STUDY ON THE BIODEGRADATION OF POLYCHLORINATED BIPHENYLS BY INDIGENOUS AEROBIC MICROORGANISMS IN TIAWAN

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Introduction

Well-known as ubiquitous environmental contaminants, polychlorinated biphenyls (PCBs) exist as complex mixtures of up to 209 potential congeners. It is possible for PCBs to be oxidatively degraded under aerobic conditions, but such processes generally occur only with congeners having five or fewer chlorines.^{1, 2} Sequential anaerobic-aerobic degradation schemes have been suggested as a means of taking advantage of the different characteristics of anaerobic and aerobic microorganisms--the former better for attacking more highly chlorinated biphenyls and the latter better for oxidizing less chlorinated biphenyls.³ The anaerobic microbial communities most often found in river sediments show varying effectiveness in reductively dechlorinating commercial PCB mixtures, typically accumulating less chlorinated ortho- and ortho- plus para-chlorinated congeners.^{4, 5} Aerobic microorganisms attack and occasionally grow on major congeners that are the products of anaerobic dechlorination.

The broad range of properties found among PCB congeners means that they are matched with certain biodegrading properties of individual aerobic microbes. For this project we considered two physicochemical properties: partition coefficient and chromatographic data. Partition coefficient refers to the retention time measured for PCB congeners analyzed with a high performance liquid chromatograph (HPLC) equipped with a C-18 column. Chromatographic data (ln RRT), one of several expressions of extra thermodynamics, reflects changes in enthalpy and entropy values in molecules that pass through a chromatographic column. Specifically, our goal was to determine relationships between DT_{50} (the time required for a PCB congener to disappear to half of its initial concentration) and these two properties.

Materials and methods

Indigenous microorganisms were eluted from sediment samples taken from the Er-Jen River in Tainan prefecture in southern Taiwan--a known site of industrial wastewater pollution for over 20 years. The microorganisms were maintained at 30°C on mineral medium containing biphenyls (1 g/liter) as a carbon source.

Retention time (RT-HPLC) values for a specific number of PCB congeners were established via isocratic liquid chromatography. The apparatus used for this experiment consisted of a high performance liquid chromatograph (Hitachi, pump L-7100) equipped with a UV-detector (L-7400) and C-18 column (E. Merck LiChoCART 250-4 cartridge Purospher[®] RP-18, 5 um). The mobile phase (1 ml/min) consisted of acetonitrile and distilled water (80:20 v:v).

PCB congener retention time (RT-GC) values were also established via isothermic gas chromatography. To minimize the effects of changes in entropy, column temperatures were set at 220°C. Most PCB congeners are liquid at that temperature, but 2, 3, 4, 5, 6, 2, 3, 4, 5, 6-decachlorobiphenyl (2, 3, 4, 5, 6, 2, 3, 4, 5, 6-CBp) exists as a solid and several dichlorobiphenyls maintain a gaseous state at that temperature. Our gas chromatograph (Varian 3600, Walnut Creek, CA) was equipped with an electron capture detector (ECD) and a DB-5 fused silica **ORGANOHALOGEN COMPOUNDS**

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capillary column (0.53 mm ID X 30 m, film thickness 1.5 μ m) (J&W Scientific, Folsom, CA). Injection port and detector temperatures were set at 280 and 300°C, respectively. Nitrogen was used as the carrier gas, with a linear velocity of 27.3 cm/s and split ratio of 15:1. Relative retention times (RRT-GC) and logarithmic values (ln RRT) were calculated for 12 PCB congeners in order to determine existing relationships between DT₅₀ and either RT-HPLC or RRT-GC (Table 1).

Results and Discussion

Results show that DT_{50} values for PCB congeners were reduced by the addition of a supporter in the form of Er-Jen River sediment (Table 1). In addition, PCB congener distribution between sediment and medium was affected by the PCB congener partition coefficient as reflected by the HPLC retention time.

| PCB congener | MS-DT ₅₀ | MM-DT ₅₀ | RT-HPLC | ln RRT |
|----------------------|---------------------|---------------------|---------|--------|
| 2, <u>2'-CB</u> | 3.26 | 3.93 | 6.09 | 0.231 |
| 2, 3-CB | 4.71 | 5.73 | 7.87 | 0.391 |
| 2, 3'-CB | 3.19 | 3.44 | 8.18 | 0.358 |
| 2, 4'-CB | 7.35 | 7.59 | 8.48 | 0.391 |
| 2, 6-CB | 3.62 | 3.57 | 6.67 | 0.231 |
| 2, 4, 2'-CB | 7.17 | 7.60 | 9.53 | 0.592 |
| 2, 5, 2 '- CB | 5.25 | 5.65 | 8.66 | 0.580 |
| 2, 6, 2'-CB | 3.81 | 3.83 | 6.80 | 0.484 |
| 2, 6, 3'-CB | 6.79 | 6.92 | 9.15 | 0.617 |
| 3, 5, 2'-CB | 10.74 | 11.39 | 14.20 | 0.679 |
| 2, 4, 2', 4'-CB | 12.28 | 13.34 | 15.61 | 0.984 |
| 2, 4, 2', 5'-CB | 11.56 | 11.80 | 14.28 | 0.962 |

Table 1. The chromatographic data and DT₅₀ of 12 PCB congeners.

MS: added sediment as supporter

MM: treated without sediment

RT-HPLC: the retention time of PCB congeners by HPLC with C-18 column

In RRT: the logarithmic values of relative retention time of PCB congeners to 2-CB.

As shown in Figure 1, a relationship was noted between the degrading power of aerobic microorganisms and the partition coefficient of PCB congeners. The relationship between the degrading power of aerobic microorganisms and the partition coefficient of PCB congeners could be shown as one linear regression equation: RT-HPLC= 0.9442_DT₅₀+3.3518 (R^2 = 0.926). PCB congeners are adsorbed onto organic matter found in river sediments; a higher partition coefficient signifies a greater degree of adsorption, which affects the PCB-degrading power of

coefficient signifies a greater degree of adsorption, which affects the PCB-degrading power of aerobic microorganisms. PCB congeners with smaller partition coefficients also have shorter DT₅₀ values.



Fig. 1. The relationships between DT₅₀ and RT-HPLC in the degradation of PCB congeners by indigenous microorganisms, which were treated with Er-Jen sediment.





Since compound retention in a chromatographic column is an expression of that compounds dissolving and partitioning behavior between a mobile and stationary phase, retention time is **ORGANOHALOGEN COMPOUNDS**

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affected by its electrochemical properties. In the absence of Er-Jen River sediment, lower In RRT values for PCB congeners were associated with lower DT_{50} values (Fig. 2). The relationship between the degrading power of aerobic microorganisms and In RRT of PCB congeners also could be shown as one linear regression equation: $\ln RRT = 0.064 \times DT_{50} + 0.0893$ ($R^2 = 0.7909$). It appears that the solubility of PCB congeners in medium affects the degrading power of aerobic microorganisms.

The capability of a microorganism to degrade a PCB congener is predictable according to its HPLC or GC retention time. A more precise prediction based on DT_{50} values could be made if quantities of both PCB congeners and microorganisms were increased.

In summary, the degrading activity of microorganisms clearly varies according to the presence of various supporters. Thus, choosing an appropriate supporter is critical to PCB bioremediation.

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