Optimizing Reductive Degradation of PAHs Using Anhydrous Ethanol with Magnesium Catalyzed by Glacial Acetic Acid

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ABSTRACT: Targeted degradation of individual polycyclic aromatic hydrocarbon (PAH) constituents like anthracene, may offer cost effective and efficient cleaning of coal tar-contaminated sites. Thus, a reductive degradation procedure of anthracene using activated magnesium with anhydrous ethanol at room temperature was developed and optimized. To determine the optimum conditions for anthracene, such as effective magnesium concentrations, glacial acetic acid volumes, and exposure time for the anthracene reduction, the experiments were designed using the response surface methodology based on the central composite design. The design also minimized the number of experiments. The main product from anthracene reduction is 9,10-dihydroanthracene. Optimum conditions for 98% degradation capacity of anthracene (2.80 \texttimes 10^{-3} mmol) were 30 mg of Mg powder (1.20 mmol), 60 \textmu L of glacial acetic acid (1.05 mmol), and 30 min exposure time. When the optimized method was tested on the coal tar specimen, twice as many reagents (i.e., Mg and glacial acetic acid) were required to obtain a 90% degradation of anthracene and fluoranthene from the coal tar. This method of using activated Mg and anhydrous ethanol selectively reduces PAHs in coal tar; in particular anthracene and fluoranthene are most efficiently removed.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that consist of two or more fused benzene rings. PAHs are lipophilic and have high desorption activation energy. They are colorless to pale solids and have low solubility in water, high melting and boiling points, and low vapor pressures. PAHs are mainly produced from the incomplete combustion of fossil fuel and organic materials, and the evaporation of petroleum derivatives. Most PAHs do not easily degrade in the environment and are classified as persistent organic pollutants. They are also considered as carcinogenic, teratogenic, and mutagenic. The United States Environmental Protection Agency (EPA) has listed 16 PAHs as priority pollutants. Seven of these PAHs, namely benz[a]-anthracene, chrysene, benzo[b]fluoranthene, benzo[k]-fluoranthene, benzo[a]pyrene, indo[1,2,3-cd]pyrene, and dibenzo[a,h]anthracene, are considered to be carcinogenic compounds. Therefore, conversion of PAHs into less toxic products is one of the strategies in the remediation of PAHs contaminated sites.

Catalytic reduction is one of the methods used for PAHs degradation. For example, transition metals (e.g., rhodium, ruthenium, palladium, etc.) have been successfully used as catalysts in degrading PAHs through hydrogenation, but the procedure requires high temperature and pressure of hydrogen to obtain relatively small nontoxic products. Thus, it is a relatively expensive procedure of PAH reduction. Birch reduction has also been used for PAH reduction, which involves the use of ammonia and alkali metals such as sodium or lithium. However, the Birch reduction has disadvantages, such as the toxicity of ammonia, difficulty in handling reactive metals, and scaling up.

Therefore, it is necessary to find an alternative metal/solvent system effective for PAH reduction, which is cheap, easily handled, and environmentally friendly. Magnesium with methanol can be such a system because it is widely used in several organic synthetic procedures. Magnesium with acidified ethanol was successfully used to remove polychlorinated biphenyls from painted surfaces. In addition, magnesium with a combined solvent of ethanol and ethyl lactate (1:1, v/v) was used to reduce some PAHs, such as dibenzo[a,h]pyrene, fluoranthene, benzo[a]pyrene, fluorene,
benz[a]anthracene, 9-fluorenone, 7H-benz[de]anthracene-7-one, 7,12-benz[a]anthracenequinone, and 9-fluorenone, from spiked soil. The degradation was 79–88% of oxygenated PAHs and 66–87% of PAHs after 24 h of reaction and at room temperature. To effectively apply such a method in contaminated sites, like the coal tar contaminant of the defunct steel mill processing plant in Sydney Nova Scotia, the degradation of PAHs needs to be fast, so that turnover can be multifold within a day.

In view of this, the PAH reduction procedure was modified by using activated Mg as the catalyst to increase degradation turnover. The Mg was activated by glacial acetic acid with anhydrous ethanol as a co-solvent to enhance the PAH degradation in coal tar. Therefore, the objectives of this work were to investigate the ability of Mg powder activated by glacial acetic acid with anhydrous ethanol to effect PAHs reduction in coal tar at room temperature and to determine the optimum conditions for PAHs reduction in coal tar.

