



# Mechanochemical destruction of pentachloronitrobenzene with reactive iron powder

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## ABSTRACT

Pentachloronitrobenzene (PCNB) has been identified as a potential persistent organic pollutant, and received concerns from many countries for regulation due to its impurities such as dioxins and furans. Considering the need for its disposal, the mechanochemical destruction approach was investigated for the applicability. PCNB was co-ground with reactive iron powder in a high energy planetary ball mill at room temperature. PCNB was found to be destructed finally, and the Dioxins and coplanar-PCBs concentrations in PCNB had been degraded from 1146 ng-TEQ/kg to 0.04 ng-TEQ/kg finally. Pentachloroaniline (PCA), 2,3,5,6-tetrachloroaniline (2,3,5,6-TeCBA) and 3,4,5,6-tetrachloroaniline (3,4,5,6-TeCBA) were detected as intermediates during the ball milling process and were destructed completely after 8 h milling. The amount of water soluble chlorides ( $\text{Cl}^-$ ) reached 95.8% of the theoretical amount of chlorine in original PCNB sample after 12 h ball milling. The solvent acetone might play a role as the main hydrogen donor, which gives rise to the amination reaction of nitro-group. Metastable structures with high molecular were proposed to be formed during the ball milling process as intermediates. Carbonization was confirmed by Raman spectrum as the final degradation product of PCNB.

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## 1. Introduction

Pentachloronitrobenzene (PCNB,  $\text{C}_6\text{Cl}_5\text{NO}_2$ , CAS No. 82-68-2), also known as quintozone or terraclor, was first developed by Bayer AG (Germany) in 1930 and primarily used as a fungicide for seed and soil treatments to control the damping-off diseases of seedlings [1]. Nowadays, PCNB is still used in many countries including China. According to the Registered Pesticide Information System maintained by the Ministry of Agriculture [2], currently there are 2 raw pesticides and 18 formulations of PCNB registered in Chinese Mainland. Shanxi Sanli Chemical Co., Ltd. and Shandong Dezhou Tianbang Agrochemical Co., Ltd. are the producers of registered PCNB raw pesticide products, with the annual production of PCNB in China was reported to be about 1000 tons [3–5].

The Pest Management Regulatory Agency (PMRA) in Canada recently completed a review of quintozone, and will prohibit the use of PCNB on recreational turf since 31 December 2010 [6]. Also the Environmental Risk Management Authority of New Zealand has decided there are grounds to reassess the use of the fungicide quintozone [7]. The PCDD/Fs have been identified as the impurities in the commercial PCNB powder, while the highest concentration of PCDD/Fs was 5.6 ng-TEQ/g active ingredient [8]. These facts imply

the possibility that PCNB might be regulated as POPs and included in the Stockholm Convention in the future. Considering the mandatory obligations of the international treaty, it is necessary to seek for potential sound disposal technology.

Mechanochemical destruction (MCD) has been considered as a promising technology to destroy solid waste containing persistent organic pollutants. Co-grinding POPs with calcium oxide (CaO) or other metal oxide/hydride, typically in planetary ball mill, has been illustrated to successfully destroy various halogenated organic compounds like POPs, including chlorinated benzenes, poly(vinyl chloride) (PVC), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), PCBs and pentachlorophenol [9–13]. In comparison, the DMCR (dehalogenation by mechanochemical reaction) method with the use of the base metal and hydrogen donors mainly aimed at efficient detoxification by stripping off the “organic halogen” entirely, without the complete destruction of the whole molecule [14]. As the solid-state reaction without organic solvents eliminates the need for solvent regeneration, it makes the corresponding processes friendlier from an environmental perspective [15]. The mechanisms of such MCD reaction when using CaO have been systematically elucidated for some contaminants like DDT and PCBs, which basically consist of dechlorination, benzyl ring leverage, and polymerization/carbonization; with the inorganic chloride and carbon as the final products [16–18]. In recent years, field applications of zero-valent-iron had been conducted for environmental remediation, for example, nano-, micro-, and millimetric

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ZVI [20–22]. Some cases have shown that the association of ZVI and other technology such as microbial dechlorination and source zone containment. But that mechanochemical treatment is an *ex situ* technique for which reactive iron is tested as dechlorination reagents without solvents for the first time. However, the mechanism of contaminants destruction by the MCD process using zero-valent-metal in a solvent-free system has not been reported yet. In the present study, the ball milling of PCNB with reactive iron powder was investigated in terms of efficiency as well as the degradation pathway.

## 2. Materials and methods

### 2.1. Materials

PCNB (95.8% in purity) was purchased from Sanli Chemical Inc. (ShanXi province, china). Reactive iron powder (98% in purity, 10–100  $\mu\text{m}$  grade, Beijing Modern Oriental Fine Chemicals Corporation, China) was stored in a dryer prior to use. Acetone (HPLC grade) was obtained from J.T. Baker Inc. (USA). Hexadeuteroacetone (acetone- $d_6$ , 99.9% in purity) was purchased from J&K Scientific Ltd. (Beijing, China). Nano-iron powder (99.9% in purity, 30 nm) was purchased from Beijing Topvender Co., Ltd.

