



## Partial degradation of carbofuran by natural pyrite



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### ABSTRACT

This work provides new insight into the degradation of 2,2-dimethyl-2,3-dihydrobenzofuran-7-yl-methylcarbamate (hereafter carbofuran) by natural pyrite as a function of pH and adsorbent loading. In the presence of *tert*-butyl alcohol i.e., OH<sup>•</sup> scavenger, the degradation efficiency of carbofuran was almost stopped. In acidic solutions (pH < 5) the degradation kinetics was pseudo first order in carbofuran as  $-\frac{d[\text{carbofuran}]}{dt} = -k_{\text{observed}} \times [\text{carbofuran}]$ . The dependence of  $k_{\text{observed}}$  on [FeS<sub>2</sub>] was given as  $k_{\text{observed}} = k_0 + [\text{FeS}_2] \times k_1$  where  $k_0 = 1.16 \times 10^{-7} \text{ h}^{-1}$  and  $k_1 = 0.137 \text{ h}^{-1}$ . The elucidation of precise steps of carbofuran degradation by pyrite has yet to be solved.

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### 1. Introduction

Pyrite (FeS<sub>2</sub> space group Pa3) is a stable metal sulfide that has received significant attention in a range of industrial and geochemical processes due to its ubiquity and unique features (Ennaoui et al., 1993; Cohn et al., 2006; Borda et al., 2003; Herbert et al., 2014). For example, the acid mine drainage occurred as a result of pyrite oxidation in the presence of H<sub>2</sub>O and O<sub>2</sub>. Pyrite is considered as a primary energy supplier for primitive life (Wächtershauser, 1988). Further, pyrite shows intrinsic conductivity and high light absorption capacity (Ennaoui et al., 1993). Recently the band gap of pyrite is shown as ~0.55 eV as opposed to widely accepted value of 0.95 eV (Herbert et al., 2013). The presence of reduced band gap on the surface as well as the existence of defects sites within this band gap hold implications for electrons transfer as required for the degradation of organic pollutants (Herbert et al., 2014, 2013; Kang et al., 2011). In this context, the S<sub>2</sub><sup>2-</sup> on pyrite surface is argued as an electron donor (Luther, 1987). The reactivity of pyrite was largely attributed to fast or slow production of OH<sup>•</sup> radicals in the presence or absence of Fenton precursors, respectively (Borda et al., 2003; Luther, 1987). Pyrite is employed as a heterogeneous catalyst for pollution control in several chemical processes such as aerobic degradation, photol-

ysis etc. (Pham et al., 2015; Lee and Kang, 2013). For example, it plays a catalytic role in the degradation of organic pollutants generated from pharmaceutical wastes (Bae et al., 2013), polyaromatic hydrocarbons (Choi et al., 2014), pesticides or pesticide precursors (Zhang et al., 2014; Tripathi et al., 2010) and domestic wastes (Kong et al., 2015).

In this research we examined the chemical kinetics of 2,2-dimethyl-2,3-dihydrobenzofuran-7-yl-methylcarbamate (hereafter carbofuran) degradation by natural pyrite under anaerobic conditions and the results were used to postulate plausible degradation mechanism/s based on experimentally identified intermediates. When such an approach is not feasible due to limitations in experimental procedures, the most probable intermediates were predicted theoretically. All the experiments were conducted in the dark under anaerobic environmental conditions. Finally, a carbofuran degradation mechanism was proposed, and the time domain distribution of different degradation products was simulated computationally. The investigation of systems in this nature is very important both from industrial and geochemical viewpoints due to its importance as an industrial catalyst (Lopez-Alvarez et al., 2011), and the role played in numerous natural processes (Luther, 1987).

Carbofuran was selected mainly due to following reasons; it is an insecticide widely used in agriculture and has a high toxicity (LD<sub>50</sub> 11 mg kg<sup>-1</sup> in mice) which acts as an inhibitor of acetyl cholinesterase (Fenoll et al., 2013). Carbofuran has a high mobility

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**Table 1**  
Physicochemical data of pyrite/water interface and carbofuran.

Parameter	Value	Source
Specific surface area, m <sup>2</sup> /g	1	Ref. Weerasooriya and Tobschall (2005)
Average particle size, μm	4–4.5	This study
Site density, sites/nm <sup>2</sup>	9	Ref. Weerasooriya and Tobschall (2005)
<sup>a</sup> pH <sub>ZPC</sub>	1.70–2.30	-do-
>FeSS <sup>-1/3</sup> + H <sup>+</sup> => FeSSH <sup>+2/3</sup>	Log K 0.93	-do-
>FeSS <sup>-1/3</sup> + 2H <sup>+</sup> => HHSS <sup>-1/3</sup>	Log K -2.87	-do-
Carbofuran	MW 221.26 au	Ref. Chapman and Cole (1982)
	K <sub>ow</sub> 17–26	-do-
	Solubility 1.59 mM at 298 K	-do-
	t <sub>1/2</sub> 27.7 (pH 7), 0.54 (pH 9)	-do-

<sup>a</sup> Value depends on equilibration time.

in soils and is soluble in water, i.e., solubility ~700 mg/L (Worthing, 1991). The maximum contaminant level (MCL) of carbofuran in drinking water is 0.04 mg L<sup>-1</sup>. Further due to high toxicity of carbofuran, new regulations have been promulgated banning its use (US Environmental Protection Agency, 2011). Semi-empirical calculations of pyrite and carbofuran systems have shown that the energy values of E<sub>LUMO</sub> and E<sub>HOMO</sub> are -3.14 and -6.14 eV, respectively, which indicate that carbofuran degradation by pyrite is theoretically feasible (Krilegman-King and Reinhard, 1994). However, investigations into the degradation of carbofuran by pyrite are depleting to date and the available information is of limited use in elucidating mechanistic pathways of carbofuran degradation. In contrast, there is substantial information on the degradation of carbofuran by photochemical (Lopez-Alvarez et al., 2011), chemical (Cohn et al., 2006; Borda et al., 2003), pyrolytic (Remya and Lin, 2011) and biological (Chaudry and Ali, 1988) methods and in most of them are routinely used in advanced oxidation processes of water treatment. In pyrolytic degradation, carbofuran has disintegrated into 83 low molecular mass fragments, viz. m/z 39–164 (Remya and Lin, 2011). Both in biological and chemical processes, however the carbofuran degradation occurred via the formation of high molecular mass fragments, viz. m/z 178–221 (Fenoll et al., 2013; Chaudry and Ali, 1988).

