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Study of photocatalytic degradation of tributyltin, dibutylin and monobutyltin in water and marine sediments

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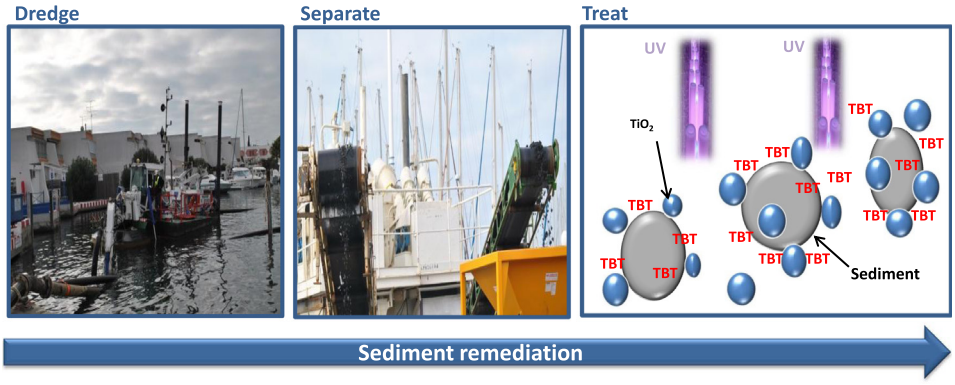
HIGHLIGHTS

- Organotins in aqueous solution are completely removed by photocatalysis.
- Organotins adsorbed on marine sediments are degraded by heteregeneous photocatalysis.
- Photocatalytic organotins degradation is mainly due to hydroxyl radical attack.
- Direct photolysis of organotins is the second mechanism of degradation.
- AOP appears as a possible way for the remediation of marine sediments.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports on the first assessment of the treatment of sediments contaminated by organotin compounds using heterogeneous photocatalysis. Photocatalysis of organotins in water was carried out under realistic concentration conditions ($\mu g\ L^{-1}$). Degradation compounds were analyzed by GC-ICP-MS; a quasi-complete degradation of tributyltin (TBT) in water (99.8%) was achieved after 30 min of photocatalytic treatment. The degradation by photolysis was about (10%) in the same conditions. For the first time decontamination of highly polluted marine sediments (certified reference material and harbor sediments) by photocatalysis proves that the use of UV and the production of hydroxyl radicals are an efficient way to treat organotins adsorbed onto marine sediment despite the complexity of the matrix. In sediment, TBT degradation yield ranged from 32% to 37% after only 2 h of irradiation (TiO_2–UV) and the by-products: dibutyltin (DBT) and monobutyltin (MBT) were degraded very rapidly in comparison with TBT. It was shown that during photocatalysis of organotins in sediments, the hydroxyl radical attack and photolysis are the two ways for the degradation of adsorbed TBT.

1. Introduction

Organotin compounds, especially tributyltin (TBT) compounds, was used in a wide range of applications including stabilizers in the PVC industry, material protection (stone, leather, paper), industrial catalysts, algicides, fungicides, bactericides and wood preservatives (Hoch, 2001). In ports and marinas, TBT has been widely applied in the past as a biocide in antifouling paint marine coatings to prevent the growth and attachment of barnacles, mussels, tube worms, algae and other marine fouling organisms. TBT is perhaps the most toxic substance that has ever been

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deliberately introduced into the marine environment by mankind (Goldberg, 1986). Marine snail and whelks imposex (hermaphroditism or sterility of females) occurs at low concentrations, in the order of ng L^{-1} (Alzieu, 1986, 1991, 1998, 2000). Owing to the high toxicity of TBT formulations in coastal ecosystems (Fent, 1996, 2004), organotins have been regulated and/or banned in antifouling paints, first in France in 1982 and later in many other countries. Studies have shown that despite the implementation of regulations or ban, high concentrations of TBT in water or in bottom sediments are still detected: in Spain (commercial and fishing harbors) (Diez et al. 2002), in France (Mediterranean marinas) (Michel and Averty, 1999; Cassi et al., 2008), in Poland (Filipkowska et al., 2011), Croatia (Furdek et al., 2012) and Argentina (Castro et al., 2012).

Even with the enforcement of regulations or prohibition, it seems, therefore, that the problem of TBT pollution of harbor sediments is still a subject of concern, especially for the disposal of contaminated dredged sediments. After dredging, sediments are considered as waste and the dumping polluted sediments in the open sea is regulated by strict criteria (Mamindy-Pajany et al., 2012). The treatment of these highly contaminated sediments seems essential before their landfilling or reuse as building materials (construction of dams, barriers, etc.).

