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# Cycling system for decomposition of gaseous benzene by hydrogen peroxide with naturally Fe-containing activated carbon

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For the removal of volatile organic compounds (VOCs) from environmental systems, gaseous benzene, a model VOC, was adsorbed on naturally Fe-containing activated carbon and subsequently, decomposed in the presence of de-ionized water, and low (0.03%, pH 6.5) and high (30%, pH 2.5) concentration H<sub>2</sub>O<sub>2</sub> solutions. The intermediates produced during benzene decomposition were analyzed and compared using gas chromatography-mass spectrometry. After the decomposition process, the activated carbon sample was air dried. Three cycles were carried out with de-ionized water and low and high concentration H<sub>2</sub>O<sub>2</sub> solutions as oxidants. The adsorption capacity of the activated carbon sample treated with DI water gradually decreased as the number of cycles increased. On the other hand, the benzene adsorption capacity of the activated carbon samples treated with the H<sub>2</sub>O<sub>2</sub> solutions was improved due to the relatively higher specific surface areas of these samples. After treatment with the low-concentration H<sub>2</sub>O<sub>2</sub> solution, intermediates such as glyoxylic acid, oxalic acid, phenol, malonic acid, and pyrocatechol were observed. After treatment with high-concentration H<sub>2</sub>O<sub>2</sub> solution, intermediates such as glyoxylic acid, formic acid, and acetic acid were formed. With increasing H<sub>2</sub>O<sub>2</sub> concentration, the number and the molecular weight of the intermediate formed by the oxidative degradation of benzene, simultaneously decreased. The Fenton reaction induced by naturally Fe-containing activated carbon and H<sub>2</sub>O<sub>2</sub> could lead to more efficient decomposition of benzene.

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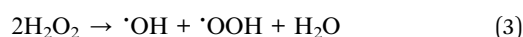
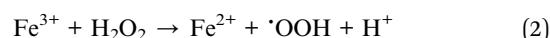
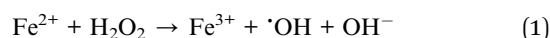
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## 1. Introduction

Volatile organic compounds (VOCs) are environmental contaminants that promote the production of ozone and photochemical smog in air, along with nitrogen oxides (NO<sub>x</sub>).<sup>1,2</sup> Derwent *et al.* defined the photochemical ozone creation potential (POCP) as a parameter for quantifying the level of contribution of a compound to ozone formation.<sup>3</sup> The POCP of a given VOC is expressed as a function of the concentration. Compounds derived from benzene such as 1,2,4-trimethylbenzene, alkylbenzenes, dialkylbenzenes, and trialkylbenzenes account for 30% of the major high-POCP compounds.<sup>4</sup> Thus, various methods of oxidizing VOCs including benzene-derived molecules have been studied. Huang *et al.* proposed the oxidation of benzene by photocatalysis on TiO<sub>2</sub> doped with transition metals (Mn, Co, Cu, and Fe) under UV irradiation. Under vacuum UV irradiation, ozone can react with phototacatalysts to produce O<sub>2</sub> and <sup>•</sup>O. After the reaction of

the produced <sup>•</sup>O with H<sub>2</sub>O, the generated <sup>•</sup>OH can oxidize gaseous benzene.<sup>5</sup> The decomposition of VOCs using hydroxyl radical (<sup>•</sup>OH) produced from H<sub>2</sub>O<sub>2</sub> has been proposed.<sup>6</sup> In the decomposition of organic compounds by hydroxyl radicals, H<sub>2</sub>O<sub>2</sub> can be decomposed into <sup>•</sup>OH using ferrous ions as catalysts in the pH range of 3–3.5, in a process well known as the Fenton reaction. In the Fenton reaction, iron(II) is oxidized to iron(III) by hydrogen peroxide, forming a hydroxyl radical and a hydroxide ion in the process (eqn (1)).<sup>7</sup> Iron(III) is then reduced to iron(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical and a proton (eqn (2)). The net effect is the disproportionation of hydrogen peroxide to create two different oxygen-radical species, with water (H<sup>+</sup> + OH<sup>-</sup>) as a byproduct (eqn (3)).



Recently, Aziz and Kim *et al.* reported the effective oxidation of VOCs on a zeolite (ZSM-5) modified with Fe under UV irradiation.<sup>8</sup> Water molecules adsorbed on ZSM-5 were oxidized to

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H<sub>2</sub>O<sub>2</sub> under UV, and the produced H<sub>2</sub>O<sub>2</sub> could effectively oxidize the VOCs adsorbed on naturally Fe-containing ZSM-5 by the Fenton reaction. Furthermore, Takeuchi *et al.* reported that, compared to a hydrophilic zeolite structure, a relatively hydrophobic zeolite exhibited comparatively high capacity for benzene adsorption.<sup>9</sup> Rey *et al.* compared the adsorption and decomposition of phenol on different pristine commercial activated carbons *versus* on the carbon samples modified with iron(III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>) or iron pentacarbonyl (Fe(CO)<sub>5</sub>).<sup>10</sup> The improved adsorption capacity and decomposition reaction were higher for the modified samples because of the Fenton reaction involving the iron compounds on the activated carbon and H<sub>2</sub>O<sub>2</sub>. Recently, Yang *et al.* reported the oxidation and decomposition of phenol on Zeolite Socony Mobil-5 (ZSM-5) modified with different concentrations of iron compounds and also found that phenol oxidation was maximal on ZSM-5 containing an optimum amount of Fe.<sup>11</sup> In the present study, the benzene adsorption capacity of the activated carbon samples modified by metals was increased. However, for pilot-scale applications, we used naturally Fe-containing activated carbon sample for the effective oxidation of benzene. In this study, (1) gaseous benzene was completely adsorbed on naturally Fe-containing activated carbon sample filled in a reactor and (2) then the various solutions (de-ionized (DI) water and low (0.03%, pH 6.5)- and high (30%, pH 2.5)-concentrated H<sub>2</sub>O<sub>2</sub> solutions) were inserted in the reactor to oxidize the benzene molecules. For the decomposition of benzene, the intermediates were analyzed and compared using gas chromatography-mass spectrometry analysis (GC-MS). Finally, after the oxidation process, (3) the activated carbon sample was dried by air. The steps from (1) to (3) were denoted as “one cycle”. Herein, three cycles were carried out with DI water and low and high concentration H<sub>2</sub>O<sub>2</sub> solutions as oxidants.

