



Abiotic degradation of methyl parathion by manganese dioxide: Kinetics and transformation pathway



Xiaoping Liao, Caixiang Zhang*, Yuan Liu, Yinwen Luo, Sisi Wu, Songhu Yuan, Zhenli Zhu

State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, PR China

HIGHLIGHTS

- Pseudo-first-order model described the degradation of methyl parathion by α -MnO₂ well.
- Removal efficiency of methyl parathion depended strongly on α -MnO₂ loading and pH.
- Cations and HA-Na affect remarkably the degradation behavior of methyl parathion.
- Hydrolysis and oxidation pathways were proposed based on the identified products.

ARTICLE INFO

Article history:

Received 7 May 2015

Received in revised form

5 February 2016

Accepted 6 February 2016

Available online 16 February 2016

Handling Editor: Min Jang

Keywords:

Methyl parathion
Manganese dioxide
Abiotic degradation
Transformation pathway

ABSTRACT

Methyl parathion, a widely used insecticide around the world, has aroused gradually extensive concern of researchers due to its degradation product such as methyl paraoxon, with higher toxicity for mammals and more recalcitrant. Given the ubiquity of manganese dioxide (MnO₂) in soils and aquatic sediments, the abiotic degradation of methyl parathion by α -MnO₂ was investigated in batch experiments. It was found that methyl parathion was decomposed up to 90% by α -MnO₂ in 30 h and the removal efficiency of methyl parathion depended strongly on the loading of α -MnO₂ and pH value in the solution where the reactions followed pseudo-first-order model well. The coexisting metal ions (such as Ca²⁺, Mg²⁺ and Mn²⁺) weakened markedly the degradation of methyl parathion by α -MnO₂. However, the effect of dissolved organic matter (HA-Na) on reaction rates presented two sides: to improve hydrolysis rate but deteriorate oxidation rate of methyl parathion. Based on the degradation products identified by gas chromatography–mass spectrometer (GC/MS) and liquid chromatography high-resolution mass spectrometer (LC/HRMS), both hydrolysis and oxidation processes were proposed to be two predominant reaction mechanisms contributing to methyl parathion degradation by α -MnO₂. This study provided meaningful information to elucidate the abiotic dissipation of methyl parathion by manganese oxide minerals in the environment.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Among organophosphorus pesticides (OPPs) as effective insecticides to inhibit the function of acetylcholine esterase (AChE) in nervous system of insects, various residues of methyl parathion had been detected ubiquitously in soil (Velasco et al., 2014), sediment (Babu et al., 2011), human adipose tissues (Wang et al., 2011) and even in groundwater system (Jurado et al., 2012). Long-term exposure of living organisms to methyl parathion, particularly for the developing children (Cooney, 1999), has been concluded to

modulate reproductive, carcinogenic and immunosuppressive effects (Coral et al., 2009). Moreover, its main oxidation product of methyl parathion through oxidative desulfuration reaction, methyl paraoxon, has been addressed to hold approximate three orders of magnitude toxicological effect than its parent compound (Straus et al., 2000). On the other hand, its major hydrolysis product, 4-nitrophenol, could also present potential risk on environment and public health due to its acute toxicity and mutagenic potential (Yi et al., 2006). Thus, those features necessitated the researchers to understand its actual fate and dissipation in the environment (Alvarenga et al., 2014).

The hydrolysis and the oxidation processes, two major attenuation modes of methyl parathion, had been substantial documented in previous literature (Janos et al., 2014; Vlyssides et al.,

* Corresponding author.

E-mail address: caixiangzhang@yahoo.com (C. Zhang).

