DEGRADATION OF CARBARYL AND 1-NAPHTHOL BY SPENT MUSHROOM COMPOST MICROORGANISMS

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ABSTRACT

The capabilities of spent mushroom compost microorganisms in degrading carbaryl and 1-naphthol were evaluated. No lag phases were observed for the two compounds. The microbial degradation kinetics of the two compounds could be interpreted very well by Pseudo-first-order model. The biodegradation rate constants of the two compounds were affected by initial biomass concentration and aeration rate significantly. The rate constants of carbaryl and 1-naphthol were 0.251 h⁻¹, 0.105 h⁻¹ respectively under the aerobic condition (aeration rate 600 ml/min and initial biomass concentration 100 mg/l). Thus, the half-life of carbaryl and 1-naphthol were 2.761 hrs, 6.600 hrs respectively.

KEYWORDS

Carbaryl; 1-Naphthol; Spent mushroom compost; Pseudo-first-order model.

INTRODUCTION

Carbaryl (1-naphthyl N-methylcarbamate), synthesized in 1953 and introduced in 1958 as a commercial formulation Sevin, is the most widely used carbamate insecticide in agriculture (Kuhr & Dorough 1976). The half-life of carbaryl in the environment ranged from 1.7 to 5.8 days in river water (Stanley & Trial 1980), 3 to 4 days on plant foliage (Kuhr & Dorough 1976) and 8 to 9 days in soils (Johnson & Stansbury 1965). The degradation of carbaryl can be affected by temperature, sun light, pH, and microorganisms. Among the various factors which determine the fate of carbaryl, microbial transformation of carbaryl plays a major role in this environmental degradation. The metabolism of carbaryl by soil organisms has been reported by Larkin and Day (1986) and Rajagopal et al. (1984). Hydrolysis was found to be the major course for microbial degradation of carbaryl in soil cultures with 1-naphthol accumulating in the medium (Rajagopal et al., 1984). 1-Naphthol is still a toxic chemical for biota though its acute oral LD₅₀ for rats is just one-tenth of that of carbaryl. However, 1-naphthol was twice as toxic to fish at a concentration of 1.3 mg/L as carbaryl in sea water (Stewart et al. 1967). Therefore in the point of view of environmental protection, the detoxification of 1-naphthol is also important as much as its parent compound (carbaryl). The biological degradation of 1-naphthol has been studied by Bollog et al. (1975) and Sikka et al. (1975).

Spent mushroom compost (SMC) is a byproduct of the mushroom industry. SMC consists of 20% organic matter including cellulose, hemicellulose, lignin, and some residual nutrients such as nitrogen, phosphorus et al. Although SMC has been sterilized before utilization, 24-30% of microbes are relatively resistant and survive after the sterilization process (Kleyn & Wetzler 1981). The microorganisms in SMC consist of bacteria, actinomycetes, and fungi.

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The objective of this study was to evaluate the biodegradability of carbaryl and 1-naphthol by spent mushroom compost microorganisms.

**MATERIALS AND METHODS**

**Materials**. Carbaryl was provided by Rhone-Poulenc Ag. Co., NC. 1-Naphthol was purchased from J.T. Baker Chemical Co., NJ. The reagents for biomass analysis were supplied by Sigma Chemical Co., MO. Fresh SMC was supplied by Mushroom Test Demonstration Facility, Pennsylvania State University.

**Experimental Design**. The experiments were taken under aerobic condition. Three 1-L flasks were used as batch-type reactors. Because abiotic degradation processes such as hydrolysis and photolysis sometimes occur during biological degradation, one reactor with microbial inhibitor (0.4% formalin) was used as control reactor to allow for correction for such processes. The other two reactors were added to 5 gm, 10 gm SMC individually to reach initial biomass concentration 50 mgFRM/l, 100 mgFRM/l after necessary incubation. To understand the effect of aeration rate on degradation rates of the two compounds, two different air flow rates (300 ml/min, 600 ml/min) were supplied at room temperature (22 ± 1°C) to individual experiments. The concentration of two compounds used was 40 mg/l. 0.46 gm K_2HPO_4 and 1.0 gm KH_2PO_4 would be added per litre solution to make a buffer solution with pH 6.8. All reactors were subsampled at prescribed intervals to measure concentrations of residual. Biomass concentrations were quantified at the beginning and the end of each experiment.