## 2. Experimental section

### 2.1. Materials

Coal activated carbon (AC, SGP-100, Samchully Co., Korea) in a pellet type powder (diameter = 4 mm, length = 10 mm) was used as an adsorbent for the VOCs. For application to a mini-column (inner diameter: 6 mm, length: 100 mm), the activated carbon powder was cut and collected with 10–14 mesh (1.4–2.0 mm) using a sieve shaker. The collected activated carbon powder was washed with DI water several times to remove impurities and then dried in a 105 °C oven for 24 h. After drying, to avoid adsorption of water by the washed activated carbon, the sample was stored in a desiccator. The low (0.03%, pH = 6.5) and high (30%, pH = 2.5) concentration H<sub>2</sub>O<sub>2</sub> solutions were prepared using H<sub>2</sub>O<sub>2</sub> (Samchun Co., Korea). The concentration of the solution was confirmed by using a measuring kit (Kyoritsu, Japan).

### 2.2. Benzene adsorption experiment

The naturally Fe-containing activated carbon powder (0.5 g) was loaded into a transparent tube ( $h = 3.2$  cm) that was used as a mini-column and was fixed with static mixers in the top and

bottom of the tube. First, to confirm the maximum benzene adsorption capacity of the prepared activated carbon, benzene gas (100 ppmv) was introduced into the column at a flow rate of 2 L min<sup>-1</sup>. The activated carbon layer and benzene gas were allowed to react for 0.001 s. To investigate the correlation between benzene decomposition and the concentration of H<sub>2</sub>O<sub>2</sub>, DI water and low and high concentration H<sub>2</sub>O<sub>2</sub> solutions were circulated in the column filled with the benzene-adsorbed activated carbon powder at a flow rate of 24 mL min<sup>-1</sup> for 2 h. Air was then introduced into the column at a flow rate of 2 L min<sup>-1</sup> to remove the decomposition benzene products or compounds desorbed from the activated carbon sample. In this study, the cycle comprising the adsorption, oxidation, and desorption processes was performed four times with de-ionized water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions as oxidants, respectively. Fig. 1 show schematic diagram of cycling system for gaseous benzene adsorption and H<sub>2</sub>O<sub>2</sub> oxidation. The output concentration of benzene gas was automatically analyzed every 5 min using a gas chromatography-flame ionization detector (GC-FID, column: Agilent HP-5 (300 cm, 0.32 mm, 0.25 μm)) with a 6-port valve. The adsorption capacity of the columns filled with the activated carbon powder samples treated with DI water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions was calculated and compared by normalizing the input and output concentrations.

### 2.3. Structural and chemical characterization

The N<sub>2</sub> adsorption/desorption isotherms of the activated carbon powder samples treated with DI water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions were characterized using an ASAP 2020 adsorption analyzer (Micromeritics, USA) at 77 K. Before the analysis, all of the samples were degassed at 573 K for 180 min. The specific surface area and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) equation from the data in the relative pressure range of 0.01–0.3 and by applying the Barrett–Joyner–Halenda (BJH) method, respectively. The crystal structure of the samples was confirmed by using an X-ray diffractometer (XRD, Bruker AXS, D2 Phaser, USA) operating at 30 kV and 10 mA with a Cu K<sub>α1</sub> radiation source ( $\lambda = 1.5418$  Å) and a nickel filter. Thermogravimetric analysis (TGA) was conducted using a thermal analyzer (SDTA851, Mettler Toledo) in the range of 25–600 °C under air flow at 60 cm<sup>3</sup> min<sup>-1</sup>. To analyze the surface functional groups of the samples, the Fourier-transform infrared spectra (FT-IR, Vertex 70, Bruker, USA) were acquired with a DLaTGS detector equipped with a KBr window. For the FT-IR analysis, pellet samples were prepared from the fine powder sample and KBr, which were compressed under a pressure of 15 MPa. Gas chromatography-mass spectrometry analysis (GC-MS, 7890B-5977A, Agilent Technologies, USA) with a column (Agilent HP-5MS UI (300 cm, 0.32 mm, 0.25 μm)) was utilized to identify the compounds or intermediates formed during oxidation of benzene by H<sub>2</sub>O<sub>2</sub>. The headspace method was applied for efficient analysis of the VOCs in the liquid solution. The liquid samples were stored in a dark room at <4 °C to prevent transformation of the VOCs. X-ray photoelectron spectroscopy (XPS,

