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# Non-thermal plasma (NTP) assisted removal of dioxins and furans in municipal solid waste incineration (MSWI) fly ash over Pt/ZSM-5 catalyst

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#### ARTICLE INFO

#### ABSTRACT

Keywords: Dioxins Furans PCDD/Fs Non-thermal plasma Catalysis The growing volume of municipal solid waste has led to increased use of incineration (MSWI), which unfortunately produces toxic and persistent pollutants such as dioxins and furans (PCDD/Fs), posing serious environmental and health risks. This study explores the use of non-thermal plasma (NTP) systems, with and without catalytic assistance, for the decomposition of PCDD/Fs in MSWI fly ash. A comprehensive investigation was carried out to evaluate the performance of 1Pt/ZSM-5 as a catalyst in the NTP-assisted systems. The results revealed that catalytic-assisted NTP significantly outperformed the NTP-alone system. The 1Pt/ZSM-5 achieved the highest decomposition efficiency and detoxification at nearly 100 % at 30 W. Furthermore, it was observed that higher input power negatively affected decomposition efficiency, resulting in increased concentrations of OCDF and 2,3,7,8-TCDD which was possibly due to competing reactions of dechlorination, chlorination, and destruction. This study underscores the importance of optimising operational conditions, particularly input power, to maximise the performance of catalytic-assisted NTP systems. The findings provide valuable insights into the decomposition mechanisms of PCDD/Fs and highlight the potential of advanced catalytic-assisted NTP systems as a sustainable solution for mitigating dioxin emissions from MSWI processes.

# 1. Introduction

The global generation of municipal solid waste (MSW) is rapidly increasing due to rapid urbanisation, population growth, and the expansion of commercial activities [11]. To address this challenge and support the transition toward sustainability, municipal solid waste incineration (MSWI) has emerged as an effective solution for managing large volumes of waste while generating renewable energy to meet rising energy demands [2].

The emissions from MSW incinerators contain various hazardous chemicals, including volatile organic compounds (VOCs), hydrogen fluoride, sulphur dioxide, nitrogen oxides (NO<sub>x</sub>), and polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) [44]. Among these hazardous chemicals, PCDD/Fs are recognised as some of the most dangerous due to their high toxicity, significant health risks, and resistance to environmental degradation [14,22,31]. PCDD/Fs adversely affect the human

immune, nervous, and reproductive systems and are also suspected [32]. Stringent emission limit values have been introduced in many countries for the monitoring and control of PCDD/F emissions from waste incinerators [29]. The most common method currently used to control dioxin and furan emissions is powdered activated carbon technology, which involves adding activated carbon as a reagent to adsorb PCDD/Fs from flue gas, followed by their capture using fabric filter bags [19]. However, this method is costly, and the disposal of used activated carbon poses additional environmental pollution risks. Therefore, the development of advanced technologies for the decomposition of PCDD/Fs formed during MSWI is crucial.

Non-thermal plasma (NTP) technology has been widely investigated for addressing environmental problems due to its advantages, such as ease of handling, system compactness, and process versatility [5,26]. The highly active species generated in NTP, including ions and free radicals [6], make it an ideal candidate for the removal of pollutants

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*Abbreviations*: HpCDD, Heptachlorodibenzo-p-dioxin; HpCDF, Heptachlorodibenzofuran; HxCDD, Hexachlorodibenzo-p-dioxin; HxCDF, Hexachlorodibenzofuran; MSW, Municipal solid waste; MSWI, Municipal solid waste incineration; NTP, Non-thermal plasma; OCDD, Octachlorodibenzo-p-dioxin; OCDF, Octachlorodibenzo-p-dioxin; PCDD, Polychlorinated dibenzo-p-dioxins; PCDF, Polychlorinated dibenzofuran; PCDD, Pentachlorodibenzo-p-dioxin; TCDF, Tetrachlorodibenzofuran; TEF, Toxic Equivalency Factor; TEQ, Toxic equivalency; VOCs, Volatile organic compounds; I-TEF, International toxic equivalent factor; I-TEQ, Total toxic equivalent quantity.

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such as VOCs and  $NO_{\times}$  [12,24,25]. However, reports on the use of NTP for the removal of PCDD/Fs are still very limited.

