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Bioavailability of methyl parathion adsorbed on clay minerals and iron oxide

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ABSTRACT

Adsorption, desorption and degradation by *Pseudomonas putida* of methyl parathion (O,O-dimethyl O-p-nitrophenyl phosphorothioate) on montmorillonite, kaolinite and goethite were studied. Metabolic activities of methyl parathion-degrading bacteria *P. putida* in the presence of minerals were also monitored by microcalorimetry to determine the degradation mechanism of methyl parathion. Montmorillonite presented higher adsorption capacity and affinity for methyl parathion than kaolinite and goethite. The percentage of degradation of methyl parathion adsorbed on minerals by *P. putida* was in the order of montmorillonite > kaolinite > goethite. The presence of minerals inhibited the exponential growth and the metabolic activity of *P. putida*. Among the examined minerals, goethite exhibited the greatest inhibitory effect on bacterial activity, while montmorillonite was the least depressing. The biodegradation of adsorbed methyl parathion by *P. putida* is apparently not controlled by the adsorption affinity of methyl parathion on minerals and may be mainly governed by the activity of the methyl parathion-degrading bacteria. The information obtained in this study is of fundamental significance for the understanding of the behavior of methyl parathion in soil environments.

1. Introduction

Bioavailability of adsorbed organic pollutants in soils and sediments affects the clean-up time and the effectiveness of bioremediation. Published results suggest that the biodegradation of organic pollutants varied significantly with contaminant structure, the types of the adsorbents, the characteristics of organisms employed and environmental conditions [1–3]. Adsorbed organic pollutants are thought to be more resistant to biodegradation than soluble phase as it is generally considered that adsorbed chemicals are unavailable to microorganisms unless desorption occurs first [4–6]. For example, adsorbed herbicide (2,4-dichlorophenoxy) acetic acid was completely protected from *Flavobacterium* sp. degradation and that adsorbed- and solution-phase bacteria degraded solution-phase herbicide with almost equal efficiencies [7]. However, some bacteria can utilize adsorbed compounds at rates slightly greater than the rate of the abiotic desorption of compounds from the adsorbents. Laor et al. [8] showed that phenanthrene mineralization was enhanced by adsorption to synthetic mineral–humic acid complexes. *Brevibacterium* sp. hydrolyzed 77% more fenamiphos adsorbed by cetyltrimethylammonium-exchanged montmorillonite than the amounts desorbed in abiotic controls within 24 h [9].

Methyl parathion has been applied in several countries which can cause irreversible phosphorylation of esterases in the central nervous system of insects and mammals and act as cholinesterase inhibitors [10]. Clay minerals are effective adsorbents for methyl parathion [11]. Nature organic matter mediates the degradation of methyl parathion in aqueous solutions containing hydrogen sulfide [12]. Methyl parathion decomposition is most effectively catalyzed by partially hydrated Cu(II)- and Al-montmorillonite and Ca-montmorillonite and kaolinite were least effective [11]. Increase in cell concentrations enhanced the degradation of methyl parathion and 50% of moisture content favored the maximum degradation of methyl parathion [13]. However, up to date, the biodegradation mechanisms of methyl parathion adsorbed on minerals are not totally understood, as is also the influence of mineral types. The aim of the current work was to investigate the level of biodegradation of methyl parathion adsorbed on montmorillonite, kaolinite and goethite by bacteria. A further objective was to determine the mechanisms of biodegradation through the

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adsorption affinity of methyl parathion for minerals and bacterial activity investigated by microcalorimetric technique. Isothermal microcalorimetric techniques have been extensively used in studies of life science and can directly and conveniently measure the heat of microbial metabolisms which is a reliable index of microbial activity [14–16].

2. Materials and methods

2.1. Minerals

The preparation of montmorillonite and kaolinite (less than 2 μm), the synthesis of goethite as well as their properties have been described elsewhere [17].

2.2. Methyl parathion

Methyl parathion (purity > 99.0%) was purchased from National Suspecting and Testing Center for Pesticide Products, China.

