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DEHALOGENATION OF DELTA-HEXACHLOROCYCLOHEXANE BY IRON SULFIDE NANOPARTICLES

Silviu-Laurentiu Badea[1], Nicolae-Ionut Cristea[2], Violeta-Carolina Niculescu[1], Stanica Enache[1], Amalia Soare[1], Athanasios Tiliakos[1], Roxana-Elena Ionete[1]

[1]National Research and Development Institute for Cryogenic and Isotopic Technologies, 4 Uzinei, 240050, Râmnicu Vâlcea, silviu.badea@icsi.ro, Romania
[2]National Research and Development Institute for Industrial Ecology-ECOIND, 57-73 Drumul Podu Dambovitei, district 6, 060652, Bucharest, Romania

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Introduction

The abiotic transformation of emerging and priority pollutants has been less studied compared to biodegradation. Iron sulfide (FeS) is a mineral with reductive properties that appears naturally in various anoxic environments, being associated with sulfate-reducing bacteria that grow in anoxic aquifers and sediments. Previous studies have reported the capacity of FeS to reductively dehalogenate various halogenated organic pollutants, such as hexachloroethane, trichloroethylene, γ-hexachlorocyclohexane (γ-HCH), hexabromocyclododecane (HBCD) and recently of α-HCH. Therefore, the objective of this study was to investigate the degradation of δ-HCH in batch experiments with iron sulfide nanoparticles, in order to mimic its transformation pathways in anoxic environments.

Materials and methods

FeS nanoparticles were synthesized by adding 250 mL solution of Na_2S (technical purity, Sigma Aldrich) 0.2 M over 250 mL solution of $FeSO_4$ 0.2 M, under a N_2 flow. Afterwards, the FeS precipitate was centrifuged, washed and freeze dried. The FeS nanoparticles were characterized by determination of specific surface, X-Ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). The dehalogenation reaction was performed in duplicates by adding 165 mL buffer mixture solution K_2HPO_4 0.1 M/ KH_2PO_4 0.1 M (in a ratio of about 94 to 6) over 1.5 g FeS nanoparticles (final pH of 8.02 ± 0.02). A control bottle was prepared by adding the same amount of δ-HCH to deoxygenated water in containing 80.88 mg/L $HgCl_2$. δ-HCH was added from an acetone solution to a theoretical concentration of approximatively 20.7 µM. The dechlorination reaction was performed for 29 days in an incubator at 30 °C and 125 rpm. For sampling, 14 mL aliquots of δ-HCH solution were taken with syringes at regular intervals and extracted with 1 mL dichloromethane. The analyzes were performed using a 1300 Trace series GC gas chromatograph coupled with a TSQ 8000 EVO triple quadrupole mass spectrometer (Thermo, Germany) configurated in Scan/SIM mode. α-HCH and its degradation products were separated on a capillary column type DB-5 with dimensions of 60 × 0.25 mm × 0.25 µm, using the following temperature program: 50° C initial temperature (constant for 1 min), then increased by 10°C/min up to 300°C (and held for 19 min).

Results and conclusions

The preliminary results show that the dehalogenation of δ-HCH by FeS followed a similar pattern (in both degradation products and kinetics) as the dehalogenation of α-HCH by FeS. The main expected degradation pathway of δ-HCH by FeS is dehydrohalogenation with formation of trichlorobenzene (1,2,4-TCB), 1,2-dichlorobenzene (1,2-DCB), and benzene as the dominant degradation products of δ-HCH. Nevertheless, the detection of monochlorobezene (MCB), in the current study, suggested that dihaloelimination might be also a significant degradation mechanism of δ-HCH by FeS. In the control bottle, the δ-HCH concentration varied from 20.6 μM at the beginning of the experiment to 17.2 μM, after 29 days, showing no significant degradation (Figure 1).

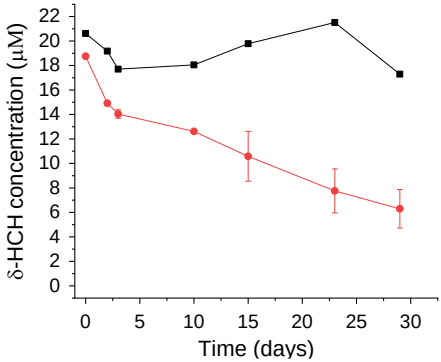

Fig. 1. The degradation curve of δ-HCH by FeS at pH value of 8 (●) and the evolution of δ-HCH concentration in the control bottle (■).

In the bottles with FeS, the δ-HCH concentration decreased from 18.7 ± 0.09 μM at the beginning of the experiment to 6.29 ± 1.57 μM, after 29 days, at the end of the experiment, the decrease in concentration being attributable both to dichlorination, but also to sorption to FeS nanoparticles. Overall, the preliminary results of this dehalogenation study showed the potential of FeS nanoparticles in dehalogenation of HCH isomers, while various dehalogenation reaction mechanisms are yet to be investigated.

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