Removal of pharmaceuticals in constructed wetlands using Typha and LECA. A pilot-scale study.

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INTRODUCTION

An ever-increasing number of xenobiotic compounds are getting detected in environmental samples worldwide. Serious concern about the contamination of water resources and drinking water supplies has aroused from the prevalence of pharmaceutical residues in the aquatic ecosystems.

Some pharmaceuticals such as ibuprofen, carbamazepine and clofibric acid are frequently detected in waters [1]. These compounds are generally quantified at low concentrations (at the ng/L or µg/L range) but, due to their persistence in the environment and to potentially cumulative effects in the organisms, studies have shown that these compounds can have some damaging effects on the aquatic ecosystems [1].

Several xenobiotic organic compounds have already been removed from contaminated waters using constructed wetlands (CW) where the processes occurring in natural wetlands can be optimized in engineered man-made ecosystems, specifically designed for wastewater treatment. Among several physico-chemical phenomena, sorption by the support matrix plays an important role in the contaminant removal mechanisms. It is important to select a matrix with a high sorption capacity, which will depend on the physico-chemical properties of the material chosen. Previous studies have shown that expanded clay (LECA) is capable to remove, by sorption, this type of substances from water [2]. CWs also take advantage of the ability of plants to adsorb, uptake and concentrate pollutants, as well as to release root exudates that enhance compound biotransformation and degradation. Wetland species such as the cattail (*Typha spp.*) have already been tested and found suitable for the removal of several organic compounds from wastewaters, being commonly used in CWs [3].

The aim of the present work was to evaluate the efficiency of a subsurface flow constructed wetland assembled with the plants *Typha spp.* and LECA as support matrix, for the removal of three pharmaceuticals, namely ibuprofen, carbamazepine and clofibric acid, from contaminated waters.

MATERIALS AND METHODS

Chemicals, support matrix and plants

The pharmaceuticals tested were carbamazebine, CAR, (CAS: 298-46-4), ibuprofen, IBU, (CAS: 15687-27-1) and clofibric acid, CA, (CAS: 882-0907).

The support matrix used was light expanded clay aggregates (LECA) with particle sizes of 1.6-5.5 mm (grade 2/4). A native plant species, cattail, *Typha sp.*, was used due to its adaptability to the assays conditions.

Characterization of the support matrix

In order to obtain a physico-chemical characterization of the support matrix, properties such as pH, electrical conductivity, porosity, bulk density and hydraulic conductivity were measured. Mineralogical composition of the LECA was determined by X-ray diffraction. The morphology and macroporous structure of the particles was analysed by optical observation of polished surfaces and thin sections at a transmitted light microscope.

Batch experiments of pharmaceuticals removal by cattails beds

A pilot-scale CW using washed LECA (2/4) as support matrix and employing subsurface flow was set up with and without plants. Four beds were planted with pre-grown cattails (density of 80 plants/m^2) and four were left unplanted as controls. Experiments were conducted in a fed batch mode with a flooding rate of 70% and 1:3 (v/v) water to matrix ratio. The pH of the solutions was monitored during the assays.

Pharmaceutical amounts were quantified by high performance liquid chromatography with UV detection at 210 nm (CAR), 222 nm (IB) and 230 nm (CA). The reverse phase analytical column used was a Zorbax Elipse XDB-C18 with 5 µm particle size. Solid phase extraction (SPE) with C_{18} columns was used whenever the measured pharmaceutical concentration fell under the limit of quantification (LOQ) of the analytical method.

RESULTS AND DISCUSSION

Characterization of the support matrix

LECA has a PZC of 8.5 and water in contact with LECA has a pH of 9.4. Its hydraulic conductivity was measured as 7.7×10^{-3} m^3 m^{-2} s^{-1}. Thin section observation shows that LECA is an extensively porous material with a highly interconnected porous structure with a wide pore size distribution. XRD results show that it is mainly composed of quartz and in smaller amounts of hercynite and anorthite. Traces of calcite were also found.

Pharmaceuticals removal by cattails beds

When planted in the LECA beds, *Typha sp.* showed an increased tolerance to the pharmaceutical compounds tested, with no visible signs of toxicity for the tested concentrations. Cattails beds showed high removal efficiencies for all compounds tested and the presence of cattails, when compared to the unplanted control beds, showed significant contributions (10% - 20%) to the pharmaceuticals removal rates.

CONCLUSIONS

LECA presents important advantages as support matrix in CWs because it has a high sorption capacity for the tested pharmaceuticals. In addition it has a pH buffer capability near neutral conditions (pH ~ 7-8) and a good control of hydraulic permeability which makes it an appropriate medium for plant growth. Cattails enhanced the pharmaceuticals removal rates, showing a good tolerance for these compounds at the tested concentrations. In conclusion, this combination of matrix and plants seems promising for setting up CWs for treating pharmaceutical contaminated waters.

REFERENCES

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