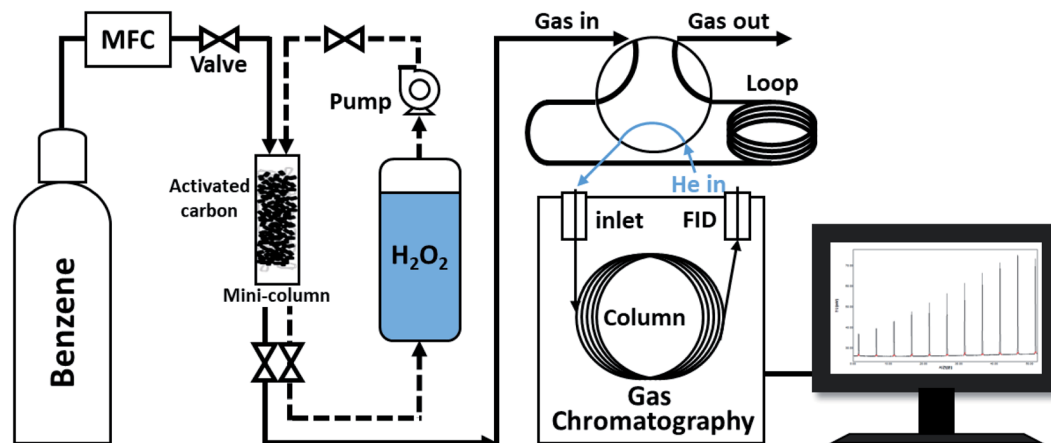


Fig. 1 Schematic diagram of cycling system for gaseous benzene adsorption and  $\text{H}_2\text{O}_2$  oxidation.

Thermo scientific, K-Alpha) was carried out with Al  $K_{\alpha}$  X-ray of 1468.8 eV and beam power of 200 W under a chamber pressure of  $7.8 \times 10^{-9}$  torr.

### 3. Results and discussion

#### 3.1. Evaluation of gaseous benzene adsorption capacity of activated carbon

Fig. 2 shows the benzene adsorption capacity of the as-cleaned activated carbon loaded into the mini-column, measured over one cycle. The maximum average benzene adsorption capacity was  $110.74 \text{ mg g}^{-1}$ , *i.e.*, the maximum amount of benzene adsorption per 1 gram of activated carbon, with breakthrough at a reaction time of  $135 \pm 15$  min. The measured values were utilized to apply to a reactor, filled with activated carbon, linked to GC-FID. After complete adsorption of benzene on the activated carbon, DI water and low- and high-concentration  $\text{H}_2\text{O}_2$  solutions were supplied to the reactor filled with the benzene-adsorbed activated carbon and air was then introduced into the column to remove the benzene decomposition products or desorbed compounds. This process, *i.e.*, benzene adsorption,

solution treatment, and air drying, is denoted as one cycle. Fig. 3 shows the adsorption capacity of the activated carbon samples after the 1<sup>st</sup> cycle. Based on the solution treatment, the benzene adsorption capacity of the activated carbon followed the order: high-concentration  $\text{H}_2\text{O}_2$  (93%) > low-concentration  $\text{H}_2\text{O}_2$  (85%) > DI water (61%).

Fig. 4 presents a comparison of the benzene adsorption capacity of the activated carbon samples treated with DI water and low- and high-concentration  $\text{H}_2\text{O}_2$  solutions. Compared to the adsorption capacity of the cleaned activated carbon, the adsorption capacity of the activated carbon sample treated with DI water gradually decreased as the number of cycles increased. The improvement of the adsorption capacity of the activated carbon samples treated with the  $\text{H}_2\text{O}_2$  solutions in the 1<sup>st</sup> cycle can be attributed to the relative increase in the specific surface area (Table 1). In particular, compared to the activated carbon sample treated with the low-concentration  $\text{H}_2\text{O}_2$  solution, the higher adsorption capacity of the activated carbon sample treated with the high-concentration  $\text{H}_2\text{O}_2$  solution may result

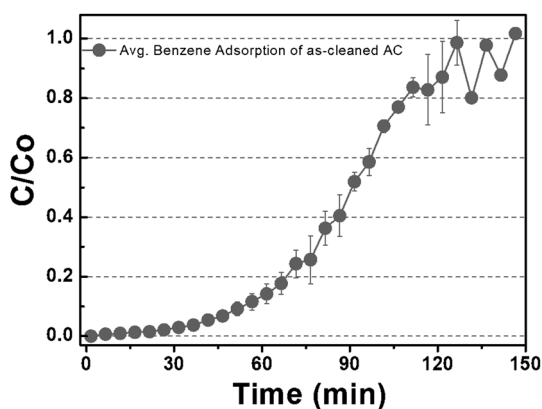


Fig. 2 Gaseous benzene adsorption capacity of the as-cleaned activated carbon sample. (The maximum adsorption capacity of gaseous benzene was observed for 120 min before inserting water and  $\text{H}_2\text{O}_2$ .)

