



# Adsorption and degradation processes of tributyltin and trimethyltin in landfill leachates treated with iron nanoparticles



Kelly Peeters<sup>a</sup>, Gaëtane Lespes<sup>b</sup>, Radmila Milačič<sup>a</sup>, Janez Ščančar<sup>a,\*</sup>

<sup>a</sup> Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

<sup>b</sup> Equipe de Chimie Analytique Bio-Inorganique et Environnement, IPREM CNRS UMR 5254, Université de Pau et des Pays de l'Adour, Hélioparc, 64053 Pau, France

## ARTICLE INFO

### Article history:

Received 27 May 2015

Received in revised form

31 July 2015

Accepted 5 August 2015

### Keywords:

Tributyltin  
Trimethyltin  
Landfill leachate  
Iron nanoparticles  
Adsorption  
Degradation  
Fenton-type process

## ABSTRACT

Biotic and abiotic degradation of toxic organotin compounds (OTCs) in landfill leachates is usually not complete. In this work adsorption and degradation processes of tributyltin (TBT) and trimethyltin (TMeT) in leachate sample treated with different iron nanoparticles (FeNPs): Fe<sup>0</sup> (nZVI), FeO and Fe<sub>3</sub>O<sub>4</sub> were investigated to find conditions for their efficient removal. One sample aliquot was kept untreated (pH 8), while the others (pH 8) FeNPs dispersed with tetramethyl ammonium hydroxide (TMAH) or by mixing were added and samples shaken under aerated conditions for 7 days. The same experiments were done in leachates in which the pH was adjusted to 3 with citric acid. Size distribution of TBT and TMeT between particles > 5 μm, 0.45–5 μm, 2.5–0.45 μm, and < 2.5 nm was determined by sequential filtration and their concentrations in a given fraction by gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICP-MS). Results revealed that most of the TBT or TMeT was present in fractions with particles > 2.5 or < 2.5 nm, respectively. At pH 8 adsorption of TBT to FeNPs prevailed, while at pH 3, the Fenton reaction provoked degradation of TBT by hydroxyl radicals. TBT was the most effectively removed (96%) when sequential treatment of leachate with nZVI (dispersed by mixing) was applied first at pH 8, followed by nZVI treatment of the aqueous phase, previously acidified to pH 3 with citric acid. Such treatment less effectively removed TMeT (about 40%). It was proven that TMAH provoked methylation of tin, so mixing was recommended for dispersion of nZVI.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

Organotin compounds (OTCs) are highly toxic even at ng L<sup>-1</sup> concentration levels (Fent, 1996). Due to their wide use in industrial and agricultural applications, they are globally present as pollutants in the environment (Hoch, 2001; Díez et al., 2002; Craig et al., 2003; Rosenberg, 2005; Milivojevič Nemanič et al., 2009; de Carvalho et al., 2010; Furdek et al., 2012; Merisiowsky et al., 2001; Michalzik et al., 2007; Pinel-Raffaitin et al., 2008; Vahčič et al., 2011; Peeters et al., 2014). The municipal waste commonly dumped on landfill sites is an important pool of OTCs that originates from household products, plastic materials and textiles, and inorganic tin from metallic cans (Pinel-Raffaitin et al., 2008; Vahčič et al., 2011; Peeters et al., 2014). Both, organic and inorganic tin species can be mobilised and released to the environment by percolation of water through the waste pile.

Tributyltin (TBT) is one of the most toxic OTCs and is, despite

its global ban (Regulation (EC) No. 782/2003, International Convention on the control of harmful anti-fouling systems on ships), still present in the marine (Furdek et al., 2012) and terrestrial environment (Silva et al., 2014), while trimethyltin (TMeT) is neurotoxic (Huong et al., 2011) and occurs in notable concentrations in landfill leachates (Merisiowsky et al., 2001; Michalzik et al., 2007; Pinel-Raffaitin et al., 2008; Vahčič et al., 2011; Peeters et al., 2014). Under landfill conditions tin is undergoing chemical and biological transformation (Peeters et al., 2014; Stasinakis et al., 2005). In this way, tin species present in waste can be modified by alkylation (i.e. hydridation, methylation, ethylation), dealkylation or transalkylation reactions, resulting in the generation of new tin compounds in liquid and gaseous phases (Pinel-Raffaitin et al., 2008).