### 2.2. Reaction procedures

A planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China) was used for the experiments. A mixture of iron powder (4.5 g) and PCNB (0.3 g) was put into a stainless steel pot at room temperature with nitrogen protection, which was sealed subsequently. The temperature of the body of pots kept stable between 34.5 and 36.2 °C. The room temperature is 28 °C. The planetary ball mill was operated at 550 rpm and the rotation direction of supporting disk changed automatically every 30 min. Two sizes of balls are used in each trial: big ball ( $\Phi$  9.60 mm); small ball ( $\Phi$  5.60 mm). The charge ratio is set as 36:1, and the total weight of balls (24 big balls and 100 small balls together) is about 180 g. The nano-iron has been added into the PCNB solution of acetone under anaerobic atmosphere. The nano-iron was not used for grinding, but to compare the reducing ability of the  $\text{NO}_2$  group with the ground iron powder (micro-meter-grade).

### 2.3. Analytical procedures

Analysis for PCDD/Fs and dl-PCB (dioxin-like PCBs: coplanar PCB mixture, 12 PCB congeners) in PCNB powder: The sample, pre-dissolved with small amount of hexane, was extracted by liquid–liquid extraction partitioning into dimethyl sulphoxide (DMSO). DMSO was collected and the solution was washed with hexane finally with DMSO left. The extraction was then diluted with MilliQ water and re-extracted into hexane. The hexane solution was then washed with potassium hydroxide and twice with MilliQ water before dehydrated by sodium sulfate. The extracts

first underwent an acid pre-clean using pure concentrated sulfuric acid. Then they were purified in a multi silica column containing acid silica, basic silica, silver nitrate silica, neutral silica and sodium sulfate. A column with activated carbon scattered silica gel was performed to separate PCDD/F and dl-PCB. Samples were analyzed by HRGC/HRMS (JMS 800D, Jeol, Japan) using the SIM mode with a resolution of 10,000. Recovery of all the recovery standards, injection standards, cleanup standards met Chinese national standard method (HJ 77.2-2008). The mean recovery percentages of PCDDs, PCDFs, dl-PCBs and PCNB are 66%, 65%, 67% and 99%, respectively.

For PCNB and HCB analysis: One portion (0.05 g) of each milled mixture was extracted with acetone for 15 min in an ultrasonic extractor. The extract was then centrifugalized at 3000 rpm for 15 min. The PCNB and possible degradation products were determined by a GC/MS (QP 2010 Plus, Shimadzu, Kyoto, Japan), equipped with a DB-5MS capillary column (0.25 mm i.d., 15 m length, 0.10  $\mu\text{m}$  film thickness, Agilent). Helium (99.999% in purity) was used as carrier gas at a constant linear velocity of 72.9  $\text{cm s}^{-1}$ . GC oven temperature was programmed from 60 °C (held for 2 min) to 220 °C (held for 1 min) at 25 °C  $\text{min}^{-1}$ , and to a final temperature of 290 °C (held for 5 min) at 20 °C  $\text{min}^{-1}$ . 1  $\mu\text{L}$  of the sample was auto-injected in the high-pressure splitless mode (high pressure 289 kPa for 2 min) when the injector temperature was set at 280 °C. The mass spectrometer was operated in EI mode and the pressure in the ion source was  $2.8 \times 10^{-4}$  Torr (1 Torr = 133.33 Pa). The temperature of ion source and interface were set at 250 and 280 °C, respectively. Mass acquisition was performed in full scan mode ( $m/z$  50–700).

A second portion (0.05 g) was used to analyse the chloride content from the dechlorination of PCNB. The sample was agitated in deionized water at 80 °C for 20 min with a magnetic stirrer. The resulting suspension was subjected to ultrasonic treatment for 20 min, then filtered through a 0.45  $\mu\text{m}$  fiber filter, and the residue was extracted two more times in the same manner. The filtrates were analyzed for chloride ions by ion chromatography (DX-100, DIONEX Co., USA) equipped with an IonPac AS4A-SC anion exchange column. The detection limits for nitrite and nitrate are 0.096  $\mu\text{g/ml}$  and 0.143  $\mu\text{g/ml}$ , respectively.

The ground samples taken at specific time from the ball milling experiment were characterized using multiple approaches. Crystalline products were identified by X-ray powder diffraction (XRD, Rigaku D/max-r B, Japan) at the following settings: Cu  $K\alpha$  radiation, 40 keV accelerating voltage, 80 mA current, 10–70°  $2\theta$  scanning range, 0.02° step and 6°  $\text{min}^{-1}$  scan speed. Raman spectra were recorded at room temperature using a Microscopic Confocal Raman Spectrometer (Renishaw RM 2000, UK) with Ar-laser beam at the 514.5 nm line. Infrared spectra were measured using a Fourier transform infrared (FTIR) spectrometer (NICOLET 6700, UK) with the KBr disk method from 400 to 4000  $\text{cm}^{-1}$ . The surface morphologies of the ground samples with different reaction time were observed using an environmental scanning electron microscope (ESEM, FEI Quanta 200 FEG). XPS analysis of the ground samples was carried out on an AEM PHI 5300X spectrometer with a

**Table 1**  
Destruction effects for the mechanochemical treatment.

	Before treatment	After 3 h treatment	After 8 h treatment
Major ingredient			
PCNB (kg/kg-dry)	0.96	0.01	0
Impurities (ng-TEQ/kg-dry)			
PCDDs	5.7	49	0
PCDFs	190	560	0
Total PCDD/Fs	195.7	609	0
DL-PCBs	950	58	0.04
Total (PCDD/Fs + DL-PCBs)	1145.7	620	0.04
HCB (kg/kg-dry)	0.04	0.02	0