Yamamoto et al. first utilised DC corona discharge with a water film to achieve a dioxin removal efficiency exceeding 90 % [43]. The study of Zhou et al. revealed that pulsed discharge streamers could effectively attach to the surface of fly ash, penetrate the particles, and decompose dioxins [48]. Zhou et al. further investigated the removal of PCDD/Fs in fly ash to examine the effects of NTP decomposition on different dioxin congeners [49]. The findings concluded that dioxin congeners with higher toxicity exhibited higher decomposition efficiencies, with 2,3,7, 8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), recognised as the most toxic PCDD/F congener, achieving an 81 % decomposition efficiency. Yoshida et al. employed a pulsed corona-induced plasma chemical process for the simultaneous removal of dioxins and NOx in a pilot-scale setup treating flue gas at 5000 Nm<sup>3</sup> h<sup>-1</sup> [45]. More than 84 % of dioxin species were decomposed based on toxic equivalency (TEQ), with a specific energy consumption of 6.1 Wh Nm<sup>-3</sup>. By comparing the decomposition efficiency of different PCDD/F congeners, it was suggested that dioxin decomposition begins with the cleavage of C-O-C bonds connecting the two benzene rings. Hung et al. applied dielectric barrier discharge (DBD) plasma to PCDD/Fs removal in 2010, demonstrating that OH radicals generated by O<sub>2</sub>, and water vapour effectively intensified the dechlorination of gaseous PCDD/Fs [15]. Zheng et al. also employed a DBD plasma system to investigate the decomposition characteristics of different PCDD/F congeners under varying input energy, discharge times, and fly ash moisture contents [47]. Their results showed that 2,3,7,8-TCDD achieved the highest decomposition efficiency of up to 92 %.

From the above literature review, it is evident that only NTP systems without catalysts have been studied for the removal of PCDD/Fs. To date, NTP systems combined with catalysts for the removal of PCDD/Fs in MSWI fly ash have not been reported. Many studies have confirmed that catalysts can play a significant role in enhancing the efficiency of NTP systems [4,7,8,39]. Without the participation of catalysts, the decomposition of PCDD/Fs in the NTP system occurs in an uncontrolled manner, where chlorination and dechlorination take place simultaneously, hindering the deep oxidation of PCDD/Fs into CO<sub>2</sub>.

Herein, a systematic investigation of an NTP-assisted catalytic system for the removal of PCDD/Fs in MSWI fly ash is essential to explain the decomposition mechanism of PCDD/Fs in the presence of catalysts. This understanding will aid future research in achieving the deep oxidation of PCDD/Fs. Platinum based catalysts have been reported in the decomposition of PCDD/Fs under thermal conditions due to its strong catalytic activity, high redox capability, and ability to promote selective dechlorination [3,23,33]. In this study, ZSM-5, with its exceptional pore structure and excellent acidity, was employed as a support for Pt nanoparticles. The catalysts were subjected to a comparative investigation of 17 different PCDD/F congeners to understand the reaction behaviour and decomposition mechanism of PCDD/Fs in MSWI fly ash within a catalytic-assisted NTP system.

# 2. Experimental

# 2.1. Materials and preparation of catalysts

The MSWI fly ash samples (No.0263) used in this work were reference material (No.490) provided by the commission of the European Communities. Pt/ZSM-5 catalysts were prepared using the conventional incipient wetness impregnation method, with a Pt loading of 1.0 wt%. Specifically, ZSM-5 (Thermo Fisher) was impregnated with an aqueous solution of chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Merck,  $\geq$ 37.50 % Pt basis) for 12 hours. After impregnation, the sample was dried at 110°C and then calcined in a muffle furnace at 550 °C for 4 hours. The calcined solids were subsequently reduced under a flow of 5 % H<sub>2</sub> in nitrogen at 50 sccm under 450 °C for 5 hours, using a heating rate of 5 °C min<sup>-1</sup>. The catalysts were named based on the theoretical Pt

loading, designated as 1Pt/ZSM-5.