Additional management of municipal solid wastes is required to prevent the release of pollutants from their treatment and disposal facilities. In 1999, the European Commission ratified a Council Directive on the 'Landfill of Waste', with the aim to reduce the negative effects of pollutants on the environment (Council Directive 1999/31/EC). To prevent environmental pollution, researchers are looking for solutions to remove OTCs from

\* Corresponding author. Fax: +386 1 2519 385.

E-mail address: [janez.scancar@ijs.si](mailto:janez.scancar@ijs.si) (J. Ščančar).

contaminated waters. Until now, remediation was only focused on the removal of TBT, but in landfill leachates it was not yet discussed. In the review article, Du et al. (2014) reported different ways of TBT removal from environmental samples. Biodegradation and phytoremediation are common remediation procedures but can be applied only, when TBT contamination levels are moderate, to prevent its toxic effects to bacteria or plants. These processes in general require long remediation period. Chemical oxidation by potassium permanganate or hydrogen peroxide, as well as electrochemical oxidation, which generates radicals, were also reported to break the bonds between the tin and butyl groups in an aqueous phase. Chemical oxidation is more effective for degrading TBT than other OTCs such as phenyltins. By applying solvent extraction TBT was removed from the aqueous phase. Diesel oil, which has been used for this purpose, offered some possibilities of its reuse in other applications. By the use of different flocculants, high amounts of TBT were removed from contaminated waters by coagulation of the suspended particulates. However, the dissolved TBT remained in solution. Adsorption processes were found to be among the most effective means to remove TBT bound to organic and inorganic particulate matter, but the cost of adsorbent is in general high. In another review article Ayanda et al. (2012) reported effective remediation of OTCs in sea water by combining hydrogen peroxide, ozone and UV treatment. The main drawback of these procedures was the need of complex and expensive treatment apparatus. Different mixtures of activated carbon with SiO<sub>2</sub>NPs, Fe<sub>3</sub>O<sub>4</sub>NPs, ZnONPs and activated carbon fly ash were also tested for removal of TBT from contaminated waters (Ayanda et al., 2013). Combination of activated carbon, nanometal oxides and fly ash increased the surface area, which resulted in high sorption capacity for TBT.

Recently, nanoparticles (NPs) have received significant interest for environmental remediation (Joo and Cheng, 2006). Among different metal NPs based remediation treatments, this one involving iron nanoparticles (FeNPs) is an attractive option as iron is inexpensive, non-toxic and environmentally compatible (Krajangpan et al., 2009; Noubactep, 2010; Singh et al., 2012; Palanisamy et al., 2013; Němeček et al., 2014). FeNPs are magnetic nanoparticles with large surface area. They have proven to be useful for adsorbing, reductively transforming or degrading numerous types of organic and inorganic environmental contaminants (Joo and Cheng, 2006; Noubactep, 2010; Singh et al., 2012; Palanisamy et al., 2013; Němeček et al., 2014). At neutral to alkaline pHs, adsorption of pollutant onto the surface of FeNPs and co-precipitation with iron corrosion products is the main process of pollutant removal (Noubactep, 2010). After remediation, iron precipitate can be simply taken away by a magnet. At acidic pHs, in aerated solutions containing dissolved Fe<sup>2+</sup> and organic ligands like citrate, oxalate or EDTA, Fenton-type reaction takes place through a series of ligand-mediated reactions, resulting in formation of H<sub>2</sub>O<sub>2</sub> and highly reactive hydroxyl (OH<sup>•</sup>) radicals. OH<sup>•</sup> radicals are strong oxidants, capable to rapidly degrade many organic and inorganic compounds (Deng and Englehardt, 2006; Gylieñe et al., 2008; Keenan and Sedlak, 2008; Zhou et al. 2009; Zhou et al., 2010; Martins et al., 2012; Babuponnusami and Muthukumar, 2014). To initiate Fenton-type reaction with FeNPs, citrate can be used as an environment-friendly alternative for toxic EDTA (Gylieñe et al., 2007). Iron forms stable complexes with citrate that generate the superoxide radical O<sub>2</sub><sup>•-</sup>, which by further reaction with Fe-complexes produces H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> is a source for the Fenton process that yields OH<sup>•</sup> radicals.