## 2. Materials and methods

### 2.1. Materials

Standards 2,2-dimethyl-2,3-dihydrobenzofuran-7-yl-N-methylcarbamate (carbofuran) and 2,3-dihydro-2,2-dimethylbenzofuran-7-ol were purchased from Chem Service, USA. HClO<sub>4</sub>, NaOH, NaClO<sub>4</sub>, Na<sub>2</sub>S, methanol, *tert*-butyl alcohol, HOCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH were obtained from Fluk (Switzerland). *N*-hydroxyamine hydrochloride, sodium acetate, and 2,2'-bipyridyl, atomic absorption iron standard solutions were from BDH (UK). Water was purified passing through a mixed bed resin to remove any anionic or cationic constituents before distillation. Stock solutions of carbofuran and 2,3-dihydro-2,2-dimethylbenzofuran-7-ol were prepared in methanol – water mixtures from the chemicals received from Sigma (USA). The half-lives of carbofuran in water ranged from 690 days at pH 5 to 1 days at pH 9 (Chapman and Cole, 1982). Therefore, the pH of the stock solution was always kept below 5 to minimize self-degradation. Pyrite samples were collected from a graphite mine (Location: Bogola, Sri Lanka) and they were purified according to the methods given elsewhere (Weerasooriya and Tobschall, 2005), particularly to remove any oxidative products such as iron(II) sulfate, melanterite etc., from the mineral phase. For all experiments sample preparations

were conducted under anaerobic conditions in a glove box which was flushed with 99.95% N<sub>2</sub> according to following procedure: three times prior to use; two times after each sample change and two times daily to remove any slow diffusive atmospheric contaminants from the glove box.

Confirmatory evidence for the identification of mineral phase was received by X-ray diffraction and FTIR analyses. The physico-chemical properties of pyrite/water interface and carbofuran used are shown in Table 1.

### 2.2. Methods

The chemical kinetics of carbofuran degradation by pyrite was examined as a function of pH, carbofuran and solid content. In control experiments, identical solutions were prepared without pyrite. The blank solutions were prepared by membrane filtering (pore size 0.45 μm) pyrite–water suspensions that were synthesized at desired experimental conditions. In selected experiments ~0.10 M *tert*-butyl alcohol was added as the OH radical scavenger. As discussed in ref. (Langford and Carey, 1975), the OH<sup>•</sup> scavenging can be monitored by detecting HOCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH. The detection of HOCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH was carried out by a GC-FID system using Porapak 3 capillary column under split–split less mode at 9.4 min retention time as confirmed against a known standard. All experiments were conducted in amber borosilicate vessels (volume ~250 mL, Ace Glass USA) capped with a glass lid with five outlets to facilitate solution transfer and pH monitoring under controlled conditions. In most cases, the mass ratio of the solid to solution was around 1:5. The uptake of water by pyrite slurry was negligible; hence errors due to changes in volume by pyrite addition were neglected because they were within the range of analytical and experimental errors. To prepare samples, first a clean vessel was capped with the lid equipped with pH electrode, anti-magnetic stirring rod, temperature probe, and N<sub>2</sub> gas inlet/outlet tubes. The batch slurry prepared with pyrite was transferred to the vessel, and stirring was initiated. Subsequently, the solution was spiked with known concentration of carbofuran and pH was recorded. In a typical kinetic experiment, the pyrite batch solution was spiked with a known carbofuran concentration. The background ionic strength was adjusted to 0.01 M with 5 M NaClO<sub>4</sub>. The pH values within 1–5 were adjusted either with 0.0921 M HClO<sub>4</sub> or 0.935 M NaOH. The temperature was maintained at 298 K. At pre-defined time intervals, samples were withdrawn into a syringe. Samples were placed in 3-ml glass vials. For the analysis of organic compounds, a 0.5-ml sample was added into a vial. A known volume (15-μl in most cases) was taken into gas tight syringe for HPLC analysis. Normally three samples were taken from each vial. In most of the cases, the conditions of pseudo order kinetics were imposed by performing experiments at excess surface sites while varying one experimental parameter at a time. Dependence of the carboruan degradation rate on proton concentration was investigated by varying system pH between ~2.0 and ~5.0. To determine the effect of solid concentration on carbofuran degradation, the pyrite content in the batch reactor was varied between 1 and 48 μM around pH ~2.

### 2.3. Analyses

Carbofuran and its degradation products were analyzed by reversed phase (RP) HPLC using Supersil C-18 column (150 m × 4.6 mm, 5 μm particle size) with a UV detector at 276 nm. The mobile phase was composed of a mixture of 60/40% acetonitrile and water under 1 mL min<sup>-1</sup> isocratic flow conditions. The inorganic degradation products, nitrate, nitrite and ammonium were determined photometrically according to the procedures given in APHA (American Public Health Association (APHA), 2005). Carbofuran degraded product identifications were carried out

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