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Penta- and 2,4,6-tri-chlorophenol biodegradation during municipal solid waste anaerobic digestion

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ABSTRACT

In this study isotopic tracing using ^{13}C labelled pentachlorophenol (PCP) and 2,4,6-trichlorophenol (2,4,6-TCP) is proposed as a tool to distinguish the loss of PCP and 2,4,6-TCP due to biodegradation from other physical processes. This isotopic approach was applied to accurately assess in situ PCP and 2,4,6-TCP degradation under methanogenic conditions in several microcosms made up of household waste. These microcosms were incubated in anaerobic conditions at 35 °C (mesophilic) and 55 °C (thermophilic) without agitation. The volume of biogas produced (CH_4 and CO_2), was followed for a period of 130 days. At this stage of stable methanogenesis, $^{13}C_6$-PCP and $^{13}C_6$-2,4,6-TCP were introduced anaerobically in microcosms and its monitoring at mesophilic and thermophilic conditions was performed in parallel by gas chromatography mass spectrometry (GC–MS) and gas chromatography isotope-ratio mass spectrometry (GC–IRMS). This study proved the almost total dechlorination of bioavailable PCP and 2,4,6-TCP into 4-CP at 35 °C. Nevertheless, high rate adsorption in particular materials of the two compounds was observed. Furthermore, Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) Spectroscopy analysis of ^{13}C labelled 2,4,6-TCP mesophilic incubations showed the partial mineralization of 4-CP at 35 °C to acetate and then to HCO^{3-}. Consequently, NMR results confirm the biogas isotopic results indicating the mineralization of ^{13}C labelled 2,4,6-TCP into ^{13}C (CH_4 and CO_2). Concerning ^{13}C labelled PCP mesophilic incubations, the isotopic composition of the biogas still natural until the day 262. In contrast, no dechlorination was observed at 55 °C. Thus PCP and 2,4,6-TCP were persistent in thermophilic conditions.
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1. Introduction

Municipal Solid Waste (MSW) anaerobic digestion in bioreactor is getting more attention as this technique produces renewable energy as electricity and heat. In fact, many countries encourage the anaerobic digestion of MSW to promote solid wastes valorization through energy and the reduction of global climate warming (CCAC, 2015).

The digestate, principal product of the MSW methanization, contains numerous toxic compounds; thus, it is necessary to monitor and quantify these compounds and their metabolites before agricultural valorization of the digestate (Robinson et al., 2001; Hiroshi et al., 2002; Öman and Junestedt, 2008). Two main pollutants, Pentachlorophenol (PCP) and 2,4,6-trichlorophenol (2,4,6-TCP), are known to be widespread as constituents of industrial wastes. The reason is that they are used in many industrial processes such as manufacture of pesticides, drugs and dyes (Neilson et al., 1991). In addition, they have been widely used as preservative agents, antiseptics and disinfectants.

PCP is used as a wood-protection agent with fungicide and bactericide properties. It has been designated as a priority pollutant and is a probable human carcinogen (ATSDR, 1998; Calabrase and Kenyon, 1991; HSDB, 1993). Moreover, it has been detected in soil, sediments, surface waters, rainwater, drinking water, aquatic organisms, and food, as well as in biological materials (human milk, urine and adipose tissue) (ATSDR, 1998). As consequence, a great deal of concern has been raised about adverse ecosystem effects due to PCP utilization. The USA Environmental Protection Agency (EPA, 1999) and the official journal of the European Union (Council directive 2455/2001/ECC, 2001) list these chlorophenols as priority pollutants because of their high risk to human health,

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carcinogenicity and considerable persistence (Chen et al., 2014).

Little is known about the fate of chlorinated phenols in the anaerobic digestion of municipal solid waste (MSW). Although these compounds are recalcitrant, it has been observed that some are transformed or completely degraded by microorganisms under anoxic conditions (for reviews, see references (Haggblom, 1992; Mohn and Tiedje, 1992; Young and Häggblom, 1995; Becker et al., 1999; Yang et al., 2009; Ye and Li, 2006; Puyol et al., 2009)). Nevertheless, the temperature effect in anaerobic digestion of aromatics compounds, especially chlorinated phenols, is a key factor. Indeed, mesophilic conditions were reported to be more favorable for aromatic compounds mineralization in anaerobic digestion systems, contrary to the thermophilic conditions (Levén and Schnürer, 2005).

As mentioned in our previous study (Limam et al., 2013) the decrease of the micropollutant concentration in the anaerobic digestion systems doesn't demonstrate its total biodegradation and mineralization into CO_2 and CH_4. Thus, we used isotopic tracing with ^{13}C labelled PCP and 2,4,6-TCP to prove the mineralization of these micropollutants to CO_2 and CH_4, and not the transformation of injected chlorophenols to other toxic metabolites.

The aim of this work was to study and to compare the fate of PCP and 2,4,6-TCP during MSW anaerobic digestion, under mesophilic and thermophilic conditions. Thus, anaerobic experimental microcosms containing reconstituted MSW were launched, in which some ^{13}C enriched PCP or 2,4,6-TCP were introduced. Using a combined molecular and isotopic approach it was then possible to monitor the specific mineralization of those compounds and to detect the accumulation of metabolites.

2. Materials and methods

2.1. Reagents and chemicals

The $^{13}C_6$-pentachlorophenol (99%) and $^{13}C_6$-2,4,6-trichlorophenol (99%) were procured from Cambridge Isotope Laboratory (Andover, USA). The potassium bicarbonate, sodium chloride, mercuric chloride, methanol, ethyl acetate, acetone and acetic anhydride, were purchased from Supelco (St Quentin Fallavier, France). All the reagents and solvents were of analytical grade. The ultra-pure water, used in all the experiments, was obtained from Milli-Q system (Eschborn, Germany).