The aim of our work was to investigate the new possibility for the remediation of OTCs in landfill leachates by the use of FeNPs. Adsorption and degradation processes of TBT and TMeT in leachates treated with nanozerovalent iron (nZVI), FeONPs and Fe<sub>3</sub>O<sub>4</sub>NPs were studied. Representative leachate sample was

treated at different pH in order to promote either adsorption onto particles that can be removed from the leachate, or degradation by Fenton-type reaction. A novel approach, which considers the chemical speciation of OTCs and their size distribution before and after the FeNPs treatment was applied to examine the association of OTCs with particles of operationally defined size present in the leachate. For this purpose sequential filtration was used and the concentration of OTCs in a given fraction determined by gas chromatography-inductively coupled plasma mass spectrometry (GC-ICP-MS).

## 2. Materials and methods

### 2.1. Reagents and procedures

Stabilized magnetic nZVI (manufactural size information approximately 25 nm) were obtained from MKNano, (Williamsville, NY USA), while the magnetic FeONPs stabilized in heptane (particle size 3.5–9.5 nm), magnetic Fe<sub>3</sub>O<sub>4</sub> nanopowder (particle size 50–100 nm) and tetramethylammonium hydroxide (TMAH) (25 wt% in methanol) used for dispersing of FeNPs came from Sigma-Aldrich (Steinheim, Germany). Citric acid monohydrate (p. a.) used for adjusting of pH of the leachate was supplied from Merck (Darmstadt, Germany). Tributyltinchloride (TBTCl, 96%) was purchased from Sigma-Aldrich and trimethyltin chloride (TMeTCl, 99%) from Acros Organics (New Jersey, NY, USA). For sequential filtration of leachate samples, the 5 μm cellulose-nitrate, 0.45 μm cellulose-acetate membrane filters and 10 kDa regenerated cellulose filters (2.5 μm) were obtained from Whatman (Vienna, Austria), Ministart (Goettingen, Germany) and Amicon (Zagreb, Croatia), respectively. To estimate the influence of microorganisms on transformation of OTCs in landfill leachate, an aliquot of the leachate sample was sterilized for 2 h at 121 °C in autoclave Geringe GE6610EM-2 (Geringe, Sweden). The reagents used for the speciation analysis of OTC are described elsewhere (Vahčić et al., 2011).

### 2.2. Speciation analysis of OTCs and validation of the analytical procedure

Speciation analysis was carried out under an optimised procedure for the determination of OTCs in landfill leachates previously developed and validated in our laboratory (Vahčić et al., 2011). It was applied in all the size fractions of the leachate samples in order to have a complete mass balance, for showing in particular if OTCs were degraded or adsorbed on FeNPs. Briefly, 10 mL aliquots of landfill leachate samples were transferred into 30 mL amber glass reactor vessels along with 0.5 mL of methanol and shaken for 2 h. 10 mL of a 0.2 mol L<sup>-1</sup> Tris-citrate buffer (pH 6) and TPrT internal standard solution (200 ng Sn L<sup>-1</sup>) were then added. For the standard addition calibration method, mixtures of methyl- and butyltins were added to sample aliquots in concentrations up to 1000 ng Sn L<sup>-1</sup>. Sample extracts were derivatized by NaBEt<sub>4</sub> (0.1 mL of 2% (m/V)), followed by the addition of 2 mL of hexane for the extraction of ethylated OTCs. Samples were then mechanically shaken for 16 h. To separate the emulsion from the organic phase, 1 mL of 25% KOH in methanol was added. The concentrations of OTCs in the organic phase were determined by GC-ICP-MS.

#### 2.2.1. Accuracy check

Since there is no certified reference material for landfill leachates available, a spike recovery test was used for the accuracy

Download English Version:

<https://daneshyari.com/en/article/6352203>

Download Persian Version:

<https://daneshyari.com/article/6352203>

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