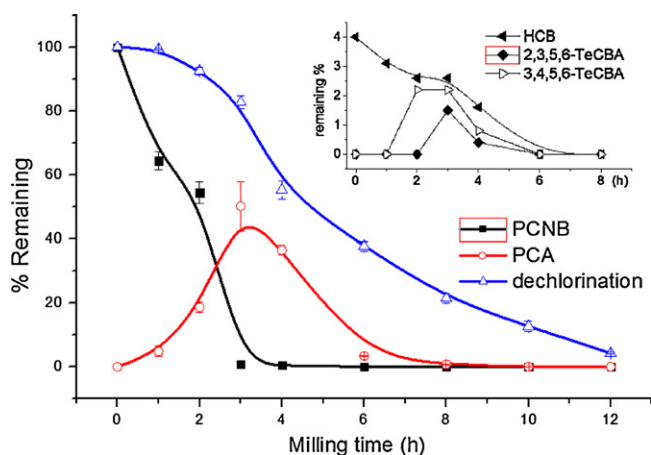


Fig. 1. Changes of the PCNB, its intermediates and dechlorination effect.

monochromatized Al K $\alpha$  X-ray source. The X-ray source was run at a reduced power of 150 W, and the pressure in the analysis chamber was maintained at less than  $10^{-8}$  Torr during each measurement. All binding energies were referenced to the neutral C 1s peak at 284.6 eV to compensate for the surface charging effects. The software package XPS peak 4.1 was used to fit the XPS spectra peaks, and the full width at half-maximum was maintained constant for all components in a particular spectrum.

### 3. Results and discussion

#### 3.1. Destruction effects

Before experiments, we have identified the PCNB purity and its impurities. The PCNB concentration is 0.96 kg/kg-dry (purity 96%). The impurities in PCNB were identified as 0.04 kg/kg-dry hexachlorobenzene (4%), 5.7 ng-TEQ/kg-dry PCDDs, 190 ng-TEQ/kg-dry PCDFs and 1146 ng-TEQ/kg-dry PCDD/Fs + DL-PCBs. Table 1 shows that the co-treatment of PCNB, HCB and dioxins could be conducted by addition of reactive iron powder and MCD method.

The MCD treatment of PCNB and iron powder was performed for 8 h, during which time the amount of chloride ions, remaining PCNB and its intermediates were measured; the percentage of non-ionic chloride was calculated from the measured amount of chloride ions and the amount of chlorine contained in the PCNB added. After 4 h

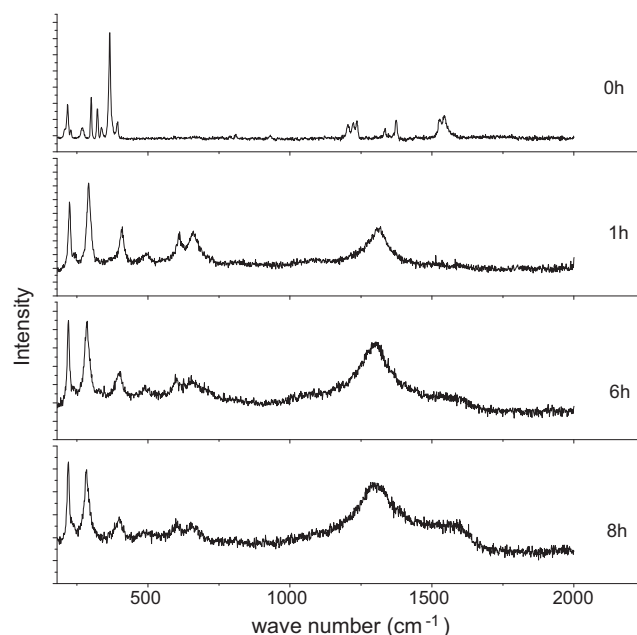


Fig. 3. Raman spectra of ground samples.

ball milling, the PCNB concentration was below the detection limit (Fig. 1). Actually no peaks could be found in the GC/MS spectrum for samples after 8 h ball milling, which implied a complete destruction of PCNB and other organic intermediates.

#### 3.2. Intermediates and products

Several intermediates were found by peak identification using US NIST(05) database searching, including: pentachloroaniline (PCA), 2,3,5,6-tetrachloroaniline (2,3,5,6-TeCBA) and 3,4,5,6-tetrachloroaniline (3,4,5,6-TeCBA). PCA was found to be the major intermediate, whose content reached the maximum at the reaction time of 3 h, when the PCNB nearly totally disappeared. The contents of 2,3,5,6-TeCBA and 3,4,5,6-TeCBA were very limited, which only accounted for 1–2% of the initial PCNB applied. Neither nitrate ( $\text{NO}_3^-$ ) nor nitrite ( $\text{NO}_2^-$ ) was detected by ion chromatography. The remained chlorines decreased gradually, while the detected ionic chloride ( $\text{Cl}^-$ ) chloride accounts for 95.8% of chlorine in the original PCNB applied at the reaction time of 12 h. However, the

