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Review article

Dioxins sources and current remediation technologies — A review

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Abstract

Dioxins are highly toxic and ubiquitous compounds that are unintentional by-products of several chemical processes on earth. According to the earth pollutant terminology, they are next to the nuclear catastrophes. It is because of their concerns over adverse health effects, a number of countries have introduced stringent emission standards. The present review focuses on entire sources of dioxins present in the environment. They are broadly classified into four major categories such as, incineration, combustion, industrial and reservoir sources. State-of-the-art remediation technologies available for reducing dioxins formation and emission from the important sources such as, flue gas, fly ash and soil were described in detail. Further, in order to get a comprehensive perception about the dioxins subject, topics such as, dioxins transfer in the environment, their mode of action, toxicity equivalence factor, exposure and health risk assessment were highlighted in brief in the introduction. A future prospects based on the findings of the review was discussed at the end.

Keywords: Dioxins; Toxicity; Health hazard; Sources; Fly ash; Flue gas; Soil; Remediation technologies

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1. Introduction

Dioxins are a class of structurally and chemically related polyhalogenated aromatic hydrocarbons that mainly includes polychlorinated dibenzo-*p*-dioxins (PCDDs or dioxins), dibenzofurans (PCDFs or furans) and the 'dioxin-like' biphenyls (PCBs). They constitute a group of persistent environmental chemicals and usually occur as a mixture of congeners. Their presence in the incinerator fly ash samples was firstly reported by Dutch and Swiss scientists in the year 1977 and 1978, respectively (Buser et al., 1978; Olie et al., 1977). However, dioxins had come to public attention in the year 1982 when an explosion at ICMESA factory in Seveso, Italy, deposited these chemicals over an area of 2.8 km^2 (Wilson, 1982).

Only 7 of the 75 possible PCDD congeners, and 10 of the 135 possible PCDF congeners, those with chlorine substitution in the 2,3,7,8 positions, have dioxin-like toxicity. Likewise, there are 209 possible PCB congeners, only 12 of which have dioxin-like toxicity (USEPA, 1994a,b). These dioxin-like PCB congeners have four or more chlorine atoms and are sometimes referred to as coplanar PCBs, since their rings can rotate into the same plane. Physical and chemical properties of each congener vary according to the degree and position of chlorine substitution. Fig. 1 and Table S-1 depict the basic structural formula of PCDDs, PCDFs, and PCBs together with the numbering convention at the positions on benzene rings where chlorine or other halogen atoms can be substituted.

1.1. Mode of transfer to the environment

The largest release of these chemicals today is open burning of household waste, municipal waste, medical waste, landfill fires, and agricultural and forest fires (Dyke et al., 1997). Dioxin and furan compounds exhibit little potential for significant leaching or volatilization once sorbed to particulate matter. The available evidence indicates that PCDDs and PCDFs, particularly the tetra- and higher chlorinated congeners, are extremely stable compounds under most environmental conditions. The only environmentally significant transformation process for these congeners is believed to be photodegradation of non-sorbed species in the gaseous phase, at the soil–air or water–air interface (Tysklind et al., 1993).

PCDDs/PCDFs entering the atmosphere are removed either by photodegradation or by deposition. Burial in-place, resuspension back into the air, or erosion of soil to water bodies appears to be the predominant fate of PCDDs/PCDFs sorbed to soil. The ultimate environmental sink of PCDDs/PCDFs is believed to be aquatic sediments. Levels of PCDDs/PCDFs in fish and invertebrates have been found to be higher than those in the water column, suggesting bioaccumulation (Atkinson, 1991). Conversely, a little information exists on the environmental transport and fate of the 12 coplanar PCBs (Sakai et al., 2001).

1.2. Mode of action

The general population exposure to dioxins chemicals occurs as an exposure to a mixture of different congeners (Masuda et al., 1998). Clearly, however, many of the effects are mediated through an interaction with the aryl hydrocarbon receptor (AhR). Dioxins induces a broad spectrum of biological responses, including induction of gene expression for cytochrome P450, CYP1A1, and CYP1A2, disruption of normal hormone signaling pathways, reproductive and developmental defects. Briefly, it indicates that the inappropriate modulation of gene expression represents the initial steps in a series of biochemical, cellular and tissue changes that result in the toxicity observed (Mandal, 2005). The variation in toxicity amount the dioxins and furans and the effect at the AhR is 10,000 fold, with TCDD being the most potent. Fig. 2, depicts a schematic model of the action of dioxin in cell.

1.3. Toxicity equivalency factor (TEF)

The toxicity of dioxins are expressed as toxic equivalent quantities (TEQs) where the most toxic congener TCDD is rated as 1.0 and the less toxic congeners as fractions of this. The toxicity of dioxins is mediated through the aryl hydrocarbon receptor; a toxic equivalency factor (TEF) is used, assuming that the effects are additive and act via a common mechanism to cause toxicity (Boening, 1998; Kerkvliet, 2002). The TEF system was initiated for dioxins and furans in 1998 by NATO/CCMS scheme, adopted internationally and termed International-TEFs (I-TEFs). Many of the other PCDDs and PCDFs and certain PCBs are less potent than TCDD but vary considerably in their respective concentrations. Each congener can be assigned a potency value relative to TCDD [TEF]. When a TEF is multiplied by the congener concentration level, a toxic equivalency (TEQ) value is obtained. In the early 1990s, WHO added TEFs for PCBs. The coplanar-polychlorinated biphenyls have less potency, but their concentrations are often much higher than concentrations of TCDD (Kang et al., 1997; Patterson et al., 1994), so their relative contribution to the total TEQ is potentially sizable. The 7 dioxin congeners, 10 furan congeners (all chlorinated in at least the 2,3,7,8 position) and the 12 PCBs which exhibit 'dioxin-like activity' were rated with

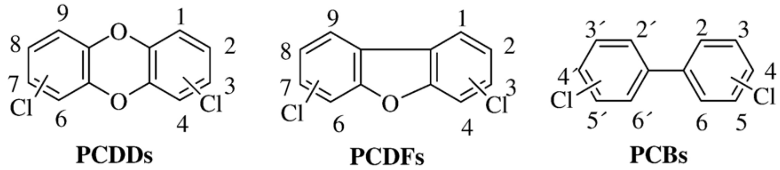

Fig. 1. Chemical structures of a) PCDD b) PCDF, and c) PCBs.

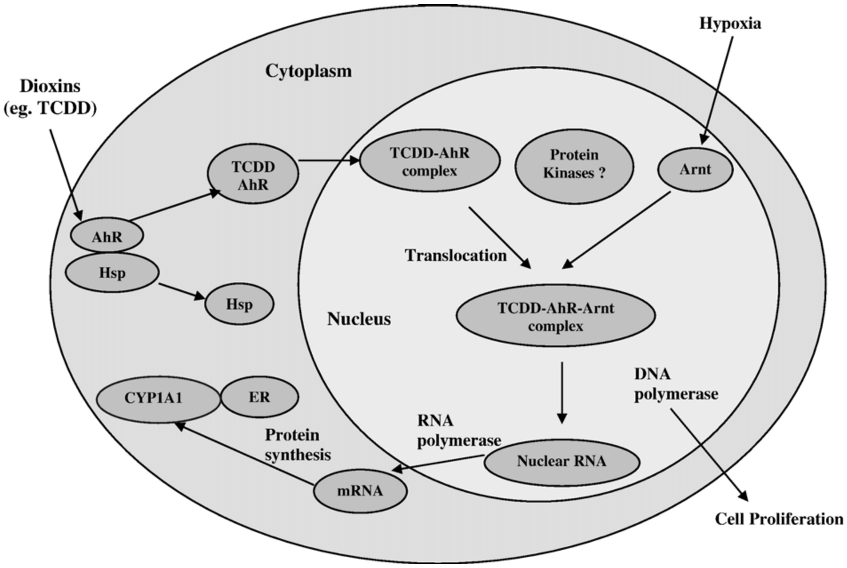

Fig. 2. A schematic model of the action of dioxins in cell (adapted from Mandal, 2005).

