

Measurement of a wide range of pharmaceutical compounds in wastewater influents by SPE-LC-MS/MS

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Abstract: A solid phase extraction (SPE) combined with liquid chromatography *tandem* mass spectrometry (LC-MS/MS) method was optimized and validated for the analysis of pharmaceuticals (PhCs) in wastewater influents. Linearity and working range, analytical thresholds, precision and accuracy were evaluated. The method was applied to the study of twenty four pharmaceuticals compounds from different therapeutic classes in wastewater influents of two Portuguese wastewater treatment plants (WWTP). The majority of the target compounds were consistently detected above quantification limits in all samples. Clofibric acid and some sexual hormones showed occurrence percentages lower than 20%. The most representative PhCs were acetaminophen, caffeine, naproxen, ibuprofen and diclofenac. Acetaminophen was the compound found at the highest concentration (up to 55 µg/L).

Keywords: pharmaceuticals; wastewater; LC-MS/MS

Results and Discussion

The validated LC-MS/MS methods were linear for all target compounds in the selected concentration range (1.5-10 µg/L for pharmaceuticals; 9 to 57 µg/L for hormones and clofibric acid): $0.9984 \leq r^2 \leq 0.9999$, $CV_m \leq 3\%$ and $VT \leq F(0.05; 1; N-3)$. The methods are precise, with $RSD < 11\%$ and 10% under repeatability and intermediate precision conditions, respectively. The instrumental limits of detection (LOD) and quantification (LOQ) were lower than the first concentration level of the working range. Target compounds show recoveries ranged from 33 % (sulfadiazine) to 141 % (diclofenac).

The occurrence studies showed a high percentage of positive samples for the majority of the target compounds, except clofibric acid and sexual hormones estrone, beta-estradiol, 17-alpha-etylnilestradiol and diethylstilbestrol, which were lower than 20%.

Wastewater influents from Beirolas and Faro-Noroeste WWTPs showed similar concentration profile of pharmaceutical compounds: 30 - 32% non-detectable, 13 - 15% higher than LOD, 10 - 12% above LOQ, 25% above 0.1 µg/L, and 17 - 19% above 1.0 µg/L.

This work contributes to a better understanding of pharmaceuticals profile on wastewater influents, being the first step for future studies related to removal efficiencies of the WWTPs.

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