

Viperous dioxins and furans: A review

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ABSTRACT

Dioxins and furans are common names for toxic chemicals that are found in very small amounts in the environment, including air, water and soil. As a result of their presence in the environment, they are also present in some foods.

"Dioxins" refers to a group of toxic chemical compounds that share certain chemical structures and biological characteristics. Dioxins can be released into the environment through forest fires, backyard burning of trash, certain industrial activities, and residue from past commercial burning of waste. Dioxins break down very slowly and past releases of dioxins from both man-made and natural sources still exist in the environment.

Almost every living creature has been exposed to dioxins. Studies have shown that exposure to dioxins at high enough levels may cause a number of adverse health effects, including cancer. The health effects associated with dioxins depend on a variety of factors including: the level of exposure, when someone was exposed, and for how long and how often someone is exposed. Humans are primarily exposed to dioxins by eating food contaminated by these chemicals. Dioxin accumulates in the fatty tissues, where they may persist for months or years. People who have been exposed to high levels of dioxin have developed chloracne, a skin disease marked by severe acne-like pimples. Studies have also shown that chemical workers who are exposed to high levels of dioxins have an increased risk of cancer.

Keywords: Dioxin, Furans, Nanoparticles, Toxicity, PCDD, TCDD.

1. INTRODUCTION

Dioxins are environmental pollutants. They are belonging to the "dirty dozen" - a group of dangerous chemicals known as persistent organic pollutants in water. Highly potential experiments have shown them affecting number of organs and systems. With different types of nanomaterial emerging for applications in water purification and water treatment devices show the effectiveness against both chemical and biological contaminants. Utilization of specific nanoparticles either embedded in membrane or on other structural media that can effectively, rapidly render unusable water to potable is being explored at a variety of sectors. Utilization of specific nanoparticles either embedded in membrane or on other structural media that can effectively, rapidly render unusable water to potable is being explored at a variety of sectors.

Dioxins are produced as unintentional by-products from the many processes in which

chlorine and chlorine-derived chemicals are produced, used and disposed off. Industrial emissions of dioxins into the environment can be transported long distances on atmospheric currents and to a lesser extent in rivers and oceanic currents. Consequently, dioxins are now globally ubiquitous. It is estimated that even if production ceases, levels in the environment will take years to decrease. This is because dioxins are persistent, taking decades or centuries to degrade, and can undergo continual recycling throughout the environment.

1.1. Toxicity of dioxin

Dioxin is a known human carcinogen. According to the U.S. Environmental Protection Agency, the general population exposure to dioxin may cause a lifetime cancer risk that is 1,000 times higher than the EPA's "acceptable" risk level. Other health problems associated with dioxin exposure include birth defects, learning disabilities, endometriosis, infertility, suppressed

immune function, reduced IQ, and hyperactive behavior in children.

2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD or TCDD, sometimes called dioxin) is the most potent of all congeners and has higher toxicity than any other synthetic molecule [1]. The dioxins can be ranked against TCDD by a system known as Toxic Equivalents (TEQ). These factors have been internationally adopted for the PCDD/Fs as well as certain types of polychlorinated biphenyls (PCBs) [2]. Current practice adopts the international toxicity equivalence factor system although older data may be reported using 2,3,7,8-TCDD concentrations alone. Other toxicity equivalents factors are in use [3] and total PCDD/F concentrations may also be reported.

1.2. Human exposure

Human exposure to dioxins is almost exclusively from food intake, especially from meat, fish and dairy products. Unusually high exposure to dioxins in humans following for example accidental/occupational exposure, together with experiments in laboratory animals, have shown effects of dioxin on health include developmental and reproductive toxicity, effects on the immune system and carcinogenicity. Even more disturbing are findings from recent studies which show that concentrations of dioxins in human tissue in the general population (of industrialized countries) are already at -- or near-those levels where health effects may occur.

