Short Communication

Unexpected promotion of PCDD/F formation by enzyme-aided Cl₂ bleaching in non-wood pulp and paper mill

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H I G H L I G H T S

- PCDD/Fs were determined in non-wood pulp mill while using enzyme-aided bleaching.
- Increases of PCDD/F levels were found when using enzyme-aided bleaching process.
- Formation of OCDD was promoted by xylanase during non-wood pulp bleaching.
- The effectiveness of enzyme on PCDD/F reduction needs further evaluation.

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Enzyme-aided Cl₂ bleaching is widely considered as promising replacements for conventional Cl₂ bleaching in wood pulp and paper mills. However, the effects of using enzyme-aided bleaching on the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the non-wood pulp and paper mills are unclear. A field study was performed to investigate PCDD/F formation when enzyme-aided Cl₂ bleaching was used to replace conventional Cl₂ bleaching in non-wood pulp and paper mills. Unexpectedly, the PCDD/F toxic equivalents (TEQs) in solid samples were higher when using enzyme-aided bleaching (0.49–5.4 pg TEQ/g) than that using conventional Cl₂ bleaching (0.15–2.44 pg TEQ/g). Large amounts of octachlorodibenzo-*p*-dioxin were formed during the enzyme-aided bleaching process. This could have been because enzyme strongly promoted the release of organic molecules bound to lignin and thus accelerated the formation of octachlorodibenzo-*p*-dioxin through organic molecular precursors. Although enzyme-aided Cl₂ bleaching was previously considered to be efficient for reducing PCDD/F releases and to be the best available technologies and best environmental practices for wood pulp and paper mills, the results obtained in this study suggested the necessity and urgency to evaluate the suitability of enzyme-aided Cl₂ bleaching for non-wood pulp and paper mills that intensively practiced in developing countries.

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1. Introduction

In the 1980s, pulp and paper mills using elemental chlorine (Cl₂) bleaching processes were found to unintentionally release polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), which are toxic, bioaccumulative, and persistent, into the environment (Voss et al., 1988; Amendola et al., 1989; Rappe et al., 1990;

Kannan et al., 2000, 2001). PCDD/Fs released from pulp and paper mills have been found to have adversely affected the surrounding environment and biota (Macdonald et al., 1998; Peek et al., 2002; Yunker et al., 2002; Oakes et al., 2013). Comprehensive investigations into the formation, emission, and control of PCDD/Fs during pulp bleaching were therefore carried out (Jokela and Salkinojasalonnen, 1992; Koistinen et al., 1992; Dimmel et al., 1993; Luthe and Prahacs, 1993; Peck and Daley, 1994; Zheng et al., 2001).

It has been found in previous studies that PCDD/Fs are mainly formed during the Cl₂ bleaching stages in pulp and paper mills

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(Fouquet et al., 1990; Hise et al., 1990; Rappe et al., 1990). Therefore, many alternatives to conventional Cl_2 bleaching have therefore been developed to decrease PCDD/F formation (Renberg et al., 1995). Enzyme-aided Cl_2 bleaching is widely considered as one of most promising “clean” bleaching processes (Torres et al., 2000; Shatalov and Pereira, 2009; Borges et al., 2013; Gangwar et al., 2014). Enzyme-aided bleaching can minimize the amounts of Cl_2 used and simultaneously increase the brightness and degree of delignification of paper products (Torres et al., 2000; Shatalov and Pereira, 2007, 2009; Borges et al., 2013; Gangwar et al., 2014). Enzyme-aided bleaching can also decrease the amounts of absorbable organic halides that are formed and discharged, and thus was considered to be efficient for reducing PCDD/F formation and release (Jokela et al., 1993; Shatalov and Pereira, 2007, 2009; Gangwar et al., 2014). However, previous studies have been focused on wood pulp bleaching, and the effects on PCDD/F formation of using enzyme-aided bleaching in non-wood pulp and paper mills are still unclear.