TEFs (Giesy and Kannan, 1998) (seeTable S-2). Thus, the toxic contribution of the PCDDs and PCDFs and certain PCBs can then be compared. In 1998 and 2005 the WHO expert meeting derived consensus TEFs for both human and wildlife risk assessment (Van den Berg et al., 1998, 2006).

1.4. Exposure and health risk assessment

People are exposed primarily through foods that are contaminated with PCDDs and PCDFs as a result of the accumulation of these substances in the food chain and in high-fat foods, such as, dairy products, eggs, animal fats, and some fish. Further, the exposure also includes industrial accidents (Baccarelli et al., 2002) and several miscellaneous exposures (Yoshimura, 2003). The approximate estimation of human exposure pathways is shown in Fig. 3.

Several adverse health effects have been associated with dioxins, including soft tissue, sarcomas, lymphomas, skin lesions (chloracne), stomach cancer, biochemical liver-test abnormalities, elevated blood lipids, fatal injury, immune system and neurological effects (Mitrou et al., 2001). Moreover, carcinogenic, genetic, reproductive, and developmental effects have been observed in many animal studies although species differ dramatically in sensitivity to these chemicals (Cole et al., 2003; Huff et al., 1994). TCDD has the LD_{50} (lethal dose) of 0.04 mg/kg for rats. However, other dioxin isomers have LD_{50} values up to 100 mg/kg for rats (Kao et al., 2001).

A number of countries and organizations have studied various approaches to the health risk assessment of dioxins with regard to dioxin as carcinogenic promoters and have defined tolerable daily intake (TDI) based on No Observed Adverse Effect Level (NOEAL) derived from animal studies (EuropeanCommission, 1994; Steenland and Deddens, 2003). In assessing the risk of 2,3,7,8-TCDD the USEPA came up with a virtual safe dose of 6 fg/kg body weight per day. The two most recent health risk assessments, carried out by the Health Council of the Netherlands in 1996 and WHO in 1998, are based on developmental effects initiated during gestation and/or lactation. The international risk assessments of dioxins are summarized inTable S-3. These doses are based on the carcinogenicity of 2,3,7,8-TCDD and provides protection from toxic effects as well. The reactions of the various member states of the European Union to these risk evaluations have put an emission limit of 0.1 ng/m^3 I-TEQ primarily waste incineration plants and tolerable daily intake of 1–4 pg I-TEQ/day/kg body.

Apart from the toxicity of dioxins and its presence in the environment, many scientists have shown the compound to be highly resistant to biodegradation. This resistance may be due to its very low water solubility and high octanol–water partition coefficients (Orazio et al., 1992). Thus, public health risk from environmental exposure to dioxins from contaminated sites can be significant. As a result, a clean-up of environmental dioxins contamination is an area requiring more attention.

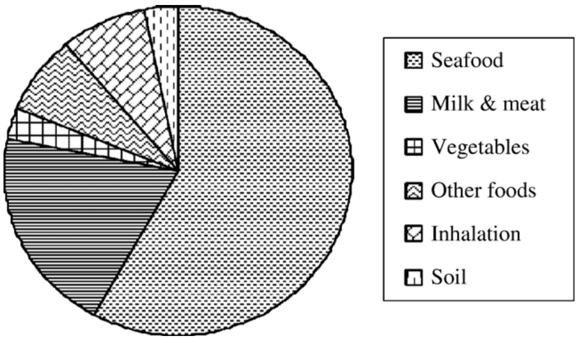

Fig. 3. Exposure of human beings to dioxins (adapted from Kishimoto et al., 2001).

2. Dioxins sources

Earlier human tissue samples show very low levels of dioxins than found today (Ligon et al., 1989). Studies of the sediments near industrial areas of the United States have shown that dioxins were very low until about 1920 (Alcock and Jones, 1996; Czuczwa et al., 1984). These studies show increases in dioxins concentrations from 1920s and continuing until about 1970. Some decline in concentrations has been observed this time. These findings can be explained by the corresponding trends of chlorophenol production (Czuczwa and Hites, 1984).

Therefore, it appears that the presence of dioxin-like compounds in environment occurs principally as a result of anthropogenic sources. These compounds are released to the environment in a variety of ways and in varying quantities depending upon the source. This ubiquitous nature of dioxins compounds suggests that multiple sources exist and that long range transport can occur. The major identified sources of environmental release have been grouped into four major categories as shown in Fig. 4.

2.1. Incineration sources

It is the largest source of dioxins release in the environment. Dioxins can be generated and released to the environment from following incineration processes.

2.1.1. Municipal solid waste incinerators

Dioxins are predominantly produced by municipal solid waste incineration processes. Several researchers have described their mechanism of formation. Overall, it is observed that the emission of dioxins and furans into the environment can be explained mainly by two principal surface catalytic processes: i) formation from precursors and ii) formation by de novo synthesis (Altwicker, 1996). An informative review on the formation and mechanism of dioxins from municipal solid waste incineration was presented (Tuppurainen et al., 1998). It was observed that several past studies demonstrated the presence of significant quantities of dioxins and dioxin precursors in municipal solid waste around 50 ng I-TEQ/kg (Abad et al., 2002).

2.1.2. Hospital waste incinerators

Hospital waste include human organs, bandages, blood tubes, test tubes, needles, syringes, tissue cell culture, and other plastic materials. Incineration has been the most widely used treatment of hospital waste in every country. However, these incinerators do not rely on advanced technologies, are high in number, burn high chlorine content waste and hence are important source of dioxin emissions (Stanmore and Clunies-Ross, 2000).

2.1.3. Hazardous waste incinerator

The harmful products of chemical processes produced from industries are called hazardous waste. Depending on the waste type, hazardous waste can be explosive, oxidizing, highly flammable, corrosive, infectious, mutagenic, irritant, toxic, or carcinogenic. A practice of separate incineration for hazardous waste has also started several years ago. Hazardous organic compounds such as chlorinated phenols can be incinerated under this method (Karademir et al., 2003).