Dioxins are lipophilic compounds which accumulate in the fat of animals. The types of foods which tend to have the highest dioxin concentrations are dairy products, meat and poultry, eggs, fish, and animal fats [4]. Green vegetables, fruits and grains are the types of foods with the lowest dioxin concentrations. Schecter et al 1997 [5] measured dioxins in pooled food samples that were collected in 1995 at supermarkets across the U.S. The pooled sample of fresh water fish had the highest level of dioxins (1.43 TEQ1), followed by butter (1.07 TEQ), hotdog/bologna (0.54 TEQ), ocean fish (0.47 TEQ), cheese (0.40 TEQ), beef (0.38 TEQ), eggs (0.34 TEQ), ice cream (0.33 TEQ), chicken (0.32 TEQ), pork (0.32 TEQ), milk (0.12 TEQ), and vegetables, fruits, grains and legumes (0.07 TEQ). A person's intake of dioxins through the diet therefore, depends on the relative intake of foods with high or low levels of contamination and the quantity consumed. For example, Patandin et al 1999 [6] investigated the dietary intake of a group of preschool children in The Netherlands and found that dairy products contributed about 50% of their intake of dioxins and related compounds,

while meat/meat products and processed foods contributed about 20% and 25%, respectively [6].

Wu BZ et al in 2012 [7] reviewed palladium nanoparticles embedded in monolithic microcellular high density polyethylene supports are synthesized as heterogeneous catalysts for remediation of 1,6-dichlorodibenzo-p-dioxin and 2,8-dichlorodibenzofuran in 200 atm of supercritical carbon dioxide containing 10 atm of hydrogen gas and at 50-90°C. Stepwise removal of chlorine atoms takes place first, followed by saturation of two benzene rings with slower reaction rates. The pseudo first order rate constant of initial hydrodechlorination for 2,8-dichlorodibenzofuran is 4.3 times greater than that for 1,6-dichlorodibenzo-p-dioxin at 78°C. The catalysts are easily separated from products and can be recyclable and reusable without complicated recovery and cleaning procedures.

Sung Ho Kim et al in 2008 [8] demonstrated suppression of dioxin emission from poly(vinyl chloride) (PVC)/titanium dioxide (TiO₂) nanohybrids. In our previous paper, we suggested a novel idea for the preparation of PVC/TiO₂ nanohybrid through TiO₂ nanoparticle-integrated hyperbranchedpoly(ε-caprolactone) (HPCL-TiO₂), aiming at a breakthrough to solve the unresolved problem in the conventional PVC/TiO₂ composites related to the poor dispersion of TiO₂ nanoparticles in PVC polymer. The integration of TiO₂ nanoparticles onto the HPCL could be successfully carried out by a dip-coating method based on the spontaneous self-assembly between TiO₂ and HPCL. In this study, three kinds of hyperbranchedpoly(ε-caprolactone)s (HnPCLs) were prepared by varying the number, n, of monomeric units on the branched backbone chains. Thereby, it was possible to control the numbers of functional ends and the contents of TiO₂ in the HnPCL-TiO₂. The loadings of TiO₂ in the HnPCL-TiO₂s were found to be 4.37, 3.26, and 2.93 wt% for n of 5, 10, and 20, respectively. The preparation of PVC/HnPCL-TiO₂ (60/40) blends was performed through solution blending of HnPCL-TiO₂ with PVC in tetrahydrofuran (THF) as solvent, and the dispersities of TiO₂ in the resulting nanohybrids were investigated by field-emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectroscopy (EDS). The FE-SEM/EDS results showed that TiO₂ nanoparticles were dispersed well in PVC matrix, while some agglomerates of TiO₂ was observed in the PVC + TiO₂ sample prepared from the solution blending of PVC with the same amount of TiO₂. The incineration experiments were performed by using a temperature-controllable electric furnace at 350 °C under the flow of ambient air, and the

