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Transformation products of oxytetracycline by heterogeneous photo-Fenton-like process

Jeong-Ann Park

Kangwon National University, Environmental Engineering, Korea, Republic of (pjaan@kangwon.ac.kr)

Oxytetracycline (OTC) is frequently detected antibiotic in surface water because it is widely used for both humans and animals; however, it is difficult to be completely removed by conventional wastewater treatment due to its recalcitrant nature. By using photo-Fenton-like process, OTC could be degraded or transformed, while only a few studies were conducted to detect its transformation products (TPs). In this study, a UHPLC (Ultra-high-performance liquid chromatography) system coupled with a Triple TOF 5600+ mass spectrometer (AB SCIEX Co., Redwood City, CA, USA) was used to identify the TPs of OTC during the heterogeneous photo-Fenton process. The heterogeneous photo-Fenton-like process was performed with MIL-100(Fe) and 50 mg/L of H₂O₂ under visible light, then 12 kinds of TPs were observed. The peak area of OTC (m/z 461) decreased immediately as the reaction went, and 8 kinds of TPs were observed only after 1 min-reaction. OTC transformed initially and mainly by decarbonylation of C1 (m/z 433), hydroxylation of the aromatic ring (m/z 477a) and C11a (m/z 477b), and demethylation at low N-C bonds (m/z 447). m/z 477a and 475 were predominantly observed because the aromatic ring is one of the most favorable target site to be oxidized by ·OH. Additionally, keto/enol at C11a-C12 is another favorable oxidation site forming m/z 477b; further hydroxylation generated m/z 493, and additional secondary alcohol oxidation led to the formation of m/z 491. A methyl group at C4 abstraction (m/z 447) was degraded further into m/z 429 by dehydration of C6-C5a, abstraction of hydrogen at C5 turned into m/z 459, and m/z 441 was formed by dehydration at C6.