Experiments with magnesium, ball milled with a small amount of graphite (10 wt.%), exhibits faster reaction kinetics than both ball-milled and unmilled Mg. In this reaction, 94% of B[*a*]P was degraded to yield six hydrogenated products (see Table 2 and Fig. 4) after 24 h; whereas with both milled and unmilled Mg, more than 80% transformation of B[*a*]P was achieved to produce three hydroaromatic products. SEM images of Mg/C (Fig. 8C) show significantly less agglomerates than its milled and unmilled counterparts, despite exposure to air. This observation is in accordance with the results of Bouaricha et al. [42] who have hypothesized that, during the milling treatment of Mg, graphene layers adsorb onto freshly created metal surfaces and thereby impede the reformation of a superficial oxide layer. In all of the experiments of this study, acetic acid was used as an activator (see Section 3.2) to break the present oxide/hydroxide layer, despite its thickness, at the surface of ball-milled or unmilled Mg, in order to allow ethanol to reach the underlying magnesium surface.

3.7. Reaction mechanism of Mg/ethanol system with B[a]P

According to the results in this study, the Mg/ethanol system has proven to be a convenient electron transfer/protic source for the reduction of benzo[*a*]pyrene. Similar to the proposed mechanisms of other dissolving-metal reducing systems [16,54], it is believed that the reduction proceeds by two subsequent single electron transfers (SET) from the magnesium metal to B[*a*]P. The role of magnesium as single electron donor [55,56] and PAHs as single electron acceptors [57,58] is an established fact. The newly formed radical–anion intermediates, from the SET, will then be protonated by nearby ethanol molecules to produce hydroaromatic derivatives of B[*a*]P. A possible reaction mechanism is illustrated in Fig. 9.

4. Conclusions

In summary, we have demonstrated a convenient method for the partial reduction of polycyclic aromatic hydrocarbons, based on the use of ball-milled Mg metal in ethanol at room temperature. The addition of acetic acid and graphite dramatically affects the reactivity and reaction rate. The present technique may be characterized by its environmentally benign nature, dually beneficial applicability (extraction of PAHs with ethanol, followed by reduction), simple procedure and low cost. Therefore, this method is promising as a practical ex situ remediation technique and also can be considered as an inexpensive alternative to other well known reduction methods for the industrial synthesis of some polycyclic hydroaromatic compounds. Current efforts are aimed at optimizing this technique and reducing other more potent carcinogenic PAHs.

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