Catalytic Degradation of Polychlorinated Biphenyls with Activated Carbon-Supported Iron

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Summary
The processes generated exhaust gas with low-concentration PCBs in large quantities after destroying high-concentration PCBs, which still cannot be disposed of. In present, activated carbon (AC) is used to adsorb residual PCBs after disposal of high level PCBs. In this study, we try to destroy PCBs of low concentration on the AC.

AC can be used as a catalyst support in many reactions, including those reducing the concentrations of organic compounds. On the other hand, the transition metal iron can be used to dechlorinate organohalogen compounds. This study presents two methods for producing AC-supported iron. A novel method prepared AC with highly dispersed Fe by the carbonization of ion-exchange resins. AC prepared by this method was called IRFe-AC. Another AC-supported iron, LaFe-AC, was produced by impregnating AC with iron ion solution. Since IRFe-AC contains a large amount of Fe, all the PCB-153 was destroyed under the conditions tested. Moreover, the biphenyl generated in the dechlorination of PCB-153 was destroyed eventually.

Key words: PCBs, activated carbon, catalyst, AC-supported, dechlorination

INTRODUCTION
Since polychlorinated biphenyls (PCBs) were first made in 1881\textsuperscript{1}, they have been used as the heat-transfer medium or electric insulation oil in electrical transformers and capacitors because of their excellent stability and thermal properties\textsuperscript{2}. In a fifty-year period, approximately 1.4 billion pounds of PCBs have been produced worldwide, and such extensive application of these compounds has resulted in widespread contamination\textsuperscript{3}. Owing to their persistence and propensity to bio-accumulate in the fatty tissues of animals, and to induce skin lesions and tumors in animals, the manufacture of PCBs in Japan ceased in 1974 with the passage of the Law Concerning the Examination and Regulation of Manufacture, Etc. of Chemical Substances (LERMCS), and was ended in the USA in 1977 with the Toxic Substances Control Act. However, a large fraction of all the PCBs that were produced is still present in the environment. During the period 1930 through 1970 cumulative losses of PCBs to the environment amounted to 354,000 tons\textsuperscript{4}. Therefore, remediation of PCB-contaminated soils, groundwater, and sediments has become a major environmental management problem.

PCBs are principally destroyed by incineration, which has become the most widely used technique for their removal\textsuperscript{5}. Under an oxygen atmosphere, however, dioxins can be generated from PCBs. Therefore, the need for the other chemical decomposition methods was recognized in amendments to the Waste Disposal and Public Cleaning Law in 1998, in Japan. According
to the Law Concerning Special Measures against PCB Waste, enacted in 2001, all PCB wastes should be destroyed within 15 years. Therefore, other methods for destroying PCBs have been proposed, including wet air oxidation\(^5\), biodegradation\(^6\), dehalogenation decomposition, including sodium metal-promoted dehalogenation\(^7\), and catalytic destruction, including reaction with superoxide\(^8\), photolysis in the presence of hydrogen donors\(^9\), and electrolytic reduction\(^10\).

Presently, these methods destroy most of the PCBs in high-concentration solutions; however, the processes generate exhaust gas with low-concentration PCBs in large quantities, which cannot be emitted without treatment. The use of activated carbon (AC) to absorb the residual PCBs has been developed and AC can be disposed of by incineration; however, this involves many problems, such as the high construction and maintenance costs of high-temperature or high-pressure equipment, the generation of dioxins in the incinerator, and the risk of PCB exposure during the conveyance and pulverization process of AC before incineration. Therefore, it is important to find an inexpensive, safe method to dispose of the low-concentration PCB waste derived from processing high-concentration solutions.

Activated carbon is not only a strong adsorbent; it can also be used as a catalyst support in many reactions\(^11\)-\(^14\). On the other hand, transition metals are reported to dechlorinate PCDD and PCDF derivatives and other chlorinated compounds\(^15\). Iron or iron compounds can be used as catalysts to decompose PCBs\(^16\). In this study, we tried to utilize the synergism between AC and iron, so AC-supported iron was made to decompose low concentrations of PCBs. Two methods were used to make AC-supported iron: one used an ion-exchange resin, and the other method impregnated AC with iron using an iron solution, followed by carbonization.