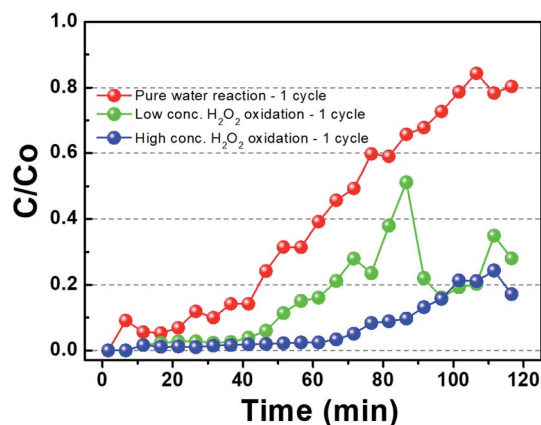


Fig. 3 Gaseous benzene adsorption by activated carbon the presence of hydrogen peroxide for 1 cycle. (Benzene was adsorbed before the saturation and then sufficiently desorbed to calculate the amount of desorption.)

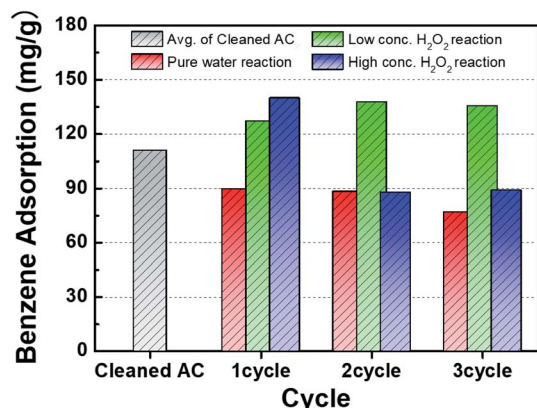


Fig. 4 Comparison of gaseous benzene adsorption on activated carbon samples after treatment with DI water and H<sub>2</sub>O<sub>2</sub> solutions during cycling.

from the higher specific surface area. The contents of H<sub>2</sub>O molecules after H<sub>2</sub>O<sub>2</sub> solution treatment were compared. The hydrophilicity in the activated carbon samples increased as observed from FT-IR analysis (Fig. 8). The activated carbon sample treated with the low-concentration H<sub>2</sub>O<sub>2</sub> solution maintained the maximum adsorption capacity during cycling. However, the adsorption capacity of the activated carbon sample treated with the high-concentration H<sub>2</sub>O<sub>2</sub> solution increased capacity in the 2<sup>nd</sup> cycle, followed by a significant decrease. Specifically, the cycling process in the high-concentration H<sub>2</sub>O<sub>2</sub> solution at pH 2.5 might confer significant hydrophilicity to originally hydrophobic activated carbon sample. Compared to the sample treated with the high-concentration H<sub>2</sub>O<sub>2</sub> solution, the relatively increased hydrophilicity of the surface of the activated carbon sample treated with the high-concentration H<sub>2</sub>O<sub>2</sub> solution may reduce adsorption capacity as benzene is typically hydrophobic.<sup>12,13</sup>

### 3.2. Characterization of the treated activated carbon samples

The specific surface area and pore structure of the activated carbon samples treated with DI water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions were characterized as shown in

Fig. 5 and Table 1. All of the samples exhibited Langmuir-type adsorption on the surfaces, where a monolayer is formed by fast adsorption. Furthermore, it is likely that the activated carbon sample consisted of narrow long pores with irregular inner shapes.<sup>14</sup> Compared to the sample treated with DI water, the surface area of the samples treated with the H<sub>2</sub>O<sub>2</sub> solutions increased, while the pore diameter was maintained at ~2.0 nm, corresponding to a size between super micropores (0.7–2 nm) and small mesopores (2–2.5 nm). Chemical treatment with H<sub>2</sub>O<sub>2</sub>, strongly acidic, or strongly alkaline solutions might lead to the formation of ultra-micropores and the increased benzene adsorption capacity.<sup>15–17</sup> Thus, after treatment with the high-concentration H<sub>2</sub>O<sub>2</sub> solution, the surface area of the activated carbon sample increased after the 2<sup>nd</sup> and 3<sup>rd</sup> cycles.

Fig. 6 shows the XRD patterns of the activated carbon samples treated with DI water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions. The profiles of all of the samples showed the broad main characteristic peaks at ~25° and ~45°, corresponding to the (002) and (100) planes in the carbon crystal structure. In addition, interestingly, peaks of Fe-related phases such as Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, which catalyze carbon formation, were observed. The Fe-related phases can participate in the Fenton reaction, creating two different oxygen-radical species (<sup>•</sup>OH and <sup>•</sup>OOH) through a disproportionation of H<sub>2</sub>O<sub>2</sub>.<sup>6,7</sup> It has been reported that the free radicals can convert benzene into phenol or other oxidation products.<sup>18,19</sup> Thus, it is expected that benzene adsorbed on the naturally Fe-containing activated carbon samples can be hydroxylated or oxidized through the Fenton reaction during treatment with the H<sub>2</sub>O<sub>2</sub> solution (eqn(1)–(3)).