#### 2.2. Characterisation of materials

The catalysts were subjected to comprehensive characterisation to investigate their physical and chemical properties. X-ray diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer using Cu Ka radiation (40 kV, 40 mA) to determine the crystal structure of the zeolites. The scanning range was  $5^{\circ}$  to  $60^{\circ}$ , with a step size of  $0.02^{\circ}$ . Nitrogen physisorption analysis was performed using a Nova 800 surface area analyser. Before the N<sub>2</sub> physisorption measurements, approximately 50 mg of each sample was degassed at 150 °C under a nitrogen atmosphere overnight. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area of the materials. Scanning electron microscopy (SEM) images were obtained using a Carl Zeiss EVO MA15 SEM, operated at 20 kV in high voltage mode. High-resolution transmission electron microscopy (HRTEM) images were captured using an FEI Titan Cubed Themis 300 G2 FEG STEM at 200 kV, and element mapping via energy-dispersive X-ray spectroscopy (EDS) was performed with an Oxford Ultim® Max system. For TEM analysis, the samples were prepared by dispersing the catalyst powders in methanol with sonication for 10 mins, and a drop of the suspension was spread onto a TEM copper grid.

#### 2.3. Experiments of the removal of PCDD/Fs in MSWI fly ash

PCDD/Fs removal experiments were carried out in a continuousflow, fixed-bed cylindrical quartz reactor (23 mm O.D.) under atmospheric pressure, and the experimental setup is shown in Fig. 1. The reactor consists of a stainless-steel rod (18 mm O.D.), which serves as the high voltage electrode and is positioned along the axis of the quartz cylinder. A copper mesh (length = 95 mm), acting as the ground electrode, was wrapped around the outer surface of the quartz reactor. In a typical experiment, 1.0 g of MSWI fly ash (pelletised with particle sizes of 250–425  $\mu$ m) was packed into the discharge zone between the high voltage electrode and the quartz reactor wall. The reactor temperature was maintained at 250°C using a tube furnace. During the reaction, the applied power of the DBD plasma was varied between 30 and 70 W, while the frequency remained constant at 20.3 kHz to investigate its effect on PCDD/Fs decomposition. The applied power was monitored using a digital oscilloscope (Tektronix MDO3024). To investigate the role of catalysts in a NTP-assisted PCDD/Fs decomposition system, 1.0 g of as -prepared 1Pt/ZSM-5 catalyst was mechanically mixed with 1.0 g



Fig. 1. Experimental setup for NTP assisted catalytic PCDD/Fs removal.

of fly ash using a pellet press. The resulting pellets (with particle sizes of  $250-425 \ \mu$ m) were packed into the above-mentioned reactor and tested under the same conditions. PCDD/Fs analysis of the original fly ash and NTP treated fly ash was carried out following the US Environmental Protection Agency Method 1613 [37]. This involved high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC-HRMS) (JMS-800D, JEOL, Japan) using a DB-5MS column. The international toxic equivalent factor (I-TEF) established by NATO was used to assess the total toxic equivalent quantity (I-TEQ) of PCDDs and PCDFs. For details on the PCDD/F congener contents and their corresponding I-TEFs, please refer to the literature [20].

For the PCDD/Fs decomposition under the NTP condition with and without catalysts, PCDD/Fs ( $X_{PCDD/Fs}$ , %) decomposition efficiency was calculated using Eq. (1):

$$XPCDD \left/ Fs = \frac{m \frac{Ash}{PCDD/Fs} - m \frac{Treated Ash}{PCDD/Fs}}{m \frac{Ash}{PCDD/Fs}} \times 100\%$$
(1)

Where  $m \frac{Ash}{PCDD/Fs}$  and  $m \frac{Treated Ash}{PCDD/Fs}$  represent the mass concentration of different PCDD/Fs congeners in the MSWI fly ash and after treatment by the NTP system, respectively.

The detoxification efficiency of the NTP systems with and without catalysts was calculated using Eq. (2),

 $X_{Detoxification} = \frac{TEQ(Ash) - TEQ(Treated Ash)}{TEQ(Ash)} \times 100\% (2)$ 

Where TEQ(Ash) and TEQ(Treated Ash) represent the toxic equivalence of the MSWI fly ash and after treatment by the NTP system, respectively.

#### 3. Results and discussion

# 3.1. The decomposition of PCDD/Fs congeners in the NTP-alone system

Table S1 lists the chemical structures of the 17 PCDD/F congeners. To investigate the relationship between decomposition performance and reaction time, the fly ash was treated using NTP at 70 W for 0.5 h and 1.0 h, respectively, as shown in Figure S1. Overall, a longer reaction time positively influenced decomposition performance. Specifically, the toxic equivalent (TEQ) of the fly ash after 1.0 h of treatment was 4180 ng kg<sup>-1</sup>, which was 67 % lower than that after 0.5 h of treatment. The extended treatment time allows more opportunity for the active species generated by plasma to break and oxidise the chemical bonds within the PCDD/F structures, enabling deeper oxidation. Based on these results, 1.0 h was selected as the discharge time for all subsequent experiments in this study.