**EXPERIMENTAL**

**Preparation of AC-supported Fe using an ion-exchange resin**

The raw resin used was a metacrylic acid type resin (Mitsubishi Chemical, WK-11). Since the resin was a weak acid type, it had to be exchanged under an alkaline aqueous solution. In such an alkaline solution, the occurring iron deposition obstructed the exchange process. So the H cations couldn’t be exchanged by iron cations directly. On the other hand, since the exchange capacity of iron cations is stronger than that of sodium cations,\(^10\) we exchanged H cations with sodium cations initially, and then exchanged the sodium cations with iron cations. The as-received ion-exchange resin (26 g) was treated in 200 m\(^3\) of 1 M NaOH solution to prepare resin exchanged with sodium. Then, this cation resin was poured with 200 m\(^3\) of 1 M Fe\(^{5+}\) solution for 1 h. The exchanged resin was then rinsed by deionized water and vacuum dried at 70 °C for 24 hours. The iron ion-exchanged resin was heated up to 700 °C at a rate of 10 °C/min and held at 700 °C for 20 minutes, in a nitrogen stream (300 m\(^3\)/min) to carbonize it\(^16\). The AC-supported iron made by using this method was called IRFe-AC.

**AC impregnated with iron ion solution**

Fifty gram of AC was added to 8.9×10\(^{-2}\) M iron(II) lactate solution at room temperature with vigorous stirring. The impregnated catalyst was dried at 105 °C for 24 hours. Then, the impregnated catalyst was heated under a nitrogen stream (300 m\(^3\)/min), up to a final temperature of 700 °C and maintained for 20 min. The AC-supported iron obtained by this method was called LaFe-AC.

**Characterization of AC-supported iron**

A sample of each AC-supported iron was decomposed in a digestion apparatus MDS-2000 (CEM, Mathews, NC) to obtain an aqueous solution of iron. Then, the solution was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (IRIS-Intrepid ICAP Thermo Electron) to measure the amount of iron supported in the AC.

The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume were derived from the N\(_2\) adsorption-desorption isotherms at 77 K using an ASAP 2400 (Shimadzu) vacuum volumetric sorption instrument. Before the N\(_2\) sorption analysis, 0.15 g samples were preheated at 403 K for about 15 hours to remove any physisorbed material from the small pores. The particle size distribution of sample was measured using a laser diffraction particle size analyzer (SALD-2100, Shimadzu). About 0.3 g of AC was put into a glass funnel (maximum i.d. at the top: 50 mm, sleeve pipe i.d.: 5 mm) and the powder was subjected to mechanical vibration.
The form and surface texture of the carbonized resin and activated carbon were examined using scanning electron microscopy (SEM) (JSM-5600T, JEOL) and energy dispersive spectroscopy (EDS) (EX-23000BU, JEOL). SEM photos of the surface of the sample were taken, and an elemental analysis of the representational point in each photo was conducted using EDS.

X-ray photoelectron spectra (XPS) were obtained with an ESCA-3200 (Shimadzu) spectrometer using Mg Kα (1253.6 eV) radiation and a retarding potential analyzer.

After carbonization at 700 °C, the AC-supported iron was characterized using X-ray diffraction (RINT-Ultima PC, Rigaku) to examine the graphite-like structure after loading the AC with Fe during carbonization, and the crystal structure of iron compounds on the AC.

To investigate the changes in the functional groups with carbonization, Fourier transform infrared spectroscopy (FTIR) analysis was used. All the IR spectra were measured at 4 cm⁻¹ resolution on an FTIR spectrometer (FT-IR8400, Shimadzu). The samples were prepared in the standard manner in KBr using the modified pitch (D15) with a KBr ratio of 1:100.

**Test decomposition system**

The PCB used in this study was PCB-153, which is the main component in Kanechlor 600, a Japanese commercial PCB mix. Fig. 1 shows a schematic diagram of the test decomposition system. The length of silica tube was 700 mm, and the inner diameter was 20 mm. One milliliter of PCB-153 solution (10 μg/mℓ -hexane) was injected at the inlet of the electric furnace and the decomposition process was continued for 2 hours. After decomposition time arrived, the reaction atmosphere of nitrogen was kept, and the decomposition equipment was air-cooled down to room temperature for 30 minutes. The exhaust gas was introduced to impingers filled with 100 mℓ -hexane) was injected at the inlet of the electric of toluene to collect products after decomposition. PCB homologues and biphenyl trapped in toluene and adsorbed on AC-supported iron after decomposition were quantified using gas chromatography-mass spectrometry.

