REMOVAL OF HAZARDOUS ORGANIC POLLUTANTS BY ADSORPTION ON MICROBIAL BIOMASS

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ABSTRACT

Removal of five toxic organic compounds from water by adsorption on microbial biomass was investigated. Lindane, diazinon, malathion, pentachlorophenol, and the PCB 2-chlorobiphenyl were adsorbed onto two types of inactive microbial biomass (a pure strain of *Rhizopus arrhizus*, and a mixed culture of activated sludge). Desorption and the thermodynamics of the adsorption process were also investigated. With the exception of malathion, the adsorptive uptake data fit the Freundlich equation and were well correlated with the octanol/water partition coefficient, but not as well correlated with water solubility of the compounds. Except for malathion the adsorption was reversible. Malathion showed unusually high apparent uptake and the removal appeared to be irreversible. The experimental evidence suggests that the disappearance of malathion resulted from a chemical reaction, while physical adsorption appears to account for removal of the other compounds.

KEYWORDS

Adsorption; Biosorption; Desorption; Hazardous organics; Microbial Biomass; PCB; Pesticides.

INTRODUCTION

The fate of hazardous organic pollutants, such as pesticides, discharged into conventional biological wastewater treatment processes is not well understood. Removal of these compounds from the wastewater stream might be, among others, the result of biodegradation, volatilization (air stripping), or adsorption by the biomass. Adsorption would result in accumulation of pollutants in the sludge with the potential environmental hazards associated with ultimate sludge disposal. On the other hand, this biological adsorption process may provide a cost-effective treatment method for biorefractory organic pollutants. Also, since many hazardous compounds are present in discharges to municipal wastewater treatment plants, a better understanding of the fate of these pollutants is needed.

Accumulation of some hazardous pollutants by selected live and dead microorganisms has been investigated by various workers (Voerman and Tammes, 1969; Grimes and Morrison, 1975; Hansen, 1979; Baughman and Paris, 1981; Lal and Saxena, 1982; McRae, 1985). Investigators at the U.S. Environmental Protection Agency have studied the fate of a number of organic priority pollutants discharged into an activated sludge pilot plant. A number of compounds have been found to accumulate in the primary and secondary sludge (Petrasek, 1983). However, comprehensive, reliable equilibrium data on adsorption of hazardous organics by biomass over a wide concentration range are not readily available.

This work and continuing research in this area is aimed at understanding the role of adsorption in biological treatment processes and developing models for predicting the fate of hazardous organic pollutants entering biological wastewater treatment plants. The purpose of this initial work is to produce reliable, reproducible adsorption data and to develop a better understanding of the microbial adsorption process. Removal of five toxic organic compounds from water by adsorption on microbial biomass was investigated. The organic chemicals (lindane, diazinon, malathion, pentachlorophenol, and the PCB 2-chlorobiphenyl) were adsorbed onto two types of microbial biomass. One biomass type was a pure strain of *Rhizopus arrhizus*, a fungus grown in the laboratory. The other biomass was a mixed culture of
activated sludge from the Hamilton, Ontario municipal wastewater treatment plant. In addition, desorption and temperature effects were also investigated.

MATERIALS AND METHODS

Chemicals

The organic chemicals used in the adsorption experiments were of +99% purity and were purchased from Crescent Chemicals Co., Hauppauge, NY. Organic solvents used for extraction were pesticide grade iso-octane and hexane. Water solutions were made with distilled/deionized water prepared in the laboratory.

Biomass

The Rhizopus arrhizus was grown in a New Brunswick Scientific Co. bench top fermentor. Sterile techniques were used to prevent contamination by stray microorganisms. The R. arrhizus was recovered by filtering through cheese cloth, washed repeatedly with tap water, and autoclaved at 250°C for 30 minutes. The biomass was then vacuum-dried and ground with a mortar and pestle to pass through a 50 mesh screen.

The activated sludge biomass was obtained by collecting return sludge from the Hamilton, Ontario municipal wastewater treatment plant. The sludge was allowed to settle and the supernatant water was decanted. This washing was repeated several times and then the sludge was recovered by centrifugation. The sludge was dried in an oven at 115°C and then ground with a mortar and pestle to pass a 50 mesh screen.

Experiments

Adsorption experiments were conducted by contacting chemical solutions of various concentrations with different quantities of biomass. Measured quantities of biomass were placed in 250 ml screw-top flasks to which was added a measured quantity (approximately 150 ml) of solution. Solutions were prepared by dissolving the various chemicals in distilled/deionized water. Controls containing the same solution but no biomass were also prepared. The flasks were agitated on an orbital shaker at 250 rpm for approximately 3 days in a constant temperature room. The solutions were then separated from the biomass by filtering through 0.45 μm membrane filters in a glass vacuum filtration apparatus. The filters were first washed with 300 ml of distilled water to remove any leachable materials. Approximately 50-75 ml of solution was filtered to bring the filter to adsorption equilibrium with the solution. This portion of the filtrate was discarded. The subsequent filtrate was then collected for analysis. Control solutions were filtered, using the same procedure. In our calculations the concentration of the control solution determined by analysis was taken to be the initial solution concentration. Uptake by the biomass was computed by a mass balance.

