ADSORPTION CHARACTERISTICS OF HALOGENATED AROMATIC POLLUTANTS (HAPs) BY A BACTERIAL PROTEIN

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Introduction

Halogenated aromatic pollutants (HAPs), which include polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and other chlorinated polynuclear aromatic hydrocarbons (PAHs), are normally toxic and are persistent chemicals in the environment.

Bioremediation has been used as an economic, safe, and environmentally preferable method for removal of HAPs. Biosorption is a more rapid and efficient removal process than biodegradation, because HAPs are sorbed by the biomass and then biomass is retrieved in a short time. The amount of biosorption by dead biomass is generally greater than or equal to that of live biomass[1]. It is possible that the amount of biosorption might be increased by the released biocompounds. Therefore, adsorption by the biocompounds released from a microorganism should also be considered. However, earlier works on biosorption mainly focused on the quantity of toxic chemicals sorbed by the cell itself. In addition, almost no studies were conducted on the kinds of biocompounds that cause the adsorption and their adsorption mechanisms.

In a previous study[2], we reported that 1,2,3,4-tetrachlorinated dibenzofuran (1,2,3,4-TCDF) and 1,2,3,4-tetrachlorinated dibenzo-*p*-dioxin (1,2,3,4-TCDD) were significantly adsorbed by a released protein when *Bacillus pumilus* PH-01 was boiled. In this research, investigations were made into the adsorption characteristics of PCDFs, PCBs, chlorinated benzenes, chlorinated naphthalenes, and some polynuclear aromatic hydrocarbons (PAHs). Based on these results, the importance of biocompounds released or secreted from microorganisms in the biosorption process is discussed.

Methods and Materials

The bacterium was isolated from a hood filter used for dioxin analysis in our lab. Fatty acid analysis and 16S rDNA sequencing results showed that the bacterium belongs to the genus *Bacillus* and is closely related to *Bacillus pumilus* NCDO 1766T. To harvest cells, *Bacillus pumilus* was inoculated into nutrient broth, then cultured overnight. The cultured medium was centrifuged at 3,000 rpm for 15 min. The supernatant was discarded, then 0.05 M of a phosphate buffer (pH 7) was added before vortexing. The washing process was performed twice. To release biocompounds, the concentrated *Bacillus pumilus* cell solution was boiled at 90 ℃ for 20 min, then centrifuged at 3,000 rpm for 20 min. The supernatant (biocompounds solution) was filtered by a syringe filter with 0.22 μm pores. A salting out method[3] using ammonium sulfate was used for protein purification.

Protein solution and HAPs (PCDFs, PCBs, chlorinated benzenes, chlorinated naphthalenes, and PAHs) were mixed in a glass centrifuge tube. The resulting solution was held at 30 ℃ and shaken at 160 rpm and for 2 hours. To extract HAPs, the sample solution was vigorously mixed with toluene.

A gas chromatography-electron capture detector (GC-ECD, HP6890, Hewlett-Packard, USA) was used for the analysis of PCDFs, PCBs, chlorinated benzenes, and chlorinated naphthalene. PAHs were analyzed by high performance liquid chromatography (HPLC, Acme, Young Lin, Korea)

Results and Discussion

In this study, we observed that the high-chlorinated congeners of PCDFs were adsorbed in larger quantities than the low-chlorinated ones (Figure 1). This can be explained by the fact that, as the number of substituted chlorines increases, the water solubility decreases and the octanol/water partition coefficient increases[4].

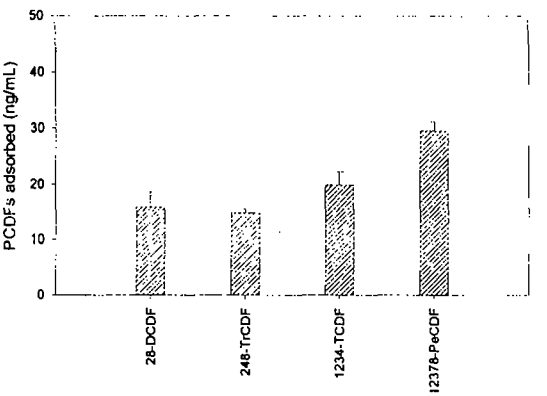

Figure 1. Adsorbed amounts of PCDFs mixture.