**Gas Chromatography-Mass Spectrometry (GC-MS) Analysis**

The analysis was performed on a GC-2010 series gas chromatograph (Shimadzu) equipped with a capil-
Results and Discussion

Carbonization behaviors of AC

Characterization of AC

Table 1 lists the surface area, pore volume, and particle size distribution of the two kinds of AC which we made, and those of the original AC was also shown. The median particle size of LaFe-AC was three times larger than that of IRFe-AC, while LaFe-AC had also higher BET surface area and greater porosity. On the other hand, the median particle of LaFe-AC was 5 % smaller than that of original AC, the surface area and the pore volume of LaFe-AC was 10 % smaller than that of original AC. Generally, BET surface area and porosity reflect the adsorption capacity of AC, and they are strongly correlated. These results imply that LaFe-AC had the adsorption capacity as original AC.

Characterization of AC-supported iron

The Fe concentration in IRFe-AC was 374mg/g-AC, which was eight times more than that in LaFe-AC (45.1 mg/g-AC). SEM images of IRFe-AC and LaFe-AC are shown in Fig. 2. The image in Fig. 2(a) shows the high density and high distribution of Fe on both the surface and within IRFe-AC. Fig. 2(b) shows the high density of Fe on the surface of LaFe-AC, and the low density of Fe inside LaFe-AC. The results of the EDS elemental analysis are shown in Fig. 3; Four points (point 1~4) were analyzed to check the deviations between location. As with the ICP-AES, there was more Fe in IRFe-AC than in LaFe-AC. Moreover, IRFe-AC also contained more oxygen than LaFe-AC. The oxygen in IRFe-AC likely originated from the carboxyl group of the ion exchange resin. The surface atomic composition was measured using XPS. The surface of both samples was composed mainly of carbon, oxygen, and iron. The proportion of Fe on IRFe-AC and LaFe-AC was 5.2 and 8.0 %, respectively. The XPS results differed from those of ICP-AES and SEM-EDS, indicating that the Fe was also inside the IRFe-AC, while most of the Fe was on the surface of LaFe-AC. Fig. 4 shows the X-ray diffraction patterns of the AC-supported iron. Fe metal was the greatest component in IRFe-AC, while FeO, was the greatest compo-

<table>
<thead>
<tr>
<th>AC</th>
<th>BET surface area (m²/g)</th>
<th>BJH description cumulative pore volume of pores (m³/g)</th>
<th>Average pore radius (Å)</th>
<th>Median particle diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BJH(adsorption) BJH(desorption) &lt;10 Å micropores</td>
<td>pore volume of all the pores (P/P0=0.98) Å</td>
<td></td>
</tr>
<tr>
<td>IRFe-AC</td>
<td>110</td>
<td>0.061 0.041 0.038</td>
<td>0.074</td>
<td>17.0</td>
</tr>
<tr>
<td>LaFe-AC</td>
<td>1447</td>
<td>0.499 0.356 0.561</td>
<td>0.668</td>
<td>18.5</td>
</tr>
<tr>
<td>AC</td>
<td>1582</td>
<td>0.550 0.396 0.614</td>
<td>0.733</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Fig. 2  SEM images of IRFe-AC (a) and LaFe-AC (b)
*The concentration of Fe improved as the color of color bar changed from black to red.
ment in LaFe-AC. Because IRFe-AC was made under a reducing atmosphere, the chemical element of Fe was the greatest component. On the other hand, a part of Fe (III) ion was reduced during the carbonization process.

**Decomposition Experiment**

The efficiency with which the two AC-supported irons destroyed PCB-153 was expressed using the decomposition rate, calculated using:

\[ \text{Decomposition rate(\%)} = \left(1 - \frac{c}{c_0}\right) \times 100\% \quad (1) \]

where \(c_0\) is the original concentration of PCB-153 before decomposition, while \(c\) is the residual concentration of PCB-153 after the decomposition process.

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**Fig. 3** EDS analysis of IRFe-AC (a) and LaFe-AC (b)

**Fig. 4** XRD patterns of IRFe-AC (a) and LaFe-AC (b)
Effect of the space velocity (SV) of the decomposition equipment

Decomposition experiment was carried out at 350 ºC for 120 min. Fig. 5 shows the decomposition rate for different SV values under nitrogen. With IRFe-AC, the decomposition rate exceeded 99.8 %. The decomposition rate of LaFe-AC with an SV of 300 h⁻¹ was 96.7 %, which was slightly higher than the value of 93.9 % for 600 h⁻¹. Although Ukisu proposed that dioxin decomposition decreased as SV increased, the results of this study did not show the clear relationship between SV and decomposition rate in the SV range of 300 to 600 h⁻¹.

