DOI: http://doi.org/10.21698/simi.2023.ab27

DETERMINATION OF FLUOROQUINOLONE ANTIBIOTICS IN WASTEWATER USING HPLC-FLD

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Keywords: *antibiotics residues, wastewater, LC, norfloxacin, ciprofloxacin*

Introduction

The excessive use of antibiotics has led to the large-scale emergence of antibiotic resistance genes, which have led to the development of antibiotic-resistant bacteria. These emerging environmental pollutants ultimately impede the effectiveness of life-saving antibiotic therapies. In order to achieve maximum efficiency with minimum waste, in recent years, analytical chemistry is increasingly focused on the development of analysis tools that can use a method with minimal sample preparation. For this reason, liquid chromatography (LC) is still the technique most widely used for the determination of organic compounds in a variety of sample matrices. In the case of the LC technique, the analysis of the molecules of interest in complex matrices requires an efficient preparation of the sample, especially if the analyte of interest is present in the medium at low concentrations.

Materials and methods

The simultaneous determination of two fluoroquinolones: norfloxacin (NOR) and ciprofloxacin (CIP) in wastewater samples was done by a simple and fast method using the High-Performance Liquid Chromatography (HPLC) technique with FLD - G1312A fluorescence (Fluorescence Detector). Due to the close hydrophobicity of the studied pharmaceutical compounds (log Kow NOR) = 0.48 and (log Kow CIP) = 0.28, a C18 stationary phase chromatographic column was used to study their retention and separation. The mobile phase used during the analysis had an isocratic elution, using an aqueous solution of H3PO4 25mM (brought to pH=3) (A) and acetonitrile (B), with a flow rate of the mobile phase of 1 mL/min. The separation time was only 7 min, with the injection volume fixed at 20 µL and at a column temperature of 30^0C.

After using the Strata XAW Polymeric cartridge with Anion Exchanger (6 ml/500mg, Phenomenex) and wastewater sample volumes of only 250 mL, the method offered good selectivity, extraction efficiency, precision with quantification limits of the order of 4.3 ng/ L for NOR and 5.6 ng/L for CIP.

Ten effluent samples were collected during three consecutive days from Bucharest Wastewater Treatment Plant (WWTP).

Results and conclusions

The developed method was applied to determine fluoroquinolone residues in wastewater samples collected from a WWTP in a municipal area. The results obtained for the analyzed wastewater samples (effluent) indicated that NOR concentrations ranged from 54.3 ng/L to 89.9 ng/L, and CIP concentrations ranged from 56.5 ng/L L to 289.8 ng/L. L, compared to NOR concentrations between 24–175 ng/L and CIP concentrations between 11–168 ng/L, as they appear in the 2013 study by Senta et al.[1].

The results of NOR and CIP for all analyzed samples are presented in Table 1.

Table 1. Pharmaceutical residues concentration determined in WWTPs samples

Effluents	Norfloxacin, ng/L	Ciprofloxacin, ng/L
EF-1	62.2	131.4
EF-2	54.3	142.1
EF-3	67.5	56.7
EF-4	73.2	203.8
EF-5	71.8	65.5
EF-6	90.5	284.5
EF-7	78.1	130.4
EF-8	98.9	109.2
EF-9	87.8	289.8
EF-10	62.4	31.8

The method developed for the determination and quantification of CIP and NOR can be used to determine trace compounds in wastewater using the C18 column. This column proved to be efficient even at the ng/L level.

Quantifying the concentrations of antibiotics from the fluoroquinolone class only in the effluent samples and not having information about the detection of fluoroquinolones in the influent samples, the efficiency of the treatment process could not be properly evaluated.

Reference

[1] SENTA, I. TERZIC, S., AHEL, M., 2013, Water Research 47, 705 -714.

Acknowledgments. This work was carried out through the "Nucleu" Program within the National Research Development and Innovation Plan 2022-2027 with the support of Romanian Ministry of Research, Innovation and Digitalization, contract no. 3N/2022, Project code PN 23 22 01 01.