2.1.4. Sewage sludge incinerator

Wastewater treatment generates a solid residue with high organic and toxic metal contents called sewage sludge. The

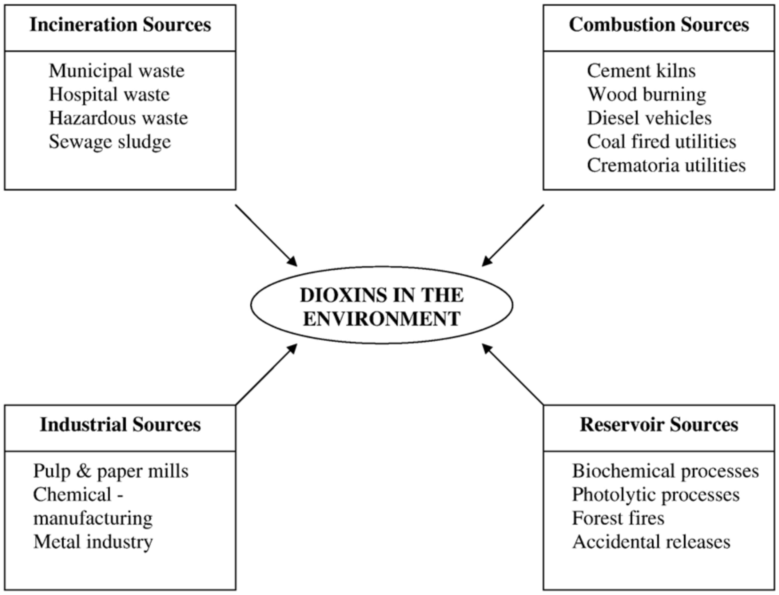

Fig. 4. Dioxins release in the environment.

limitations facing land filling and recycling and the planned ban on sea disposal has led to the use of incineration processes for the disposal of sewage sludge. A few studies were reported on the sewage sludge incineration (Fullana et al., 2004).

2.2. Combustion sources

2.2.1. Cement kilns

The switch to burning hazardous waste as fuels for cement kilns has created problem for individuals and organizations. About 16% of the facilities burn hazardous waste as an auxiliary fuel; limited data suggests that PCDD/PCDF levels in clinker dust and stack emissions of these kilns may be significantly higher than the kilns which do not burn hazardous waste (Abad et al., 2004; Eduljee, 1999).

2.2.2. Wood burning

A number of studies have found dioxins in the emissions and ash/soot from wood fires in non industrial situations (Stanmore, 2004). According to the European Emission Inventory, wood combustion is at present one of the most important air emission sources for dioxins (Quass et al., 2000). In an appealing review paper it is reported that the dioxins emission from wood burning is about 945 g I-TEQ/year (Lavric et al., 2004).

2.2.3. Diesel vehicles

A very scant literature available on emission of dioxin from diesel vehicles. Researchers from Sweden and Norway have studied dioxin emission from diesel vehicles (Marklund et al., 1990; Oehme et al., 1991). As these studies depend on the fuel used in a particular country more studies are required in order to reach a conclusive estimation.

2.2.4. Crematoria

Crematoria procedures can be a ready source of organic material and chlorine, and hence are possible source of dioxins emission (Alcock et al., 1999). Inventory estimates rate this source as 0.3% of European output (Landesrumweltanmt, 1997) and 0.24% of US output (USEPA, 1998).

2.2.5. Coal-fired utilities

Although emission of dioxins compared to the wood burning is very less, they are numerous, large in size and their high stacks indicate that they could impact very large areas (Chen, 2004; Harrad et al., 1991). Considering the large scale usage the importance of these facilities is very much unknown.

2.3. Industrial sources

2.3.1. Pulp and paper mills

The manufacture of bleached pulp and paper has in the past resulted in dioxin releases to water, land and paper products. These compounds can be formed through the chlorination of naturally occurring phenolic compounds such as those present in wood pulp (Rappe et al., 1987). It is reported that the waste generated from a pulp mill of China produces dioxins concentration of 300 pg/l I-TEQ (Zheng et al., 2001).

2.3.2. Metals industry

The metallurgical processes such as high temperature steel production, smelting operations, and scrap metal recovery furnaces are found to be typical sources of dioxins (Anderson and Fisher, 2002). Processes in the primary metals industry, such as sintering of iron ore, have also been identified as potential sources (Cieplik et al., 2003; Wang et al., 2003). In several countries the annual release of dioxins is estimated to be 500–4000 g I-TEQ (Anderson and Fisher, 2002).

2.3.3. Chemical manufacturing

PCDDs and PCDFs can be formed as by-products from the manufacture of chlorinated compounds such as chlorinated phenols, PCBs, phenoxy herbicides, chlorinated benzenes, chlorinated aliphatic compounds, chlorinated catalysts and halogenated diphenyl ethers (Oberg et al., 1992, 1993; Sidhu and Edwards, 2002). Although the manufacture of many chlorinated phenolic intermediates and products, as well as PCBs, was terminated in the late 1970s in the United States, production continued around the world until 1990, and continued, limited use and disposal of these compounds can result in release of dioxins into the environment.

2.4. Reservoir sources

The persistent and hydrophobic nature of these compounds causes them to accumulate in soils, sediments, landfill sites, vegetation and organic matter. They have potential for redistribution and circulation of dioxins in the environment. The dioxin compounds in the “reservoirs” can be redistributed and circulated in the environment by dust or sediment resuspension and transport (Kjeller and Rappe, 1995; Rotard et al., 1994).

The major reservoir sources include:

2.4.1. Biological processes

The action of microorganisms on chlorinated phenolic compounds results in the formation of dioxins under certain environmental conditions (Siewers and Schacht, 1994).

2.4.2. Photochemical processes

Dioxins like OCDD (1,2,3,4,5,6, 7,8,9-octachlorodibenzo-dioxin), HPCD (1,2,3,4,5,6,7,8-heptachlorodibenzodioxin) formation occurs by photolytic radical reactions of pentachlorophenol (Baker and Hites, 2000; Tysklind et al., 1993).

2.4.3. Accidental sources

The incidents of dioxins release at Seveso, Italy and Yusho Japan can be considered as an accidental release of dioxins into atmosphere. Further, forest fires and volcanoes also come under this category (Clement and Tashiro, 1991; Ruokojarvi et al., 2000).

2.4.4. Miscellaneous sources

Miscellaneous sources includes formation of dioxins in FBC (Fluidized Bed Combustion) boilers, thermal oxygen cutting of scrap metal at demolition sites, power generation, PVC in house fires, Kraft liquor boilers, laboratory waste, drum and barrel reclaimers, tire combustors, carbon reactivation furnaces and scrap electric wire recovery facilities, etc. (Anthony et al., 2001; Carroll, 1996; Menzel et al., 1998).

3. Techniques of dioxin remediation, reduction and prevention

It was observed that dioxins enter into the environment mainly from the flue gas originated from incineration and combustion processes, formation of fly ash (originated from incineration and combustion processes) and dioxins contaminated soil occurred due to industrial and reservoir sources. Therefore, it was decided to highlight a comprehensive state-of-the-art study on the remediation, reduction and prevention of these components which are threatening the environment.

3.1. Treatment of flue gases

Incineration and combustion processes releases large amount of flue gases which are one of the bulk sources of dioxin emissions in the environment. The formation of dioxins in the flue gases of the incinerator system occurs by precursors and de novo synthesis at temperature of 300–500 °C. A schematic diagram of a typical incinerator system is shown in Fig. 5. The composition of dioxins in the flue gases varies from 1–500 ng I-TEQ/m^3. Therefore, it is important to treat the flue gas to reduce its concentration to an acceptable limit (0.1 ng I-TEQ/Nm^3) before entering into the environment.

Following methods were adopted for the reduction in emission of dioxins.