2. RESULTS AND DISCUSSION

2.1. Effect of Magnesium Activation. Using a commercial Mg powder without activation was found to be ineffective for the anthracene reduction, as shown in Figure 1.

![Figure 1](image1.png)

Figure 1. Effect of Mg activation and Mg particle size on reduction of anthracene in anhydrous ethanol at room temperature. (A) Non-catalyzed Mg powder, (B) catalyzed Mg turnings, and (C) catalyzed Mg powder. The reaction conditions are 250 ppm anthracene (C), 30 mg Mg, glacial acetic acid (30 μL), and 3 h reaction time. Error bars represent the relative standard deviation (RSD)%, n = 3.

In addition, particle size has a clear effect on the removal efficiency of anthracene, where small-size Mg particles (≤150 μm) are more efficient for anthracene reduction (>90% removal efficiency) than Mg turnings (~50% removal efficiency), as shown in Figure 1, bars B and C. This is due to the large surface area of Mg powder that is available for reaction with anthracene molecules. Activation of Mg powder using glacial acetic acid is a necessary process to remove the formed layers of magnesium oxide (MgO) and magnesium hydroxide (Mg(OH)₂) from the Mg surface. These layers prevent the interaction between Mg and the substrate (e.g., anthracene). Mg activation can be achieved by using methyl iodide or ethyl bromide, but this method is not favored because a side reaction with the Mg can occur through the Grignard reagent formation. Mercury chloride also can be used, but it is highly toxic. Stirring of Mg during the reaction is an important process and helps to remove the oxide layers and reduces the reaction time (<1 h), but it is not favored for large-scale reduction using Mg turnings because the glass reactor can be damaged by abrasion, whereas slower stirring is not effective with large-scale reductions. Acid treatment is another method to remove the oxidized layers from Mg surface, by which Mg is activated through increasing the active sites on the Mg surface. In this work, glacial acetic acid was used as the activator because it is water-free, which improves the reaction efficiency, easy to handle, and environmentally friendly.

The Mg cleaning using glacial acetic acid includes the reaction between the acid and the oxide layers (MgO and Mg(OH)₂), as shown in eqs 1 and 2:

\[
\text{MgO(s)} + 2\text{CH}_3\text{COOH(l)} \rightarrow \text{Mg(CH}_3\text{COO)}_2(\text{sol}) + \text{H}_2\text{O(l)}
\]

(1)

\[
\text{Mg(OH)}_2(s) + 2\text{CH}_3\text{COOH(l)} \rightarrow \text{Mg(CH}_3\text{COO)}_2(\text{sol}) + 2\text{H}_2\text{O(l)}
\]

(2)

2.2. Effect of Magnesium with Ethanol. Aprotic solvent (dried acetonitrile) was used with Mg catalyzed by glacial acetic acid for anthracene reduction to understand the role of co-solvent in anthracene reduction, and to compare with anhydrous ethanol (Figure 2). The results indicate that ethanol is an essential co-solvent with catalyzed Mg for anthracene reduction, whereas dry acetonitrile did not show any efficiency in anthracene reduction. Anhydrous ethanol works as a proton source, as shown in the reaction mechanism (Scheme 1). In addition, using anhydrous ethanol as a co-solvent has several advantages, such as being nontoxic, cheap, and a high ability to extract PAHs. Mg reacts with anhydrous ethanol to produce hydrogen gas and magnesium ethoxide, as shown in eq 3. Anthracene degradation increases with increasing reaction time, where a high conversion of anthracene (>90%) occurs at time ~3 h (see inset plot in Figure 2).

\[
\text{Mg(s)} + \text{CH}_3\text{CH}_2\text{OH(l)} \rightarrow \text{Mg(OCH}_3\text{CH}_3)_2(\text{sol}) + \text{H}_2(\text{g})
\]

(3)
Scheme 1. Proposed Mechanism for the Anthracene Reduction Using the Mg Catalyzed by Glacial Acetic Acid, Which Is a Modification of Mechanism Earlier Proposed by Elie

Due to these side reactions shown in eqs 1–3, the amount of Mg powder (1.20 mmol) and glacial acetic acid (1.05 mmol) are used in excess compared to the amount of anthracene used (2.80 × 10^{-3} mmol). Therefore, the reaction is not stochiometric.

