

# MECHANOCHEMICAL DESTRUCTION OF PCNB WITH REDUCTIVE IRON POWDER

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## Introduction

Pentachloronitrobenzene (CAS No.82-68-2), also known as quintozone or terraclor, is an organochlorine fungicide which is applied to seeds, soils, and plants. It is also used to prevent the formation of slime in industrial water[1]. Pentachloronitrobenzene is a fungicide that is degraded in anoxic soils and sediments through unknown processes that are often thought to be biologically mediated. In the presence of mineral surfaces, Fe(II) promotes the reduction of nitroaromatic compounds[2]. Many investigations have been focused on the biodegradation of PCNB. Recently, much more concerns have been given to chemical degradation such as Fe(II) reduction and gamma radiation[3, 4]. In this paper we try to use the reductive iron powder for the destruction of PCNB.

Mechanochemical destruction (MCD) has received attentions as a promising technology to destroy solid waste containing persistent organic pollutants[5]. It is a proven non-combustion technology and does not require heating or off-gas treatment. The degradation mechanisms of MCD with calcium oxide have been systematically studied for both DDT and Dioxins[6, 7]. Then DMCR method had been developed by Birke which utilize the Base metal and hydrogen donor to accelerate destruction[8]. However, this reaction usually takes place in the solid-liquid phase. The degradation mechanism of MCD by zero-valent-metal without hydrogen donors has not been investigated, so in our study, the reductive iron powder and PCNB were used to investigate the mechanism and effects of destruction.

## Materials and methods

Reductive iron powder (98% purity; Beijing Modern Oriental Fine Chemicals Corporation) was stored in a dryer prior to use. Pentachloronitrobenzene (C<sub>6</sub>Cl<sub>5</sub>NO<sub>2</sub>, 95% in purity) was purchased from Shanxi Sanli chemical Co., Ltd. A planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China) was used for the experiments. A mixture of CaO and DP with different ratios was put into a stainless steel pot in a vacuum control system, and the pot was sealed subsequently. The planetary ball mill was operated at 550 rpm and the rotation direction of supporting disk changed automatically every 30 minutes. Ground products were identified by X-ray powder diffraction (XRD, Rigaku D/max-r B, Japan); Microscopic Confocal Raman Spectrometer (Renishaw RM 2000, UK); Fourier transform infrared (FTIR) spectrometer (NICOLET 6700 FTIR).

## Results and discussion

### Destruction

The MCD treatment of PCNB and iron powder was performed for 8h, 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 initially added as PCNB. After 8h, the PCNB concentration was below the detection limit. As a matter of fact, no peaks could be found in the GCMS spectrum after 8h grinding which means the organic materials have been destructed successfully. However, at this time the released ionic chloride could only achieve 76.9% (in figure1, non-ionic chloride 23.1%). The final product may contain some high molecular weight organic compounds with some chlorine and oxygen substituents[6]. The peaks

of Nitrate and Nitrite ions cannot be found in Ion Chromatograph analyses. After 3h grinding, the PCNB concentration decreased sharply near zero, and the main intermediate product PCA could be found clearly. What could result in such a sudden change must be determined in the next step.

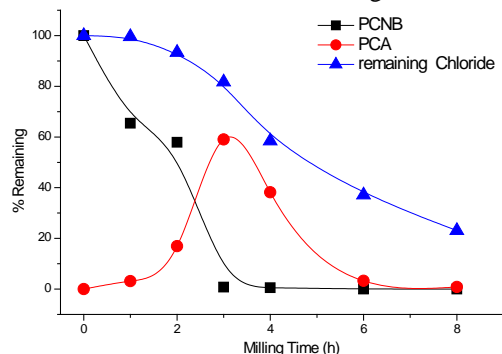


Fig. 1. Changes of the PCNB, PCA and non-ionic chloride

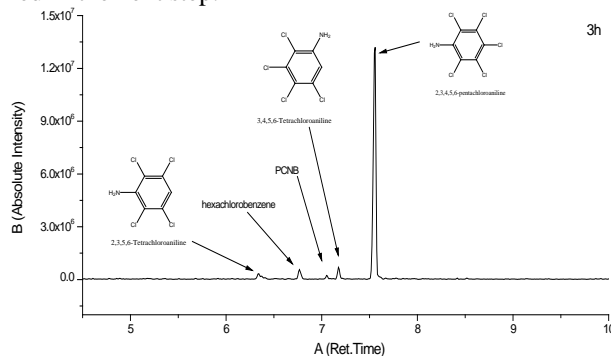


Fig. 2. GC/MS chromatogram of the degradation products

In PCNB mechanochemical destruction treatment, both 2,3,5,6-tetrachlorobenzeneamine and 3,4,5,6-tetrachlorobenzeneamine have been identified as the minor intermediates (1-2%), which means dechlorination reactions have taken place in MCD treatment. In contrast, after 3h grinding, the 58.9% of PCNB have been transferred to PCA, the Cl bonding of benzene ring is much more stable than the (-NO<sub>2</sub>) bonding of benzene. Another question of mechanism is raised before us: what is the major mechanism for destruction? Although the amination reaction of nitro-group is significant in MCD treatment, this is the first step for the overall destruction. Because the carbon is the final product of MCD by Laman spectrum, the polymerization is the main destruction mechanism. So the 2,3,5,6-tetrachlorobenzeneamine and 3,4,5,6-tetrachlorobenzeneamine are the byproducts (Fig. 2). But this does not mean dechlorination is not the main destruction pathway (Fig. 3). From the curve of non-ionic chloride, it can be drawn process of polymerization is earlier than the dechlorination. After 8h grinding, the organic compounds are destroyed and have no peaks in GCMS which means the amounts of unidentified materials (polymerized products) increased, but the ionic chloride has not achieved 100%.