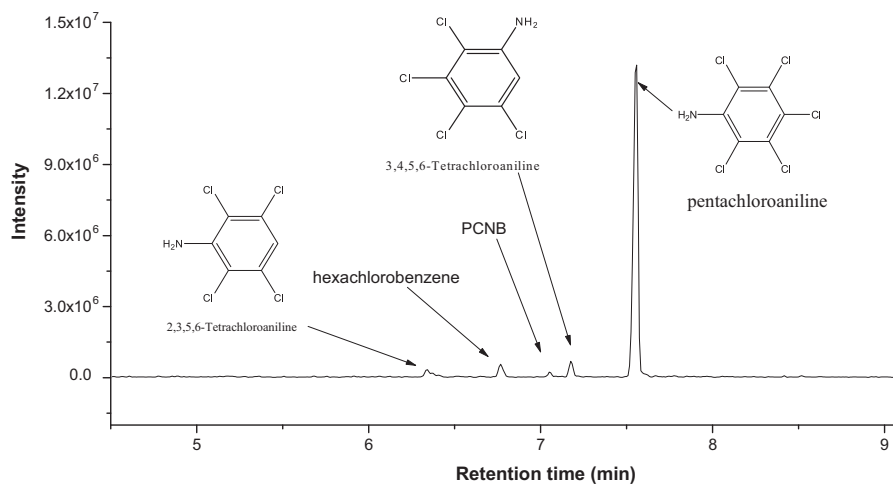
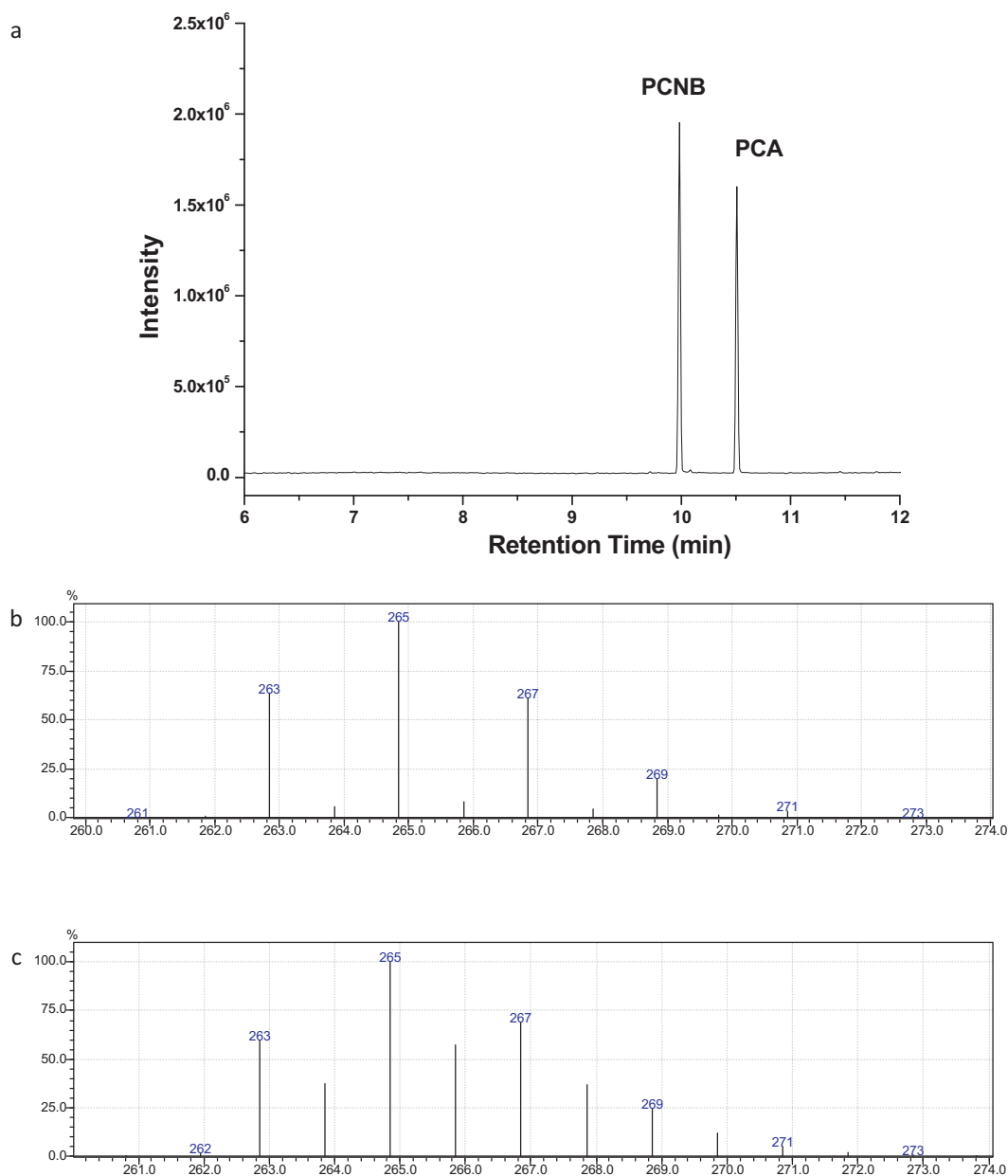


Fig. 2. GC/MS chromatogram of the degradation products obtained by 3 h MCD treatment.



**Fig. 4.** GC/MS spectra for the comparison study. (a) The chromatogram of 2 h ground sample dissolved in acetone and hexadeuteroacetone- $d_6$ , respectively. (b) PCA mass spectrum of 2 h ground sample dissolved in acetone. (c) PCA mass spectrum of 2 h ground sample dissolved in hexadeuteroacetone- $d_6$ .

$Cl^-$  detected only accounts for 76.9% of the chlorine in original PCNB at the reaction time of 8 h, when no peaks found in the GC/MS spectrum. This means there is a time interval between organics destruction and dechlorination, which is similar with the phenomenon in DDT destruction with calcium oxide [16]. There might be some kind of high molecular compounds containing chlorine existing in the ground sample between 8 h and 12 h, with the molecular weight beyond the detection range of GC/MS equipment adopted in this study (Fig. 2).