2.3. Anthracene Reduction Mechanism. Reduction of anthracene using activated Mg with anhydrous ethanol gives 9,10-dihydroanthracene as the main product. A proposed modified mechanism of this reaction based upon that described by Elie is shown in Scheme 1. A single electron transfer (SET) is the first step in the mechanism, where a single electron transfers from Mg (the electron donor) to anthracene (the electron acceptor) to form a radical anion (I) at position 9 or 10 of the anthracene molecule. Then, (I) is protonated to form the protonated radical (II). The second electron transfers from Mg to (II) to form anion (III), which in turn is protonated by ethanol molecules to produce 9,10-dihydroanthracene (IV).

2.4. Optimization of Anthracene Reduction. The single-factor-at-a-time approach is widely reported in the literature, in which a single factor is studied and other factors remain constant. Nevertheless, that approach is not fully successful because it ignores the interactions between the factors and requires many experiments. However, the experimental design methodology reduces the number of experiments and takes into account the interactions between the factors.

2.4.1. Screening of Variables. The screening variables of the anthracene reduction using the Mg catalyzed by glacial acetic acid were achieved using four factors, namely Mg powder dosage, glacial acetic acid, graphite, and time. Graphite was introduced as a possible factor since Elie et al. reported a catalytic function in their experiments. Using the data shown in Table 1, the significance of each factor was then determined by a Pareto chart (Figure 3), in which the significance of each factor is shown to be proportional to the length of the corresponding line bar. For example, glacial acetic acid and Mg have a significant effect (p ≤ 0.05 at 95% confidence level), having values of 12.12 and 11.00, respectively. However, graphite has an insignificant effect (p = 0.2199), as shown in Appendix (Table S1). This result was proven by other experiments, designed to study the effect of the added graphite. For example, experiment #4 in Table 1 was repeated with graphite (30 mg), and experiment #8 was also repeated but without graphite. There is no apparent effect on reduction of anthracene in both the cases. Therefore, the three factors that have a clear effect on removal % of anthracene reduction are Mg dosage, glacial acetic acid, and time. Among them, glacial acetic acid has the highest effect followed by Mg and time, respectively.

2.4.2. Optimization Using Central Composite Design (CCD). The use of response surface methodology (RSM) based on CCD is widely reported in the literature because it is simple and easy to use, minimizes the number of experiments, and provides useful information on the effects of factors and their interactions. The experiments achieved for the optimization of anthracene reduction using activated Mg with anhydrous ethanol are listed in Table 2. Three factors (i.e., Mg powder, glacial acetic acid, and time) were studied and each factor has three levels: low (−1), medium (0), and high (+1). Increasing the Mg dosage increases the removal % of anthracene. The same trend can be observed when the glacial acetic acid volume increases. Using the highest Mg dosage and high glacial acetic acid dosage gave the ability to obtain high removal % of anthracene during a relatively short time (30
The results of analysis of variance (ANOVA) of the CCD model are listed in Appendix (Table S2), where the $p$-values of the three factors (Mg powder, glacial acetic acid, and time) are less than 0.05, which indicate that they have a clear significant influence on anthracene reduction. In addition, $F$-values are large and the lack of fit is insignificant, which leads us to conclude that the model is in a good agreement with the data used.\(^{35}\) Depending on the ANOVA analysis, the final mathematical equation, in terms of actual factors, for removal calculation is as follows (eq 4)

$$\text{removal} = +71.86 + 11.90 \times A + 12.80 \times B + 6.68 \times C + 1.95 \times AB - 1.45 \times AC - 0.43 \times BC - 8.451 \times E - 0.003 \times A^2 - 4.01 \times B^2 + 2.99 \times C^2$$

(where, $A$: Mg, B: glacial acetic acid, and C: time) \(^{(4)}\)