Fig. 7(a) shows the TGA curves of raw activated carbon and the activated carbon samples treated with DI water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions. For the raw activated carbon sample, weight losses of ~1% and ~4% at 80 and 300 °C, respectively, caused by evaporation water molecules of the water molecules on the surface and in the pores (Fig. 7(b)). For the activated carbon sample with the maximum amount of adsorbed benzene, a weight loss of ~15% was observed up to 300 °C. As previously measured, the maximum benzene adsorption for the activated carbon used in this study was 110.74 mg g<sup>-1</sup>, corresponding to ~10% of the total weight of the activated carbon. Thus, the weight loss of ~15% may be the sum of adsorbed benzene (~10%) and water molecules (~4%). The

Table 1 Characteristics of specific surface area and pore structure for the activated carbon samples after treatment with DI water and H<sub>2</sub>O<sub>2</sub> solutions during cycling

Activated carbon	Cycle	BET surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Meso surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Micro surface area <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	Micro pore volume <sup>c</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter <sup>d</sup> (nm)
Raw	—	682	212	470	0.23	2.06
Pure water reaction	1	675	176	499	0.23	2.06
Low conc. H <sub>2</sub> O <sub>2</sub> oxidation	1	714	190	524	0.25	2.05
Low conc. H <sub>2</sub> O <sub>2</sub> oxidation	3	681	184	497	0.23	2.06
High conc. H <sub>2</sub> O <sub>2</sub> oxidation	1	743	203	539	0.26	2.05
High conc. H <sub>2</sub> O <sub>2</sub> oxidation	3	775	238	537	0.25	2.05

<sup>a</sup> Calculated using BET equation. <sup>b</sup> Calculated using *t*-plot equation. <sup>c</sup> Pore volume evaluated from the N<sub>2</sub> adsorption–desorption isotherms. <sup>d</sup> Peak pore size determined from BJH desorption branch.

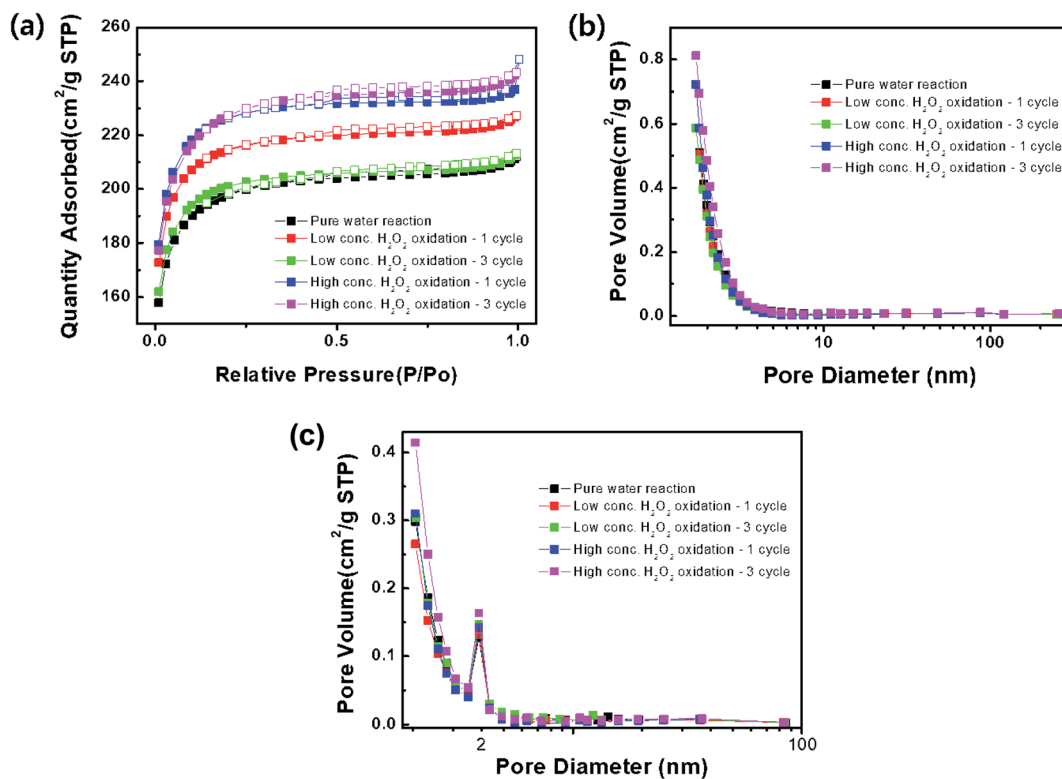


Fig. 5 (a) N<sub>2</sub> adsorption (closed squares)–desorption (open squares) isotherms, (b) BJH adsorption and (c) desorption branch.

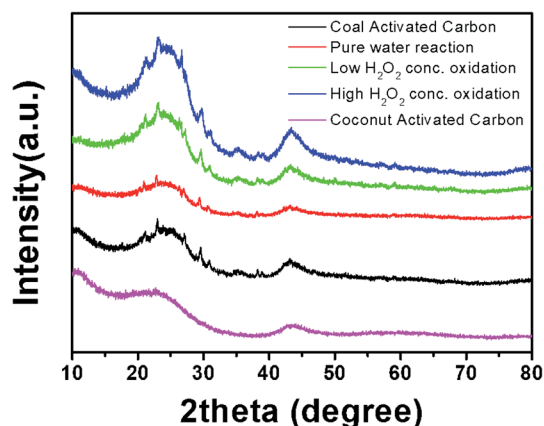


Fig. 6 XRD patterns of activated carbon samples after treatment with DI water and H<sub>2</sub>O<sub>2</sub> solutions during cycling.

weight losses in the activated carbon sample treated with the low-concentration H<sub>2</sub>O<sub>2</sub> solution might result from minor water evaporation at 80 °C (~1%) and the evaporation of benzene at >80 °C. Compared to the activated carbon sample treated with the low-concentration H<sub>2</sub>O<sub>2</sub> solution, the activated carbon sample treated with and high-concentration H<sub>2</sub>O<sub>2</sub> solution exhibited a greater weight loss of ~3% at 80 °C, suggesting a partial transition of the activated carbon sample from hydrophobic to hydrophilic.<sup>12,13</sup>