Fig. 2. Decomposition of 17 PCDD/F congeners under pure NTP conditions at varying discharge powers (30 W to 70 W): (a)-(b) concentration distribution, and (c)-(d) decomposition efficiency of 17 PCDD/Fs.

Fig. 2 presents the results of the 17 PCDD/Fs mass concentration in the original MSWI fly ash and remaining mass concentration and decomposition efficiency of the 17 PCDD/Fs congeners in the MSWI fly ash after treatment in the NTP-alone system under varying operating voltages. 2,3,7,8-TCDD, recognised as the most toxic PCDD/F congener, achieved a decomposition efficiency of 80 % at 30 W, the highest among the seven PCDD congeners. This observation is consistent with previous studies, which have shown that dioxin congeners with greater toxicity tend to achieve higher decomposition efficiencies [47,49]. Furthermore, the decomposition efficiency of PCDD/Fs is influenced by the number of chlorine substitutions in their structure. For example, the decomposition efficiency of 2,3,7,8-TCDF was 81.7 % at 30 W. However, as the number of chlorine substitutions increased from 4 to 8, the decomposition efficiency of 1,2,3,6,7,8-HxCDF decreased to 73.3 %. The decomposition efficiency of OCDD, which contains eight chlorine atoms, was only 21.7 %, four times lower than that of 2,3,7,8-TCDF. This observation can be attributed to the fact that more energy is required to break the PCDD/F structure as the number of C-Cl bonds increases, resulting in lower decomposition performance under the same conditions [47]. Thompson et al. reported that each chlorine substitution in dibenzofuran or dibenzo-p-dioxin increases the enthalpy of formation by 1.64 kcal mol<sup>-1</sup> [34]. Furthermore, group additivity and semi-empirical methods predicted that the enthalpy of formation of dioxin compounds decreases linearly with successive chlorination, indicating an increase in the stability of the compounds [10,30,36].

In addition to the number of chlorine substitutions, the position of these substitutions also plays a significant role in determining decomposition efficiency. For instance, the decomposition efficiency of 1,2,3,6,7,8-HxCDD is higher than that of 1,2,3,4,7,8-HxCDD. Chlorine atoms, being electron-withdrawing groups, influence the electron distribution of the molecule through conjugation effects depending on their substitution positions (ortho, meta, or para) on the benzene ring [17, 46]. Hou et al. applied DFT calculations to 1,2,3,7,8-PCDD and observed that chlorine substitution at positions 4, 9, and 6 progressively increased the difficulty of decomposition, consistent with the principle of distal preference [13]. Consequently, in this study, the decomposition efficiency of 1,2,3,4,7,8-HxCDF at 30 W was 74.5 %, approximately 20 % higher than that of 1,2,3,7,8,9-HxCDF which has a more symmetrical structure with chlorine substituted at position 9 instead of position 4. This observation aligns with the findings of Hou et al. [13].

Unlike other studies in the literature, increasing the input power in an NTP-only system does not always enhance the decomposition of PCDD/Fs. In this study, an input power of 30 W exhibited the best performance for PCDD/F removal compared to other power levels. For example, the decomposition efficiency of 2,3,7,8-TCDD at 30 W reached 80 %. However, when the power was increased to 50 W, the decomposition efficiency decreased to 67.5 %, and it dramatically dropped to -21.2 % at 70 W. This finding indicates that at higher applied voltages, certain PCDD/F congeners are generated, confirming that during the NTP-assisted decomposition process, dechlorination, chlorination, and destruction reactions occur simultaneously [28].

The NTP system generates abundant active species such as ions, radicals, and O<sub>3</sub> [6]. Increasing the input power enhances the concentration of these active species, which can rapidly dissociate chemical bonds such as C–Cl, C–O, and C–C bonds in the benzene ring of PCDD/Fs [9,15,49]. In the absence of catalysts, the bonds dissociation can occur randomly. The resulting substances can subsequently react with each other or with certain PCDD/F molecules. During the formation process of dioxins and furans, chlorination reactions often lead to complete chlorination. OCDF, as a fully chlorinated congener with all available positions substituted by chlorine atoms, exhibits high thermodynamic stability due to its highly chlorinated structure [1]. Consequently, OCDF is one of the most abundant congeners in the formation process of PCDFs. This also explains the increase in OCDF concentration from approximately 4000 ng kg<sup>-1</sup> to 20,000 ng kg<sup>-1</sup> after NTP treatment at 70 W. Unlike PCDDs, the distribution of PCDF congeners is primarily

controlled by the dechlorination process of OCDF [16,35]. This observation explained the increase in the concentration of most PCDF congeners under higher input power.