3.1.1. Particulate matter collection

It is possible to eliminate particle bound dioxins with a dust collector. At temperatures below 200 °C the collection of particle bound dioxins overcomes the de novo synthesis. The removal of particle-bound dioxins from the waste gas coming from an iron ore sintering plant with a cloth filter yielded a reduction of the dioxins up to 73% (Ergebnisse, 1996). Dioxin removal efficiencies of the electrostatic precipitator IZAYDAS Incinerator (Turkey) were examined in a trial burn. It was showed that removal efficiencies of greater than 90% for all congeners and homologues of dioxins (Karademir et al., 2003).

A fabric filters and electrostatic precipitators (ESP) have more efficiency in the removal of particle bound dioxins and are currently used as dust collectors during the incineration processes. Electrostatic precipitator having strong electrical field is generally used for the collection of particulate matter or dust. A product consisting of particulate matter or dust and hydrated lime, settles to the bottom of the reactor vessel. It was observed that with the use of the combined system, dioxins removal rates of 90–92% can be achieved (Kim et al., 2000). However, there are technical difficulties of removing the dust from the waste gas of incinerators at high temperatures. Some heavy metal salts because of their relatively high vapor pressure could not be removed from the waste gas in sufficient amounts.

3.1.2. Scrubbers or spray absorber and electrostatic precipitators

Scrubbers followed by electrostatic precipitators have been in use for many years in waste incinerator for reduction of dioxin emissions. The absorbent (lime slurry) is atomized in the spray tower. The gas is first absorbed by the liquid phase and then by the solid phase. The lime slurry mixes with the combustion gases within the reactor. The neutralizing capacity of the lime reduces the percentage of acid gas constituents (e.g. HCl and SO_2 gas) in the reactor. It was also observed that the addition of coke made from bituminous coal in a quantity of up to 500 mg/m^3 a much higher dioxin collection efficiency of approx. 90% can be achieved (Maier-Schwinning and Herden, 1996).

3.1.3. Sorbent or flow injection process

The flow injection process is generally based on the injection of finely grained coke stemming from anthracite or bituminous coal mixed with limestone, lime or inert material into the waste gas flow with a temperature of approx. 120 °C. So the material is suspended in the flow homogeneously and subsequently settles in a layer on the surface of the cloth filter. The inert material which is added in an amount of more than 80% serves to take up the heat that is developed by the exothermic reactions involved in the adsorption process. It also helps to prevent ignition of the coke (Cudahy and Helsel, 2000).

The use of naturally and synthetically occurring zeolites is also found to be a good alternative (Abad et al., 2003). Flow injection processes are being used in Europe and USA in a number of waste incineration plants for the collection of dioxins, HCl, HF and SO_2. Due to the necessary high amounts of inert material, the residual matters left from the process are

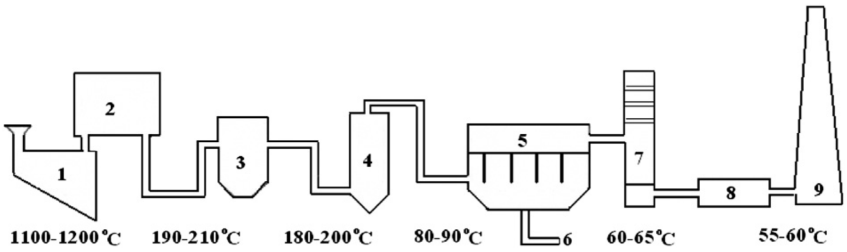

Fig. 5. A schematic diagram of the incinerator system: 1) bunker waste, 2) boiler, 3) electrostatic precipitator, 4) spray absorber or dry sorbent injection, 5) bag filter or fabric filter, 6) fly ash for treatment, 7) wet scrubber, 8) AC (Activated Carbon) unit, and 9) Chimney.

considerable. With this process dioxins removal efficiency of 99% can be achieved.

3.1.4. Fluidized-bed process with adsorbent recycling

From the process engineering point of view the fluidized-bed process lies between the flow injection process and the fixed-bed as well as moving-bed adsorbent process. The advantage of the fluidized-bed process lies in the high residence times of the adsorbent and in better utilization of sorbent because of the more favorable mass transfer conditions and longer solids retention times in the system.

In this process, the flue gas passes through the grate from the bottom and forms a fluid bed of coke stemming from bituminous coal and inert material with a temperature of about 100 to 120 °C. A limestone or lime can be used as inert material and the amount of coke can be higher than in the flow injection process. The adsorbent is separated from the flue gas in a dust collector and re-circulated to the fluidized bed. Usually the adsorbent can be recycled many times, so that, it is possible to collect other acid components such as HCl, HF and SO_2. The advantages of the fluidized-bed process, lies in the high residence times of the adsorbent and in better utilization of sorbent because of the more favorable mass and heat transfer conditions and longer solids retention time in the system (Liljelind et al., 2001; Shiomitsu et al., 2002).

3.1.5. Fixed-bed or moving-bed processes

This process uses the same adsorbent as that of the fluidized-bed process. But, the coke moves slowly from top to bottom while the waste gas flows in opposite direction. The activated coke takes up contaminants during its entire residence time in the reactor, which may be several 1000 operating hours. The time period during which an effective exchange of matter takes place is in fixed-bed or moving-bed processes about 10 times longer than in flow injection or fluidized-bed processes (Fell and Tuczek, 1998). The difference between fixed-bed and moving-bed process is in the former the bed of activated coke of cross-flow adsorbers is not moved during the time adsorption takes place and the spent coke is withdrawn and replaced by new coke. In moving-bed reactors the coke bed travels continuously. A very high dioxins separation efficiency of more than 99% can be achieved with the moving-bed process (Karademir et al., 2004).

Fixed bed process used for the waste gas cleaning has some problems like blocking due to moisture absorption and corrosion. Therefore in current flue gas cleaning plants, the fixed-bed process has been largely replaced by the turbulent-contact method applied in the moving-bed process with continuously exchanged adsorbent.

3.1.6. Catalytic decomposition of dioxins

A method of selective catalytic reduction for the NOx gases can be also applied for the dioxins remediation. The present evidence shows that the catalysts used in selective reduction of the NOx in the flue gas suppressed the formation of dioxins by 85% (Goemans et al., 2004). It proves that a single, effectively designed catalyst can be used in the removal of the oxides of nitrogen and dioxins (Liljelind et al., 2001). The catalysts are mostly composed of the oxides of Ti, V and W. Additionally, oxides of Pt and Au supported on silica-boria-alumina are found to be effective for the destruction of dioxins at 200 °C (Everaert and Baeyens, 2004).

To avoid blockage of the catalyst with coarse fly ash particles and ammonium sulfate the catalyst for the destruction of dioxins is usually applied after the cleaning stages. The advantage of selective catalytic reduction (SCR) over the other methods is the elimination of complicated disposal problems of residual matter. On the contrary, the catalyst lacks the capacity of removing as wide spectrum of contaminants as activated coke (Andersson et al., 1998).

3.1.7. Electron irradiation processes

It is a new process for destruction of dioxins compounds in the flue gas. The method has following features: i) no possibility of secondary pollution because of the direct decomposition of dioxins which is different from the recovery method using a filter, ii) no need for temperature control, and iii) very simple process resulting in easy installation to existent incinerators.