Fig. 8 shows the FT-IR spectra of the activated carbon samples treated with DI water and low- and high-concentration

H<sub>2</sub>O<sub>2</sub> solutions. The main characteristic peak at 3550–3200 cm<sup>-1</sup> corresponds to the hydroxyl (O–H) stretching group, which may be related to the hydrogen bonding from adsorbed water molecules, alcohol, or phenol compounds.<sup>15,20,21</sup> In particular, the FT-IR profiles of the samples treated with the H<sub>2</sub>O<sub>2</sub> solutions showed the characteristic peak corresponding to the O=C=O group at ~2349 cm.<sup>22–24</sup> Compared to the sample treated with the low-concentration H<sub>2</sub>O<sub>2</sub> solution, the characteristic peak at 3550–3200 cm<sup>-1</sup> in the profile of the activated carbon sample treated with the high-concentration H<sub>2</sub>O<sub>2</sub> solution indicates relatively increased hydrophilicity of the activated carbon because of the hydroxyl (O–H) group.<sup>25–27</sup> Even though the activated carbon sample treated with the high-concentration H<sub>2</sub>O<sub>2</sub> solution has higher surface area than low-concentration H<sub>2</sub>O<sub>2</sub> solution, the benzene adsorption capacity of the activated carbon sample treated with high-concentration H<sub>2</sub>O<sub>2</sub> was reduced because of the increased hydrophilicity of catalyst.<sup>20,21,27</sup> Fig. 9 shows the XPS C 1s and Fe 2p spectra of the activated carbon samples before and after treatment with DI water and H<sub>2</sub>O<sub>2</sub> solutions. Especially, the chemical state and the existence of Fe in the activated carbon samples prepared with coal as a carbon source was compared with the activated carbon prepared with coconut as a carbon source. In the C 1s spectra, all the sample exhibited the XPS characteristic peaks at 282.8, 286.0, and 286.6 eV corresponding to graphitic carbon (C–C), hydrocarbon (C–H), and hydroxyl group (C–OH), respectively.<sup>28,29</sup> However, in contrast to the activated carbon prepared with coconut, the activated carbon samples prepared with coal contained the chemical states of Fe<sup>2+</sup> (~708.4 eV) and Fe<sup>3+</sup>

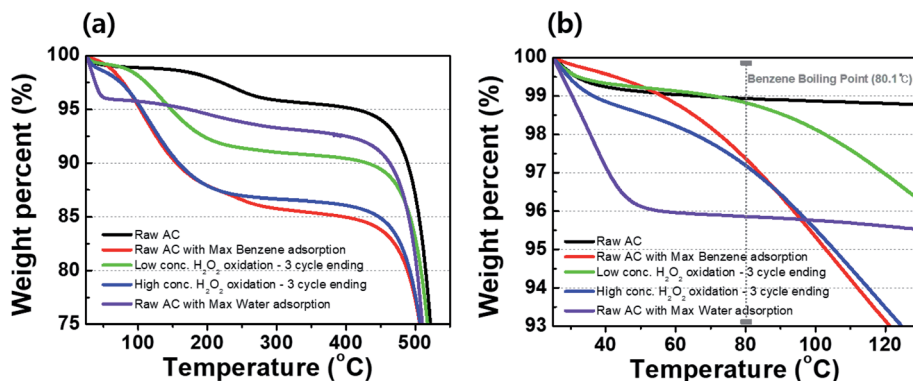


Fig. 7 TGA curves of activated carbon samples after treatment with DI water and  $\text{H}_2\text{O}_2$  solutions during cycling in (a) the wide range and (b) the vicinity of a boiling point of benzene.

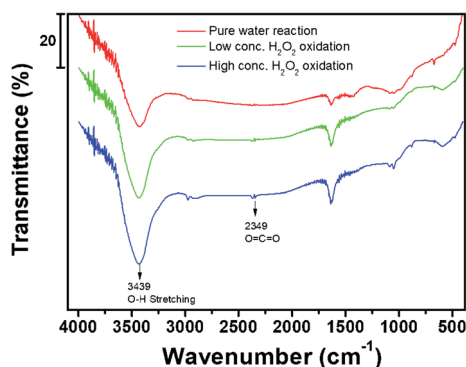
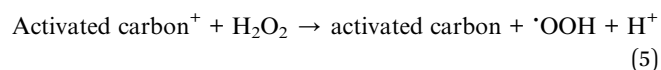
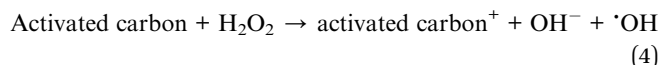


Fig. 8 FT-IR spectra of activated carbon samples after treatment with DI water and  $\text{H}_2\text{O}_2$  solutions during cycling.