The color of initial mixture of PCNB and reactive iron powder was yellow, which was changed to be black after 6 h or 8 h ball milling. The Raman spectra from the ground samples was shown in Fig. 3. With the ongoing ball milling, firstly a band with the peak at  $1312\text{ cm}^{-1}$  then another band with peak at  $1582\text{ cm}^{-1}$  appeared, with the intensity strengthened gradually. According to Tuinstra and Koenig, single crystals of graphite show one single line at  $1575\text{ cm}^{-1}$  on the Raman spectra; while other graphite

materials like stress-annealed pyrolytic graphite, commercial graphite, activated charcoal, lampblack, and vitreous carbon show another line at  $1355\text{ cm}^{-1}$  [19]. These two bands were actually identical with so called "D-band" ( $1330\text{--}1380\text{ cm}^{-1}$ ) and "G-band" ( $1540\text{--}1580\text{ cm}^{-1}$ ). It is well known that the sharp G-peak in the spectra is characteristic for scattering by the optic phonons of graphite ( $sp^2$ -bonded carbon atoms). The D-peak in the Raman spectra is usually diffused and is characteristic for scattering from disordered carbon ( $sp^2$ -bonded carbon atoms) [23,24]. The appearance order of G- and D-peaks on the Raman spectra revealed that firstly amorphous carbon was formed during the ball milling process, some of which was then converted into graphite. This phenomenon was identical with those in other mechanochemical destruction studies using calcium oxide (CaO) instead of iron [25,26]. The destruction portion of PCNB in ball milling without reactive iron powder after 8 h is 9.2%, and the amorphous carbon and graphite did not appear.

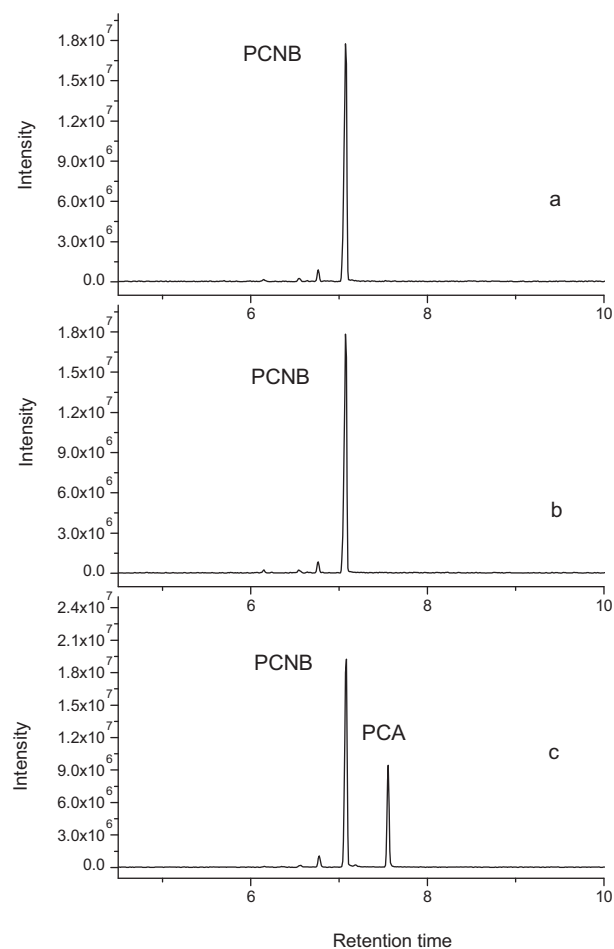
### 3.3. Hydrogen source

No hydrogen atom is contained in the molecule of PCNB, nor has any hydrogen containing reagent been employed in the ball milling pot. The formation of  $-NH_2$  indicates the involvement of hydrogen donors in the process. One possibility would be that  $-NH_2$  was formed not in the pot but outside the pot, when the samples were contacted with acetone as the extraction reagent. For confirmation and clarification purpose, a comparison study was conducted. Aliquots of powder samples after 2 h ball milling were dissolved in the acetone and the acetone- $d_6$ , respectively, and then injected for GC/MS analysis. As shown in Fig. 4a, the retention times of both PCNB and PCA in two solutions are identical. However the mass spectra corresponding to PCA were different. The main bars in the standard mass spectrum of PCNB (e.g.  $m/z$  263, 265, 267, 269) were found in both Fig. 4b and c, while some bars intensified significantly in Fig. 4c, e.g.  $m/z$  264, 266, 268, 270. Such differences should be caused by a deuterium atom contained in the  $-NH_2$  group when using acetone- $d_6$ . Therefore the possibility proposed above was confirmed, i.e. the ground samples did react with the acetone during the extraction process, resulting the hydrogen atoms in acetone transfer into the  $-NH_2$  of polychlorinated aniline. Meanwhile, the moisture adsorbed on the surface of solid materials might be the hydrogen donor. Such reaction occurring proceeding after the field of mechanical stress, therefore is a sort of “posteffect”. Unlike the reactions occurring in the field of mechanical stress which would most likely involve mechanically activated species, the role of mechanical action in this “posteffect” reduces mostly to the generation of radicals, while the subsequent free-radical process obeys the rules inherent in them [15]. In this study, the electron spin resonance (ESR) could not be conducted to detect radicals, due to the magnetism of iron.