2.3. Bacteria and growth conditions

The used bacterium (*Pseudomonas putida*) capable of using methyl parathion as the sole source of carbon and energy was isolated from the soil near Shanongda Pesticides Company in Hubei Province, China. *P. putida* was isolated from enrichment cultures by adding soil inoculant to mineral salts media (3.0 g L^{-1} K_2HPO_4, 1.5 g L^{-1} KH_2PO_4, 0.01 g L^{-1} NaCl, 0.1 g L^{-1} $MgSO_4$, 0.001 g L^{-1} $FeSO_4{\cdot}7H_2O$ and 1 g L^{-1} $(NH_4)_2SO_4$, pH 7.0–7.2) containing methyl parathion.

P. putida was grown in 100 mL of mineral salts media containing yeast extract (200 mg L^{-1}) and methyl parathion (100 mg L^{-1}) at 30 °C and 180 rpm for 12 h. Cells were harvested and washed twice with mineral salts media solution and suspended in the same buffer.

2.4. Batch equilibrium adsorption

Two grams of montmorillonite, kaolinite or goethite was mixed with 100 mL of $CaCl_2$ (0.05 mol L^{-1} as background electrolyte) and the pH of the suspension was adjusted to 7.0 with HCl or NaOH (0.01 mol L^{-1}). One milliliter of the mineral suspension and 4 mL of methyl parathion solutions with different concentrations (0–40 mg L^{-1}) were added in a 50 mL of Teflon tubes. The mixture was shaken at 30 °C for 24 h in the dark and centrifuged at 20,000 × *g* for 10 min. The supernatant was filtered through a separate 0.45 μm membrane syringe filter. The concentration of methyl parathion in the supernatant was determined by high-performance liquid chromatograph (HPLC) equipped with UV detector at 275 nm wavelength. Analyses were performed on a reverse phase C_8 column (Zorbax Eclipse XDB, 5 μm, 4.6 mm × 150 mm) using a mobile phase of methanol–water (70:30, v/v). The flow rate was 0.7 mL min^{-1} and the injection volume was 20 μL. The amount of methyl parathion adsorbed on the minerals was calculated by the difference between the amount of methyl parathion added and that remaining in the supernatant. A blank experiment (without minerals) at each concentration was also conducted in order to deduct the amount of methyl parathion adsorption on the tubes and degradation during equilibrium time.

2.5. Desorption experiments

Forty milligrams of mineral and 2 mL of $CaCl_2$ (0.05 mol L^{-1}) containing 0.4 mg methyl parathion were mixed in the centrifuge tube. The mixture was shaken at 30 °C for 24 h in the dark and centrifuged at 20,000 × *g* for 10 min. The residue was washed with 2 mL of $CaCl_2$ for 1, 7, 12 and 24 h. Each washing was repeated until no more methyl parathion was detected in the supernatant.

2.6. Bioavailability assays

The degradation kinetic of free methyl parathion was determined in a batch system. Fifty milliliters of mineral salts media solution containing different concentrations (10, 20 or 40 mg L^{-1}) of methyl parathion was placed in 100 mL of Erlenmeyer flasks and then inoculated with *P. putida* (10^8 cells). At certain time intervals, 2 mL of samples were taken from the flasks and filtered through a separate 0.45 μm membrane syringe filter for HPLC analysis. Uninoculated experiments were also conducted.

To evaluate the availability of the immobilized methyl parathion to *P. putida*, a degradation assay was adapted from the method described by Neera et al. [9]. Methyl parathion adsorbed by 8 mg of montmorillonite, kaolinite or goethite was suspended in 2 mL of mineral salts media solution in 10 mL of Teflon tubes and then inoculated with *P. putida* (10^8 cells). At regular intervals, the mixture was centrifuged at 20,000 × *g* for 10 min and methyl parathion in the supernatant was filtered through a separate 0.45 μm membrane syringe filter for HPLC analysis. Adsorbed methyl parathion, as well as its hydrolysis product, p-nitrophenol, was extracted by dispersing the pellet in 2 mL of methanol. All supernatant was pooled for analysis.

