Development of a system for treatment of wastewaters, containing antibiotic substances

Abstract

Due to the widespread use of antibiotics in modern society, these substances are also present in low concentrations in the environment. While this does not cause direct negative effects on organisms, it contributes to the spread of bacterial resistance to antibiotics, which is becoming an increasingly pronounced health problem.

The purpose of this doctoral dissertation was to determine which advanced oxidation process and what doses of oxidants shoudl be used in order that antibiotics become suitable for conventional biological treatment. To achieve that it is necessary to reduce toxicity and increase biodegradability of the antibiotics. The use of oxidation as a pretreatment before conventional biological treatment could effectively limit the spread of non-biodegradable antibiotics into the environment.

Veterinary, poorly biodegradable and environmentally sustainable Tiamulin was used as the model antibiotic. Two antibiotics were used to compare and confirm the effects of oxidation techiques; biodegradable betalactam Amoxicillin and non biodegradable fluoroquinolone Levofloxacin. We tested three advanced oxidation techniques; ozone, ozone in combination with hydrogen peroxide, and Fenton reagent. The aim was to achieve partial mineralization and, above all, to increase the biodegradability of antibiotics both in water and in the biological sludge matrix.

The doses of ozone required to significantly improve biodegradability are for Tiamulin 660 mg O_3 g^{-1} (biodegradability improved from 17 to 60 %) and for Levofloxacin 534 mg O_3 g^{-1} (100 % biodegradability achieved). Ozonation of Amoxicillin with 267 mg of O_3 g^{-1} has the opposite effect, as it reduces biodegradability from 100 to 80 %. Mineralization rates ranged from 13 % for Tiamulin, 39 % for Levofloxacin and 49 % for Amoxicillin. *Vibrio fischery* toxicity was not eliminated by ozonation neither with Tiamulin nor with Levofloxacin. The structural changes caused by ozonation in Tiamulin begin with the attack of ozone on the vinyl double bond and the formation of a carboxyl group, followed by the oxidation of sulfur and nitrogen atom, and then the gradual decomposition of the molecule. The disintegration of the vinyl double bond and the formation of a carboxyl group also results a loss of antibiotic activity of the molecule.

Fenton oxidation gives comparable effects as ozonation, however by application of comparativelly high oxidant doses. To achieve 80 % biodegradability of levofloxacin, 1.955 mg of H_2O_2 g^{-1} is needed, which is in terms of oxidant equivalent to 2.760 mg of O_3 g^{-1}. Analogous to ozonation, toxicity with Fenton's reagent cannot be eliminated.

In the case of tiamulin and levofloxacin, the removal of TOC and COD follows zero-order kinetics, however in two stages, where the reaction rate is higher in the first stage of the reaction. The stepwise nature of the reaction may be justified by the analysis of structural changes of the molecule during ozonation, as intermediates appear in the process, which react further with ozone forming end products, which no longer react with ozone. For amoxicillin, however, measurements indicated that the removal of TOC and COD follows variable-order kinetics (from zero to first).

Antibiotic-contaminated (400 mg L^{-1}) biological sludge was also ozonated, showing a synergy between the effect of sludge solubilisation and antibiotic deactivation. Inhibition of biogas production was completely eliminated by ozonation of sludge in doses between 36 and 70 mg of O_3 g_{vss}^{-1} and at the same time the yield of methane in biogas was increased.

The results of the study show that when using advanced oxidation techniques there is no single guide on what to use for which antibiotic, because the results are poorly predictable, especially in terms of oxidation products, which may have completely different properties than the parent molecule. Nevertheless, ozonation undoubtedly has great potential for use in industrial scale biological treatment systems, especially as an antibiotic treatment technique for contaminated sludge prior to anaerobic stabilization.

Keywords

Antibiotics, biological treatment, biodegradability, advanced oxidation processes, sludge waste, oxidation, ozone, toxicity.