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Review

Recent developments and prospects of dioxins and furans remediation

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ABSTRACT

Rapid urbanization and industrialization of anthropogenic activities have exerted immense pressure on the environment. Polyhalogenated organic compounds, especially dioxins and furans are regarded as ubiquitously persistent environmental pollutants in the ecosystem. The recalcitrant nature of dioxins and furans induce toxicity in both humans and wildlife. Dioxins and furans are generated by defective technological chemical processes that occur during the manufacture of herbicides and pesticides, use of fertilizers, bleaching of paper and wood pulp and incomplete combustion process. However, incineration and incomplete combustion of solid waste are the main cause for the discharge of dioxins and furans to the environment. During incineration and incomplete combustion, noxious flue gas and ashes are released into the atmosphere and contaminate the soil and water systems; thereby affecting the ecology. According to World Health Organization fact sheet 2016, more than 90% of human exposure to dioxins is through the food chain, especially from dairy products, seafood and meat. These pollutants are mutagenic, carcinogenic, immunotoxic and teratogenic for lower and higher forms of life i.e. microorganisms to humans. This review describes the sources of dioxins and furans pollution, hazardous effects on the ecosystem and recent techniques to minimize and treat dioxins and furans contaminants in the environment. This paper also previews the significance of conventional and latest remediation techniques prevailing around the globe for treating dioxins and furans entry into the ecosystem.

1. Introduction

The rapid urbanization and industrialization has opened the door for modernization in various industrial sectors and has exerted immense pressure on the environment. Polyhalogenated organic compounds are the most detrimental contaminant persistent in all components of the ecosystem and exhibit negative reputation to the environment. Dioxins, furans and their congeners are a group of persistent pollutants with halogenated aromatic compounds that are inevitably emanated from incomplete combustion and incineration process. Commonly known dioxins and furans are polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs).

According to the United States Environmental Protection Agency (US-EPA), dioxins and furans are considered as the abbreviation for the family of chemically-related compounds that share a similar chemical structure and characteristics. These environmental pollutants exhibit longer half-lives (Milbrath et al., 2009; Matsumoto et al., 2015), hence, are highly persistent in the ecosystem. They are produced as a result of defective technological chemical processes that occurs during the production of herbicides and pesticides (Holt et al., 2010), use of fertilizers (Elskens et al., 2013), bleaching of paper and wood pulp (Andelin et al., 1989) and incomplete combustion process (Zhang et al., 2017).

PCDD/Fs are highly toxic and carcinogenic to ecosystem due to their chronic implications on biota. They are reported as immunosuppressant's (Kerkvliet, 1995) and endocrine disruptors (Costa et al., 2014) that lead to a disruption in the fundamental growth and development of cells, thereby; affecting the neurodevelopment (Ten Tusscher et al., 2014) and reproductive systems (Van Luong et al., 2018). Almost all living organisms are exposed to dioxins and furans as a part of food chain since dioxins get absorbed in fat tissue (Pirard and De Pauw, 2006) and furans are produced during thermal processing of food (Fan, 2005; Knutsen et al., 2017). Boda et al. (2018) demonstrated the associations of dioxins in breast milk and cord blood sex hormones in Vietnamese newborn infants residing near the former US Air Force base. In general, the total concentration or toxicity of complex congener's mixture is reckoned by the concept of International Toxic Equivalents (I-TEQ) whereas individual congeners are ascribed to a specific International Toxic Equivalency Factor (I-TEF) by North Atlantic Treaty Organization/Committee on The Challenges of Modern Society (NATO/CCMS), 1988.

In India, the annual release of PCDD/Fs is estimated at 8656.55 g TEQ using United Nations Environment Programme Toolkit during

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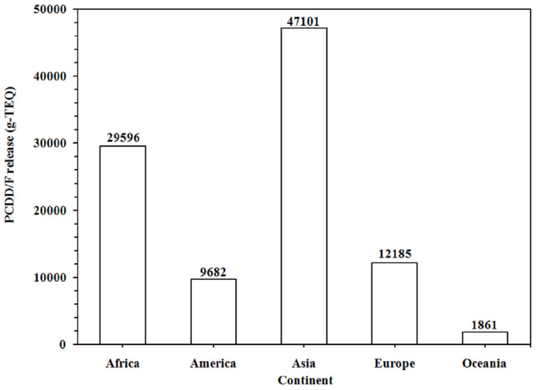

Fig. 1. Continent wise emission of PCDD/Fs.

2009–2010. Waste incineration (66.75%) and ferrous/non-ferrous metal production (20.22%) sectors are the major sources for the PCDD/F emission into the environment. According to Kumari et al. (2017), the emission factor of dioxin/furans for open burning municipal solid waste on streets and landfill sites are reported as 40 μg TEQ/MT and 300 μg TEQ/MT, respectively. The implementation of Stockholm Convention is exhibited by the Ministry of Environment and Forests (MoEF), Government of India for effective control of persistent organic pollutants release into the environment. The Indian government has planned to promote and introduce Best Available Techniques (BAT) and Best Environmental Practice (BEP) to reduce PCDD/F emission, especially in waste incineration and ferrous and non-ferrous metal production categories. Fig. 1 depicts the continental emission of PCDD/Fs (Wang et al., 2016). The release of PCDD/Fs is higher in the continent with least/under-developed countries due to naive industrial technology and substandard environmental management system.