2.7. Microcalorimetry

A TAM III thermal activity monitor (Thermometric AB, Sweden) was used for all heat effect measurements. In the measuring mode, dynamic range is ±50 mW and the maximum baseline error of the heat flow after 24 h is ±225 nW. The heat flows through high-sensitivity thermopiles surrounded by a heat sink, which is stabilized at $\pm 1 \times 10^{-4}$ °C. The magnitude of the heat exchange of a thermopile with a heat sink is proportional to the voltage signal. The output signal collected as heat power and versus time was gathered continuously by TAM assistant software. Before experiment, stainless steel ampoules were sterilized by rinsing in 75% ethanol and sterilized distilled–deionized water for 10 min and dried under a laminar flow hood.

To assess the influence of substrate concentration on microbial activity, the thermal effects from *P. putida* utilizing different concentrations of methyl parathion were obtained by using 4 mL of stainless steel ampoules. These ampoules were hermetically closed by Teflon sealing discs to avoid evaporation inside the apparatus. Experiments were carried out at 30 ± 0.02 °C. All determinations of thermal effect were performed in ampoules with 2 mL of mineral salts media solution containing different concentrations (10, 20, 30 and 40 mg L^{-1}) of methyl parathion. Then 0.02 mL of bacterial suspension (10^8 cells) was inoculated in the above ampoules. After gentle shaking at 75 rpm for 60 s, the ampoules were lowered to the preheating position for 15 min and then to the measuring positions. Once the baseline was stable, data were recorded until the signal returned to the baseline.

As for the determination of the metabolic activity of *P. putida* in the presence of minerals, 8 mg of montmorillonite, kaolinite or goethite, 1.6 mL of sterilized distilled–deionized water, 0.4 mL of sterilized beef-extracted peptone medium and 0.02 mL of bacterial culture containing about 10^8 cells were introduced aseptically into the ampoules. The later procedures were the same as described above.

The values of peak height (PH) and corresponding peak time (PT) of each power–time curve were picked through the TAM assistant software kit (Thermometric AB, Sweden). The microbial growth rate constant (k) determined by microcalorimetry is based on the assumption that the heat evolved from metabolism

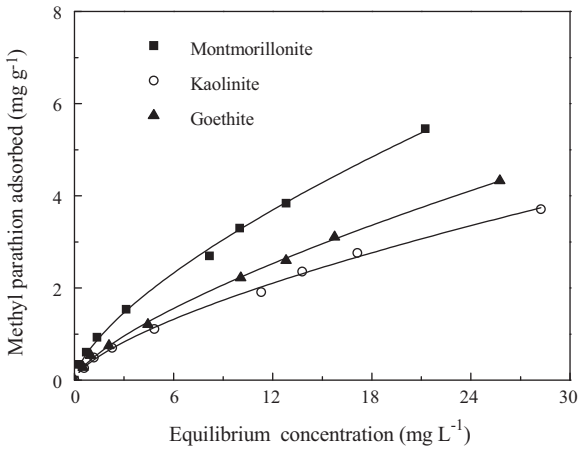

Fig. 1. Adsorption isotherms of methyl parathion on minerals.

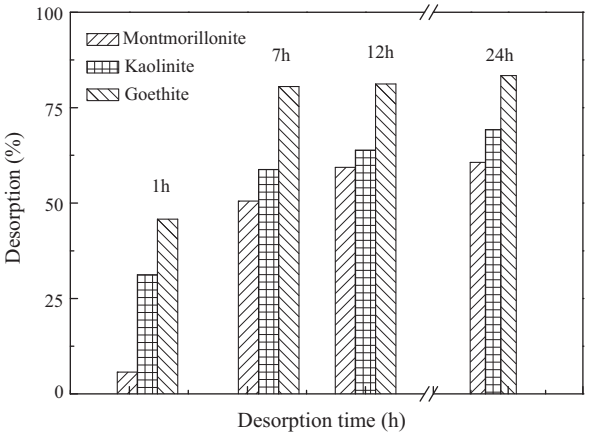

Fig. 2. The percent desorption of methyl parathion from minerals.

in the vegetative stage was proportional to the rate of cell division [18]. This parameter was calculated by fitting a logarithmic growth model based on data of the power–time curve in the logarithmic growth stage (the rise part of the first peak in the curve).