Dechlorination and chlorination are likely competing reactions, with the specific pathway determined by local reaction conditions such as chlorine source concentration, reaction time, temperature, and input power. Therefore, identifying the optimal operating conditions for the NTP-assisted PCDD/Fs removal system is crucial to achieving effective and complete decomposition of PCDD/Fs.

# 3.2. Characterisation of MSWI fly ash particles

To better understand the decomposition of PCDD/F congeners in the NTP-alone system, SEM and EDX mapping were employed to investigate the morphological changes in the fly ash and the changes in elemental concentrations in MSWI fly ash.

Fig. 3 illustrates the surface changes of the MSWI fly ash before and after NTP treatment. Compared to the fresh fly ash, the surfaces of the NTP-treated fly ash appeared significantly rougher. Additionally, relatively large particles in the fly ash dissociated into smaller particles after discharge. These results indicate that the DBD plasma can penetrate fly ash particles and fragment larger particles into smaller pieces.

Figure S2 presents the EDX mapping of fresh fly ash and treated fly ash under three different input power. The results show that the weight percentage of chlorine in fresh fly ash was 2.95 %, which dropped significantly to 0.69 % after discharge in the NTP system under 30 W. This clearly demonstrates that the PCDD/Fs in the fly ash were decomposed by the DBD plasma, consistent with observations discussed in the previous section. However, the chlorine concentration in the treated fly ash under 70 W was 2.64 %, similar to that of the fresh fly ash. This can be attributed to some PCDD/F congeners undergoing dechlorination at 70 W, where the dissociated chlorine reacted with other substances to form new PCDD/Fs, resulting in a similar chlorine concentration in the fly ash. This finding also provides evidence supporting the hypothesis that dechlorination, chlorination, and destruction reactions occur simultaneously in the NTP system.

#### 3.3. Characterisation of catalysts

The decomposition behaviour of PCDD/Fs in the NTP-alone system was systematically discussed. The non-selective reaction mechanism in the NTP-alone system led to random dissociation of chemical bonds in PCDD/Fs, resulting in the formation of by-products and the rechlorination of PCDD/Fs. To achieve the deep decomposition of PCDD/Fs, 1Pt/ZSM-5 was employed in this study. Systematic characterisation was carried out, and the catalytic performance of the catalyst in PCDD/Fs removal was thoroughly investigated.

Fig. 4 presents the powder XRD patterns of the ZSM-5 and the assynthesised 1Pt/ZSM-5 catalysts. The characteristic diffraction peaks at  $2\theta = 7.9^{\circ}$ ,  $8.9^{\circ}$ , and in the range of  $23^{\circ}$  to  $25^{\circ}$  (highlighted in the shaded area) confirm the well-crystallized MFI structure of the ZSM-5 zeolite, indicating that the zeolite framework remains undamaged after the impregnation process [27]. In addition to the zeolite peaks, diffraction peaks corresponding to platinum were observed at  $2\theta$ =  $39.7^{\circ}$  and  $46.2^{\circ}$ , corresponding to the (111) and (200) crystal planes of metallic Platinum, respectively [24]. These peaks indicate the successful deposition of Pt onto the ZSM-5 support.

The N<sub>2</sub> adsorption-desorption isotherms of the ZSM-5 and 1Pt/ZSM-5 catalysts are shown in Figure S3, with the corresponding porous properties summarised in Table S2. Both samples exhibit a steep increase in N<sub>2</sub> uptake at low relative pressures (P/P<sub>0</sub> < 0.01), confirming the presence of micropores in the supports [38]. The surface areas of ZSM-5 and 1Pt/ZSM-5 were 794 m<sup>2</sup> g<sup>-1</sup> and 703 m<sup>2</sup> g<sup>-1</sup>, respectively. The slight decrease in surface area for 1Pt/ZSM-5 can be attributed to the deposition of Pt nanoparticles on the surface of ZSM-5.