Recently, Hirota and Kojima studied the decomposition behavior of dioxin and furan isomers under electron-beam irradiation in incinerator gases at a temperature of 473 K. They noticed a significant decomposition for all PCDD isomers, which resulted from oxidation reactions with OH radicals yielded by electron-beam irradiation (Hirota and Kojima, 2005). With this process dioxins can be reduced up to 99%. It involves gas-phase degradation of dioxin molecules by OH radicals formed under the action of ionizing radiation on gas macro components (Gerasimov, 2001). The benefits of this process are decomposition products are only organic acids and low energy consumption.

All the aforementioned processes with their dioxins reducing measures are presented inTable S-4.

3.2. Treatment of fly ash

The incineration processes of hospital, hazardous, sewage sludge and municipal solid waste produces thick solid residues or cake called fly ash. It contains dioxins and heavy metals. These pollutants are extremely harmful to soil, marine and fresh water ecosystems, especially when they bioaccumulate through earthy and aquatic food webs. The dioxins concentration in fly ash varies from 100–5000 ng/kg. In many countries, the environmental protection legislation classifies municipal solid waste incineration fly ash as hazardous material and further treatment is required before they are released in to the atmosphere or disposed of in landfills.

Following methods were practiced for the destruction of dioxins in fly ash; however, many of them are limited only to the laboratory stage.

3.2.1. Thermal treatment

Thermal treatment is a process by which heat is applied to the waste in order to sanitize it. The primary function of thermal treatment is to convert the waste to a stable and usable end product and reduce the amount that requires final disposal in landfills (Cheung et al., 2007; Lundin and Marklund, 2007). It is observed that dioxins present in fly ash can be decomposed by thermal treatment under suitable conditions. The work of Vogg and Stieglitz revealed that in an inert atmosphere, thermal treatment of dioxins at 300 °C for 2 h resulted in 90% decomposition of dioxins (Vogg and Stieglitz, 1986). Further in an oxidative atmosphere, thermal treatment at 600 °C for 2 h resulted in 95% decomposition of dioxins, but at lower temperatures dioxins are formed.

It is reported in a review that more than 95% destruction of dioxins can be obtained using thermal treatment equipments such as electrical, oven, coke-bed melting furnace, rotary kiln with electric heater, sintering in LPG burning furnace, plasma melting furnace, etc (Buekens and Huang, 1998).

3.2.2. Non-thermal plasma

The application of non-thermal plasma technology on toxic substance process has been widely studied (Nifuku et al., 1997; Obata and Fujihira, 1998). This process has several advantages over the conventional control devices. It performs effectively and economically at very low concentrations under ambient temperature condition and low maintenance. It doesn't require auxiliary fuel and eliminates disposal problems and sensitivity to poisoning by sulfur or halogen containing compounds. Researchers are paying attention on this new technology for application to environmental protection.

Zhou et al. (2003) applied non-thermal nanosecond plasma to destroy dioxins contained fly ash. They found that a positive pulse discharge provides a higher destruction effect on the compounds contained than does a negative one. They reported that different isomer compounds show different toxic removal effects and the higher the toxicity of the compounds is, the higher is the destruction efficiency. Among all of the congener contained in the fly ash, the isomer 2 3,7,8-TCDD which has the highest toxicity shows the highest destruction efficiency up to 81%.

3.2.3. UV irradiation (photolytic)

A photocatatlytic degradation of dioxins using semiconductors films such as TiO_2, ZnO, CdS, and Fe_2O_3 under UV or solar light is a highly promising method, as it operates at ambient temperature and pressure with low energy photons. This process use light to generate conduction band (CB) electrons and valence band (VB) holes (e^- and h^+) which are able to initiate redox chemical reactions on semiconductors. TiO_2 has been predominantly used as a semiconductor photocatalyst. The VB holes of TiO_2 are powerful oxidants that initiate the degradation reactions of a wide variety of organic compounds (Kim et al., 2006). It was reported that a complete degradation of 2-chlorordibenzo-*p*-dioxin and 2,7-dichlorodibenzo-*p*-dioxin was observed after 2 and 90 h, respectively, in UV illuminated aqueous suspension with no significant intermediates detection. The products obtained after the completion of process were CO_2 and HCl (Pelizzetti et al., 1988).

Choi et al. in their work of photocatalytic degradation of highly chlorinated dioxin compounds found that degradation rates of dioxins decreased with the number of chlorine and increases with the intensity of light and the TiO_2 coating weight (Choi et al., 2000). The photolysis products from 2,3,7,8-TCDD do not bind to either the Ah receptor or the estrogen receptor in vitro (Konstantinov et al., 2000).

3.2.4. Chemical reaction

A chemical reagent method involves use of a reagent and medium for the decomposition of polychlorinated aromatic compounds. In the past years, research was mainly focused on the removal and destruction of dioxins and incineration was favored over the other methods. Nevertheless, the interest in the recovery of reusable materials (e.g., PCBs are present mostly in transformer oils) and the necessity to treat contaminated products with low concentration of PCBs have renewed the interest in the dechlorination methods. The dehalogenation methods mostly involve use of low-valent metal such as alkali metal in alcohol, Mg and Zn/acidic or basic solution (Krishnamurthy and Brown, 1980).

Mitoma et al. have studied detoxification of highly toxic polychlorinated aromatic compounds using metallic calcium in ethanol (Mitoma et al., 2004). They found that metallic calcium can be kept stable under atmospheric conditions for a long period as compared to metallic sodium since the surface is coated with $CaCO_3$, which is formed in contact with air. Moreover, ethanol, which is one of the safe solvents for humans, acts not only as a solvent but also as an accelerator due to its ability to remove the carbonated coating. This decomposition method for dioxins is therefore one of the most environment friendly and economic detoxification methods with respect to the energy and safety of the reagents. Concentration for each isomer of PCDDs, PCDFs and PCBs was reduced in 98–100% conversions by treatment in ethanol at room temperature. The TEQ for the total residues of isomers was reduced from 22000 to 210 pg-TEQ at room temperature.

3.2.5. Hydrothermal treatment

As a large amount of fly ashes are generated annually, there is a continuing interest in establishing ways in which they may be used. It is well known that fly ashes demonstrate satisfactory performance when intermixed with Portland cements. However, fly ashes contain toxic dioxins compounds. Therefore, identification of further means to facilitate the use of fly ashes and avoid the need to dispose then as hazardous wastes is rather desirable. Fly ashes reacted with suitable additives have been reported to produce new types of cementitious materials (Derojas et al., 1993; Jing et al., 2007).

A hydrothermal treatment is a physico-chemical process based on the T/RH/t relation (temperature, relative humidity, time). Fly ashes were put into water or a solution and subject to hydrothermal treatment at high pressure and temperature. An effective solution for dioxins decomposition was found to be NaOH containing methanol; fly ashes containing 1100 ng/g total dioxins subjected to hydrothermal treatment using this solution at 300 °C for 20 min were found to have only 0.45 ng/g total dioxins. It was suggested that the process is superior to purely thermal treatment at the same temperature and the regenerated fly ashes can be used in the cement industries (Ma and Brown, 1997).