**Biomass and Chemical Analysis**. Microbial biomass was determined using Folin-Reactive Material (FRM) as a measure of biomass. To quantify the FRM of the microbial biomass the method developed by Lowry et al. (1951). Carbaryl and 1-naphthol were analyzed on high performance liquid chromatograph with LC-8 column (Supelco Co. Bellefont, PA).

**Transformation Kinetics**. The kinetics of carbaryl and 1-naphthol were described by Pseudo-first-order model in which

\[
\frac{dS}{dt} = k_1 S
\]

where \(k_1\) is the Pseudo-first-order rate constant; \(S\) is the chemical concentration. To calculate the Pseudo-first-order biodegradation rate constants, the concentration of residual carbaryl and 1-naphthol must be corrected for loss due to abiotic processes. The biodegradation kinetics could also be described by Second-order model in which

\[
\frac{dS}{dt} = k_2 X S
\]

where \(k_2\) is the Second-order rate constant; \(X\) is the biomass concentration; \(S\) is the chemical concentration. Because biomass concentration did not change significantly during the experiments, Second-order biodegradation rate constants were obtained by dividing Pseudo-first-order biodegradation rate constants by the initial biomass concentration.

**RESULTS AND DISCUSSION**

The stability of carbaryl and 1-naphthol in aqueous solution was known to be pH-dependent. Therefore, strongly buffering capacity was used in the study. Routine examination of the reactor broth was also conducted and no case was a shift of greater than 0.1 pH unit observed in any reactors at the termination of each experiment. The increment of microbial biomass concentration was less than 10 % of initial biomass concentration in each reactor. Carbaryl and 1-naphthol could be biodegraded easily by SMC microorganisms.

In the experiment of carbaryl degradation by SMC microorganisms, no lag phase was observed. Figure 1 shows 1-naphthol formation during degradation of carbaryl. This phenomenon was also reported by several researchers (Larkin & Day 1985, Rajagopal et al. 1984). It means that hydrolysis would be the major pathway of carbaryl degradation. The accumulation of 1-naphthol was high to 10 mg/l and then decreased, which shows that the formed 1-naphthol was further biodegraded and substituted for carbaryl as a major carbon and energy source gradually. Table 1 shows that the degradation rate of carbaryl was affected by initial biomass concentration significantly. While the concentration of residual carbaryl in the reactor with initial biomass 100 mg/l was down to 0.044 mg/l after 24 hrs aeration, the residual carbaryl in the reactor with initial biomass 50
Degradation of carbaryl and 1-naphthol

mg/l still had 1.183 mg/l. Thomas et al. (1986) have reported that the degradation of carbaryl by mixed cultures of bacteria proceeded at a logarithmic rate. The same phenomenon was also observed in degrading carbaryl by SMC cultures. These data were found to fit the Pseudo-first-order model very well. The rate constants of carbaryl degradation in the reactor with various biomass concentrations (0, 50, 100 mg/l) were 0.006, 0.134, 0.257 hr⁻¹ respectively (Table 1).

![Graph: Formation of 1-naphthol during degradation of carbaryl](image)

**Fig. 1** Formation of 1-naphthol during degradation of carbaryl

<table>
<thead>
<tr>
<th>Compound</th>
<th>Q(ml/min)</th>
<th>FRM(mg/l)</th>
<th>k₁(hr⁻¹)</th>
<th>t₁/₂(hrs)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbaryl</td>
<td>300</td>
<td>0</td>
<td>0.006</td>
<td>115.500</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>100</td>
<td>0.150</td>
<td>4.620</td>
<td>0.988</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0</td>
<td>0.006</td>
<td>112.683</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>50</td>
<td>0.134</td>
<td>5.172</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>100</td>
<td>0.257</td>
<td>2.696</td>
<td>0.982</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>300</td>
<td>0</td>
<td>0.008</td>
<td>86.625</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>100</td>
<td>0.043</td>
<td>16.116</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0</td>
<td>0.010</td>
<td>69.300</td>
<td>0.970</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>50</td>
<td>0.070</td>
<td>9.900</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>100</td>
<td>0.115</td>
<td>6.026</td>
<td>0.998</td>
</tr>
</tbody>
</table>