Manufacture of pulp and paper product using non-wood raw materials are still intensively practiced in developing countries, such as China, India and Russia (Qi and Ning, 2013). There are numerous non-wood pulp and paper mills in China and other developing countries. The global annual production of non-wood pulp was 15,756 thousand tonnes (Qi and Ning, 2013). The proportion of non-wood pulp took less than 5% of total pulp and paper in the world (Qi and Ning, 2013). However, the non-wood materials contribute about 60% of raw materials in Chinese pulp and paper industry in the 1990s in China (Zheng et al., 1997). The non-wood raw materials used in these mills are mainly reeds, wheat straw, and so on (Zheng et al., 1997, 2001). Non-wood plants usually contain less lignin, more silica, and more colored material than woody plants (Yu et al., 2002). Thus, the formation mechanism of PCDD/Fs in non-wood pulp and paper mills could be different from that in wood pulp and paper mills. PCDD/F formation and emissions from non-wood pulp and paper mills using Cl_2 bleaching processes have been studied in detail (Zheng et al., 1997, 2001; Wang et al., 2012; Wang et al., 2014). Zheng et al. reported PCDD/F concentrations and profiles in six non-wood pulp and paper mills (Zheng et al., 1997, 2001). Wang et al. recently described the PCDD/F formation and emissions from six Chinese non-wood pulp and paper mills (Wang et al., 2012). However, all the investigated pulp and paper mills adopted Cl_2 bleaching processes. Up to date, no studies

of the formation of PCDD/Fs in non-wood pulp and mills using enzyme-aided bleaching processes have yet been performed to our knowledge. It is still unclear whether using enzyme-aided bleaching, which is widely recognized to be a promising clean bleaching process, could decrease PCDD/F emissions for non-wood pulp and paper mills. It is therefore important that PCDD/F concentrations and profiles in non-wood pulp and paper mills using enzyme-aided bleaching should be evaluated and compared with PCDD/F concentrations and profiles in mills using conventional Cl_2 bleaching, which are still intensively used. Such comparisons would be significant for suggesting the best available technologies and best environmental practices (BAT/BEP) for non-wood pulp and paper mills from the viewpoint of decreasing PCDD/F releases.

In this study, we aimed to evaluate the possible effectiveness of PCDD/F emission reduction when using enzyme-aided bleaching processes to replace conventional Cl_2 bleaching processes in non-wood pulp and paper mills. A field study in a Chinese non-wood pulp and paper mill was performed, and the PCDD/F concentrations and profiles in the raw materials, pulp, products, sludge, and effluents before and after the conventional the Cl_2 bleaching had been replaced with an enzyme-aided bleaching process were determined. The results were expected to provide the first insight about whether the enzyme-aided bleaching are the BAT/BEP technique associated with PCDD/F emission reductions for non-wood pulp and paper mill or not.

2. Materials and methods

2.1. Information on the investigated pulp and paper mill

The study was performed at a non-wood pulp and paper mill in China. Wheat straw was used as the raw material and a conventional Cl_2 bleaching sequence, which involved C (chlorine), E (alkaline extraction), and H (hypochlorite) processes was adopted as shown in Fig. 1. Xylanase is a widely used enzyme in pulp and paper mills (Shatalov and Pereira, 2007, 2009; Gangwar et al., 2014). Xylanase pretreatment can increase the brightness of the product, increase the degree of delignification of the pulp achieved, and decrease the amount of Cl_2 required by about 20%. Xylanase aided bleaching was used as substitute of conventional Cl_2 in this mill. We analyzed samples from the mill when it was using a conventional Cl_2 bleaching process and when it was using a

Fig. 1. A schematic about the processes for using conventional Cl_2 bleaching and enzyme-aided Cl_2 bleaching and the sampling points for solid samples and effluent samples.

xylanase-aided chlorine bleaching process to compare the concentrations and profiles of PCDD/Fs formed when the different bleaching processes were used.

2.2. Sample collection, pretreatment, and PCDD/F analysis

The solid samples were collected from different process stages (Fig. 1) including raw materials (R), chlorine bleaching (C), alkaline extraction (E), hypochlorite bleaching (H), paper product (P) and sludge (S) when conventional Cl_2 bleaching was used. When enzyme-aided Cl_2 bleaching process was used, the solid samples from various process stages were collected again. The effluent samples were also collected from different process stages including chlorine bleaching (C), alkaline extraction (E), and discharged wastewater (W) when it was using a conventional Cl_2 process and again when it was using an enzyme-aided Cl_2 bleaching process. Each effluent sample was 20 L in volume. The PCDD/Fs in each effluent sample were enriched by passing the sample through a glass column packed with XAD-2 resin.