3.2.6. Supercritical water oxidation (SCWO)

A waste treatment process using supercritical water, which exists as a phase above the critical temperature (647.3 K) and critical pressure (22.12 MPa) has proved to be a novel way for an effective dioxin remediation. Sako et al. applied the process for the decomposition of dioxins in fly ashes with oxidizer such as air, pure oxygen gas and hydrogen peroxide (Sako et al., 1997). They performed a reaction under the conditions of temperature 673 K, pressure 30 MPa and time 30 min. They observed the importance of behavior of a strong oxidizer and found that the decomposition yield of dioxins is 99.7% with the use of supercritical water and hydrogen peroxide. They have also successfully examined the process for dechlorination of PCBs from transformer oil (Sako et al., 1999).

Recently, the same group studied a hybrid process for the destruction of dioxins in fly ashes (Sako et al., 2004). They performed extraction of dioxins from fly ashes using supercritical fluid (CO_2) and concentration by adsorption, and destruction by SCWO. In the extraction–adsorption process, dioxins contained in fly ashes can be transferred and concentrated to the adsorbent (activated carbon). Then, the adsorbent containing dioxins is completely destructed by SCWO.

The dioxins destruction efficiencies from fly ash and current remediation technologies are presented in Table S-5.

3.3. Remediation of soil and sediment

Environmental problems created by forest fires, oil tanker accidents and oil spillage from cars and trucks, leaky containers, industrial accidents and poorly disposed of wastes are much more common cause for concern. The reservoir processes outlined in Section 2.4 mainly contributes to the contamination of soil. Numerous tons of soil and sediment in the world were contaminated with dioxins that need an appropriate remediation method. The most common soil contaminants are petroleum-based, ex. diesel fuel, gasoline polyaromatic hydrocarbons (PAH), etc. Many PAHs are known carcinogens and others are suspected problem chemicals which tend to spread through soil by diffusion and convection.

Soil remediations involve two distinct classes: *in-situ*, or on-site, and *ex-situ*, or off-site. On-site cleanups are often preferred because they are cheaper. On the other hand, *ex-situ* remediation has the added bonus of taking the bulk of contaminants off-site before they can spread further. In addition, *in-situ* situations are limited because only the topside of the soil is accessible. These environmental limitations force *in-situ* remediation to fall into three categories: washing, venting and bioremediation. Off-site facilities have the luxury of more complete control over the cleaning chemical processes.

Following on- and off-site methods can be used for the remediation of soil.

3.3.1. Radiolytic degradation

Ionizing radiation in the form of high-energy electron beams and gamma rays is a potential non-thermal destruction technique. Theoretical and some empirical assessments suggest that these high-energy sources may be well suited to transforming dioxin to innocuous products. Gamma radiolysis has been shown to be effective in the degradation of PCDD and PCBs in organic solvents and in the disinfection of wastewaters (Farooq et al., 1993; Nickelsen et al., 1992; Zhao et al., 2007).

Using a cobalt-60 gamma ray source, Hllarides et al. extensively studied dioxin destruction on artificially contaminated soil (Gray and Hilarides, 1995; Hilarides et al., 1994). A standard soil (EPASSM-91) was artificially contaminated with 2,3,7,8-TCDD to 100 ppb, and in the presence of 25% water and 2% surfactant (RA-40) and at a high irradiation dose (800 kGy), greater than 92% TCDD destruction was achieved, resulting in a final TCDD concentration of less than 7 ppb. The results of these experiments demonstrate that radiolytic destruction of TCDD bound to soil using gamma radiation can be achieved. The role of surfactant was very useful and was thought to mobilize TCDD molecule to a more favorable location in the soil, thereby modifying target size and density to make the direct effects of radiolysis more effective. The study of by-products and theoretical target theory calculations indicate that TCDD destruction proceeds through reductive dechlorination.

Recently, Mucka et al. found that addition of promoters to the toxicants increases the percentage of destruction under electron beam radiation. They observed a positive influence of active carbon and Cu_2O oxide on dechlorination of PCBs in alkaline 2-propanol solution using radiolytic degradation method (Mucka et al., 2000).

3.3.2. Base catalyzed dechlorination

The base-catalyzed decomposition (BCD) process is a chemical dehalogenation process (Chen et al., 1997). It involves the addition of an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide to the contaminated medium. BCD is initiated in a medium temperature thermal desorber (MTTD) at temperatures ranging from 315–426 °C. Alkali is added to the contaminated medium in proportions ranging from 1 to about 20% by weight. A hydrogen donor compound is added to the mixture to provide hydrogen ions for reaction, if these ions are not already present in the contaminated material. The BCD process then chemically detoxifies the chlorinated organic contaminants by removing chlorine from the contaminants and replacing it with hydrogen.

Pittman Jr. and Jinabo He, have studied dechlorination of chlorinated hydrocarbons and pesticides. They used Na/NH_3 to de-halogenate polychlorinated compounds from the soils and sludges. Several soils, purposely contaminated with 1,1,1-trichloroethane, 1-chlorooctane and tetrachloroethylene, were remediated by slurring the soils in NH_3 followed by addition of sodium. The consumption of sodium per mole of chlorine removed was examined as a function of both the hazardous substrate's concentration in the soil and the amount of water present. The Na consumption per Cl removed increases as the amount of water increases and as the substrate concentration in soil decreases. PCB and dioxin-contaminated oils were remediated with Na/NH_3 as were PCB-contaminated soils and sludges from contaminated sites. Ca/NH_3 treatments also successfully remediated PCB-contaminated clay, sandy and organic soils but laboratory studies demonstrated that Ca was less efficient than Na when substantial amounts of water were present (Pittman and He, 2002).

3.3.3. Subcritical water treatment

Water which is held in liquid state above 100 °C by applying a pressure is called subcritical water. It has properties similar to the organic solvents and can act as a benign medium. It has been used to extract PCBs and other organic pollutants from soil and sediment (Weber et al., 2002). Hashimoto and co-workers examined the process of subcritical water extraction for removing dioxins from contaminated soil (Hashimoto et al., 2004). They observed 99.4% extraction of dioxins at a temperature of 350 °C within 30 min; however, it took a much longer time at lower temperatures. In one of the experiment, by the addition of OCDDs to the soil they found that dechlorination is a major reaction pathway.

A use of zero-valent (ZVI) iron in reductive dechlorination of PCDDs and remediation of contaminated soils with subcritical water as reaction medium and extractive solvent was studied by Kluyev and co-workers (Kluyev et al., 2002). They observed by using iron powder as a matrix higher chlorinated congeners were practically completely reduced to less than tetra-substituted homologues. Zero-valent iron has become accepted as one of the most effective means of environmental remediation. It is inexpensive, easy to handle and effective in treating a wide range of chlorinated compounds or heavy metals. It has been widely applied *in-situ, ex-situ* or as part of a controlled treatment process in wastewater, drinking water soil amendment stabilization and mine tailing applications.

3.3.4. Thermal desorption

Thermal desorption is a separation process frequently used to remediate many Superfund sites (Depercin, 1995). It is an *ex-situ* remediation technology that uses heat to physically separate petroleum hydrocarbons from excavated soils. Thermal desorbers are designed to heat soils to temperatures sufficient to cause constituents to volatilize and desorb (physically separate) from the soil.