- a air flow rate;
- b initial biomass concentration expressed by Folin-Reactive Material;
- c Pseudo-first-order degradation rate constant;
- d half-life of compound due to degradation; t₁/₂ = 0.693/k₁;
- e coefficient of correlation.

As the loss due to abiotic processes was considered, the biodegradation rate constants were calculated and listed in Table 2. A little change existed between degradation rate constants and biodegradation rate constants, which means that the loss of carbaryl due to abiotic processes just played a minor role in the degradation of carbaryl. Table 2 also shows that the biodegradation rate constant of carbaryl was proportional to the initial biomass concentration in reactor. Thus, the Second-order rate constant of degradation of carbaryl almost did not change under the same aeration rate. However, as aeration rate decreased from 600 ml/min to 300 ml/min, the degradation rate of carbaryl would reduce by 40%.

To get more understanding of the degradation of 1-naphthol, some further experiments were done. The degradation rate of 1-naphthol was also affected by initial biomass concentration and aeration rate (Table 2). The influence of aeration rate on biodegradation rate of 1-naphthol was much larger than that of carbaryl. This phenomena may be due to the fact that hydroxylation is the major pathway of biodegradation of 1-naphthol (Larkin and Day 1986) while hydrolysis is the major pathway of biodegradation of carbaryl. Thus, oxygen concentration (aeration rate) played a more important role in biodegradation of 1-naphthol than in that of
Moreover, Table 2 also shows that biodegradation rate of 1-naphthol was only half of that of carbaryl under aeration rate 600 mg/l condition, which means that SMC microorganisms could biodegrade carbaryl more efficiently.

**TABLE 2. Biodegradation Rates of Carbaryl and 1-Naphthol**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Q(ml/min)</th>
<th>FRM(mg/l)</th>
<th>k₁(hr⁻¹)</th>
<th>t₁/₂(hrs)</th>
<th>k₂(l/mg/hr)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbaryl</td>
<td>300</td>
<td>100</td>
<td>0.144</td>
<td>4.813</td>
<td>0.00144</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>50</td>
<td>0.128</td>
<td>5.414</td>
<td>0.00256</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>100</td>
<td>0.251</td>
<td>2.761</td>
<td>0.00251</td>
<td>0.981</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>300</td>
<td>100</td>
<td>0.037</td>
<td>18.730</td>
<td>0.00037</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>50</td>
<td>0.060</td>
<td>11.550</td>
<td>0.00120</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>100</td>
<td>0.105</td>
<td>6.600</td>
<td>0.00105</td>
<td>0.997</td>
</tr>
</tbody>
</table>

*a* air flow rate;  
*b* initial biomass concentration expressed by Folin-Reactive Material;  
*c* Pseudo-first-order degradation rate constant;  
*d* half-life of compound due to degradation;  
*e* Second-order biodegradation rate constant;  
*f* coefficient of correlation.

**CONCLUSIONS**

The spent mushroom compost microorganisms were able to degrade carbaryl and 1-naphthol successfully. The cultures were more efficient in degrading carbaryl than 1-naphthol. The biodegradation rates of carbaryl and 1-naphthol were proportional to initial biomass concentration in solution. Because hydrolysis is the major pathway of carbaryl degradation while hydroxylation is the major pathway of 1-naphthol degradation, the effect of aeration rate on degradation rate of 1-naphthol was more significant than that of carbaryl. All the degradation kinetics of the two compounds could be fitted very well by Pseudo-first-order model.

**REFERENCES**