exhaust gases resulting from the incineration process were collected. Prior to the identification of the components emitted in the incineration process, the GC experiments for calibration were performed on several commercial standards of dioxin and organic compounds known to be dioxin precursors. The GC results on the exhaust gases from the incineration of samples showed that the emissions of dioxin and precursors were largely suppressed with the increasing content of TiO₂ in PVC/HnPCL-TiO₂, i.e., the order of PVC/H5PCL-TiO₂ > PVC/H10PCL-TiO₂ > PVC/H20PCL-TiO₂, as compared with those in the neat PVC/HnPCL without TiO₂. Especially, the PVC/H5PCL-TiO₂ with a maximum TiO₂ loading of 1.6 wt% showed removal efficiencies of ca. 60% up to 70% over the dioxin and dioxin precursors, which is equivalent to one and half to several times as much as the PVC + TiO₂ samples prepared through the conventional route. The remarkable enhancement of the suppression of dioxin emission in the PVC/HnPCL-TiO₂ might be attributed to the improvement of the degree of TiO₂ dispersion in the nanohybrid.

Sung Ho et al 2007 [9] presented suppression of dioxin emission from poly(vinyl chloride) (PVC)/titanium dioxide (TiO₂) nanohybrids. In our previous paper, we suggested a novel idea for the preparation of PVC/TiO₂ nanohybrid through TiO₂ nanoparticle-integrated hyperbranchedpoly(e-caprolactone) (HPCL-TiO₂), aiming at a breakthrough to solve the unresolved problem in the conventional PVC/TiO₂ composites related to the poor dispersion of TiO₂ nanoparticles in PVC polymer. The integration of TiO₂ nanoparticles onto the HPCL could be successfully carried out by a dip-coating method based on the spontaneous self-assembly between TiO₂ and HPCL. In this study, three kinds of hyperbranchedpoly(e-caprolactone)s (H_n PCLs) were prepared by varying the number, n, of monomeric units on the branched backbone chains. Thereby, it was possible to control the numbers of functional ends and the contents of TiO₂ in the H_n PCL-TiO₂. The loadings of TiO₂ in the HnPCL-TiO₂s were found to be 4.37, 3.26, and 2.93 wt% for n of 5, 10, and 20, respectively. The preparation of PVC/H_n PCL-TiO₂ (60/40) blends was performed through solution blending of H_n PCL-TiO₂ with PVC in tetrahydrofuran (THF) as solvent, and the dispersities of TiO₂ in the resulting nanohybrids were investigated by field-emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectroscopy (EDS). The FE-SEM/EDS results showed that TiO₂ nanoparticles were dispersed well in PVC matrix, while some agglomerates of TiO₂ was observed in the PVC + TiO₂ sample prepared from the solution blending

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Yoo H et al in 2007 [9] reviewed measure and compare the amount of dioxin emitted from both TEPVC and PVC incineration, estimating the dioxin inhibition efficiency of TEPVC. TEPVC and PVC were first combusted in a well-controlled, small-scale incinerator at 700 °C. Synthetic air was introduced as the air for combustion. The combustion gas was trapped using a thimble filter, water and diethylene glycol impingers in a cold-bath, and amberlite XAD-2 resin absorption tubes, sequentially along the stream. The thus-treated samples were extracted, spiked with internal standards, and purified through a multi-layer silica-gel column and alumina column. Finally, the samples were condensed and used for dioxin analysis based on HRGC/HRMS. The TEPVC shows reduced dioxin emission due to the enhanced dispersibility of TiO₂ nanoparticles by nanoparticle encapsulation.

Li-Fan Zhao et al in 2007 [10] aimed to study rapid and sensitive densitometry bioassay of dioxins. It is known that dioxin ligand can bind heterodimeric aryl hydrocarbon receptor (AhR) and trigger the formation of the complex of dioxin-AhR, AhR nuclear translocator (Arnt), and dioxin-responsive element (DRE). We have established a rapid and sensitive method using nanoparticle-modified DRE probes based on dioxin-dependent binding of DRE to AhR complex. Dioxins can trigger the binding of nanoparticle-modified DRE probe to AhR complex. The nanoparticle-modified DRE probes in the dioxin-AhR-Arnt-DRE complexes immobilized on the microplates were detected by measuring optical density after silver