3. Results

3.1. Equilibrium adsorption of methyl parathion

The adsorption isotherms of methyl parathion on clay minerals and iron oxide are shown in Fig. 1. Methyl parathion adsorbed by montmorillonite, kaolinite and goethite fitted a Langmuir equation which can be described as $X = X_m KC/(1 + KC)$, where X is the amount of methyl parathion adsorbed per unit mass of minerals, X_m is the maximum amount of methyl parathion that may be adsorbed, K is a constant related to the adsorption energy and C is the equilibrium methyl parathion concentration. The greater the K value, the higher the affinity between methyl parathion and minerals. As presented in Table 1, the maximum amount of methyl parathion adsorption on montmorillonite (11.03 mg g^{-1}) was greater than those on goethite (9.56 mg g^{-1}) and kaolinite (7.35 mg g^{-1}). The estimated K values were in the order of montmorillonite (0.044) > kaolinite (0.035) > goethite (0.031), indicating that the affinity of methyl parathion adsorption on montmorillonite is higher than that on kaolinite or goethite.

3.2. Desorption of methyl parathion

As shown in Fig. 2, the percent desorption of methyl parathion by $CaCl_2$ from montmorillonite, kaolinite and goethite was 5.64–59.26%, 31.06–63.89% and 45.71–80.64% before 12 h. Only a small percentage (<5%) of adsorbed methyl parathion was desorbed from minerals after 12 h and the percent desorption was 60.61%, 69.44% and 83.50% for montmorillonite, kaolinite and goethite, respectively, at 24 h. These results imply that the binding strength of methyl parathion on minerals follows the sequence of montmorillonite > kaolinite > goethite, which is in accordance with the Langmuir constant (K) values.

Table 1
Langmuir parameters for methyl parathion adsorption on minerals.

Minerals	X_m (mg g^{-1})	K (L mg^{-1})	r
Montmorillonite	11.03	0.044	0.98
Kaolinite	7.35	0.035	0.99
Goethite	9.56	0.031	0.99

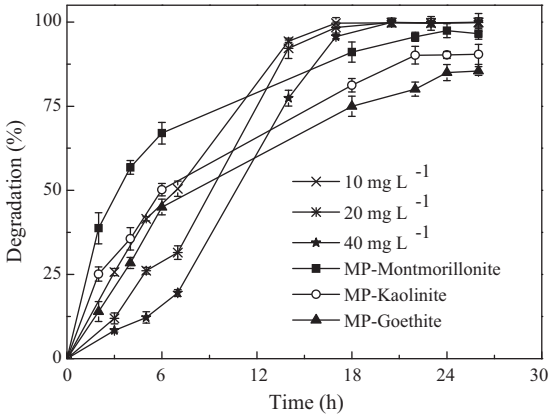

Fig. 3. Degradation of free and adsorbed methyl parathion (MP) by *Pseudomonas putida*.

3.3. Microbial degradation of methyl parathion

Fig. 3 shows the degradation of free and adsorbed methyl parathion by *P. putida*. As for free methyl parathion, the percent degradation of methyl parathion decreased from 50.53 to 19.86% with the increase of pesticide concentration from 10 to 40 mg L^{-1} within 7 h. Methyl parathion was degraded completely by the bacterium within 26 h. Only 5.64% of methyl parathion was transformed during the same period without inoculation (data not shown). Compared to the free methyl parathion system, the percentage of degradation of mineral-adsorbed methyl parathion was higher at the first 7 h. For example, the percent degradation was more than 50% for adsorbed methyl parathion, while less than 30% of degradation was observed for free pesticide at the initial concentrations of 20 and 40 mg L^{-1} during the same period. However, the degradation of free methyl parathion increased rapidly and exceeded that of adsorbed pesticide after 18 h. As for adsorbed methyl parathion, the percentage of degradation followed the sequence of montmorillonite > kaolinite > goethite during the examined period. The results suggest that methyl parathion adsorbed on montmorillonite may be easier to degrade by *P. putida* than that on kaolinite or goethite.

