



Mechanochemical removal of carbamazepine



Mohamed Samara, Ahmed Nasser*, Uri Mingelgrin

Institute of Soils, Water and Environmental Sciences, Volcani Center, ARO, Bet Dagan 50250, Israel

HIGHLIGHTS

- Breakdown of carbamazepine (CBZ) by surface reactions.
- CBZ sorption on Al-montmorillonite enhanced its degradation.
- CBZ ball milling with magnetite generated a complete disappearance of the drug.

ARTICLE INFO

Article history:

Received 1 May 2016

Received in revised form

21 June 2016

Accepted 22 June 2016

Available online 6 July 2016

Handling Editor: T. Cutright

Keywords:

Mechanochemistry

Carbamazepine

Ball milling

Magnetite

Al-montmorillonite

ABSTRACT

Carbamazepine (CBZ) is a drug used for treating epilepsy, neuropathic pain, schizophrenia and bipolar disorder. Its widespread use is indicated by its listing in the WHO's Model List of Essential Medicines. The accumulation of CBZ in various environmental compartments, specifically in crops irrigated with treated effluent or grown on soils containing biosolids, is often reported. Being a persistent PPCP (a pharmaceutical and personal care product), developing procedures to remove CBZ is of great importance. In the present study, the breakdown of CBZ by surface reactions in contact with various minerals was attempted. While Al-montmorillonite enhanced CBZ disappearance without the need to apply mechanical force, the efficiency of magnetite in enhancing the disappearance increased considerably upon applying such force. Ball milling with magnetite generated a virtually complete disappearance of CBZ (~94% of the applied CBZ disappeared after milling for 30 min). HPLC, LC/MS and FTIR were employed in an attempt to elucidate the rate of disappearance and degradation mechanisms of CBZ. A small amount of the hydrolysis product iminostilbene was identified by LC/MS and the breaking off of carbamic acid from the fused rings skeleton of CBZ was indicated by FTIR spectroscopy, confirming the formation of iminostilbene.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Traces of various PPCPs (pharmaceuticals and personal care products) are often detected in treated wastewater effluents and sludges (Zhu and Chen, 2014; McClellan and Halden, 2010). Certain compounds belonging to this broad group of chemicals are ubiquitous, indicating their resistance to breakdown under conditions prevailing in standard effluent treatment facilities as well as in the natural environment. One of the most commonly detected PPCP is carbamazepine (CBZ) (Clara et al., 2004; Stamatelatou et al., 2003).

CBZ is a drug commonly used in the treatment of epilepsy and neuropathic pain as well as of schizophrenia and bipolar disorder. It is listed in the WHO Model List of Essential Medicines (WHO, 2015),

namely, the WHO considers this drug a must for any general health system.

Numerous field and laboratory studies record the extent of accumulation of carbamazepine in the environment and specifically in food crops grown on soils irrigated with treated sewage effluent or loaded with biosolids (Grossberger et al., 2014; Shenker et al., 2011). It was demonstrated that the concentration of CBZ in domestic effluents or sludges as well as in the soils to which these waste products were applied or the crops grown on such soils, did not pose a significant risk to human health (Prosser and Sibley, 2014). Yet, the resistance of CBZ to natural attenuation requires special care in the release to the environment of effluents or solid wastes from sources which may be rich in that compound, such as production plants or medical facilities, due to the risk of accumulation of CBZ to harmful levels. Hence, an efficient and environmentally friendly technique for the breakdown of carbamazepine is of considerable value.

* Corresponding author.

E-mail address: nasser@agri.gov.il (A. Nasser).

Most procedures used for breaking down organic pollutants are based on biological processes (Khan et al., 2004). However, such biotic procedures are often rather slow and cease to be effective when any one of many environmental variables (such as salinity or the concentration of toxic residues left in the polluted medium) exceed some threshold value (Mulder et al., 2001). Abiotic processes are often free of these shortcomings.

A mechanochemical process is defined as a chemical reaction which is driven by the application of a mechanical force. The application of the force may be by such means as milling, grinding or compression. Application of a mechanical force may cleave solid particles and thereby increase their surface area while exposing freshly formed surfaces. Such freshly exposed surfaces often contain chemically active sites, including free radicals which come into being due to bond breakage at the planes of cleavage (Zhang et al., 2014; Nasser and Mingelgrin, 2014). The application of a mechanical force may also induce mass transfer that will bring in contact the substrate molecules and the surface sites at which the desired solid phase reaction takes place (Nasser et al., 2000; Harchova et al., 2007; Kalinkin et al., 2006).

A variety of minerals, including montmorillonite, manganese oxides, calcium oxide and iron oxides were shown to induce a wide range of abiotic transformations of organic pollutants (Pizzigallo et al., 1995, 2004; Di Leo, 2000; Nasser et al., 1997; Mingelgrin and Saltzman, 1979; Mortland and Halloran, 1976) and successful application of mechanical force to enhance degradation of slowly-degradable pollutants at surfaces of various minerals was often reported in the past (Caschili et al., 2006; Pizzigallo et al., 1995, 2004). Examples include the mechanochemical degradation of 2,4-D and of atrazine (Nasser et al., 2000; Shin et al., 2000) when ground in contact with manganese oxide. Mechanochemical degradation of γ -hexachlorocyclohexane on CaO and of catechol in contact with birnessite was demonstrated more recently (Di Leo et al., 2012; Nomura et al., 2012). Degradation of imazaquin upon grinding with a number of minerals, including Cu-montmorillonite, a manganese oxide and iron oxides was also reported (Nasser et al., 2009). Light grinding for 5 min in the presence of Cu-montmorillonite, which was the most effective mineral in degrading imazaquin, brought about the degradation of over 90% of the imazaquin. A review of mechanochemically-induced surface transformations of environmentally-relevant compounds was published by Nasser and Mingelgrin (2012).

