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Review

Environmental remediation techniques of tributyltin contamination in soil and water: A review

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HIGHLIGHTS

- A critical review of remediation techniques for TBT contaminated soil and water.
- The first review paper covers global TBT-antifouling paints legislation process.
- Laboratory, pilot-scale and full-scale TBT clean-up techniques are reviewed.
- Efficiency, feasibility and cost of the clean-up techniques are compared.

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ABSTRACT

Tributyltin (TBT) compounds are active constituents of organotin antifouling paints which were used to prevent the growth of 'fouling' organisms on marine structures and vessels since 1950s. Due to the widespread applications as antifouling agent on commercial and military marine vessels, TBT compounds entered various ecosystems and are still being found in sewage sludge, sediments and waterways. Since the adverse toxic effects of TBT to non-targeted aquatic life were discovered in 1980s, significant effort has been directed towards the clean-up of TBT-contaminated marine sediments and waterways. Most of published research papers regarding TBT compounds mainly focus on their properties, environmental fates, levels and toxicity. This paper firstly reviews the global TBT legislation development from 1980s to 2008, and also presents a critical review of environmental disposal and remediation techniques of TBT contaminated soil and water. The efficiency, feasibility and cost of recent TBT clean-up techniques by thermal treatment, biodegradation, advanced chemical oxidation and physio-chemical adsorption are also critically reviewed.

Contents

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1. Introduction

Tributyltin (TBT) is a synthetic organotin compounds and widely used from the 1950s to 2008 as the active constituent of organotin antifouling paints on commercial and military marine vessels, as well as on small recreational watercraft [1]. Tributyltin (TBT) compounds conform to the following general formula $(CH_3CH_2CH_2CH_2)_3Sn\text{-}X$, where X is an anion (normally a halogen ion such as Cl^-), or a covalently-bonded functional group. World production of organotin compounds increased from about 40,000 tonne/year in 1985 and peaked at 50,000 tonne/year in 1996 [2]. Ship fouling is the unwanted growth of biological materials, such as barnacles, algae and other marine organisms, on ships' hulls immersed in seawater. Antifouling paints are applied to ships' hulls to prevent the growth of these marine organisms to reduce friction between the hulls of ships and water. Effective antifouling techniques using antifouling paints enable ships to travel more smoothly and faster in water and so reduce fuel costs. It has been reported that a 1 mm thick layer of algal slime increases hull friction by 80% and causes a 15% loss in ship speed, whereas a 5% thickness increase in fouling for a tanker of 250,000 tons deadweight will increase fuel usage by 17% [3]. Effective antifouling paints are thus very important for the shipping industry for both economic and environmental reasons. Copper-based (Cu_2O) antifouling paints were used originally but they become ineffective within a year and longer acting biocides are needed. TBT-based antifouling paints swiftly kill marine organisms such as barnacles, algae and mussels and are much longer lasting than those based on copper oxide.

TBT antifouling paint was introduced in the late 1950s and soon became widely adopted on a global scale as a very effective antifouling agent. However, adverse effects of TBT on oyster growth were observed in oyster farms on the Atlantic coast of France in 1980s [4] and it raised serious concerns on the toxicity of TBT to marine ecosystems and waterways, even at very low concentrations. Research has demonstrated that lower level organisms typically show impairment at concentrations as low as 1 ng TBT/L while higher-level organisms show health impairment at concentrations as low as 1 μg TBT/L [1]. In the last 40 years scientific studies have shown that TBT-based anti-fouling paints release highly toxic TBT into aquatic systems from relatively diffuse sources such as TBT-based antifouling paint surfaces and from intense point-sources such as shipyards and hardstand areas within commercial harbours and marinas [5]. TBT compounds have the tendency to accumulate in sewage sludge, sediments and biota. Degradation of TBT in the aquatic environment is a slow process. Half-lives range from 1 to 3 weeks under optimal conditions to several years under anaerobic conditions, and therefore TBT compounds pose a substantial risk of toxicity and have significant chronic impacts on non-targeted marine species, habitats and ecosystems. Human health is therefore also at risk due to consumption of affected seafood [6–13].

The environmental concentration levels, physical and chemical properties, toxicity, human exposure and distribution of TBT in aquatic systems have been well studied and documented [2,8, 14–20]. However, most of published research and review papers regarding TBT compounds are mainly focusing on their properties, environmental fates, levels and toxicity. Since the discovery of the adverse impact of TBT antifouling agent on untargeted marine lives, significant efforts have been put into clean-up of the TBT-contaminated marine sediments and waterways. This paper gives an overview of the development of international TBT legislation, the environmental sources and then focuses on laboratory, pilot-scale studies and full-scale projects on remediation of TBT-contaminated sediment and water in the past 20 years. The efficiency, feasibility and cost of recent TBT clean-up techniques by thermal treatment, biodegradation, advanced chemical oxidation and physio-chemical-adsorption are also overviewed and critically compared.

2. Sources of TBT contaminant in the marine environment

The principal source of TBT contamination of the marine environment is TBT-based antifouling paint. TBT can enter marine systems through three major pathways:

2.1. TBT leached into seawater from antifouling paint applied to the hulls of ships

There are two main types of antifouling paint: free-association and self-polishing antifouling paint [1]. Both of these antifouling paints consist of a film-forming material with a biocidal ingredient (TBT) and a pigment. TBT-based copolymer paints have a constant leach rate of 1.6 μg (Sn)/cm^{-2}/day but the initial leaching rate of a freshly painted surface can be as high as 6 mg (Sn)/cm^{-2}/day, which reduces to the designed constant rate after several weeks. Therefore a 3-day docking of a commercial ship at a harbour mooring can release more than 200 g TBT into the water and if freshly painted, this amount can reach 600 g. As a result the dissolved

Fig. 1. Pieces of antifoulant paint removed from the grounding site [22].