2.2. Preparation of the inocula

The inocula used in this study were obtained by the centrifugation of 12 portions of 200 mL leachate obtained from a municipal solid waste (MSW) landfill. The leachate centrifugation is performed during 10 min at 8500g and a temperature of 4 °C (AllegraTM X-22R Centrifuge, Beckman Coulter, France). In the experiments, 6 MSW inocula were used for the $^{13}C_6$-PCP degradation study and 6 MSW inocula were used for the $^{13}C_6$-2,4,6-TCP degradation study.

2.3. Micropollutants degradation assays

Experimental microcosms were prepared, for each compound, in triplicate for both temperature (35 °C ±2 °C and 55 °C ±2 °C) as described previously (Qu et al., 2009). These incubations were composed of 330 mL glass bottles closed with a screw cap and a septum (Fischer Scientific Bioblock, Illkirch, France) filled with a volume of $NaHCO_3$ buffer solution of 210 mL at pH=8.3 and 10 g of a representative composition of a reconstituted French Solid Waste (MODECOM Composition in percentage: putrescible 28.6, papers and cardboards 25.4, textiles and sanitary textiles 5.7, plastics 11.1, glasses 13.1, metals 4.1, not classified fuels 3.3, incombustible not classified 6.8 and special waste 0.5.).

Then, the prepared MSW inocula were introduced at the same time to the twelve bottles devoted to $^{13}C_6$-PCP and $^{13}C_6$-2,4,6-TCP degradation assays and an atmosphere of Nitrogen was established. The biogas (CH_4 and CO_2) composition was analyzed immediately after the equilibration by connecting the bottle to a gas chromatograph (LGC CP2003P Varian) equipped with two parallel chromatographic columns coupled to thermal conductivity detectors (TCD). The measurement conditions were same as in (Vigneron et al., 2007). Briefly, the biogas composition was analyzed by a gas chromatograph (μGC CP2003P Varian) equipped with two parallel chromatographic columns: a Poraplot U and a molecular-sieve (Varian). The carrier gas was helium. Detection was achieved with a thermal conductivity detector (TCD).

After 130 days of incubation, until reaching the stable methanogenesis phase, the $^{13}C_6$-PCP and $^{13}C_6$-2,4,6-TCP microcosms were amended with respectively 0.28 mg $^{13}C_6$-PCP and 1.06 mg $^{13}C_6$-2,4,6-TCP, to yield the initial dissolved concentrations of 1320 μg L^{-1} for $^{13}C_6$-PCP and 5037 μg L^{-1} for $^{13}C_6$-2,4,6-TCP. Two incubations were realised for each compound at mesophilic and thermophilic conditions. Moreover, a control incubation for each temperature was performed by injecting 300 mg of mercuric chloride ($HgCl_2$) diluted in 15 mL sterile water. The ($HgCl_2$) obtained concentration allows the microorganisms activity inhibition in the control incubation (Tuominen et al., 1994).

The mesophilic and thermophilic incubated microcosms were kept in the dark under methanogenic conditions for a new period of 262 days for $^{13}C_6$-PCP and 360 days for $^{13}C_6$-2,4,6-TCP. Biogas (CH_4 and CO_2) isotopic composition survey was done during this period under mesophilic and thermophilic conditions. Also a quantitative analysis of $^{13}C_6$-2,4,6-TCP and $^{13}C_6$-PCP is done by GC–MS.

2.4. Analytical methods

2.4.1. $^{13}C_6$-PCP and $^{13}C_6$-2,4,6-TCP quantitative analysis

Leachate was retrieved regularly from each incubation for $^{13}C_6$-PCP and $^{13}C_6$-2,4,6-TCP analysis. Their concentrations were determined experimentally as described previously in detail (Limam et al., 2010). Briefly, after dilution of 100 μL of sample in 5 mL milli-Q water, the diluted leachate sample is introduced in a 20 mL Polytetrafluoroethylene (PTFE)-capped glass vial. 2 g Sodium chloride, 200 mg $KHCO_3$ and 30 μL of acetic anhydride were added. In order to achieve the derivatization reaction, a reaction time of 5 min at 80 °C is maintained. Then, a polydimethylsiloxane (PDMS) solid-phase microextraction (SPME) fiber (100 μm) was injected in the headspace of the 20 mL PTFE-capped glass vial. Finally the extraction of $^{13}C_6$-PCP and $^{13}C_6$-2,4,6-TCP was done at 80 °C and under 500 rpm rotation speed for 30 min After that, the SPME fiber was desorbed in the injector at 250 °C for 5 min Analysis was performed automatically by Combi PAL autosampler (CTC Analytics, Switzerland). The headspace-SPME (HS-SPME) extract was introduced in the Splitless injector. The detection was performed by the quadrupole mass spectrometer coupled to the Ultra gas chromatograph (Thermo Fisher Scientific, France).

The chromatographic separation was achieved using a 60 m length, 0.25 mm I. D., 0.25 μm film thickness Zebron 5 MS column (5% phenyl-methyl polysiloxane, Phenomenex). The oven temperature program was the following: 40 °C for 5 min, increase in three steps, at 20 °C min^{-1} to 120 °C, then at 2 °C min^{-1} to 164 °C, and finally at 35 °C min^{-1} to 280 °C. Finally, oven temperature was maintained 2 min at 280 °C. The injector temperature was kept at 250 °C and the spiltless-time was 5 min The GC separation was performed in the constant flow mode. The carrier gas was Helium with a column flow rate of 1.2 mL min^{-1}. The transfer line and the ion source were held at 280 °C. MS detector mode was the electron

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