enhancement. Results showed that as little as 0.01 pM of TCDD could be detected. Dioxins could be quantified accurately with the linear range from 1 nM to 0.01 pM. The coefficient of variation was 5~8% in this bioassay. The optical density of nanoparticle-based silver enhancement was produced in a dose- and time- dependent manner. The dioxin concentrations in fly ash samples determined by this bioassay were comparable with that by the standard HRGC/HRMS. Thus this bioassay is a sensitive and convenient cell-free bioassay of dioxin that is suitable for screening of dioxins in environmental or food matrices.

Suppression of the emission of dioxin and its precursors as a result of the co-incineration of poly(vinyl chloride) (PVC) with TiO₂-encapsulating polystyrene (TEPS), in which TiO₂ nanoparticles with the capacity to adsorb dioxin and its precursors are encapsulated without significant agglomeration. Field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were used to show that spherical PS particles encapsulating a uniform dispersion of TiO₂ nanoparticles are obtained through the dispersion polymerization of styrene in an aqueous ethanol medium. To facilitate the encapsulation, the surface of the TiO₂ nanoparticles was modified with a polymerizable organic silane linker prior to polymerization. For comparison purposes, experiments were performed in which PVC was co-incinerated with neat PS (PVC/PS), TiO₂-encapsulating PS (PVC/TEPS), and mechanically mixed TiO₂/PS (PVC/PS-MTiO₂). Qualitative and quantitative investigations of the suppression of the emission of a model dioxin and its precursors were performed by analyzing the exhaust gases from the co-incinerations using gas chromatography/mass spectrometry (GC/MS). The results show that the addition of TiO₂ nanoparticles into co-incineration systems reduces the concentration of the dioxin and its precursors in exhaust gases. Moreover, the quantitative removal efficiencies for PVC/TEPS and PVC/PS-MTiO₂ indicate that the suppression is successfully enhanced by the TiO₂-encapsulation: increases in the dispersity of the nanoparticles result in improved adsorption of the dioxin and its precursors [11].

Sherry Rier et al 2002 [12] reviewed evidence that dioxin and dioxin-like compounds are potent modulators of immune and endocrine function critical to the pathobiology of endometriosis. Furthermore, perspectives on the potential mechanism of dioxin and dioxin-like compound-induced toxicity in endometriosis, important knowledge needs, potential animal models for endometriosis studies, and

considerations integral to future human case-control studies.

Zeolite is a crystalline hydrated aluminosilicate of alkaline and earth metals. It is an effective sorbent and ion-exchange media for metal ions which was evaluated as an ion exchange media for the removal of heavy metals from acids mine waste water. Magnetite Nanoparticles embedded Zeolite is prepared for better treatment of Dioxins contaminated water which can make potable one for regular use. Magnetite particles can be synthesized by coprecipitation of iron (II) and iron (III) aqueous salts solution in alkaline medium. Because of strong magnetic dipole, magnetite particles tend to aggregate. Polymeric compounds with special functional groups or surfactants can be added into solution in order to stabilize the solution. This technology is having lots of advantages over methods but still needs lots of research before the successful industrial application.

Dioxin and dioxin-like compounds, or DLCs, are found throughout the environment, in soil, water, and air. People are exposed to these unintentional environmental contaminants primarily through the food supply, although at low levels, particularly by eating animal fat in meat, dairy products, and fish. While the amount of DLCs in the environment has declined since the late 1970s, the public continues to be concerned about the safety of the food supply and the potential adverse health effects of DLC exposure, especially in groups such as developing fetuses and infants, who are more sensitive to the toxic effects of these compounds. Dioxins and Dioxin-like Compounds in the Food Supply: Strategies to Decrease Exposure, recommends policy options to reduce exposure to these contaminants while considering how implementing these options could both reduce health risks and affect nutrition, particularly in sensitive and highly exposed groups, if dietary changes are suggested.