There have been very few publications on the specific treatment of organotin in water and/or in sediment. Several techniques have been identified for the remediation of TBT from contaminated sediments: physical separation (hydrocycloning and froth flotation) (Reed et al., 2001), land deposition (Novak and Trapp, 2005), biodegradation (Saeki et al., 2007), thermal treatment (Mostofizadeh, 2001; Song et al., 2005), chemical oxidation (Mailhot et al., 1999; Pensaert et al., 2005) and electrochemical treatment (Stichnothe et al., 2001; Voulvoulis and Lester, 2006; Arevalo and Calmano, 2007). Anaerobic treatment of TBT adsorbed on sewage sludge was minimal (Voulvoulis and Lester, 2006) and this process appears to be not adapted for treating TBT. In this context, Advanced oxidation could be considered as a potential solution to decontaminate marine sediments. Among the advanced oxidative processes (AOP), heterogeneous photocatalysis appears as an interesting technique for the treatment of persistent organic pollution (Brosillon et al., 2011; Plantard et al., 2012). Indeed, TiO_2 activation under UV irradiation ($\lambda < 390$ nm) allows the generation of highly reactive $OH^{\cdot}$ free radicals from water or hydroxide ions. Navio et al. have studied the photocatalysis (UV/TiO_2) of TBT (Navio et al., 1993, 1996) and triphenyltin (TPT) (Navio et al., 1997) in an aqueous solution at a very high concentration (5 mg L^{-1}) in comparison with the levels found in raw water. TBT was partially degraded after 30 h of UV irradiation whereas dibutyltin (DBT) and monobutyltin (MBT) were under the limit of detection in less than 12 h. TPT (C_0 = 2.5 mg L^{-1}) was completely degraded after 2 h 30 min whereas diphenyltin and monophenyltin remain in solution as by-product of TPT degradation after 2 h 10 min.

The goal of this study is to investigate the possibility to treat sediments contaminated with organotin compounds by heterogeneous photocatalysis. Firstly, photocatalysis of organotin in water was carried out in order to confirm previous findings (Navio et al., 1996, 1997). Unlike previous research, very low levels of organotin – close to those found in raw water – were studied: 5 μg(Sn) L^{-1} in this study vs 5 mg(Sn) L^{-1} in the literature (Navio et al., 1996; Bangkedphol et al., 2010). This experimental approach necessitated the ability to monitor low levels of organotin in both water and solid matrixes with an adapted analytical method. Decontamination of different marine sediments (certified reference material and harbor sediments) by photocatalysis was then examined.

2. Materials and methods

2.1. Reagents and environmental samples

Chloride forms of MBT(95%), DBT(97%) and TBT(96%) were obtained from LGC Promochem (Molsheim, France). Tripropyltin chloride (TPrT, 98%) was obtained from Strem Chemicals (Bischeim, France). Stock organotin solutions containing 1000 mg(Sn) L^{-1} were prepared in methanol. When stored at +4 °C in the dark, they are stable for at least one year (Lespes, 1995). Methanol, sodium acetate, nitric and acetic acids and isooctane were purchased from Fisher Bioblock Scientific (Illkirch, France). Deionised MilliQ water (18.2 MΩ cm) was used. Tertbutanol (tButOH, purity 99.5%) was purchased from Sigma Aldrich (Saint-Quentin Fallavier, France). Sodium tetraethylborate ($NaBEt_4$) used for derivatization was obtained from Strem Chemicals. $NaBEt_4$ solutions (2% in deionised water) were prepared daily and stored at +4 °C in the dark. Glassware was decontaminated overnight in a 10% (v/v) nitric acid solution and rinsed thoroughly with deionised water prior to use (Bancon-Montigny et al., 1999, 2001). TiO_2 (P 25 Degussa) was used as a photocatalyst in this study (BET: 54 m^2 g^{-1}; average particle diameter: 20 nm).

Tests were performed on the PACS-2 marine sediment reference material (National Research Council of Canada-NRCC). This was collected from Esquimalt harbour, B.C, freeze dried, passed through a No. 120 (125 μm) screen, blended and bottled. Certified values and their uncertainties are reported as mass fractions (based on dry mass) in Table 1. Studied surface sediments were collected in February 2009 from a yachting harbor on the south-east French Mediterranean coast (Port-Camargue, Languedoc-Roussillon,) using a Shipek grab.

Table 1
Organotins, metals and organic carbon (POC) concentrations in PACS and surface sediments of Port-Camargue. The location in the harbor of the samples PC19, PC21, PC25 are given in Fig. 1 in Briant et al. (2013). (Italics: standard deviation)

		Organic carbone (%)	MBT	DBT	TBT	As	Co	Cr	Cu	Mn	Ni	Pb	Ti	Zn
			ng(Sn) g^{-1}			mg kg^{-1}								
Certified reference material PACS 2	Certified values	3.3	700	1100	832	26.2	11.5	91	310	440	39.5	183	4400	364
				±135	*±95*	*±1.5*	*±0.3*	*±5*	*±12*	*±19*	*±2.3*	*±8*	*±300*	*±23*
	Measured values		579	958	871									
			±28	*±40*	*±19*									
Port-Camargue marina	PC19	0.57	112	235	308	7.2	3.3	22	160	202	11.4	29	1370	84
			±3	*±7*	*±11*	*±0.2*	*±0.1*	*±1*	*±5*	*±6*	*±0.3*	*±1*	*±41*	*±3*
	PC21	2.96	710	5066	10738	10.7	4.6	37	1497	206	17	94	2253	475
			±22	*±127*	*±161*	*±0.3*	*±0.1*	*±1*	*±45*	*±6*	*±1*	*±3*	*±68*	*±14*
	PC25	0.82	364	1276	3136	15.1	7.3	54	321	353	29	66	2052	301
			±12	*±16*	*±85*	*±0.5*	*±0.2*	*±2*	*±10*	*±11*	*±1*	*±2*	*±62*	*±9*

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