### 3.4. Fate of nitro-group ( $-NO_2$ )

Neither nitrate ( $NO_3^-$ ) nor nitrite ( $NO_2^-$ ) was detected in the ground samples by ion chromatography. It is necessary to study the fate of  $-NO_2$  during the grinding. Klupinski et al. proposed that nitroaromatic compounds in aqueous media may act as Lewis bases at vacant lattice sites of iron oxides where they could then be reduced by proximate Fe(II), present either as a sorbed complex or as part of a distinct nanoscale mixed valent mineral phase [27]. In the present study, one proposed reaction is the electron transfer from ground iron powder which leads to the oxygen adsorption, while the nitro-group ( $-NO_2$ ) becomes a metastable structure with negative electricity. The ground sample after 3 h ball milling was kept still in air for 3 months, and then was dissolved in the acetone for GC/MS testing. PCA was found at the GC/MS spectrum, which illustrates the good stability of metastable structure mentioned above.

In addition, supplementary experiments had been designed to testify changes of the ( $-NO_2$ ) group in MCD treatment. Fig. 5 shows a comparison of GC/MS spectra from the solutions of PCNB in acetone (100 ppm) added with different iron materials, including original reactive iron powders, reactive iron powders after 6 h ball milling treatment (without PCNB), and nano-iron powder. Fig. 5a shows the experiment in which original iron powders (0.05 g, 10–100  $\mu$ m, see Supporting material) were put into PCNB solution of acetone (100 ppm), the PCNB has no change. Fig. 5b shows the experiment that the 8 h ground iron powders (only iron powder, no PCNB) were put into PCNB solution of acetone (100 ppm), and PCNB has no change either! This is an effectively evidence that the mechanochemical destruction process involves the reaction of nitro-group. In order to compare with the reactivity of nano-iron powders, the commercial nano-iron powder (30 nm) was used to



**Fig. 5.** Reactions of PCNB solution in acetone and iron powders. (a) 100 ppm PCNB solution with original iron powders. (b) 100 ppm PCNB solution with 6 h ground iron powders (charge ratio is 36:1). (c) 100 ppm PCNB solution with 30 nm iron powder.

see if amination reaction of nitro-group will take place (Fig. 5c). The nano-iron powders were put into PCNB solution of acetone under anaerobic atmosphere. As shown in Fig. 5c, part of PCNB has been reduced to PCA. When comparing Fig. 5b with Fig. 5c, it can be deduced that 8 h milling is not sufficient to change the iron powders to nanostructure iron, which will be verified by SEM picture. The SEM images obtained from the powders (PCNB and iron) experiencing different grinding time were as shown in Fig. 6. The particle size of powders decreased along the grinding process. After 8 h grinding, lots of submicron size hollow spheres were observed, with the size of these spheres ranging from 1  $\mu$ m to 20  $\mu$ m. Such sizes were much larger than that of nano-iron; therefore the degradation should not be attributed to the nano-iron particles generated during the ball milling process. We also have done the XPS analyses for the N 1s kept stable between 1.15 and 1.95% on the surface of the ground sample and original sample. We proposed that N element is still in the final solids, but the ( $-NO_2$ ) group has been destroyed.

### 3.5. Degradation pathway

Based on the results from two comparison experiments above, the mechanochemical degradation of PCNB in solid phase in the pot should be the main mechanism, while the reaction between the powder sample and the acetone as the extraction reagent outside the pot was the minor mechanism. The detection results of

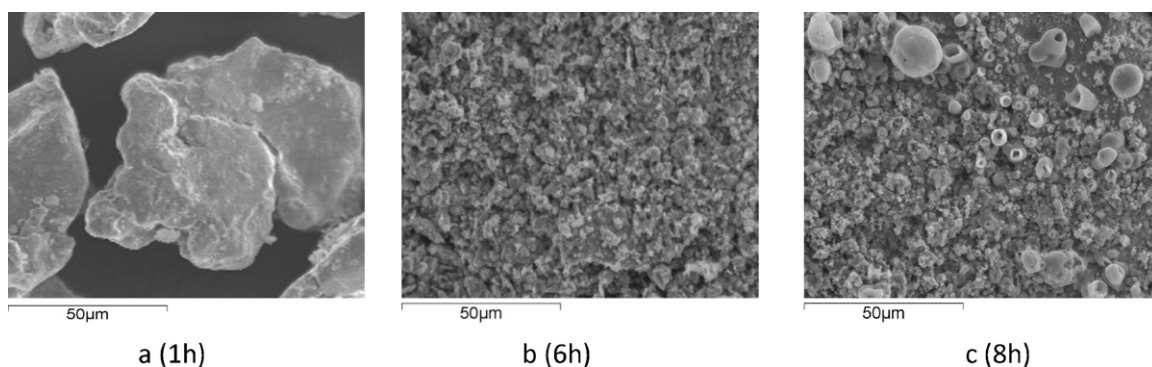


Fig. 6. SEM of the ground samples.