1.3. Dioxin and Furans

Dioxins and furans are common names for toxic chemicals that are found in very small amounts in the environment, including air, water and soil. As a result of their presence in the environment, they are also present in some foods. Exposure to dioxins and furans has been associated with a wide range of adverse health effects in laboratory animals and humans. The type and occurrence of these effects typically depend on the level and duration of exposure.

Bhupander Kumar et al in 2012 [13] studied seventeen congeners of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans (PCDDs/Fs) in selected solid wastes

analyzed by HRGC-HRMS applying the isotopic dilution technique. Recovery rates of spiked $^{13}\text{C}_{12}$ -labeled standard compounds were calculated and found within the accepted ranges for all the samples. The observed concentration of 17 PCDDs/Fs was 13763.00 pg g⁻¹, 256.66 pg g⁻¹, 1857.63 pg g⁻¹ and 9.64 pg g⁻¹ dw, in sewage sludge, paper mill sludge, industrial contaminated soil and flyash, respectively. The 2,3,7,8-TeCDD substituted toxic equivalent (I-TEQ) was 77.068 pg I-TEQ g⁻¹, 11.319 pg I-TEQ g⁻¹, 96.316 pg I-TEQ g⁻¹ and 0.401 pg I-TEQ g⁻¹, respectively. OCDD, Hep-CDD, OCDF, Hep-CDF and TCDF were the dominant congeners. In this study, the ratio of $\sum\text{PCDD}/\sum\text{PCDF}$ was 10.39, 4.91, 4.28 and 3.97 for sewage sludge, paper mill sludge, soil and flyash, respectively which indicates that PCDD/Fs sources in the studied samples were contaminated significantly with the mechanism of the precursor formation routes.

Sen S et al in 2010 [14] reviewed Furan ring systems are abundantly available in secondary plant metabolites. Due to their remarkable properties, many synthetic furans are utilized as pharmaceuticals. Hence a series of N-(furan-2-ylmethylene) benz- imines derivatives has been synthesized by reaction between furan-2--carboxaldehyde and various aromatic anilines to yield the Schiff's bases. The newly synthesized compounds showed potent CNS depressant and analgesic activities. Prior to determination of the Pharmacological activity LD50 was determined.

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) concentrations were measured in seabirds from Rio de Janeiro, Brazil. Samples of *Sula Leucogaster* were collected in 2008-2011 on Ilha Grande bay. Detectable hepatic concentrations of PCDD/Fs and PCBs were found in all samples analyzed. The concentrations were below the range of concern established by WHO. Study aims to integrate information from analysis of seabirds with chemicals, and primary results coming from these studies may allow identification of scientific evidence, helping the containment of pollution sources. Furthermore, the data is the first measurements of PCDD/Fs and PCBs congeners in seabirds from this area, and suggests that future studies should take note of the results in order to test for a greater range of compounds and species and to determine levels of environmental contamination [15].

Furan is a food processing contaminant classified as possibly carcinogenic to humans. As the occurrence of furan has been reported in a variety of foods processed in sealed containers, the objective of this work was to investigate if the

contaminant can be found in home-cooked foods prepared in a pressure cooker. For that, several foods including beans, soy beans, whole rice, beef, pork, potato, and cassava were pressure-cooked and analyzed for the furan content by gas chromatography coupled to mass spectrometry preceded by a headspace solid phase microextraction (HS-SPME-GC/MS). Furan was not found above the limit of quantification in the pressure-cooked samples. No furan has either been found in reheated samples after 24 hours under cold storage. Although levels up to 173 µg/kg were already reported for commercial canned/jarred foods, it seems that the cooking in a pressure cooker may not represent a concern in relation to the occurrence of furan in foods [16].