SEM analysis of 1Pt/ZSM-5, as shown in Figure S4, reveals the lath-



Fig. 3. SEM images of (a) MSWI fly ash, treated MSWI fly ash under different plasma input power; (b) 30 W, (c) 50 W, and (d) 70 W.



Fig. 4. XRD patterns of (a) the ZSM-5 supports, and (b) as-prepared 1Pt/ZSM-5 catalysts (after calcination in air at 550 °C).

shaped morphology of the supports, with crystal size ranging from approximately 150 to 400 nm. The size and dispersion of metal on the catalyst support play an important role in determining the utilisation efficiency and overall catalytic performance [6]. HRTEM was used to investigate the size and dispersion of Pt nanoparticles in the 1Pt/ZSM-5 catalyst. The results are presented in Fig. 5. As shown in Fig. 5(a), the HRTEM image reveal the presence of small metal particles, while the EDS mapping confirms the uniform distribution of Pt on the 1Pt/ZSM-5 catalysts. The particle size distribution, presented in Fig. 5(b), indicates that the average Pt nanoparticle size in 1Pt/ZSM-5 is  $6.62 \pm 0.26$  nm. Additionally, cumulative frequency analysis, also presented in Fig. 5(b), shows that over 90 % of the Pt nanoparticles in 1Pt/ZSM-5 are smaller than 9.61 nm (d(90) = 9.61 nm). The small particle size and uniform distribution of Pt nanoparticles on the catalyst can be attributed to the large surface area and porous structure of ZSM-5.

3.4. The decomposition of PCDD/Fs congeners in the catalytic-assisted NTP system

Fig. 6 presents the results for the remaining mass concentration and decomposition efficiency of the 17 PCDD/Fs congeners in the MSWI fly ash after treatment in the catalytic-assisted NTP system under varying operating voltages. With the participation of 1Pt/ZSM in the reaction system, the decomposition behaviour of PCDD/Fs showed significant differences compared to the NTP-alone system, indicating changes in the underlying reaction mechanisms. In the NTP-alone system, the decomposition efficiency of PCDF congeners was lower than that of PCDDs, primarily due to the re-chlorination process that formed OCDF. For instance, the decomposition efficiency of 1,2,3,4,7,8,9-HpCDF was only 53.4 % at 30 W in the NTP-alone system. However, with the participation of 1Pt/ZSM-5, the decomposition efficiencies of all PCDFs increased significantly, achieving nearly 100 % at 30 W. This observation



Fig. 5. (a) HRTEM image of 1Pt/ZSM-5, (b) Pt particles size distribution of 1Pt/ZSM-5, (c) and (d) TEM-EDS mapping of Pt on 1Pt/ZSM-5.

confirms that the inclusion of the catalyst enables the deep destruction of PCDD/Fs rather than merely breaking chlorine bonds, thus avoiding re-chlorination. In addition to PCDFs, nearly 100 % decomposition was achieved for all other PCDD congeners, except for 2,3,7,8-TCDD, under 30 W. This performance outperforms that of the NTP-alone system under the same conditions. Meanwhile, the decomposition efficiency of 2,3,7,8-TCDD also reached an impressive 86.4 %. The superior performance of 1Pt/ZSM-5 catalytic-assisted NTP systems compared to NTPalone systems can be attributed to the ability of catalysts to (i) lower the activation energy of reactions, (ii) selectively adsorb reaction intermediates, and (iii) provide additional active sites that synergise with the reactive species generated by NTP [40–42].

In the catalytic-assisted decomposition system, the power of the DBD plasma still negatively impacts the removal of PCDD/Fs. The decomposition efficiency of PCDD/F congeners decreased with increasing input power, particularly for 2,3,7,8-TCDD and OCDF. The mass concentration of 2,3,7,8-TCDD increased from 20.4 ng kg<sup>-1</sup> to 219.6 ng kg<sup>-1</sup>, and the OCDF concentration rose from 6.17 ng kg<sup>-1</sup> to 11,864 ng kg<sup>-1</sup> when the power was increased from 30 W to 70 W. As discussed in the NTP-alone chapter, it is believed that dechlorination, chlorination, and destruction reactions occur simultaneously during the decomposition of PCDD/Fs. The negative impact of increasing input power on PCDD/Fs decomposition can be explained by the following possible reasons: (i) With increasing input power, the concentration of high-energy electrons and reactive species (such as OH, O, and N2<sup>+</sup>) increases significantly, leading to a higher probability of random molecular bond dissociation and non-selective reactions. (ii) At lower power levels, the catalyst effectively promotes dechlorination reactions,

decomposing highly chlorinated congeners. However, with increasing power, re-chlorination reactions may dominate. (iii) At high power levels, the large number of high-energy electrons may directly interact with the catalyst surface, damaging or deactivating the active sites of the catalysts.