The model validity was evaluated by ANOVA analysis, where the correlation coefficient ($R^2$) is 0.91 and the adjusted $R^2$ is 0.89 at a confidence level of 95%. In addition, the standard deviation is 7.1% and the lack of fit is not significant. The model accuracy can be evaluated through the homogenous distribution of externally studentized residuals and predicted probability values around the straight line (Figure S1A). In addition, Figure S1B shows the distribution of the real values obtained from experiments and the predicted values from the model around the straight line ($y = x$), which explains a good agreement between the actual and predicted values.\(^{36}\) Therefore, this model can be used for optimizing the PAHs reduction using the Mg/ethanol system. Depending on Figure 4, the optimum conditions for anthracene reduction are 30 mg of Mg, 60 $\mu$L of glacial acetic acid, and a reaction time of 30 min. The result of the gas chromatography flame ionization detector (GC-FID) analysis of the anthracene before and after the reaction using Mg catalyzed by glacial acetic acid at the optimum conditions mentioned above is shown in Appendix (Figure S2). Clearly, the anthracene reduction using Mg catalyzed by glacial acetic acid gives the 9,10-dydranthracene as the main product, which is also reported in the literature.\(^{28}\)

### 2.5. Optimization of Coal Tar Reduction.

The coal tar used in this study consists mainly of light PAHs such as naphthalene, phenanthrene, fluoranthene, and pyrene (Figure 5 and Table 3). The concentration of these PAHs extracted from the coal tar using anhydrous ethanol was determined using standard calibration curves and their concentrations are listed in Table 3.

The use of the optimum conditions from anthracene reduction experiments was found to be insufficient for obtaining high removal of some of PAHs in the coal tar because it includes multiple PAHs. Use of 30 mg of Mg and 60

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**Table 2. Central Composite Design Using the Three Significant Factors at Three Levels for Optimizing the Anthracene Reduction**

<table>
<thead>
<tr>
<th>#</th>
<th>Mg (mg)</th>
<th>glacial acetic acid ((\mu)L)</th>
<th>time (h)</th>
<th>removal (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>78.0</td>
</tr>
<tr>
<td>2</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>60.0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>75.0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>−1</td>
<td>65.1</td>
</tr>
<tr>
<td>5</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>98.5</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>65.0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>−1</td>
<td>0</td>
<td>61.0</td>
</tr>
<tr>
<td>8</td>
<td>−1</td>
<td>−1</td>
<td>−1</td>
<td>42.0</td>
</tr>
<tr>
<td>9</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>78.7</td>
</tr>
<tr>
<td>10</td>
<td>−1</td>
<td>−1</td>
<td>+1</td>
<td>50.0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>+1</td>
<td>0</td>
<td>80.0</td>
</tr>
<tr>
<td>12</td>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>84.0</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>+1</td>
<td>90.0</td>
</tr>
<tr>
<td>14</td>
<td>−1</td>
<td>0</td>
<td>0</td>
<td>65.0</td>
</tr>
<tr>
<td>15</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>98.0</td>
</tr>
<tr>
<td>16</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>74.4</td>
</tr>
<tr>
<td>17</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
<td>59.8</td>
</tr>
</tbody>
</table>

$^a$The mean of three experiments, RSD% < 3.0%.
μL of glacial acetic acid gave 56% removal of anthracene and 89% removal of fluoranthene. The sum of the concentrations of anthracene and fluoranthene in coal tar is close to 500 ppm. Therefore, the double dosage of reagents (Mg powder + glacial acetic acid) was added to anhydrous ethanol extract of coal tar to increase the PAH removal. Thus, increasing the dosage to 60 mg of Mg powder and to 120 μL of glacial acetic acid increases the anthracene removal to 89% and fluoranthene to 90%. Triple dosage (90 mg of Mg powder + 180 μL glacial acetic acid) did not show any improvement of PAH degradation (Figures 6 and 7; Table 4).

The reduction of PAHs using activated Mg and anhydrous ethanol is selective because only anthracene (9) and fluoranthene (14) in the coal tar were reduced with high removal %. The main products from anthracene and fluoranthene are 9,10-dihydroanthracene and 2,3-dihydrofluorantheme, respectively. The light PAHs, such as naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, phenanthrene, and pyrene, were not reduced by the anhydrous ethanol with Mg catalyzed by glacial acetic acid under the conditions used. The current reaction conditions can be described as being mild conditions; therefore, reduction of the light PAHs (naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene) requires harsher conditions, or coordination of these PAHs with iron cyclopentadienyl cation to be reduced.37