2004). Generally, hydrolysis process was acknowledged to be the predominant transformation pathway controlling the fate of methyl parathion in the environment. Multiple natural minerals ordinary distributed in the environment had been confirmed to possess the potentiality to catalyze the hydrolysis of methyl parathion, such as montmorillonite (Seger and Maciel, 2006), cerium dioxide (Janos et al., 2014) and goethite (Torrents and Stone, 1994). The reduced sulfur species existed widely in subsurface and marine environments (e.g. HS^- and S_n^{2-}) was also proven to improve the hydrolysis rate of methyl parathion as nucleophilic reagents to attack the carbon atom of the alkoxy group (Guo and Jans, 2006). Additionally, the mixed mechanisms (electrophilic and nucleophilic substitutions) were involved in the hydrolyzation of methyl parathion by divalent metal ions (such as Cu(II), Pb(II) and Zn(II)) (Smolen and Stone, 1997).

Besides, the oxidation transformation of the thiophosphate functionality to its corresponding oxon form ($\text{P}=\text{O}$), a more toxic compound than its parent, is also prevalent in the environment matrix (Seger and Maciel, 2006) or during the advanced treatment processes (Vlyssides et al., 2004). For instance, the partially hydrated montmorillonite clays (e.g., in Cu^{2+} and Zn^{2+}) also appeared to effectively catalyze the oxidation of methyl parathion and chlorpyrifos (Seger and Maciel, 2006). Parathion and chlorpyrifos could be also oxidized to its corresponding $\text{P}=\text{O}$ by the hypochlorous acid (HOCl) (Duirk et al., 2009).

As well known, manganese dioxides (MnO_2) are ubiquitous in natural soils and sediments (Remucal and Ginder-Vogel, 2014). Meanwhile, it has played an important role on the biogeochemical cycles of inorganic and organic compounds because of its distinctive physicochemical properties such as large surface area, low point of zero charge and high crystallinity and oxidizing ability (Negra et al., 2005). Therefore, MnO_2 particles have been applied efficiently to degrade a variety of contaminants. Of which, the hydrolysis behavior of herbicide atrazine on synthetic birnessite ($\delta\text{-MnO}_2$) was investigated (Shin and Cheney, 2005). The oxidation degradation of endocrine disruptors and antibiotics by MnO_2 had been also observed (Lu and Gan, 2013; Lin et al., 2009). Generally, the oxidation mechanism of MnO_2 was ascribed to radicals formed via electron transfer (Stone, 1987). However, it is not clear the possible hydrolysis and oxidation mechanism is synchronous for methyl parathion degradation by MnO_2 .

To elucidate the attenuation of methyl parathion in natural environments, the degradation behavior by MnO_2 is imperative to explore. In this study, the abiotic degradation of methyl parathion by MnO_2 including hydrolysis and oxidation processes were discussed separately. Moreover, some main factors such as pH, metal ions (e.g. Ca^{2+} , Mg^{2+} and Mn^{2+}), and dissolved organic matter (e.g. HA-Na) were also studied to understand the reaction mechanisms well. This results offer useful information related to the fate and dissipation of methyl parathion and other OPPs in actual environment matrix.

2. Materials and methods

2.1. Chemicals and oxide preparation

Methyl parathion standard (>99.6%) was purchased from Pesticide Research Institute (Shanghai, China). Methyl paraoxon was purchased from Fluka (Pestanal, analytical standard, $\geq 98\%$). The commercial 4-nitrophenol (AR, 98%) and sodium humate (AR) was obtained from Shanghai Aladdin reagent Co., Ltd. Acetonitrile, n-hexane and dichloromethane (DCM) were of HPLC grade and were purchased from ANPEL Laboratory Technologies (Shanghai, China). Other chemical reagents used in the experiment were of analytical grade and were obtained from the Sinopharm Chemical

Reagents Co., Ltd (Shanghai, China). All of above reagents were used as received without further purification. Ultrapure water (18.2 M Ω cm resistivity) prepared from ultra-pure water system (Heal Force NW, China) was used in all experiments.