The PCDD/F analysis was performed using an isotope dilution high-resolution gas chromatography/high resolution mass spectrometry method based on U.S. Environmental Protection Agency method 1613B that has been described previously (Fang et al., 2007, 2008). Briefly, each sample was air-dried, then an aliquot was spiked with a mixture containing $^{13}\text{C}_{12}$ -labeled PCDD/F internal standards, Soxhlet extracted with 250 mL 1:1 *n*-hexane/dichloromethane, then concentrated using a rotary evaporator. The extractions were then purified by successively passing through an acidic and basic silica column, a multilayer silica column (containing, from top to bottom, anhydrous sodium sulfate, 1 g silica gel, 10 g silica gel containing 44% w/w sulfuric acid, 1 g silica gel, 5 g silica gel containing 33% w/w sodium hydroxide, 1 g silica gel, 2 g silica gel containing 10% w/w AgNO_3 , and 1 g silica gel), and a basic alumina column. The cleaned extract was evaporated to about 20 μL under a stream of nitrogen. Before instrumental analysis, $^{13}\text{C}_{12}$ -labeled 1,2,3,4-tetrachlorodibenzo-*p*-dioxin and 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin injection standards were added for evaluating the recoveries of internal standards. All of the $^{13}\text{C}_{12}$ -labeled internal and performance standards and the calibration solution were purchased from Wellington Laboratories (Guelph, Canada).

The PCDD/F congener concentrations in the sample extracts were analyzed using a high-resolution gas chromatograph (Agilent 6890 GC; Agilent Technologies, Santa Clara, CA, USA) coupled to a high-resolution mass spectrometer (Autospec Ultima; Waters, Milford, MA, USA) (Fang et al., 2007, 2008). Two ions in the molecular ion cluster of each analyte were monitored. Separation was achieved using a DB-5 MS column (60 m long, 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies). The oven temperature programs were used as below: 160 $^{\circ}\text{C}$ initial for 2 min; increased at

7.5 $^{\circ}\text{C min}^{-1}$ to 220 $^{\circ}\text{C}$ and hold for 16 min; increased at 5 $^{\circ}\text{C min}^{-1}$ to 235 $^{\circ}\text{C}$ and hold for 7 min; increased at 5 $^{\circ}\text{C min}^{-1}$ to 330 $^{\circ}\text{C}$ and hold for 1 min. 1 μL was injected with in splitless mode. The mass spectrometer was operated in electron impact ionization mode (electron energy 37 eV) in selected ion monitoring mode and at a resolution >10,000. The source temperature was 270 $^{\circ}\text{C}$.

The quality control and quality assurance procedures included checking the instrument stability and relative response factors by analyzing calibration standards before samples were analyzed. For a peak in a sample to be identified as an analyte, the retention time of the peak had to be within 2 s of the retention time of the corresponding $^{13}\text{C}_{12}$ -labeled internal standard and the isotope ratio (the ratio of the areas of the peaks in the two ions monitored) for the peak had to be within 15% of the theoretical value. The recoveries of the $^{13}\text{C}_{12}$ -labeled internal standards were 67%–135%, and met the requirements of U.S. Environmental Protection Agency method 1613B. One blank sample was analyzed with each batch of samples. Our laboratory has often participated in interlaboratory PCDD/F analysis assessments. The z-scores for our laboratory in interlaboratory assessments for PCDD/F TEQs have normally been between -1 and $+1$, indicating that PCDD/Fs are determined with satisfactory accuracy in our laboratory.

3. Results and discussion

3.1. Comparison of the PCDD/F concentrations between enzyme-aided Cl_2 bleaching and conventional Cl_2 bleaching processes

Xylanase is the most widely used enzyme in pulp and paper mills (Shatalov and Pereira, 2007, 2009; Gangwar et al., 2014). Xylanase was used in the enzyme-aided Cl_2 bleaching process in the investigated mill. Concentrations and profiles of PCDD/Fs formed during enzyme-aided Cl_2 bleaching and conventional Cl_2 bleaching were compared. Analyzing the samples from enzyme-aided Cl_2 and conventional Cl_2 bleaching processes performed at the same plant made it much easier to compare the results because the same facilities were used and the mass flow of pulp was the same. The PCDD/F TEQs in the solid samples and effluents collected from the mill when conventional Cl_2 bleaching was performed are shown in Fig. 2(a). The PCDD/F TEQ in the raw materials was 0.07 pg TEQ/g. The PCDD/F TEQ in the pulp after stage C had increased to 0.40 pg TEQ/g, 5.35 times higher than in the raw materials. The PCDD/F TEQ in the solid pulp after stage E was 0.15 pg TEQ/g, 62.1% lower than after stage C. The PCDD/F TEQ in the pulp after stage H had increased to 0.53 pg TEQ/g, 3.53 times higher than after stage E. The PCDD/F TEQ after stage H was even higher than after stage C. After being bleached, the pulp was fed into a paper briquetting machine to make paper, and the PCDD/F TEQ in the paper product was 1.02 pg TEQ/g. The PCDD/F TEQs in the effluents after stages C and E were 1.95 and 2.57 pg TEQ/L, respectively. The PCDD/F TEQ in