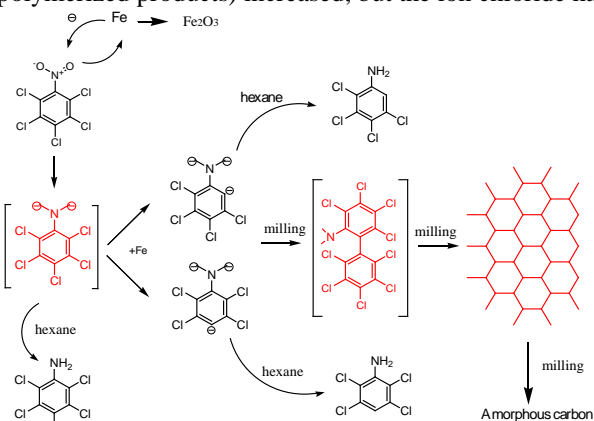


Fig. 3. Proposed pathways for degradation

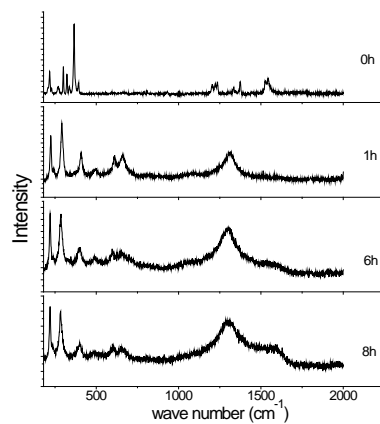


Fig. 4. Laman spectra of ground samples with time

### Final products identification

In order to see what happened in the surfaces of the ground sample, Scanning Electron Microscope was used to analyze the products. From the SEM of different grinding time powders, the particle size of powders had been decreased. After 6 grinding, the PCNB and iron powders were compressed closely. And After 8h grinding, lots of

submicron size hollow spheres can be seen clearly. The size of these spheres ranges from 1 $\mu\text{m}$  to 20 $\mu\text{m}$  which means the structure of the ground sample for several hours is not the nanometer structure.

Figure 4 shows the Raman spectra of ground samples. The color of the untreated sample was yellow, while the color of the samples of 6h and 8h were black. The most probable explanation is that carbon has been formed during the treatment which then is verified by the Raman spectra: absorption peaks at 1312  $\text{cm}^{-1}$  corresponding to the typical Raman peaks of amorphous carbon have been identified clearly while the peaks at 1582  $\text{cm}^{-1}$  corresponding to the typical Raman spectra of graphite could only be seen from 8h sample. The widened pattern implies a broad distribution of the formed domain sizes. In other researches, the peaks of both graphite carbon and amorphous carbon could appear simultaneously in the presence of Calcium oxide. But in our research, the formation of graphite carbon seems more difficult than amorphous carbon. Theoretically, the graphite carbon structure is the most stable for the carbon, but the presence of iron powder hindered the formation of graphite. We assume the iron powder serve as the electron donors and MCD-reaction leads to high temperature on the surface of the powders. Though the reason cannot be explained by the situ monitoring methods, the formation of amorphous carbon shows the carbonization of the organic phase with the progress of destruction reaction. Since some peaks in ground sample of low content PCNB will not appear by Raman spectra, the weight ratio (Fe/PCNB=5:1) has been chosen in order to reveal what happened in the reaction. After 8h grinding, the peaks at 660  $\text{cm}^{-1}$  corresponding to C-Cl bonding could be found distinctly. These are the incomplete reacted products for Fe and PCNB which indicate the high molecular weight organic compounds with some chlorine and oxygen substituents formed in the process. The dechlorination and polymerization reaction did not occur in some sequence. This phenomenon can explain why the released ion chlorine could not reach 100% when the PCNB and PCA have been destructed completely.

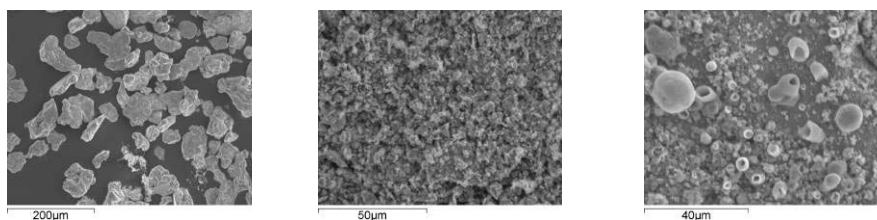


Fig 5 SEM a (1h) b (6h) c (8h)

## Acknowledgement

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