

Recalcitrant Organic Pollutants Remediation by Natural Mineral Pyrite(天然の黄鉄鉱による離分解性有機汚染物質の浄化)

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論 文 内 容 要 旨

This study aims to investigate the applicability of natural mineral iron disulfide (pyrite) in remediation of recalcitrant organic pollutants. Degradation experiments of several classes of organic compounds were conducted in aqueous pyrite solution. The reaction controlling factor and reaction mechanism were determined.

Trichloroethylene (TCE) was representative for the chlorinated aliphatic compounds. The transformation of TCE in pyrite aqueous suspension under different oxygen conditions was investigated in laboratory batch experiments. TCE transformation was pursued by monitoring its disappearance and products released with time. The effect of oxygen was studied by varying the initial dissolved oxygen concentration (DO_i) inside each reactor. Transformation rates depended strongly on DO_i in the system. In anaerobic pyrite suspension, TCE did not transform as it did under aerobic conditions. The transformation rate increased with an increase in DO_i . The TCE transformation kinetics was fitted to a pseudo-first-order reaction with a rate constant k (h^{-1}) varying from 0.004 to 0.013 for closed systems with DO_i varying from 0.017 to 0.268 mmol/L under the experimental conditions. In the aerobic systems, TCE transformed to several organic acids including dichloroacetic acid, glyoxylic acid, oxalic acid, formic acid and finally to CO_2 and chloride ion. Dichloroacetic acid was the only chlorinated intermediate found. Both TCE and the

pyrite surface were oxidized in the presence of O₂. Oxygen consumption profiles showed O₂ was the common oxidant in both TCE and pyrite oxidation reactions. Ferric ion cannot be used as an alternative oxidant to oxygen for TCE transformation.

Besides of aliphatic compounds representative by TCE and several organic acids, aromatic compounds were also able to degrade in pyrite aerobic solution. Degradation of aromatic compounds including benzene and several chlorinated benzenes (from mono-chlorinated benzene (CB), di-chlorinated benzenes (di-CBs) to tri-chlorobenzenes (tri-CBs) in aerobic pyrite suspension were investigated using laboratory batch experiments at 25 °C and room pressure. At first, chlorobenzene was studied as a model compound for all considered aromatic compounds. CB degraded in aerobic pyrite suspension, transformed to several organic acids and finally to CO₂ and Cl⁻. Transformations of remaining aromatic compounds were pursued by measuring their degradation rates and CO₂ and Cl⁻ released with time. Transformation kinetics was fitted to the pseudo-first-order reactions to calculate degradation rate constant of each compound. Degradation rates of the aromatic compounds were different depend on their chemical structures; which are the number and position of chlorine substituents on the benzene ring in this study. Compounds with the highest number of chlorine substituent at m-positions have highest degradation rate (1,3,5 triCB > 1,3 diCB > others). Three chlorine substituents closed together (1,2,3 triCB) generated steric hindrance effects, therefore 1,2,3 triCB is most stable to the degradation reaction. The degradation rates of all compounds were in the following order: 1,3,5 triCB > 1,3 diCB > 1,2,4 triCB ≅ 1,2 diCB ≅ CB ≅ benzene > 1,4 diCB > 1,2,3 triCB. The final products of the transformations were CO₂ and Cl⁻. Oxygen was the common oxidant for pyrite and aromatic compounds. The presence of aromatic compounds reduced the oxidation rate of pyrite, which representative by the reducing of ferrous and sulfate ions release to aqueous solution.

Hydroxyl radical (.OH) was detected in pyrite aqueous suspension. Quantity of .OH was calculated by comparing radical from pyrite suspension with the radical produced from hydrogen peroxide (H₂O₂) solutions catalyzed by horseradish peroxidase (HRP). In pyrite solutions under aerobic condition, amount of .OH released increased with time. There was accumulation of radical in aqueous solution with time. Under anaerobic condition, amount

of radical produced was insignificant compare to the amount produced under aerobic condition. The effect of different initial oxygen concentrations on the production of radical was visible after 168h reacted. At the beginning stage when oxygen was still available in all systems, the amount of hydroxyl radical produced was similar for all different initial oxygen concentrations. However, at the later stage when oxygen was consumed by the pyrite oxidation reactions, the system has higher initial oxygen concentration, the more radical was detected. The generation of hydroxyl radical can play the central role in degradation of organic compounds. Under aerobic conditions, a significant quantity radical produced can degraded several organic compounds. Based on the experimental data obtained for the degradation of several aromatic compounds, the mechanism for organic compounds degradation in aqueous pyrite system has been proposed. The main pathway involved in the reaction at the reactive sites on the pyrite surface. Organic compounds degradation reactions were competitive with pyrite oxidation reaction for the reactive sites on the surface and for the .OH oxidant.