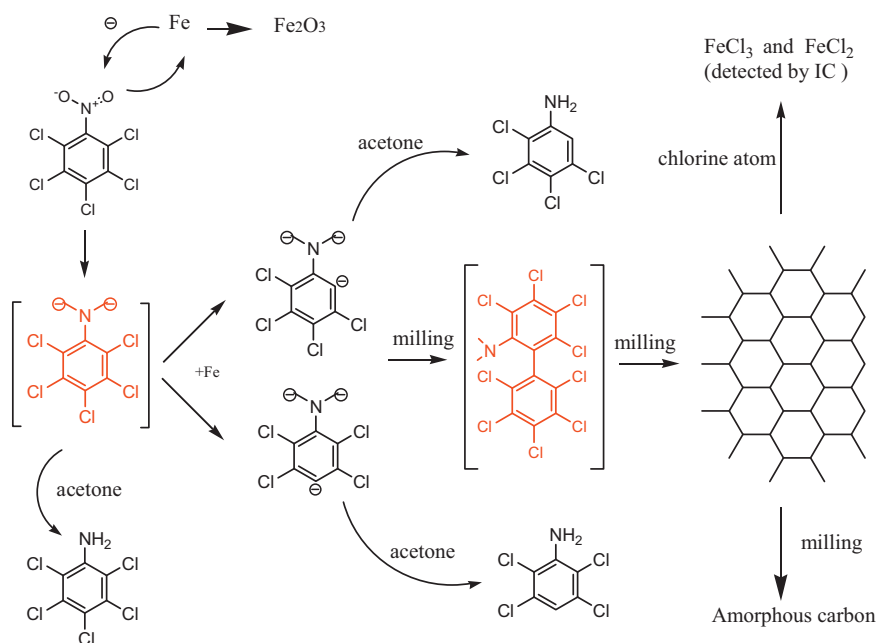


Fig. 7. Proposed pathways for degradation of PCNB with iron powder by MCD treatment.

organic intermediates and products described above illustrated that the degradation pathway of PCNB under the ball milling condition in this study should be: (1) the nitro group ( $-\text{NO}_2$ ) was activated by ball milling in the pot and the amino group ( $-\text{NH}_2$ ) was detected in the presence of hydrogen donors such as acetone outside the pot; (2) the chlorine atoms were removed from the benzyl ring; (3) carbon was formed via polymerization. Other researchers have testified the mechanism that dechlorination/polymerization pathway exist if amorphous carbon and graphite were produced. This pathway was induced by electron transfer. This was followed by the dissociation of a chloride ion, which formed a radical. These radicals could then in turn form high-molecular-weight compounds through polymerization, leading to some non-extractable compounds [28,29]. Their conclusions could support our mechanism of Fe and PCNB reaction for the degradation pathway.

On the basis of the above results and established theories in previous studies, a possible pathway was proposed, as shown in Fig. 7. The meaning of results is that although the amination of nitro-group will reduce the toxicity of PCNB in ball milling process, it does not mean the safe MCD disposal of chlorinated organic compounds. The signal of the most safe treatment measure for mechanochemical destruction is the final carbonization of organics. So in MCD

application, the moment when organic compound peaks no longer appeared in GC/MS spectrum of the ground sample is the terminal time of reaction.

For the future work, the reactivity measurement of iron powder and scrap iron might be interesting. Unlike the approach used for the aqueous phase [30–32], the methodology applicable in solid phase should be established.

#### 4. Conclusions

The MCD method could destruct the PCNB powder with reactive iron powder successfully, and the impurities such as dioxins and HCB could also be destructed simultaneously. The toxic equivalent quantity of the PCNB powder has been degraded from 1146 ng-TEQ/kg-dry to 0.04 ng-TEQ/kg-dry.

Pentachloroaniline (PCA), 2,3,5,6-tetrachloroaniline (2,3,5,6-TeCBA) and 3,4,5,6-tetrachloroaniline (3,4,5,6-TeCBA) were detected as intermediates during the ball milling process and were destructed completely after 8 h milling.

Graphite and amorphous carbon were confirmed by Raman spectrum as the final degradation product of PCNB with the mechanism of carbonization.

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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.jhazmat.2011.10.045.