Fig. 2. PCDD/F TEQs in the (a) solid samples and (b) effluent samples collected when the Cl_2 and enzyme-aided bleaching processes were adopted.

the sludge produced during treatment of the mixed effluent was 2.44 pg TEQ/g. The PCDD/F TEQ in the wastewater was dramatically decreased during the wastewater treatment process, to 0.80 pg TEQ/L in the discharged wastewater.

Enzyme-aided bleaching is an expected promising alternative to conventional Cl_2 bleaching to decrease the use of Cl_2 during pulp bleaching. Using enzyme-aided bleaching can decrease the amounts of Cl_2 required while increasing the brightness and degree of delignification of the product (Torres et al., 2000; Shatalov and Pereira, 2007; Gangwar et al., 2014). It has also been found that enzymes can decrease the amounts of absorbable organic halides formed during bleaching (Jokela et al., 1993; Gangwar et al., 2014), and therefore that using enzymes can be expected to decrease the amounts of PCDD/Fs formed. However, the PCDD/F TEQs in the pulp after the C stage, the pulp after the E stage, the product, and the sludge when the enzyme-aided bleaching process was used were

2.73, 0.49, 0.99, and 5.40 pg TEQ/g, respectively, as shown in Fig. 2(b). These PCDD/F concentrations were unexpectedly higher than the concentrations when conventional Cl_2 bleaching was used even though about 20% less Cl_2 were required when the enzyme-aided process was performed. The PCDD/F TEQ was almost six times higher in the pulp after the enzyme-aided C stage than in the pulp after the conventional Cl_2 bleaching C stage. The PCDD/F TEQ was also clearly higher in the pulp after the enzyme-aided E stage than in the pulp after the Cl_2 bleaching E stage.

The PCDD/F TEQs in the effluent after the enzyme-aided C stage, the effluent after the enzyme-aided E stage, and the discharged wastewater were 0.68, 1.43, and 0.61 pg TEQ/L, respectively, as shown in Fig. 2(b). The PCDD/F TEQs in the effluent after the C stage, the effluent after the E stage, and the discharged wastewater were about 65%, 44%, and 24% lower, respectively, when enzyme-aided bleaching was performed than when conventional Cl_2 bleaching

Fig. 3. PCDD/F congener profiles in the solid samples and effluent samples collected when the (a) Cl_2 and (b) enzyme-aided Cl_2 bleaching processes were adopted. (CDD = chlorodibenzo-*p*-dioxin, CDF = chlorodibenzofuran, O = octa, Hp = hepta, Hx = hexa, Pe = penta, T = tetra).

was performed. The increase in the solid sample PCDD/F TEQs and decrease in the effluent PCDD/F TEQs caused by using the enzyme-aided process suggested that most of the PCDD/Fs formed were found in the solid phases.

3.2. Comparison of PCDD/F congener profiles between enzyme-aided Cl_2 bleaching and conventional Cl_2 bleaching processes

The dominant congeners in the raw materials used in the mill were OCDD and 2,3,7,8-TCDF, as shown in Fig. 3(a). OCDD contributed 49% of the total PCDD/F concentration, more than any other congener. The PCDD/F profiles in the pulp after stages C, E, and H and in the product when Cl_2 bleaching was performed were all dominated by 2,3,7,8-TCDF and OCDD. OCDD, 2,3,7,8-TCDF, and 1,2,3,4,6,7,8-HpCDD dominated the PCDD/F profiles in the effluents produced after stages C and E, and 2,3,7,8-TCDD contributed little. OCDD, OCDF, and 1,2,3,4,6,7,8-HpCDD were the dominant congeners in the sludge, but 1,2,3,4,7,8-HxCDF, OCDF, and OCDD were the dominant congeners in the discharged wastewater, indicating that the wastewater treatment process may have altered the PCDD/F profile.