The adsorbed amounts of high-chlorinated PCBs were higher than those of low-chlorinated PCBs (Figure 2). This result coincides with the PCDFs adsorption pattern and can also be explained by the log K_{ow} values of the PCB congeners, as expected from the structural similarities between PCBs and PCDD/Fs. A difference in the adsorption rates of PCB isomers from the same homologues was also found. For TeCBs and HxCBs, when the number of ortho-substituted chlorines was small and chlorine was located at a meta position of 3, the adsorption rates were high. However, the adsorption of HpCBs isomers did not coincide with these results.

The adsorption patterns of chlorinated benzenes and chlorinated naphthalenes were similar to those of PCDFs and PCBs. The adsorbed amounts of high-chlorinated congeners were larger than those of low-chlorinated ones, and chlorinated naphthalenes, which have two benzene rings, were more adsorbed than chlorinated benzenes (Figure 3).

PAHs adsorption experiment was also carried out. However, we couldn't find any characteristic the adsorption pattern with different structures of PAHs (Figure 4); it notes that PAHs used in this study were not chlorinated ones.

Considering overall adsorption characteristics of HAPs, it seems that the protein may adsorb most of the hydrophobic organic chemicals. The fact that significant amounts of HAPs were adsorbed on the protein, however, implies that biocompounds released or secreted from microorganisms can have an effect on the movement or fate of HAPs in the environment.

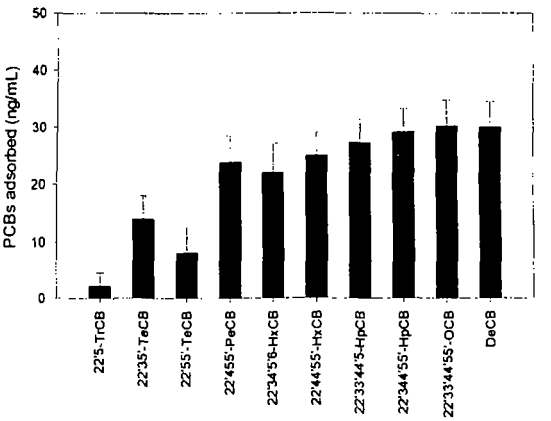

Figure 2. Adsorbed amounts of PCBs mixture.

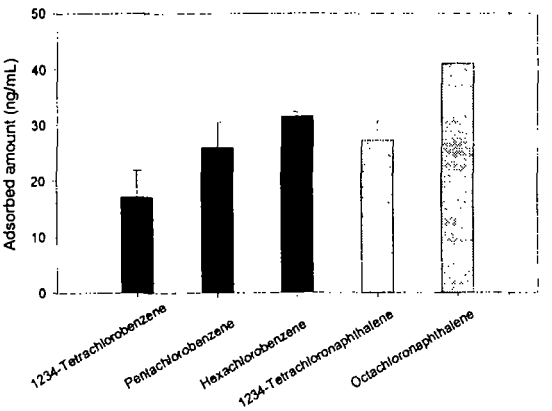

Figure 3. Adsorbed amounts of chlorinated benzenes and naphthalenes mixture.

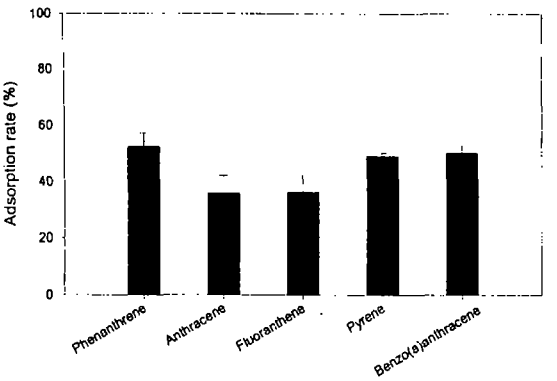

Figure 4. Adsorption rate of PAHs mixture.

Acknowledgements

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