Desorption experiments were done by first contacting the biomass with adsorbate solutions as in the adsorption experiments. The biomass was then allowed to settle in the adsorption flasks and the majority of the supernatant solution was decanted and replaced by distilled/deionized water. The flasks were then sealed and put back on the shaker for 3 days. The decanted solutions were filtered and the quantities of biomass collected on the filters were measured. The quantity of biomass in the decantate was subtracted from the original quantity of biomass to provide the biomass quantity basis for desorption. The filtrates were analyzed and the adsorptive uptakes were calculated. After desorption equilibrium was reached the solutions were filtered and the filtrates analyzed. The equilibrium loading after desorption was computed by a mass balance.

All samples were prepared for analysis by extracting the solutes from the water solutions with pesticide grade hexanes or iso-octane. The extractions were done in Teflon sealed septum bottles by shaking the solvent/water mixture on a wrist-action shaker at maximum speed for 30 minutes. The solvent solutions were analyzed using a Hewlett-Packard Model 5830A gas chromatograph with an electron capture detector and a digital integrator. Standard solutions were extracted in the same manner as the samples, and were analyzed along with the samples. Sample concentrations were determined by linear interpolation between the adjacent lower and higher standards.

A nonlinear least squares routine using Marquardt's compromise was used to fit the Freundlich equation to the equilibrium data:

\[ q = K C_{eq}^{1/n} \]  (1)

where

- \( q \) = equilibrium concentration of adsorbate on biomass, μg/g
- \( C_{eq} \) = equilibrium concentration of adsorbate in solution, μg/l.

The parameters \( K \) and \( 1/n \) were determined by using the true dependent variable, \( C_{eq} \), and taking the initial concentration and the biomass concentration as the independent variables. Because the data covers a wide concentration range, a reduced least squares technique was used so that the regression line would not favour the higher concentration values. In this case, the parameters which minimize
Hazardous organic pollutants were determined, where

\[ Y_{\text{obs}} = \text{observed values of dependent variable} \]

\[ Y_{\text{model}} = \text{values of dependent variable predicted by the model} \]

**RESULTS**

**Adsorption Isotherms**

Selected adsorption isotherms at 20°C are shown in Figures 1-5 with the fitted Freundlich equation lines. Tables 1 and 2 give the Freundlich parameters for each isotherm where \( q \) is in \( \mu g/g \) and \( C_{eq} \) is in \( \mu g/l \).

**Fig. 1** Adsorption of lindane on activated sludge.

<table>
<thead>
<tr>
<th>Compound</th>
<th>K</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lindane</td>
<td>2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>28.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Diazinon</td>
<td>1.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Malathion</td>
<td>3.7</td>
<td>1.2</td>
</tr>
<tr>
<td>2-Chlorobiphenyl</td>
<td>64.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Fig. 2  Adsorption of pentachlorophenol on *R. arrhizus*.

Fig. 3  Adsorption of diazinon on activated sludge.
Hazardous organic pollutants

Fig. 4  Apparent adsorption of malathion on activated sludge.

Fig. 5  Adsorption of 2-chlorobiphenyl on *R. arrhizus*. 
TABLE 2  Freundlich Parameters for Activated Sludge Adsorption Isotherms

<table>
<thead>
<tr>
<th>Compound</th>
<th>K</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lindane</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>10.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Diazinon</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Malathion</td>
<td>408.5</td>
<td>0.5</td>
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</table>

Tables 3 and 4 give the equilibrium adsorption capacity of the biomass at some different solution concentrations.

TABLE 3  Equilibrium Adsorption Capacity of R. arrhizus

<table>
<thead>
<tr>
<th>Compound</th>
<th>Adsorption Capacity at Stated Concentration. µg/g</th>
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<tbody>
<tr>
<td></td>
<td>10 µg/l</td>
</tr>
<tr>
<td>Lindane</td>
<td>24</td>
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<tr>
<td>Pentachlorophenol</td>
<td>230</td>
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<tr>
<td>Diazinon</td>
<td>12</td>
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<tr>
<td>Malathion</td>
<td>57</td>
</tr>
<tr>
<td>2-Chlorobiphenyl</td>
<td>773</td>
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</tbody>
</table>

TABLE 4  Equilibrium Adsorption Capacity of Activated Sludge

<table>
<thead>
<tr>
<th>Compound</th>
<th>Adsorption Capacity at Stated Concentration. µg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 µg/l</td>
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<tr>
<td>Lindane</td>
<td>15</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>69</td>
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<tr>
<td>Diazinon</td>
<td>4</td>
</tr>
<tr>
<td>Malathion</td>
<td>1410</td>
</tr>
</tbody>
</table>