The overall objective of the present work is to explore the possibility of eliminating carbamazepine by a mechanochemical process. Surface reactions involving various minerals were explored. Magnetite, birnessite, hematite, titanium oxide, Cu-montmorillonite and Al-montmorillonite were tested and the efficacy of both manual grinding and ball milling was assessed. Magnetite was singled out to be studied in considerable detail since it displayed an exceptionally high capacity for breaking down CBZ upon application of mild grinding for a short duration. An advantage of employing a reaction involving magnetite is that due to the magnetic properties of that mineral, the separation of the spent magnetite after its addition to a CBZ-loaded medium may be easily achieved using a magnetic field (Zhu et al., 2014).

2. Materials and methods

2.1. Materials

Carbamazepine (CBZ; $C_{15}H_{12}N_2O$; 5H-dibenzo[b,f]azepine-5-carboxamide; Diagram 1) was acquired from Sigma-Aldrich, Switzerland (purity $\geq 98\%$). A CBZ stock solution (500 $\mu\text{g/mL}$), was prepared in acetonitrile (ACN), and then stored in glass vials sealed with caps lined with Teflon septa at -18°C .

The minerals used were obtained as follows: Al- and Cu-montmorillonite, were prepared from Na-montmorillonite purchased from Fisher Scientific, USA as described in the Methods section. Manganese oxide (birnessite, $\delta\text{-MnO}_2$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$), were synthesized as described by Nasser et al. (2009), titanium dioxide (TiO_2 , 99.8% purity), was purchased from Aldrich, Germany. Three samples of magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$), which differed in their particle size were investigated. Magnetite with particle diameter $<500\ \mu\text{m}$ was supplied by the Geological Survey of Israel; magnetite with particle diameter $<5\ \mu\text{m}$ and magnetite with particle diameter $<0.05\ \mu\text{m}$ were purchased from Sigma-Aldrich, Switzerland and were 98% pure.

Reagents were of analytical grade and purchased from Sigma-Aldrich, Switzerland. Solvents were of LCMS grade and supplied by BioLab Ltd, Israel.

2.2. Methods

2.2.1. Preparation of the homoionic montmorillonites

The empirical formula of montmorillonite is $(\text{M}^{+q})_{0.4/q}(\text{Al})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$, where M represents the exchangeable cation (which in the present study is predominantly Ca, Cu or Al), and q is the valence of the exchangeable cation. Iron (as well as other cations), commonly replace some Al and Si atoms in the mineral matrix (Al may also substitute for the Si), thus producing a net negative charge which is compensated by the exchangeable cation. Al- and Cu-montmorillonites were prepared by equilibrating the original Na-montmorillonite with a 1 N solution of the chloride salt of the desired exchangeable cation at a mineral:solution ratio of 1:10 (w/v). This step was repeated three times and then the solid phase was rinsed four times with distilled water.

2.2.2. Application of mechanical force

To 1 g samples of the minerals which were spread in a thin layer on glass Petri dishes, a total of 1 mL of the stock 500 $\mu\text{g/mL}$ CBZ solution was slowly added so as to ensure complete uptake of the added liquid by the solid phase. The wetted samples were well mixed and then dried in a fume hood until the ACN was totally evaporated ($\sim 2\ \text{h}$). The virtually complete evaporation of ACN was ascertained by the disappearance of all traces of gloss from the surface of the intermittently mixed, thinly spread, spiked mineral sample and by its return to room temperature after the cooling caused by the solvent's evaporation. The validity of this procedure was established by measuring the load of ACN left in selected samples by the procedure of Channing et al., 2001). Immediately following the complete removal of ACN, 0.25 g samples of the various minerals loaded with CBZ were manually ground for 5 min, using a mortar (3 cm radius) and pestle. At the point in time at which the grinding was completed (T_0), weighed portions ($\sim 0.125\ \text{g}$) of the solid samples were added to a 4 mL of ACN in 12 mL glass bottles. The resulting suspensions underwent sonication at room temperature for 30 min in a sonication bath (Sonicator, USA). The suspensions were finally centrifuged (Hettich, Germany) at 3500 rpm for 10 min and the liquid phase separated and stored in glass bottles at -18°C for future analysis. Samples of 0.5 g CBZ-loaded magnetite, (which displayed a high potential for enhancing mechanochemical removal of CBZ in the manual grinding tests), were milled in a ball mill (Retsch model MM2, Germany), equipped with 2 agate grinding balls (7 mm in diameter), at 2000 rpm for 30 min. The milled samples were extracted with ACN as described above immediately following milling (T_0), and after incubation for various durations of up to 120 h following the milling. Ground minerals which were not loaded with CBZ were also extracted with ACN and the extracts were used as a reference. All tests were run in triplicates.

Download English Version:

<https://daneshyari.com/en/article/4407372>

Download Persian Version:

<https://daneshyari.com/article/4407372>

[Daneshyari.com](https://daneshyari.com)