Clemencia Rodriguez et al 2008 [17] reviewed assessment of potential health impacts of dioxin and dioxin-like compounds in recycled water for indirect potable reuse was conducted. Toxic equivalency factors (TEFs) for 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs) congeners have been developed by the World Health Organization to simplify the risk assessment of complex mixtures. Samples of secondary treated wastewater in Perth, Australia were examined pre-and post-tertiary treatment in one full-scale and one pilot water reclamation plant. Risk quotients (RQs) were estimated by expressing the middle-bound toxic equivalent (TEQ) and the upper-bound TEQ concentration in each sampling point as a function of the estimated health target value. The results indicate that reverse osmosis (RO) is able to reduce the concentration of PCDD, PCDF and dioxin-like PCBs and produce water of high quality (RQ after RO=0.15). No increased human health risk from dioxin and dioxin-like compounds is anticipated if highly treated recycled water is used to augment drinking water supplies in Perth. Recommendations for a verification monitoring program are offered.

Earlier research on furan, its presence in variety of food and showed carcinogenic on high dose animals tests, hence considered possibly carcinogenic to human. So, it is dire need to monitor furan in processing food. In 2004, FDA performed comprehensive study using large number of food samples and found furan level up to 120 ppb. After this, European Food Safety Authority (EFSA) followed the FDA initiative and began to collect information on the methods of analysis, occurrence and formation in food, exposure through consumption, and the toxicity of furan. Furan level more than 100 µg/ kg were found in coffee, baby food, and sauces and soups [18]. Afterwards EFSA regularly call for more

information on the occurrence of furan in foods [19].

1.4. How to avoid dioxin and furan

Do not eat beef or pork, which have some of the largest concentrations of dioxin of all food sources. Limit your intake of ocean fish; do not eat any freshwater fish. Chicken has the lowest dioxin content of all meats, but is still significant. Vegetarian meat substitutes such as tofu, beans, and rice have essentially no contamination.

If your family drinks milk, drink only skim milk, since dioxin is carried in the butterfat. Avoid all full-fat dairy products, such as butter, cheese and ice cream. Use non-fat skim-milk products or non-dairy substitutes. If you are female and are considering having children, it is essential that you eat a non-dairy, low-fat vegetarian diet for several years before you have children. Dioxin is passed from the woman's body to the infant through the placenta and in breast milk, which contains more dioxin than any other food (in relation to an infant's body weight) for women who consume meat and milk.

- Prepare meat and fish in a way that minimizes your exposure by trimming visible fat from food. Bake, broil, roast, barbecue or microwave instead of frying, and drain off extra fat after cooking.
- Healthy Eating, and enjoy a variety of foods. Vegetables, fruit and grains contain fewer dioxins and furans than meat, milk products and fish.
- Follow provincial/territorial government advisories about eating certain types of fish.
- Do not burn garbage, especially construction materials that might contain wood preservatives or plastic.
- Limit the amount of wood you burn in your fireplace or stove, and learn about wood-burning techniques that release fewer dioxins.
- Do not smoke, and keep your family away from second-hand smoke as much as possible.

2. CONCLUSION

Polychlorinated dibenzodioxins (dioxins) and polychlorinated dibenzofurans (furans) are highly persistent compounds with a strong affinity for sediments and a high potential for accumulating in biological tissues. They enter the environment mainly through the incineration of waste, and pulp and paper processing, and have been found in very small amounts in all compartments of the environment including air, water, soil, sediments, animals and foods. Large exposures can lead to a variety of serious health

problems. Large doses of dioxins and furans are known to cause serious health problems, including cancer, in laboratory animals. The impact of these substances on humans and wildlife, which are exposed to smaller doses, is less certain. As a result, the level of health risk from dioxins and furans is controversial.

By taking these steps, you can reduce your family's exposure to dioxins and furans, and help to limit the overall release of these substances into the environment.

- Do not burn garbage, especially construction materials that might contain wood preservatives or plastic.
- Limit the amount of wood you burn in your fireplace or stove, and learn about wood-burning techniques that release fewer dioxins.
- Enjoy a variety of foods. Vegetables, fruit and grains contain fewer dioxins and furans than meat, milk products and fish.
- Follow provincial/territorial government advisories about eating certain types of fish.
- Do not smoke, and keep your family away from second-hand smoke as much as possible.

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