



Determination of pharmaceutical compounds in wastewaters from constructed wetlands using ultra-high performance liquid chromatography with fluorescence detection

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Introduction

Pharmaceutical compounds constitute an important group of active compounds which can produce deleterious effects over aquatic ecosystems when they reach them through wastewaters¹. For this reason, it is necessary to develop treatment methods which permit the elimination of these compounds. Nevertheless, in small communities, the construction of traditional treatment facilities could not be the most suitable option and constructed wetlands (CW) have revealed as a sustainable and economic solution². In this work, we present a methodology based in solid phase extraction (SPE) combined with ultra-high performance liquid chromatography with fluorescence detection (UHPLC-FD) for the determination of five different drugs (acetylsalicylic acid, naproxen, ibuprofen, gemfibrozil and ciprofloxacin) and its application to samples from a pond-CW system.

Materials and Methods

The pond-CW system under study is located in a university area and it consists of a facultative lagoon and a horizontal flow CW. It has been operating since 1999 treating raw wastewater from the campus. The efficiencies for BOD₅ (biological oxygen demand), COD (chemical oxygen demand), total suspended solids and turbidity have been moderately high, over 75%.

OASIS HLB SPE cartridges were used to extract the pharmaceuticals from 250 mL of wastewater at pH=7. After the elution of the target compounds using 5 mL of HPLC methanol, the extracts were dried under a stream of nitrogen and after that, the extracts were reconstituted in 1 mL of methanol, achieving a preconcentration factor of 250.

Regarding the chromatographic procedure, it was performed using an ACQUITY UPLC system with a fluorescence detector and an ACQUITY BEH C₁₈ column (50 x 2.1 mm, 1.7 µm). The separation of the target compounds was done in gradient mode in 7.5 minutes. Excitation and emission wavelengths were also optimized for each compound.

Results and Discussion

The SPE-UHPLC-FD method was applied to real wastewater samples obtained in a natural wastewater treatment plant. Samples from influent, the facultative lagoon effluent and the CW effluent were analysed every week from February to May 2018. The concentrations of the pollutants in the influent were significantly different from those of the effluent. Moreover, the method allowed the evaluation of the removal efficiencies of this natural treatment system.

Naproxen and ibuprofen showed the highest concentrations of detected compounds while acetylsalicylic acid cannot be quantified in any sample.

Conclusion

The development of a SPE-UHPLC-FD method for the determination of pharmaceutical compounds in wastewaters have been successful. Despite of many interferences from the matrix, the developed method has shown a great selectivity and sensitivity, resulting to be appropriate for the determination of the target pharmaceuticals, even at trace concentrations.

Bibliography

¹ A. Wick *et al.* Fate of beta blockers and psycho-active drugs in conventional wastewater treatment, *Water Res*, 2009, 43, 1060–1074

² J.A. Herrera-Melián, *et al.*, Study on the removal of hormones from domestic wastewaters with lab-scale constructed wetlands with different substrates and flow directions, *Environ Sci Pollut Res Int*,