3.4. Microbial activity of P. putida

The power–time curves for the growth of *P. putida* at different concentrations of methyl parathion in mineral salts media system are shown in Fig. 4. The signal displayed was mainly caused from *P.*

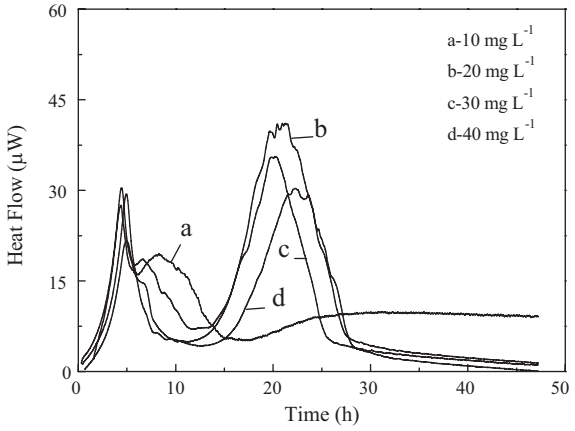

Fig. 4. Power–time curves of *Pseudomonas putida* utilizing different concentrations of methyl parathion in MSM system.

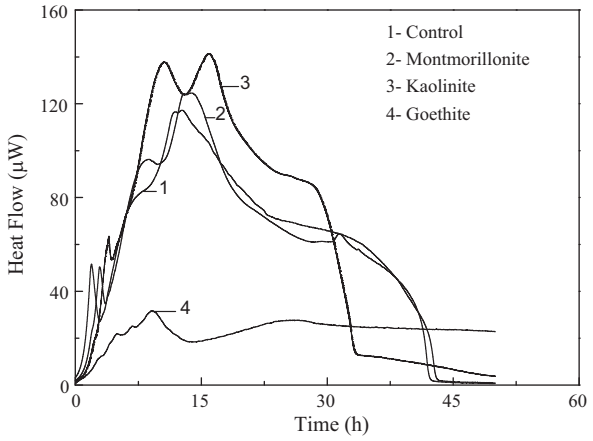

Fig. 5. Power–time curves of *Pseudomonas putida* metabolism in the presence of minerals in beef-extracted peptone system.

Table 2
Thermokinetic parameters of *Pseudomonas putida* utilizing different concentrations of methyl parathion in mineral salts media system.

Concentration (mg L^{-1})	PT (h)	PH (μW)	k (h^{-1})	R^2
10	4.40	27.5	0.7030 ± 0.0031	0.9863
20	4.41	30.4	0.6529 ± 0.0005	0.9994
30	4.91	29.4	0.6235 ± 0.0011	0.9972
40	4.86	21.5	0.5974 ± 0.0032	0.9737

PT is the time at which the calorimetric signal reaches its maximum amplitude at the logarithmic growth stage. PH and k is the maximum heat output and the growth rate constant at the logarithmic growth stage. R is a correlation coefficient used to judge the goodness-of-fit of a logarithmic growth model.

putida metabolism, methyl parathion being the sole carbon source in the ampoule. As shown in Fig. 4, the metabolism of *P. putida* changed with methyl parathion concentrations. The PT value was 4.40 h in the presence of 10 mg L^{-1} of methyl parathion, while the value increased to 4.86 h at a methyl parathion concentration of 40 mg L^{-1}. This increase of the peak time could be in response to the lengthy period of adaptation of the *P. putida* in this nutrient condition [19]. The growth rate constant (k) and the PH value decreased from 0.7030 to 0.5974 h^{-1} and from 27.5 to 21.5 W, respectively, with the increase of methyl parathion concentrations from 10 to 40 mg L^{-1} (Table 2). These results suggest that higher concentrations of methyl parathion inhibit substantially bacterial activity.