Although they are not designed to decompose organic constituents, thermal desorbers can, depending upon the specific organics present and the temperature of the desorber system, cause some of the constituents to completely or partially decompose. The vaporized hydrocarbons are generally treated in a secondary treatment unit (e.g., an afterburner, catalytic oxidation chamber, condenser, or carbon adsorption unit) prior to discharge to the atmosphere. Afterburners and oxidizers destroy the organic constituents. Condensers and carbon adsorption units trap organic compounds for subsequent treatment or disposal. Kasai et al. (2000) and Harjanto et al. (2002), have proposed a thermal remediation process based on a zone combustion method for the remediation of soils contaminated by dioxins. The process uses stable combustion of coke particles in the packed bed to soils. They removed 98.9% of dioxins from the soil in a laboratory scale experiment. They also observed increase in the removal efficiency with the pre-treatment of soil such as drying, pre-granulation and addition of limestone.

3.3.5. In-situ photolysis

In this method dioxins can undergo photolysis by sunlight under proper conditions. It is cost effective and less destructive to the site. An organic solvent mixture is added to the contaminated soil and time is then allowed for dioxin solubilization, transport and photodegradation. For this purpose, the surface of the soil is sprayed with the low-toxicity organic solvent and allowed to photodegrade under the sunlight. Several researchers have used this approach, finding that dioxins on the soil surface rapidly decomposed after being sprayed with various organics such as isooctane, hexane, cyclohexane, etc. (Balmer et al., 2000; Goncalves et al., 2006). Dougherty et al. (1993), found that solar-induced photolytic reactions can be a principal mechanism for the transformation of these chemicals to less toxic degradation products. Convective upward movement of the dioxins as the volatile solvents evaporated was the major transport mechanism in these studies. The effectiveness of this process depends on a balance between two rate controlling factors: convective transport to the surface and sunlight availability for photodegradation.

The *in-situ* vitrification is another developing process for on-site soil decontamination which means to make glass out of something. It involves the use of electricity to melt the waste and surrounding soil in place, then cooling it to form glass. The pollutants that cannot be destroyed by the heat are encapsulated within the glass, so they cannot leach into the surrounding soil or groundwater.

3.3.6. Solvent and liquefied gas extraction

Solvent extraction is a physico-chemical means of separating organic contaminants from soil and sediment, thereby concentrating and reducing the volume of contaminants that needs to be destroyed. This is an *ex-situ* process and requires the contaminated site soil to be excavated and mixed with the solvent. Eventually, it produces relatively clean soil and sediment that can be returned to the site (Silva et al., 2005).

Liquefied gas solvent extraction (LG-SX) technology uses liquefied gas solvents to extract organics from soil. Gases, when liquefied under pressure, have unique physical properties that enhance their use as solvents. The low viscosities, densities, and surface tensions of these gases result in significantly higher rates of extraction compared to conventional liquid solvents. Due to their high volatility, gases are also easily recovered from the suspended solids matrix, minimizing solvent losses. Liquefied carbon dioxide and propane solvent is typically used to treat soils and sediments (Saldana et al., 2005).

Contaminated solids, slurries, or wastewaters are fed into the extraction system along with solvent. Typically, more than 99% of the organics are extracted from the feed. After the solvent and organics are separated from the treated feed, the solvent and organic mixture passes to the solvent recovery system. Once in the solvent recovery system, the solvent is vaporized and recycled as fresh solvent. The organics are drawn off and either reused or disposed of. Treated feed is discharged from the extraction system as slurry. The slurry is filtered and dewatered. The reclaimed water is recycled to the extraction system and the filter cake is sent to disposal or reused.

The U.S. Environmental Protection Agency's (EPA) evaluated a pilot scale solvent extraction process that uses liquefied propane to extract organic contaminants from soil and sediments. Approximately 1000 pounds of soil, with an average polychlorinated biphenyl (PCB) concentration of 260 mg/kg, was obtained from a remote Superfund site. Results showed that PCB removal efficiencies varied between 91.4 and 99.4%, with the propane-extracted soils retaining low concentrations of PCBs (19.0–1.8 mg/kg). Overall extraction efficiency was found to be dependant upon the number of extraction cycles used (Meckes et al., 1997).

3.3.7. Steam distillation

A distillation in which vaporization of the volatile constituents of a liquid mixture takes place at a lower temperature (than the boiling points of the either of the pure liquids) by the introduction of steam directly into the charge; steam used in this manner is known as open steam. It is an ideal way to separate volatile compounds from nonvolatile contaminants in high yield. Steam distillation is effective with microwave energy to treat contaminated soil and sediments. Microwaves are electromagnetic radiation with a wavelength ranging from 1 mm to 1 m in free space with a frequency between 300 GHz to 300 MHz, respectively. In the microwave process, heat is internally generated within the material, rather than originating from external sources. The heating is very fast as the material is heated by energy conversion rather than by energy transfer, as, in contrast, occurs in conventional techniques. Microwave radiation penetrates the sample and heats water throughout the matrix. The developing steam caused volatile and semi-volatile organic pollutants to be removed from the soil without decomposition. The temperature necessary for microwave induced steam distillation was less than 100 °C. Microwave treatments can be adjusted to individual waste streams: depending on the soil, the contaminants and their concentrations, remediation treatment can be conducted in several steps until the desired clean-up level is reached. All contaminants could be removed to non-detectable or trace levels (Windgasse and Dauerman, 1992).

Steam distillation was found to be effective for the removal of 2,7-dichlorodibenzo-*p*-dioxin (DCDD) from DCDD-applied soil. The DCDD concentration (250 μg/50 g soil) in the original soil decreased to less than 5% after steam distillation for only 20 min. The results suggest that steam distillation could be a new remedial method for soils contaminated with dioxins (Mino and Moriyama, 2001).

3.3.8. Mechanochemical (MC)

In this technology the mechanical energy is transferred from the milling bodies to the solid system through shear stresses or compression, depending on the device used. A significant part of the milling energy is converted into heat and a minor part is used to induce breaks, stretches and compression at micro and macroscopic level or for performing a reaction. MC degradation can be easily performed using *ball mills* that are readily available in different sizes (treatment of materials up to several tons is possible) and constructions. The pollutants are eliminated directly inside a contaminated material, regardless of complex structure and strong nature of the pollutant. This method has a high potential to dispose of organic wastes at any desired locations with flexible operation due to its use of a portable facility composed of a mill and a washing tank with a filter. Although this method needs a dechlorinating reagent such as CaO in the grinding operation, it does not require any heating operation. To support use of the MC dechlorination method, it would be useful to have a correlation between the dechlorination rate of organic waste and the grinding (MC) conditions to determine the optimum condition in a scaled-up MC reactor (Mio et al., 2002; Napola et al., 2006).

In a laboratory experiment, it was shown that polyhalogenated pollutants such as polychlorinated biphenyls (PCBs) or pentachlorophenol (PCP) to their parent hydrocarbons in high yields, i.e., biphenyl and phenol, respectively by applying magnesium, aluminum or sodium metal plus a low acidic hydrogen source (Birke et al., 2004). For instance, PCBs in contaminated soils, filter dusts, transformer oils, or as pure substances are dechlorinated to harmless chloride and their parent hydrocarbon biphenyl (over 90%). The method offers several economic and ecological benefits: ball milling requires a low energy input only. Because of the strikingly benign reaction conditions, toxic compounds can be converted to defined and usable products. No harmful emissions to the environment have to be expected. This opened up the development of novel, innovative *ex-situ* dioxins remediation and decontamination processes.