## References

- [1] D.O. Tas, S.G. Pavlostathis, Effect of nitrate reduction on the microbial reductive transformation of pentachloronitrobenzene, *Environ. Sci. Technol.* 42 (2008) 3234–3240.
- [2] The Institute for the Control of Agrochemicals (ICAMA) Comprehensive Inquiry System of China Pesticide Information Network (in English). Available at: <http://www.chinapesticide.gov.cn/en/index.html>.
- [3] Z.Y. Wang. To cancel the tax drawback policy for glyphosate to promote the integration of production. *AgriGoodsHerald*. July 30, 2010 (in Chinese). Available at: [http://www.nzdb.com.cn/html/xwrd/2010-6/30/11\\_7\\_53\\_C7B8D.html](http://www.nzdb.com.cn/html/xwrd/2010-6/30/11_7_53_C7B8D.html).
- [4] T.N. Brown, F. Wania, Screening chemicals for the potential to be persistent organic pollutants: a case study of arctic contaminants, *Environ. Sci. Technol.* 42 (2008) 5202–5209.
- [5] USEPA Reregistration Eligibility Decision for Pentachloronitrobenzene, 2006. Available at: [http://www.epa.gov/oppsrrd1/REDs/pcnb\\_red.pdf](http://www.epa.gov/oppsrrd1/REDs/pcnb_red.pdf).
- [6] Health Canada Pest Management Regulatory Agency Re-evaluation decision: quitozene, 2010. Available at: [http://dsp-psd.pwgsc.gc.ca/collections/collection\\_2010/arla-pmra/H113-28-2010-6-eng.pdf](http://dsp-psd.pwgsc.gc.ca/collections/collection_2010/arla-pmra/H113-28-2010-6-eng.pdf).
- [7] Environmental risk management authority decision on grounds for reassessment of a substance: quitozene, 2010. Available at: <http://www.ermanz.govt.nz/find/WebResultsDetails.aspx?ID=1678>.
- [8] Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) impurities in pesticides: a neglected source of contemporary relevance, *Environ. Sci. Technol.* 44 (2010) 5409–5415.
- [9] Y. Nomura, S. Nakai, M. Hosomi, Elucidation of degradation mechanism of dioxins during mechanochemical treatment, *Environ. Sci. Technol.* 39 (2005) 3799–3804.
- [10] H. Mio, S. Saeki, J. Kano, F. Saito, Estimation of mechanochemical dechlorination rate of poly (vinyl chloride), *Environ. Sci. Technol.* 36 (2002) 1344–1348.
- [11] T. Inoue, M. Miyazaki, M. Kamitani, J. Kano, F. Saito, Dechlorination of polyvinyl chloride by its grinding with KOH and NaOH, *Adv. Powder Technol.* 16 (2005) 27–34.
- [12] Y. Tanaka, Q.W. Zhang, F. Saito, Decomposition of monochlorobiphenyl by grinding with rare earth oxides, *J. Chem. Eng. Jpn.* 39 (2006) 469–474.
- [13] J.H. Yan, Z. Peng, S.Y. Lu, X.D. Li, M.J. Ni, K.F. Cen, H.F. Dai, Degradation of PCDD/Fs by mechanochemical treatment of fly ash from medical waste incineration, *J. Hazard. Mater.* 147 (2007) 652–657.
- [14] V. Birke, J. Mattik, D. Runne, Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants, *J. Mater. Sci.* 39 (2004) 5111–5116.
- [15] Z.V. Todres, *Organic Mechanochemistry and Its Practical Applications*, CRC Taylor & Francis Group, LLC, 2006, p. 9.
- [16] S.A. Rowlands, A.K. Hall, P.G. McCormick, R. Street, R.J. Hart, G.F. Ebell, P. Donecker, Destruction of toxic materials, *Nature* 367 (1994) 223.
- [17] A.K. Hall, J.M. Harrowfield, R.J. Hart, P.G. McCormick, Mechanochemical reaction of DDT with calcium oxide, *Environ. Sci. Technol.* 30 (1996) 3401–3407.
- [18] I.W. Nah, K.Y. Hwang, Y.G. Shul, Effect of metal and glycol on mechanochemical dechlorination of polychlorinated biphenyls (PCBs), *Chemosphere* 73 (2008) 138–141.
- [19] F. Tuinstra, J.L. Koenig, Raman spectrum of graphite, *J. Chem. Phys.* 53 (1970) 1126–1130.
- [20] S. Comba, A. Di Molfetta, R. Sethi, A Comparison between field applications of nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers, *Water Air Soil Pollut.* 215 (2011) 595–607.
- [21] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable reactive barriers: a critical review, *Environ. Eng. Sci.* 24 (2007) 401–423.
- [22] C. Noubactep, The fundamental mechanism of aqueous contaminant removal by metallic iron, *Water SA* 36 (5) (2010) 663–670.
- [23] V.V. Uglov, A.K. Kuleshov, D.P. Rusalsky, M.P. Samzov, A.N. Dementshenok, Friction coefficient, microstructure and thermal stability of amorphous a-C coatings, *Surf. Coat. Technol.* 158–159 (2002) 699–703.
- [24] V.V. Uglov, A.K. Kuleshov, M.P. Samtsov, M.V. Astashinskaya, Raman light scattering in hydrogenated metal-carbon composite films, *J. Appl. Spectrosc.* 73 (2006) 388–393.
- [25] W. Zhang, J. Huang, G. Yu, S. Deng, W. Zhu, Mechanochemical destruction of dechlorane plus with calcium oxide, *Chemosphere* 81 (2010) 345–350.
- [26] Y. Tanaka, Q. Zhang, F. Saito, Mechanochemical dechlorination of chlorinated compounds, *J. Mater. Sci.* 39 (2004) 5497–5501.
- [27] T.P. Klupinski, Y.P. Chin, S.J. Traina, Abiotic degradation of pentachloronitrobenzene by Fe(II): reactions on goethite and iron oxide nanoparticles, *Environ. Sci. Technol.* 38 (2004) 4353–4360.
- [28] Xingbao Gao, Wei Wang, Xiao Liu, Low-temperature dechlorination of hexachlorobenzene on solid supports and the pathway hypothesis, *Chemosphere* 71 (2008) 1093–1099.
- [29] Xingbao Gao, Wei Wang, Xiao Liu, Dechlorination reaction of hexachlorobenzene with calcium oxide at 300–400 °C, *J. Hazard. Mater.* 169 (2009) 279–284.
- [30] C. Noubactep, T. Licha, T.B. Scott, M. Fall, M. Sauter, Exploring the influence of operational parameters on the reactivity of elemental iron materials, *J. Hazard. Mater.* 172 (2–3) (2009) 943–951.
- [31] C. Noubactep, Characterizing the effects of shaking intensity on the kinetics of metallic iron dissolution in EDTA, *J. Hazard. Mater.* 170 (2–3) (2009) 1149–1155.
- [32] C. Noubactep, Characterizing the reactivity of metallic iron upon methylene blue discoloration in Fe<sub>0</sub>/MnO<sub>2</sub>/H<sub>2</sub>O systems, *J. Hazard. Mater.* 168 (2–3) (2009) 1613–1616.