The PCDD/F congener profiles in the samples when the enzyme-aided chlorine bleaching process was shown in Fig. 3(b). It can be seen that the dominant congeners in the pulp after the enzyme-aided C stage were OCDD and 1,2,3,4,6,7,8-HpCDD. When the conventional Cl_2 bleaching process was used in mill, the dominant PCDD/F congeners after stage C were 2,3,7,8-TCDF and OCDD. The congener profile in the pulp after the enzyme-aided bleaching stage C process was quite different from the profile after the conventional Cl_2 bleaching stage C, indicating that the presence of the enzyme affected the PCDD/F formation mechanisms. It has previously been found that the less chlorinated PCDD/F congeners may be formed through the chlorination of DBD and DBF in pulp and the chlorination of nonextractable precursors (Dimmel et al., 1993). We found that enzyme-aided chlorine bleaching caused more OCDD to be formed during stages C and E (causing OCDD to contribute a much larger proportion of the total PCDD/F concentrations in the pulp and effluents from stages C and E) than when conventional Cl_2 bleaching was adopted.

Unlike during the enzyme-aided stage C, 2,3,7,8-TCDF was formed, to some extent, during the enzyme-aided stage E. OCDD, 1,2,3,4,6,7,8-HpCDD, and 2,3,7,8-TCDF dominated the PCDD/F profiles in the product. The dominant PCDD/F congeners at the corresponding stages when conventional Cl_2 bleaching was performed were OCDD and 2,3,7,8-TCDF. The PCDD/F profiles in both the sludge samples produced during effluent treatment and the discharged wastewater were dominated by OCDD, OCDF and 1,2,3,4,6,7,8-HpCDD which together contributed more than 80% of the total PCDD/F concentrations. Similar PCDD/F congener profiles in the sludge and discharged wastewater when conventional Cl_2 bleaching was performed with that using enzyme-aided bleaching suggested that similar PCDD/F formation mechanisms occurred during wastewater treatment whichever bleaching process was adopted.

Comparing the PCDD/F profiles in the samples collected when enzyme-aided bleaching and conventional Cl_2 bleaching were adopted led us to suggest that the increase in the amount of OCDD formed as a result of the presence of the enzyme directly caused the PCDD/F TEQs to be higher in the samples collected when enzyme-aided bleaching was adopted than when conventional Cl_2 bleaching was adopted. The reason for this is speculated below. It has been found that xylanase can attack lignin–carbohydrate complexes and release lignin-bound compounds (Preiss et al., 1987; Ruttimann-Johnson and Lamar, 1996; Shatalov and Pereira, 2007). Therefore, it was suggested that adding xylanase could cause large

amounts of organic molecules to be released from lignin-bound compounds in non-wood pulp, meaning that much more organic molecules (such as phenols) will undergo a condensation reaction when xylanase is present during bleaching than when no xylanase is present. Adding xylanase to the bleaching process will therefore lead to much more formation of OCDD and increase the total PCDD/F TEQ during enzyme-aided bleaching relative to conventional Cl_2 bleaching in non-wood pulp and paper mills. Further study associated with the potential effect of xylanase on the release of organic molecules bound to lignin and their subsequent condensations in the non-wood pulp is needed.

4. Conclusions

Pulp and paper mills are important sources of PCDD/Fs (Huang and Buekens, 1995; Fiedler, 2007). The global annual production of non-wood pulp was about 15,756 thousand tonnes (Qi and Ning, 2013). Non-wood raw materials are intensively used in pulp and paper mills in developing countries than are used in developed countries (wood is the main raw material in developed countries). The different raw materials used in developing countries could mean different PCDD/F formation mechanisms occur. Widely recognized advanced techniques that are used in wood pulp and paper mills in developed countries might therefore not be suitable for the sustainable development of non-wood pulp and paper mills that still intensively practiced in developing countries.

This study firstly reported that enzyme-aided bleaching, which is widely expected to be a promising substitute for conventional Cl_2 bleaching in wood pulp and paper mills, unexpectedly promotes increased PCDD/F TEQs in non-wood pulp and paper mill. The results strongly suggested urgency and necessity of further assessment about the effectiveness of enzyme-aided bleaching, which recognized as the BAT/BEP for wood pulp and paper mills, in PCDD/F reductions for non-wood pulp and paper mills.

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