### 3. CONCLUSIONS

Activated Mg with anhydrous ethanol is an effective system to convert some of the PAHs (e.g., anthracene and fluoranthene) to hydrogenated PAHs with high removal (~90%) during a relatively short time (30 min). The experimental design approach is a useful methodology that can be used to optimize the PAH reduction using activated Mg and anhydrous ethanol. The PAH reduction is mainly affected by three factors: Mg powder dosage, glacial acetic acid volume, and reaction time. The order of these factors from the highest to the lowest significant effect is as follows: Mg powder dosage > glacial acetic acid volume > time. The products of the PAH reduction are less toxic compared to their parent compounds. Therefore, Mg activated by glacial acetic acid with anhydrous ethanol can be considered as a promising route for environmental remediation for the removal of PAHs from PAH-contaminated coal tar.

### 4. MATERIALS AND METHODS

#### 4.1. Chemicals

Anthracene (>90%) was purchased from Alfa Aesar and used as received. Nitrobenzene (99%) as an internal standard was purchased from Fisher Scientific (New Jersey), toluene (99.5%) was purchased from Caledon Laboratories Ltd. (Georgetown, ON, Canada), acetonitrile (high-performance liquid chromatography grade, 99.9%) was purchased from ACP Chemicals (Montreal, Canada), and anhydrous ethanol was purchased from Commercial Alcohols (Brampton, ON, Canada). All of these chemicals were used without further purification except acetonitrile, which was dried over molecular sieves for 2 weeks. Glacial acetic acid (>99.85%), magnesium powder (≤150 μm, 98% purity),

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Table 3. PAH Compounds Identified in Anhydrous Ethanol Extract of Coal Tar before and after Reduction

<table>
<thead>
<tr>
<th>peak no.</th>
<th>compound name</th>
<th>conc. in coal tar (mg/L)</th>
<th>N/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>nitrobenzene (internal standard)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>naphthalene</td>
<td>1823</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2-methylnaphthalene</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1-methylnaphthalene</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>acenaphthylene</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>fluorene</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>9,10-dihydroanthracene</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>phenanthrene</td>
<td>631</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>anthracene</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>carbazole</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>9-methylnaphthalene</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>4H-cyclopenta[def]phenanthrene</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1,2-dihydrofluorantheme</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>fluoranthene</td>
<td>370</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>pyrene</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>benz[a]anthracene</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>chrysene</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

"Peak numbers refer to peaks in chromatograms in Figure 7. b RSD% < 5%, n = 3."
magnesium turnings (∼4000 μm, 98% purity), and graphite (99.99%) were purchased from Sigma-Aldrich, Canada. Coal tar samples were collected from Sydney Tar Ponds, Nova Scotia, Canada, according to the coal tar sampling methodology.38

4.2. Anthracene and Coal Tar Reduction Experiments. Initially, anthracene was used as a representative model compound of PAHs and subjected to reductive degradation with Mg powder in anhydrous ethanol. Then, the optimum conditions were used for PAHs reduction in coal tar. The method used in this study is based on a procedure used in a previous study.27 Briefly, a 2.0 mL solution of anthracene (250 ppm) in anhydrous ethanol, in a 20 mL poly(tetrafluoroethylene) (PTFE) vial was added with a desirable amount (0.010–0.030 g) of Mg powder, which was previously well grounded using agate mortar and pestle. The reaction started by adding a desirable volume of glacial acetic acid (10–60 μL), which was used as an activator, and the reaction mixture was rapidly stirred for various time intervals (0.5–3.0 h) at room temperature (21.5 °C). The reaction was quenched by adding 2.0 mL of toluene, then the mixture was sonicated for 15 min, and filtered using nylon microfilter paper. For product separation, 4.0 mL of deionized water was added, and then the mixture was centrifuged (3000 rpm) for 20 min. The toluene extracts were stored at 4 °C in 5 mL sealed glass vials with

<table>
<thead>
<tr>
<th>symbol</th>
<th>Mg powder (mg)</th>
<th>glacial acetic acid (μL)</th>
<th>time (h)</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>60</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>60</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>90</td>
<td>180</td>
<td>0.5</td>
</tr>
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</table>

Figure 6. Chromatogram of GC-FID analysis of reduction of coal tar soluble in anhydrous ethanol using Mg catalyzed by glacial acetic acid under the conditions (A–C) listed in Table 4. Peak numbers correspond to compounds listed in Table 3.