( $\sim 711.3$  eV) mainly resulting from  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ , respectively, which may contribute to the Fenton reaction during treatment with the  $\text{H}_2\text{O}_2$  solution.<sup>30</sup>

### 3.3. Benzene decomposition

In the Fenton reaction, the Fe-related phases and  $\text{H}_2\text{O}_2$  could produce two oxygen-radical species *via* the disproportionation of  $\text{H}_2\text{O}_2$ .<sup>31</sup> Thus, during treatment with the  $\text{H}_2\text{O}_2$  solution, benzene adsorbed on the naturally Fe-containing activated carbon samples can be hydroxylated or oxidized to phenol or other oxidation products.<sup>18,19</sup> It was reported that  $\text{H}_2\text{O}_2$  on activated carbon could be decomposed into hydroxyl groups based on the Haber–Weiss mechanism and that the formation rate of hydroxy radicals at  $\text{pH} > 8.0$  might be low.<sup>32–34</sup>



The intermediates adsorbed on the activated carbon samples treated with DI water ( $\text{pH} = 7.0$ ) and low- ( $\text{pH} = 6.5$ ) and high

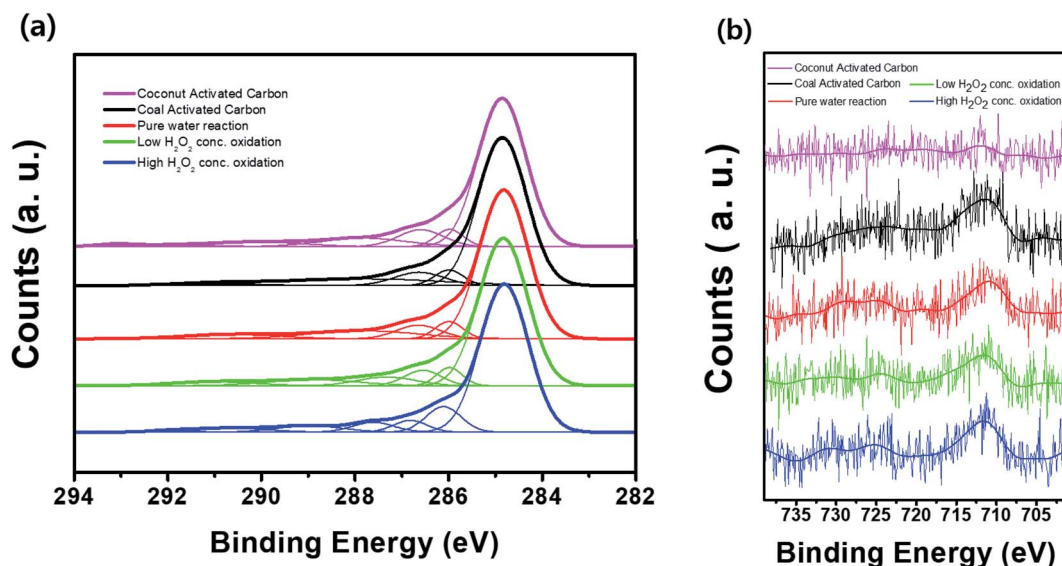

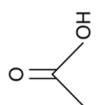
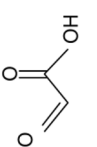
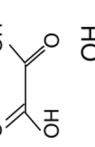
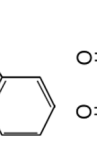
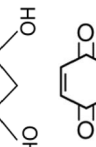
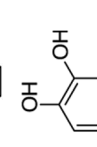
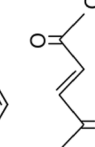
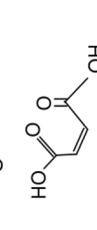



Fig. 9 XPS (a) C 1s and (b) Fe 2p spectra of the activated carbon samples before and after treatment with DI water and  $\text{H}_2\text{O}_2$  solutions during cycling.

Table 2 Comparison of intermediates adsorbed on the activated carbon samples treated with DI water and H<sub>2</sub>O<sub>2</sub> solution

Results		Low H <sub>2</sub> O <sub>2</sub>		High H <sub>2</sub> O <sub>2</sub>			
Reaction	Pure water	Molecular weight	Intermediates	Molecular weight	Intermediates		
Division	Molecular weight	Intermediates	Molecular weight	Intermediates	Structure	Reference	
1	—	—	—	46.03	Formic acid	 <chem>O=C(O)</chem>	Liu <i>et al.</i> , 2017 (ref. 19); Hara, 2017 (ref. 18)
2	—	—	—	60.05	Acetic acid	 <chem>CC(=O)O</chem>	Liu <i>et al.</i> , 2017 (ref. 19); Hara, 2017 (ref. 18)
3	74.04	Glyoxylic acid	74.04	Glyoxylic acid	 <chem>O=C(O)C=O</chem>	Hara, 2017 (ref. 18)	
4	90.03	Oxalic acid	90.03	Oxalic acid	 <chem>O=C(O)C(=O)O</chem>	Liu <i>et al.</i> , 2017 (ref. 19); Hara, 2017 (ref. 18)	
5	—	—	94.11	Phenol	 <chem>Oc1ccccc1</chem>	Liu <i>et al.</i> , 2017 (ref. 19); Hara, 2017 (ref. 18)	
6	104.06	Malonic acid	104.06	Malonic acid	 <chem>O=C(O)CC(=O)O</chem>	Hara, 2017 (ref. 18)	
7	108.10	<i>p</i> -Benzoquinone	—	—	 <chem>O=C1C=CC(=O)C=C1</chem>	Liu <i>et al.</i> , 2017 (ref. 19)	
8	—	—	110.01	Pyrocatechol	 <chem>Oc1ccccc1O</chem>	Liu <i>et al.</i> , 2017 (ref. 19)	
9	116.07	Fumaric acid	—	—	 <chem>O=C(O)/C=C/C(=O)O</chem>	Hara, 2017 (ref. 18)	
10	116.07	Maleic acid	—	—	 <chem>O=C(O)C=CC(=O)O</chem>	Hara, 2017 (ref. 18)	

