REMOVING PHARMACEUTICAL RESIDUES FROM CONTAMINATED WASTEWATERS USING EXPANDED CLAY AGGREGATES

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Pharmaceutical compounds (PhCs) are ingested in large quantities by humans in treatment and prevention of disease, but they are only partially absorbed by the organisms being excreted together with their metabolites. The sewage treatment plants (STP) are only able to partially remove some of these compounds and, despite the low concentrations present in the wastewaters (ng-µg/L), these xenobiotics can still pose a serious threat to the aquatic environments.

Sub-surface flow constructed wetland systems (SSF-CWS) are biological systems used in wastewater treatment, and clay materials can be used as support matrices for these systems. Clay materials act not only as filters but they also can potentially remove organic pollutants due to its sorption properties.

In this study a processed clay material, light expanded clay aggregates (LECA), was tested for their sorption capacity towards three widespread water polluting pharmaceuticals, namely clofibric acid (CA), ibuprofen (IB) and carbamazepine (CB). Sorption assays were done with aqueous solutions of the individual compounds and with their mixture at different concentrations from 1.0 to 50.0 mg L^{-1}. The sorptive properties of LECA were also investigated using wastewater spiked with a mixture of the three compounds at the same concentrations tested for the aqueous solutions.

Reversed phase HPLC with UV-Vis detection at 210, 222 and 227 nm for CB, IB and CA respectively was used to measure the compounds

concentrations. For the single-compound solutions the HPLC analyses were performed in isocratic mode with a mobile phase composed by 75:25 acetonitrile:water with 0.1% (v/v) phosphoric acid. For the solutions containing the three compounds, the separation was performed using the same elution solvents and a gradient program. The total run time was 8 minutes, the flow rate was 1.0 mL min^{-1} and the injection volume was 20 µL. Calibration curves were constructed for standard solutions of CB, IB and CA individually, as well as solutions containing the three mixed compounds. The average areas of the compounds' peaks were plotted against the standards concentrations resulting in linear correlations with R^2 equal to or higher than 0.999 in every calibration curve. Whenever the measured concentrations were below the method's LOQs of 0.27 mg L^{-1}, 0.39 mg L^{-1} and 0.13 mg L^{-1} for CB, IB and CA respectively, the samples were pre-concentrated on LiChrolut® RP-18. All data were analyzed by the analysis of variance method (ANOVA, single factor) at different significance levels.

Results for the individual compounds in aqueous solutions have shown that LECA presents higher removal rates for IB and CB (44 – 92% and 60 – 95% respectively) whereas for CA the removal rates are moderate but still significant (30– 58%). In any case, and for all the studied compounds, the % removal decreased with the increasing load, the lower % removal still correspond to increasing absolute amounts sorbed. When the three compounds are put simultaneously in contact with LECA there are evidences of competitive sorption among the studied compounds, with CB being the less affected compound of the three. When all the compounds were dissolved in wastewater, there was a slight loss of removal efficiency, probably due to an increased solubility in the aqueous media owing to the organic matter present in the wastewater or to competitive sorption effects.

Considering the hydraulic and physico-chemical properties of LECA which make this material suitable for constructed wetlands applications, its sorption properties evidenced in this work make it especially interesting for applications aiming at the removal of this kind of pollutants from wastewaters.