3.3.9. Biodegradation process

Bioremediation is a treatment process which uses microorganisms such as fungi and bacteria to degrade hazardous substances into nontoxic substances (Ballerstedt et al., 1997; Mori and Kondo, 2002). The microorganisms break down the organic contaminants into harmless products- mainly carbon dioxide and water. Once the contaminants are degraded, the microbial population is reduced because they have used their entire food source. The extent of biodegradation is highly dependent on the toxicity and initial concentrations of the contaminants, their biodegradability, the properties of the contaminated soil and the type of microorganism selected. There are mainly two types of microorganisms: indigenous and exogenous. The former are those microorganisms that are found already living at a given site. To stimulate the growth of these indigenous microorganisms, the proper soil temperature, oxygen, and nutrient content may need to be provided. If the biological activity needed to degrade a particular contaminant is not present in the soil at the site, microorganisms from other locations, whose effectiveness has been tested, can be added to the contaminated soil. These are called exogenous microorganisms.

Bioremediation can take place under aerobic and anaerobic conditions. With sufficient oxygen, microorganisms will convert many organic contaminants to carbon dioxide and water. Anaerobic conditions support biological activity in which no oxygen is present so the microorganisms break down chemical compounds in the soil to release the energy they need. A key difference between aerobic (oxidative) and anaerobic breakdown is the former predominantly used for lower chlorinated congeners and the later for high chlorinated congeners (hydrodechlorination).

Sometimes, during aerobic and anaerobic processes of breaking down the original contaminants, intermediate products that are less, equally, or more toxic than the original contaminants are created. Kao and Wu (2000) have invented an *ex-situ* method in which a chemical pre-treatment (partial oxidation) in combination with bioremediation was developed to efficiently remediate TCDD-contaminated soils. In a slurry reactor, they used Fenton's Reagent as an oxidizing agent to transform TCDD to compounds more amenable for biodegradation. They observed up to 99% TCDD was transformed after the chemical pre-treatment process. The slurry reactor was then converted to a bioreactor for the biodegradation experiment. They concluded that the two-stage partial oxidation followed by biodegradation system has the potential to be developed to remediate TCDD-contaminated soils on-site.

On this topic, an appealing review titled "Degradation of dioxin like compounds by microorganisms" was presented (Wittich, 1998).

Table S-6 depicts the technologies used for soil decontamination along with their efficiency.

4. Future prospects and conclusions

Dioxins compounds are environmentally and biologically stable and, as a result, human exposure is chronic and wide spread. An exposure to such type of chemicals can damage the immune system, leading to increased susceptibility and it can disrupt the functions of several hormones. Major routes of dioxins entering into the atmosphere are incineration and combustion sources and therefore, more attention is required for the enhanced understanding of the precursor and de novo mechanisms of dioxins formation. The interaction between chlorine and precursors must be well understood. Further, it is important to identify the conditions under which chlorine, carbon and oxygen can become limiting reactants in the incineration and combustion chamber. The relationship between the rate of carbon consumption and the rate of production of dioxins should be clarified.

Over the past several years, there has been a shift in the major sources of dioxins, in large part due to the stringent regulations and focused voluntary efforts. Production of pesticides used to be associated with relatively high levels of contamination with dioxins. Many of these products have been banned. Bleaching of paper and pulp products using free chlorine in Kraft mills led to the production of dioxins. But the use of alternative processes reduced dioxin formation. Therefore, the chemical industries are taking proper measures to avoid the generation of dioxins. Although incineration process of municipal solid waste once used to be the major source, its contribution to the current emission inventories is now decreasing. However, medical waste incineration is still a major source of dioxins. Polyvinyl chloride (PVC) plastic, as the dominant source of organically bound chlorine in the medical waste stream, is the main cause of dioxin formation by the incineration of medical wastes. Therefore, health professionals have a responsibility to work to reduce dioxin exposure from medical sources. Health care institutions should implement policies to reduce the use of PVC plastics as much as possible, thus achieving major reductions in medically related dioxin formation.

Emissions of these toxic contaminants are believed to have reduced in some industrial countries and there are suggestive data indicating that background levels in human blood and milk in Germany, the Netherlands, and United States have declined, recently. The other important sources of dioxin family compounds today involve combustion processes and reservoir sources. Uncontrolled burning and collection of small sources are the significant sources of new dioxins emissions today. Attempts should be made in order to tap these sources.

The atmospheric transport of dioxins from the source to the site is a complex process and different sources introduce intricate mixtures of dioxins into the environment; no single congener can be used to attribute the occurrence of dioxins in a sample to specific source. Therefore, improved knowledge of the transport mechanisms is required. In this view, there is a strong need for the development of fast and accurate analytical tools. The development of continuous emission monitor (CEM) technology could be an answer for this.

In order to avoid the formation of dioxins in the flue gas it is important to manipulate properly the process parameters such as temperature, residence time and turbulence of the combustion chamber and the post combustion flue gas treatment facilities, etc. A number of technologies are available for removing or destroying dioxins from gases. Waste incineration plants commonly use bag house filters (fabric filters) equipped with activated carbon injection, or fixed bed carbon filters in order to fulfill the emission limits for dioxin. SCR-catalysts (selective catalytic reduction) for NOx reduction combined with an oxidation catalyst are also known to be an effective method to destroy dioxins. Among other recent developments are the installation of systems of catalytic destruction of dioxins and use of better filter materials. The company *Caldo Environmental Engineering* commercializes ceramic filters that can be used at high temperatures and that allow a continuous removal of particles from air or other gases (Calado(UK)). These materials are very resistant in extreme conditions of temperature (>450 °C) and/or of chemical corrosion. In the year 2000, W. L. Gore and Associates proposed a system of destruction of dioxins through the use of catalytic filters REMEDIA D/F. These filters consist of membranes of expanded (PTFE), containing the catalytic system (Gore(USA)). In this process, the membrane captures the fine particles in the surface of the filter, the dioxins and furans pass through the membrane and react instantaneously with the catalyst giving as products CO_2, H_2O and HCL.

The treatment of fly ash and soil for the destruction of dioxins is a broader area of investigation. The currently practiced *ex-situ* thermal treatment methods are energy demanding and hence, alternative techniques are required to save the consumption of energy. The use of photolytic techniques for *in-situ* destruction of dioxins seems to be very economical but their effectiveness largely depends on the sunlight availability for photodegradation. The application of supercritical water for the remediation of dioxins presenting in the fly ash and soil finds to be a promising one, however, more studies are required in order to make the process realistic. Solvent and liquefied gas extraction, steam distillation and mechanochemical are upcoming technologies and may have the potential to eliminate dioxins efficiently from the contaminated soils. Nevertheless, a single pilot scale study is reported (USEPA) on the use of liquefied gas for the removal of PCBs from soil and the present information on removal high molecular weight, toxic, dioxin compounds are very limited. Amongst all the methods described biodegradation is the cheapest method for the destruction of dioxins; however efficient hybrid organisms have to be constructed in the laboratory for the maximum destruction of these compounds. Since biodegradation is a slow process, due to the low bioavailability of dioxins, their rates can be increased by the use of bio-emulsifiers and chemical pre-treatment of the soil.

In our opinion, the use of super critical water, liquefied gas and biodegradation (along with the chemical pre-treatment) have a higher potential and reinforcing the need for more research for the development of sustainable methods of treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envint.2007.07.009.

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