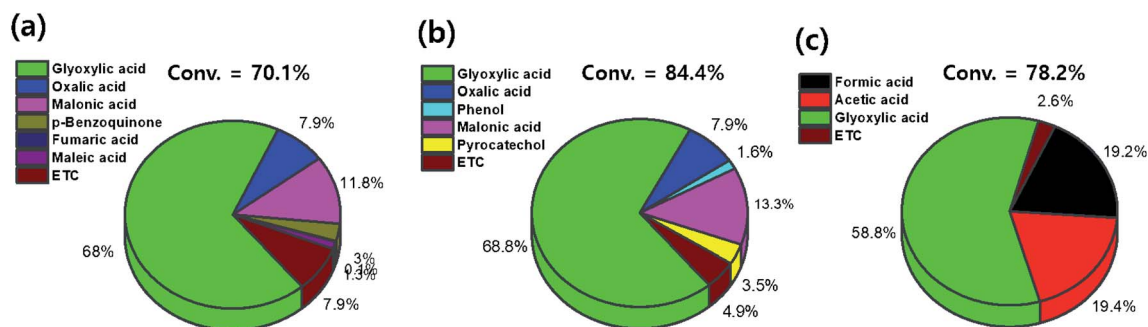


Fig. 10 Conversion of benzene and selectivity of the intermediates on activated carbon treated with (a) pure water, (b) low-conc. H<sub>2</sub>O<sub>2</sub>, and (c) high-conc. H<sub>2</sub>O<sub>2</sub> solutions.

(pH = 2.5)-concentration H<sub>2</sub>O<sub>2</sub> solutions were characterized using GC-MS (Table 2).

Furthermore, the conversion of benzene and selectivity of intermediates after treatments were determined from the GC-FID data as follows:

$$\text{Conversion} = \frac{(\text{benzene ads. (mg g}^{-1}) - \text{benzene des. (mg g}^{-1}))}{\text{benzene ads. (mg g}^{-1})} \times 100(\%) \quad (6)$$

$$\text{Selectivity} = \frac{\text{portion of one intermediate}}{\text{all intermediates}} \times 100(\%) \quad (7)$$

The conversion values of benzene after treatments with DI water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions were 70.1%, 84.4%, and 78.2%, respectively. After treatment with the low-concentration H<sub>2</sub>O<sub>2</sub> solution, intermediates such as glyoxylic acid (68.8%), oxalic acid (7.9%), phenol (1.6%), malonic acid (13.3%), and pyrocatechol (3.5%) were observed (Fig. 10). Furthermore, after treatment with the high-concentration H<sub>2</sub>O<sub>2</sub> solution, intermediates such as formic acid (19.2%) and acetic acid (19.4%) were dominantly detected. With increasing H<sub>2</sub>O<sub>2</sub> concentration, the number and the molecular weight of the intermediates, formed by the oxidative degradation of benzene, simultaneously decreased. In general, organic compounds and aromatic compounds can be effectively oxidized by the hydroxy groups formed in the H<sub>2</sub>O<sub>2</sub> solution upon treatment with Fe or UV radiation.<sup>8,35</sup> However, it is interesting that even after the oxidative degradation of benzene *via* treatment with DI water, various resulting intermediates such as glyoxylic acid, oxalic acid, malonic acid, *p*-benzoquinone, fumaric acid, and maleic acid were observed. This demonstrates that benzene can be decomposed into various intermediates by heat generated from the reaction of activated carbon with DI water or H<sub>2</sub>O<sub>2</sub> solution.<sup>19,36–39</sup> Thus, the paths for decomposition of benzene involve benzene ring excitation or pyrolysis.<sup>40,41</sup> However, herein, in the first step (in DI water), benzene was decomposed into maleic acid and fumaric acid (Table 2). The decomposition intermediates were then decomposed into glyoxylic acid, malonic acid, and oxalic acid through the 2<sup>nd</sup> step (in low-concentration H<sub>2</sub>O<sub>2</sub> solution). Finally, the intermediates were

decomposed into acetic acid and/or formic acid through high-concentration H<sub>2</sub>O<sub>2</sub> solution. Consequently, in this study, the Fenton reaction in the presence of the naturally Fe-containing activated carbon and H<sub>2</sub>O<sub>2</sub> could lead to more efficient decomposition of benzene due to the hydroxyl radicals produced during the Fenton reaction.

## 4. Conclusions

In summary, gaseous benzene adsorbed on naturally Fe-containing activated carbon was decomposed using de-ionized water and low- and high-concentration H<sub>2</sub>O<sub>2</sub> solutions. Compared to the activated carbon sample treated with DI water, the benzene adsorption capacity of the activated carbon samples treated with the H<sub>2</sub>O<sub>2</sub> solutions was improved due to an increase in the specific surface area. In addition, with increasing H<sub>2</sub>O<sub>2</sub> concentration, the number and molecular weight of the intermediates, formed by the oxidative degradation of benzene simultaneously decreased. Consequently, the Fenton reaction in the presence of the naturally Fe-containing activated carbon and H<sub>2</sub>O<sub>2</sub> could lead to the more efficient decomposition of benzene due to the hydroxyl radicals produced during the reaction.

## Conflicts of interest

There are no conflicts to declare.

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