The power–time curves for the metabolism of *P. putida* in a beef-extracted peptone system as influenced by various minerals are shown in Fig. 5. The corresponding thermokinetic parameters of microbial metabolism were listed in Table 3. The PT value of free *P. putida* was 1.93 h, while the values increased to 2.89, 3.99 and 9.12 h in the presence of montmorillonite, kaolinite and goethite, respectively. Compared with the system of free *P. putida*, the k value decreased by 69.0%, 37.8% and 24.6%, respectively, in goethite, kaolinite and montmorillonite systems. The above results indicate that the presence of minerals inhibited the activity of *P. putida* and the depressing effect was in the order of goethite > kaolinite > montmorillonite.

Table 3
Thermokinetic parameters of *Pseudomonas putida* metabolism in presence of minerals.

Systems	PT (h)	PH (μW)	k (h^{-1})	R^2
Free	1.93	51.58	1.3699 ± 0.0085	0.9842
Montmorillonite	2.89	50.44	1.0327 ± 0.0032	0.9944
Kaolinite	3.99	63.47	0.8521 ± 0.0026	0.9932
Goethite	9.12	31.71	0.4251 ± 0.0024	0.9656

PT is the time at which the calorimetric signal reaches its maximum amplitude at the logarithmic growth stage. PH and k is the maximum heat output and the growth rate constant at the logarithmic growth stage. R is a correlation coefficient used to judge the goodness-of-fit of a logarithmic growth model.

4. Discussion

Our microcalorimetric data showed that goethite displayed the strongest inhibitory effect on the metabolic activity of *P. putida*, while montmorillonite presented the lowest depressing effect (Fig. 5 and Table 3). Rong et al. [20] also reported that compared with kaolinite and montmorillonite, goethite significantly depressed the sporulation and the total metabolic activity of *Bacillus thuringiensis*. The stronger inhibitory effect of goethite on bacterial activity may be ascribed to the following reasons: (1) at the pH condition studied, the negatively charged bacteria were easily attached to the positively charged goethite via electrostatic attraction forces. Jiang et al. [21] found that goethite showed the greatest adsorption capacity for *P. putida*, while montmorillonite was the least; (2) the size of goethite was roughly in the range of twenty to hundreds of nanometers, which was smaller than that of bacterial cells. Nanogoethite may strongly bond to the surfaces of bacteria by penetrating the outer membrane and piercing the peptidoglycan layer [22]. Therefore, these tight attachment of goethite to bacterial surface could not only reduce the surface available for nutrient uptake, but also somewhat "hurt" the bacteria and probably depress its activity. Compared with goethite, the lower depressing effects of montmorillonite and kaolinite may be ascribed to the inhibitory effect of Al^{3+} (aq) from these minerals on *P. putida* [23]. Additionally, montmorillonite was also considered to play an important role in buffering the pH of suspension within the optimal range for bacterial growth [24].

Kaolinite and goethite on which methyl parathion was loosely adsorbed had a higher capability of protecting methyl parathion against degradation by *P. putida* than montmorillonite on which methyl parathion was tightly adsorbed. It suggests that the degradation of methyl parathion in soil system is not governed by the affinity of methyl parathion adsorption on clay minerals and iron oxide. Greater extents of protection provided by goethite than by montmorillonite and kaolinite may be due to the significant decrease in the activity of *P. putida* in the presence of goethite. Studies on the effects of concentrations of methyl parathion on the degradation and activity of *P. putida* also show that higher concentrations of methyl parathion can result in the decrease of the percent biodegradation through inhibiting the activity of *P. putida* (Fig. 4 and Table 2). These results further confirmed that the degradation of methyl parathion adsorbed on minerals might be mainly

controlled by the interaction mechanisms of bacteria with minerals and the resultant bacterial activity.

In conclusion, the degradation of methyl parathion adsorbed on montmorillonite by *P. putida* was higher than that on kaolinite and goethite. The biodegradation of methyl parathion was not controlled by the adsorption affinity of methyl parathion for minerals. The activity of the degrading bacteria appears to be responsible for the degradation of methyl parathion in soil environments.

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