# 3.5. The detoxification efficiency of the NTP alone system and the catalytic-assisted NTP system

Fig. 7 presents the TEQ and detoxification efficiency of different MSWI ash samples. TEQ is a measure used to estimate the overall toxicity of a mixture of PCDD/Fs. It expresses the toxicity of the mixture in terms of a reference compound, 2,3,7,8-TCDD, which is the most toxic dioxin and is assigned a Toxic Equivalency Factor (TEF) of 1 [18]. The results indicate that both the NTP-alone system and the catalytic-assisted NTP system can effectively remove PCDD/Fs under lower applied voltages. At 30 W, the detoxification efficiency of the NTP-alone system was approximately 75 %, while nearly 100 % detoxification was achieved with the participation of catalysts. Although a significant amount of OCDF was generated in the catalytic-assisted NTP system at high input power, where the concentration increased from  $3630 \text{ ng kg}^{-1}$  to  $11,864 \text{ ng kg}^{-1}$  at 70 W, the system still maintained a high detoxification efficiency. This is due to the low toxicity of OCDF, which has a TEF of only 0.001 [21]. Herein, although some PCDD/F congeners were found to increase in concentration after NTP treatment, overall, the NTP system in combination with catalysts demonstrated enhanced performance, enabling deeper oxidation of PCDD/Fs compared to the NTP-alone system.



Fig. 6. NTP assisted decomposition of 17 PCDD/Fs over 1Pt/ZSM-5: (a)-(b) concentration distribution, and (c)-(d) decomposition efficiency of 17 PCDD/Fs.



Fig. 7. (a): Toxic equivalency, and (b): Detoxification efficiency of PCDD/Fs over the pure NTP condition and 1Pt/ZSM-5 with different input energy.

#### 4. Conclusions

This study systematically investigated the decomposition behaviour of PCDD/Fs in MSWI fly ash using a non-thermal plasma system, both with and without catalytic assistance. The findings demonstrate the strong potential of NTP technology for PCDD/F degradation and emphasise the critical role of catalysts in enhancing efficiency and selectivity.

In the NTP-alone system, up to 80 % decomposition efficiency of 2,3,7,8-TCDD was achieved at 30 W. However, performance declined at higher power due to competing dechlorination and re-chlorination re-actions, leading to the formation of more stable and toxic by-products such as OCDF. The decomposition behaviour was also strongly influenced by the number and position of chlorine atoms on the PCDD/F molecules.

Compared to the NTP-alone system, the catalytic-assisted system exhibited superior performance, achieving nearly 100 % detoxification efficiency at 30 W, significantly surpassing the NTP-alone system. This enhancement was particularly notable in the decomposition of PCDFs, which tended to re-chlorinate in the NTP-alone system but were significantly decomposed in the presence of the catalyst. However, at higher input power levels, the decomposition efficiency declined, accompanied by a substantial increase in OCDF concentration from 3630 ng·kg<sup>-1</sup> to 11,864 ng·kg<sup>-1</sup> at 70 W. Several possible factors contributed to this decline: (i) the generation of more active species under high voltage, which likely enhanced non-selective decomposition reactions; (ii) competition between dechlorination and re-chlorination reactions; and (iii) potential deactivation of the catalyst. In the future, more in-situ experiments, and simulations should be carried out to get a deeper understanding of the decomposition mechanisms of PCDD/Fs in NTP system, particularly in the presence of catalysts.

Overall, this study demonstrates that optimising the operating conditions, particularly the input power, is important for maximising the performance of catalytic-assisted NTP systems. The findings provide valuable insights into the mechanisms governing PCDD/F decomposition and the role of catalysts in enhancing the efficiency and selectivity of NTP systems, offering a new approach to solving the challenge of MSWI fly ash treatment.

# CRediT authorship contribution statement

Williams Paul: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. Maryam Khatibi: Investigation. Yibing Mu: Writing – original draft, Methodology, Investigation, Conceptualization.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.117121.

# Data availability

Data will be made available on request.

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