The pathways and kinetics of trichloroethylene (TCE) degradation in aerobic pyrite suspension were investigated. The degradation of TCE and its intermediates were confirmed by the detection of hydroxyl radical in aerobic pyrite suspension. Hydroxyl radical generated in aqueous pyrite suspension after 16h shaken at 25 °C was quantified using fluorescent method. This radical can play a decisive role in the degradation of TCE and its degradation intermediates. The laboratory batch experiments under the same conditions as TCE experiments were conducted to determine the degradation pathways and rates for all identified intermediates of TCE reactions. Kinetic model was developed, formulated, and solved analytically based on the understanding of various processes is consistent with results obtained in the kinetic experiments. The reaction pathway of TCE oxidation has been proposed, in which the degradation of TCE to formic acid and finally to CO₂ was the main route. Degradation of TCE to oxalic acid and dichloroacetic acid were found as minor pathways.

論文審査結果の要旨

現在、世界各地で難分解性有機化合物による土壌・地下水汚染問題が生じており、安全かつ安価な処理方法が求められている。黄鉄鉱は自然界に広く分布する天然鉱物であり、一部の有機塩素化合物と反応する事例が報告されてきたが、これまでのところその反応が起こる条件は嫌気的環境下だけであった。本論文は、トリクロロエチレン (TCE) とクロロベンゼン (CB) 類を代表物質として、これまで報告のない好气的条件における黄鉄鉱と難分解性の有機化合物との反応を取り上げ、その反応条件の詳細を明らかにするとともに、反応機構を速度論的に解明することを目的としたもので、全5章で構成される。

第1章は緒論である。第2章では、TCEを含む水溶液を入れた回分容器中に粉碎、整粒、表面洗浄した黄鉄鉱を投入し酸素を存在させた状態で反応させると黄鉄鉱の溶解を伴いながら TCE の分解が進行すること、酸素の供給を遮断すると TCE の分解は起こらないことを示している。また、分解は擬一次反応で整理されること、溶存酸素濃度を変えて TCE 分解挙動を追跡し、分解速度が酸素濃度に依存すること、Fe(III)イオンは分解反応に寄与しないこと、主要分解生成物がジクロロ酢酸、グリオキシル酸、シュウ酸、ギ酸と二酸化炭素であることを明らかにしている。第3章では、クロロベンゼン類あるいはベンゼンについて2章と同様の実験を行い、TCEと同様これらの化合物も黄鉄鉱の溶解に伴って好气的に分解されることを示している。また、分解速度は化合物によって大きく異なり、検討した8種類の中では、1,3,5-トリクロロベンゼンの分解速度が最も大きく、次いで1,3-ジクロロベンゼンが大きいことを示している。第4章では、まず反応溶液中で発生するヒドロキシルラジカル量を定量し、有機化合物の分解反応がこのヒドロキシルラジカルによってもたらされていることを示している。その上で、反応生成物の大半を検出していると考えられる TCE の分解反応について、その反応機構を速度論的に解析し、TCE から有機酸類を経て二酸化炭素に完全分解される経路で、ほぼ実験結果を表現できることを明らかにしている。第5章は結論である。

以上、本論文により自然界に広く分布する天然鉱物の黄鉄鉱が介在する好气的分解経路により TCE やクロロベンゼン類などの難分解性有機化合物が容易に分解可能であることが、その反応機構を含めて世界で始めて示されたことは、環境中での難分解性有機化合物の自然減衰を理解するうえで、またその反応機構を難分解性有機化合物により汚染された環境の浄化に利用する上でも、重要な知見を提供するものであり、環境科学、応用化学、環境修復工学など広範な学術領域に対する貢献が少なくない。

よって、本論文は博士(学術)の学位論文として合格と認める。