Fig. 5 (b) shows the products partition after decomposition. As PCBs homologues and biphenyl had low ratio during the products, PCB-153 may cleave to small fraction in this reaction. As well, according to the FTIR results (shown in Fig. 6), IRFe-AC contains ether (1650 cm⁻¹) and ketone (1220 cm⁻¹) groups, while LaFe-AC has a ketone group (1660 cm⁻¹) that can damage the oxygen bridge in dioxin. The fact indicated that the bridge between two benzene nuclei was probably damaged by acidic oxides on the AC surface.

Influence of stove temperature

At 300 and 350 ºC, the decomposition rate of PCB-153 with IRFe-AC was 97.9 and 99.9 %, respectively. Especially at 350 ºC, the PCB-153 was eventually converted to biphenyl and other substances (Fig. 7(b)). On the other hand, the decomposition rate of PCB-153 with LaFe-AC as the catalyst was 30.9 % at 300 ºC and 93.9 % at 350 ºC (Fig. 7(a)). At 350 ºC, with LaFe-AC, about 90 % of the products were biphenyl and other substances (Fig. 7(b)). In case of 300 ºC, re-
Fig. 6  FT-IR spectra of IRFe-AC and LaFe-AC

Fig. 7  Decomposition rate (a), decomposition products (b) and ratio of PCB homologues with different stove temperatures
Residual PCB-153 was found on AC-supported iron and was not trapped in toluene. It can be considered that at low temperature adsorption process played more important role than decomposition process.

Influence of Experimental time

When IRFe-AC was used as a catalyst, the decomposition rate did not vary much with time, as shown in Fig. 8. With experimental times of 30, 60, and 120 min, all the decomposition rate with IRFe-AC were over 99%. On the other hand, using LaFe-AC as a catalyst, the decomposition rate increased with the reaction time improved, and the amount of residual PCB was reduced as the reaction time increased. For experimental times of 30, 60, and 120 min, the decomposition rate with LaFe-AC were 64.5, 77.5, and 93.9%. Therefore, decomposition reaction was fast when IRFe-AC used as a catalyst, and 30 min was sufficient for PCB-153 decomposition. While LaFe-AC was used as a catalyst, the decomposition process was slowly. For the residual PCB-153 was detected on LaFe-AC and was not trapped in toluene, it had a possibility that adsorption process was converted to decomposition process as the experimental time improved.

The effects of AC-supported iron characteristics on the decomposition rate

Despite the smaller BET surface area and porosity of IRFe-AC, the decomposition rate with IRFe-AC was higher than that with LaFe-AC under the same conditions. Therefore, the catalytic reaction might play a more important role than the adsorption process.

Previously, we showed that the decomposition rate was low when iron compounds were used as a catalyst.

![Fig. 8 Decomposition rate (a), decomposition products (b) and ratio of PCB homologues with different experimental time](image-url)
to destroy PCBs under an air atmosphere\textsuperscript{10}. Nevertheless, in this study, AC-supported iron had a high decomposition capacity under \(N_2\) atmosphere. The AC-supported iron appears to have a higher catalytic capacity than iron, iron compounds\textsuperscript{18}. Under \(N_2\) atmosphere, at 350 °C, the decomposition rate with AC alone was about 82\% (as shown in Fig. 7). Both of IRFe-AC and LaFe-AC showed higher catalytic capacity than AC alone under the same condition. As well, according to the decomposition products, the homologues of PCBs by AC alone were more than by AC-supported iron. Because at the higher temperature of 350 °C, AC-supported iron showed a higher catalytic capacity than AC alone, we could suppose that it had the same tendency at the lower temperature of 300°C. Therefore, AC-supported iron appears to have a higher catalytic capacity than AC alone.

**CONCLUSIONS**

AC-supported iron can be used as a catalyst for the decomposition of PCBs.

A novel method for preparing activated carbon with Fe from an ion-exchange resin was proposed. When a large amount of highly dispersed Fe was loaded on the AC, all the PCB-153 was destroyed within 30 min at 300 °C. With the IRFe-AC catalyst, under \(N_2\) atmosphere, the decomposition rate of PCB-153 exceeded 99.8 \%, and the main product of biphenyl was destroyed eventually. The decomposition process likely destroyed the bridge between the benzene rings of the PCB by acidic oxides on the AC surface.

With LaFe-AC, which was AC impregnated with iron ion solution, the decomposition rate of PCB-153 was 99.9 \% under air at 350 °C and a reaction time of 120 min. With LaFe-AC, the decomposition rate improved as the reaction time increased.

**REFERENCES**

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