Figure 7. Evaluation of Mg powder catalyzed by glacial acetic acid in anhydrous ethanol for PAHs reduction in coal tar at room temperature. Reaction conditions (A–C) are listed in Table 4. Error bars represents RSD%, n = 3.

Table 4. Reaction Conditions Used for PAHs Reduction in Coal Tar
PTFE-lined caps. The toluene extracts as well as reductive degradation on the PAHs were confirmed using gas chromatography–mass spectrometry (GC–MS) and gas chromatography flame ionization detector (GC-FID). For coal tar degradation, 0.200 g of coal tar was dissolved in 60.0 mL of anhydrous ethanol, sonicated, then filtered using nylon 0.45 μm PTFE CHROMIC. Approximately 40% of the coal tar dissolved. A solution of 2.0 mL of coal tar in anhydrous ethanol was added to 0.030 g of Mg and 60 μL of glacial acetic acid. The reaction mixture in a sealed vial was stirred rapidly for 30 min. Then, the reaction was stopped and the product was separated using the same steps used for anthracene reduction.

4.3. Experimental Design. The experimental design for the anthracene reduction was achieved using the Design-Expert 9.0.0 software. This experimental design was carried out through two stages: screening of variables and optimization using central composite design. In the stage of variables screening, a half factorial design (2^3) for four factors (magnesium dosage, glacial acetic acid dosage, graphite dosage, and time) was investigated to determine the importance of these factors. The factor that has a less significant effect can be ignored to reduce the number of experiments. The stage of screening variables includes eight runs listed in Table 1. In the screening of variables, each factor has two levels: low and high, which were coded by −1 for low and +1 for high levels. The minimum and maximum values of each factor were chosen according to the preliminary experiments and literature. The second stage is optimization using the response surface methodology (RSM) based on the central composite design (CCD). RSM is a mathematical and statistical technique used for modeling and analysis of experimental data via study of the relation between the response (e.g., removal (%)) and the variables (factors) to obtain the optimum response. In addition, CCD is a kind of RSM including central points with factorial or fractional factorial design and it is widely used for the second-order model. For optimizing the anthracene reduction, three significant factors (i.e., Mg concentration (10−30 mg), glacial acetic acid volume (10−60 μL), and exposure time (0.5−3.0 h)) were investigated. Each factor has three levels: low (−1), medium (0), and high (+1). The experiments were 17 runs and conducted in triplicates (Table 2).

4.4. Samples Analysis. To confirm degradation of the PAHs, the samples were analyzed on GC–MS (Agilent 7683 series II, Wilmington) and GC-FID (Trace Ultra Thermo Scientific). The GC–MS is equipped with an Agilent 5973 mass selective detector, which was used at the operation conditions of 70 eV electron ionization energy, 40−550 m/z scan range, and 250 °C mass interface temperature. The GC column is a DB-5 capillary column (30 m × 0.25 mm i.d. × 0.25 m film thickness) with a helium flow rate of 1.5 mL/min. The temperature of GC oven was programmed at the initial temperature of 80 °C for 1 min then was increased to 300 °C with a heating rate of 10 °C/min and held for 2 min at the final temperature. The injection volume and the injector temperature were 2 μL and 300 °C, respectively. The analysis was achieved in splitless mode. For quantitative analysis, calibration curves of PAHs were achieved in triplicates with good linearity (R^2 > 0.97). The compounds were identified by GC–MS through matching the spectrum obtained with the reference spectra in the NIST library. GC-FID equipped with the same column type of GC–MS is mentioned above. The detector and the injector temperature were 300 °C. The GC-FID oven temperature was programmed to be the same as that of GC–MS. The hydrogen and air flow rates were 40 and 300 mL/min, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00247.

Statistical procedure and selection of optimal parameter for designing anthracene reduction experiments; GC-FID analysis of anthracene and reaction products of anthracene reduction using Mg/EtOH system; results of analysis of variance (ANOVA) of four factors (Mg, graphite, glacial acetic acid, and time) chosen for anthracene reduction experimental design (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES


(32) Wittyarak, I.; Imyin, A.; Wongravee, K. Simultaneous removal of As(III) and As(V) from wastewater by co-precipitation using an experimental design approach. *Desalination Water Treat.* 2016, 57, 16571−16582.