The toxicity potential and the persistent nature of dioxins and furans in living creatures has led to a great interest in developing technologies to treat and control the release of these harmful chemicals into the environment. Dioxins and furans enter the atmosphere by combustion, thereby; researchers focussed on the mechanism of formation and envisaged that de-novo mechanisms and presence of precursor are the main rationales behind the formation of dioxins and furans. Based on this understanding, several technologies have been developed for the treatment and control of dioxins and furans release into the environment. This review discusses on the formation mechanisms and technologies developed for the control and treatment of PCDD/Fs.

2. Dioxins and furans formation

Dioxins and furans are mainly generated during combustion reaction along with fly ash, combustion gases and slag. The complete mechanism behind the formation of dioxins and furans are not completely elucidated since the phenomenon is highly complex and includes a series of solid and gas phase reactions. The formation pathways of dioxins and furans are highly influenced by the precursor, reactive species, nature of the catalyst, presence of chlorine compound and temperature. The PCDD/Fs are derived based on two main hypotheses, namely, homogeneous (pyrosynthesis) and heterogeneous reactions (de novo process and catalytic assisted precursor coupling). Dioxins and furans formation mechanism may occur independently or simultaneously (Lopes et al., 2015). The schematic representation of the formation of dioxins and furans is depicted in Fig. 2.

2.1. Homogeneous formation mechanism

Homogeneous formation pathway involves high temperature (400-800 °C) gas phase reaction through pyrosynthesis reaction. The most common precursor for gas phase formation of PCDD/Fs is chlorinated aromatic hydrocarbons (chlorobenzenes, chlorophenols and aliphatic precursors). During the process, short-chain chlorinated hydrocarbon precursor is converted to PCDD/Fs by oxidation and reduction process at high temperature. In gas phase formation of PCCD/Fs, three principle methods take place in chlorinated phenol, namely, the coupling of precursor and radical species (self-condensation), cyclization reaction and chlorination/dechlorination reactions. In case of chlorinated benzenes, oxidation and pyrolysis of chlorobenzenes produce more PCDF congeners than PCDDs. Recently, Truong et al. (2008) reported the mechanism of pyrolysis of hydroquinone produced PCDD/F congeners under rich and lean oxidation conditions.

2.2. Heterogeneous formation mechanism

Heterogeneous formation reaction takes place in the post-combustion zone between 200 and 400 °C. This mechanism involves two main routes, namely, de novo process and catalytic assisted precursor coupling. In case of de novo pathway, the carbon matrix structure undergoes simultaneous oxidation and chlorination reactions at 200-400 °C in the presence of oxygen to break down and transforms the matrix to emit PCDD/Fs. This formation mechanism is predominant in the flue gas cooling section of industrial incinerators. The formation of PCDD/Fs is influenced by gas phase materials (oxygen), solid phase materials (carbon forms), chlorine, temperature and reaction time. Fängmark et al. (1994) demonstrated the importance of fly ash in the formation of chlorinated aromatics. During metallurgical processes of de novo synthesis, measurable amount of PCDD/Fs is present in the solid phase and flows of off-gases (Zhang and Buekens, 2016; Buekens et al., 2001). However, transition metal ions like copper play an important role in both ring condensation and chlorination, and catalysis the dioxin and furan generation. In heterogeneous catalysis, mechanism for the formation of PCDD/Fs on a copper-catalyst surface is explained by Langmuir-Hinshelwood reaction and Eley-Rideal reaction pathways. Qian et al. (2005) demonstrated that transition metals promoted the formation of PCDD/Fs from pentachlorophenol while earthy alkaline metals suppressed the PCDD/Fs formation. Phenyl coupling reaction and surface reaction of brominated arenes in the generation of PCDD/Fs resembled Ullmann type reaction. Duan et al. (2011) reported that catalytic assisted precursor coupling is highly influenced by the catalyst, oxidation and halogenides.

3. Root of dioxins and furans pollution

3.1. Natural sources

Nature is a large chemical laboratory where a wide range of reactions takes place giving rise to many new compositions. Dioxins and furans are examples of such compositions which are considered as the most lethal chemicals. Dioxins and furans are naturally emitted by fumes from volcanic eruptions, forest fires and natural combustion processes like open burning of materials (Reiner et al., 2006). Salamanca et al. (2016) reported that forest fires increased the PCDD/Fs concentration in coastal waters of central Chile.

3.2. Anthropogenic sources

The concentration of dioxins and furans in the environment showed a significant increase after the progress of chemical industries and the concentration of these toxic chemicals was at the peak in the environment in late 1970s and early 1980s. Therefore, PCDD/Fs formation is mainly influenced by anthropogenic sources than the natural sources. The main anthropogenic sources of dioxins and furans are categorised into four sources (Fig. 3), incineration, combustion process, industrial processes and reservoirs.