Amorphous MnO_2 was synthesized referred to the method described by Baldwin et al. (2001). The details can be found in supporting information (SI). The specific surface area of MnO_2 was measured to be 183.47 m 2 g $^{-1}$ (ASAP2020, Micromeritics, USA) (SI Fig. S1). The pore size of MnO_2 could be attributed primarily to the occurrence of the stacked arbitrary of small plate-like particles (Sing et al., 1985). The powder was identified to be $\alpha\text{-MnO}_2$ phase (JCPDS no. 44-0141, $a = b = 9.78$ Å, $c = 2.87$ Å) (Bruker AXS D8-Focus, German) (SI Fig. S2) (Su et al., 2013). The morphology of $\alpha\text{-MnO}_2$ showed that small plate-like particles were agglomerated to form irregular spherical structures with a size of 1–15 μm (FEG-SEM-EDX SU 8010, Japan) (SI Fig. S3a). The particles had a diameter of about 10 nm (TEM-EDX Philips CM12, Netherlands). The presence of manganese and oxygen of $\alpha\text{-MnO}_2$ was identified by the EDX analysis (SI Fig. S3b and d).

2.2. Experiment methods

One gram per liter of methyl parathion was prepared in hexane solution as the stock solution. Then, a certain volume of stock solution added into volumetric flask using syringe was completely dried under a gentle nitrogen stream. Subsequently, ultrapure water containing 0.2‰ sodium azide and 0.01 M NaCl was added into the flask to inhibit the biodegradation of methyl parathion and to keep the suitable ion strength.

Batch experiments were conducted in 10-mL borosilicate glass bottles with an alumina crimp and a PTFE-faced septa by adding a known concentration of aqueous solution of methyl parathion with an accurate amount of $\alpha\text{-MnO}_2$. The reaction bottles were shaken continuously in a water bath shaker (150 rev min $^{-1}$) at 25 ± 1 °C in the dark. The influence of pH on the degradation was investigated under the condition of 20.5 μM methyl parathion, 0.57 M $\alpha\text{-MnO}_2$ and 0.01 M NaCl. The reaction solution pH was adjusted using 0.01 M buffers of acetic acid and its sodium salt (pH 4.5–5.5), and 4-morpholinepropanesulfonic acid (MOPS) and its sodium salt (pH 6.5–7.5) (Lu and Gan, 2013). The co-solutes effects of cations (Ca^{2+} , Mg^{2+} and Mn^{2+}) were also evaluated by adding 0.01 M corresponding chlorine salts at pH 4.5. As for the effect of organic matter on the degradation, the content of HA-Na varied from 0.1 mg L $^{-1}$ to 10 mg L $^{-1}$ was added in reaction solutions at pH 4.5 (Lin et al., 2009). In addition, the control experiments carried out under the same condition without the sodium azide and NaCl revealed that the influences of biology inhibitor and electrolyte were negligible.

Preliminary experiments were conducted to evaluate whether the oxygen contained in the solution affected the degradation of methyl parathion by $\alpha\text{-MnO}_2$. Almost the same degradation behavior under the N_2 -purging anoxic condition and non- N_2 -purging air condition indicated that the influence of the oxygen was negligible (SI Fig. S4). Thus, all the experiments were conducted without excluding oxygen. In addition, the adsorption capacity of methyl parathion by $\alpha\text{-MnO}_2$ was also investigated by calculating the difference of contents in reactions obtained with two approaches: (i) samples were centrifuged for 5 min at a speed of 3500 rev min $^{-1}$. The supernatants were passed through 0.22 μm PTFE membrane filters (CNW, Shanghai) and then transferred to 2 mL vials for HPLC analysis; (ii) excess L-ascorbic acid (2 g) was added into the reaction solution and shaken immediately for 30 s until the oxide particles were completely dissolved in the solution. Then, the samples were extracted using liquid–liquid extraction method by 3 \times 5 mL DCM and analyzed by gas chromatography (GC) equipped with a nitrogen–phosphorus detector (NPD) (GC-

Download English Version:

<https://daneshyari.com/en/article/6306821>

Download Persian Version:

<https://daneshyari.com/article/6306821>

[Daneshyari.com](https://daneshyari.com)