Temperature Effects

The effect of temperature on adsorptive uptake was investigated for lindane, diazinon and malathion. A simplified linear equilibrium relationship of the form \( q = K C \) was fit to the adsorption data at different temperatures because of the strong correlation of the Freundlich model parameters. Assuming that the van't Hoff equation applies to the equilibrium constant, \( K \):

\[
\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}
\]

where

- \( T \) = temperature, °K
- \( \Delta H \) = energy of adsorption, cal/mole
- \( R \) = gas constant, cal/mole °K

or

\[
\ln K = -\frac{\Delta H}{R} \left( \frac{1}{T} \right) + \ln K_0
\]

If \( \Delta H \) is assumed to be constant over the temperature range in question, \( \Delta H \) can be determined from values of \( K \) at different temperatures. Estimated values of \( \Delta H \) are given in Table 5. Although these values may not be of great accuracy, the orders of magnitude give some insight into the adsorption phenomena.
Desorption isotherms for lindane and diazinon for both types of biomass were essentially identical to the adsorption isotherms indicating complete reversibility. Adsorption of malathion was reversible at 5°C, however at 20°C desorption did not occur. In fact additional uptake appeared to take place.

DISCUSSION

Lindane

The isotherms for lindane on both *R. arrhizus* and activated sludge are essentially linear (1/n \approx 1.0). A large ultimate adsorption capacity and low energy of adsorption could account for the linear isotherm. Because of the low solubility of lindane (approximately 10 mg/l), the isotherm cannot be carried to a point where saturation of the potential adsorption sites limits the uptake capacity. Results of the temperature experiments indicate that adsorption is exothermic, as would be expected, and that the energy of adsorption is in the range where physical adsorption rather than chemisorption is the dominant mechanism. The adsorption energies are of the same order as reported for other organic compounds adsorbed into activated carbon (Weber and Gould, 1966). The adsorptive uptake on the biomass is, however, significantly lower than that reported for lindane adsorbed on activated carbon (Dobbs and Cohen, 1980). The desorption experiments show that lindane adsorption is completely reversible. This result also indicates that lindane adsorption is primarily a physical adsorption phenomenon.

Diazinon

Diazinon, which has a water solubility of approximately 40 mg/l, exhibited lower adsorptive uptake than lindane as would be expected. The adsorptive capacities for both biomass types were similar. The isotherm for activated sludge is essentially linear while the best fit of the Freundlich equation for *R. arrhizus* is slightly nonlinear. The nonlinearity may be more an artifact of the fitting technique than a representation of physical phenomena since the two fitted parameters are highly correlated. The low energies of adsorption for diazinon indicate that a physical adsorption process is dominant. The low positive value of ΔH for activated sludge, indicating an endothermic process, may be due to the inaccuracy of the calculation since adsorption is generally an exothermic process. The adsorption of diazinon appears to be completely reversible, indicating a low binding energy characteristic of physical adsorption.

Malathion

Based on its greater water solubility (approximately 150 mg/l) malathion would be expected to exhibit lower adsorptive uptake than diazinon and lindane. Based on its significantly higher uptake and the large positive values of ΔH it is probable that a chemical reaction is involved in the removal of malathion from solution. Malathion is known to be subject to decomposition by various enzymatic reactions (Büchel, 1983). It may be that enzymes associated with the biomass result in decomposition of the malathion and produce the apparent high uptake. At lower temperatures the reaction may be significantly slower, accounting for the lower apparent uptake at 5°C. The desorption experiments at 5°C indicate that malathion uptake is reversible. The observed uptake at 5°C may be primarily adsorption while at 20°C the apparent uptake may be mainly the result of chemical reaction. Desorption experiments conducted at 20°C show that the removal of malathion is not reversible which tends to confirm the proposed hypothesis of a chemical reaction. Further work in this direction continues.

Pentachlorophenol

Although its water solubility (approximately 14 mg/l) is slightly greater than that of lindane, pentachlorophenol exhibits significantly higher adsorption than lindane. The isotherms for pentachlorophenol are slightly nonlinear indicating a...
tendency toward saturation at higher concentrations. Adsorptive uptake is less than that reported for activated carbon (Dobbs and Cohen, 1980).

2-Chlorobiphenyl

With the lowest water solubility of the compounds tested (approximately 5.9 mg/l), 2-chlorobiphenyl shows the greatest adsorption. Although the regressions routine suggests that the PCB adsorption isotherm is essentially linear, there is experimental evidence that it may not be (Figure 5). Additional experimental work on this is currently under way.

CONCLUSIONS

The results of these experiments indicate that adsorption is an important process in the removal of hazardous organic pollutants in biological treatment systems. Where physical adsorption is involved the adsorption is reversible indicating that hazardous compounds can return to water solution from waste sludges. While the uptake capacity of biomass is generally less than that of activated carbon, it is high enough to provide significant removal of trace quantities of hazardous compounds combined with domestic or nonhazardous industrial pollutants. The results of the malathion experiments show that even with dead biomass more complex behaviour than physical adsorption may be involved for some chemicals. Enzymatic reactions not involving metabolic activity may take place in biological systems. Knowledge of the byproducts of these reactions is of concern since other hazardous compounds may result. Further investigation is needed to develop predictive models for the biological adsorption process.

ACKNOWLEDGEMENT

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REFERENCES


