Sorption behavior of granular matrices for application in pharmaceutical removal by SSF constructed wetlands

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INTRODUCTION

In recent years, the occurrence and fate of pharmaceutically active compounds (PhACs) in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry. Clofibric acid, ibuprofen and carbamazepine are some of the most frequently found PhACs in environmental monitoring studies.

Some xenobiotics have already been successfully removed from contaminated waters using constructed wetlands (CW). Depuration of wastewaters in CWs is achieved by the concerted action between plant rhizomes, microorganisms and matrix component. CWs efficiency can be significantly improved by careful selection of the matrix, plants and microorganism used.

Among several physico-chemical phenomena, sorption by the matrix plays an important role in the PhACs removal mechanism. It is important to select a matrix with a high sorption capacity, which depends on the physico-chemical properties of the material chosen.

Previous studies carried out by the authors showed that expanded clay (LECA) presents a high sorptive affinity by clofibric acid [1]. The aim of the present work was to evaluate the capacity of LECA to remove other PhACs, namely ibuprofen and carbamazepine, and compare the results obtained with these pharmaceuticals with those obtained previously with clofibric acid. In addition, other materials were tested for the removal of clofibric acid and the results were compared with those obtained with LECA. The ultimate objective of this work will be to optimize the performance of this component in the overall performance of a constructed wetlands system designed for the removal of PhACs from wastewaters.

MATERIALS AND METHODS

Chemicals and support matrices

In the assays, solutions of clofibric acid (CA), ibuprofen (IB) and carbamazepine (CZ) were used with concentrations ranging from 1 to 50 ppm. The concentrations of these chemicals in water were quantified by UV/Vis spectrophotometry (λ_{CA} = 227.6 nm; λ_{IB} = 210.0 nm; λ_{CZ} = 285.0 nm). Three different types of support matrix were used: light expanded clay aggregates (LECA), sepiolite and exfoliated vermiculite. In our assays two types of LECA were used, with particle sizes of 1.6-5.5 mm (grade 2/4) and 5.5-12.5 mm (grade 3/8).

Characterization of the support matrices

In order to obtain a physico-chemical characterization of the several support matrices, the following properties were studied: pH, electrical conductivity, porosity and bulk density. The mineralogical composition of the support matrices was determined by X-ray diffraction. The morphology and macroporous structure of the particles was analyzed by optical observation of polished surfaces and thin sections at a transmitted light microscope.

Sorption of pharmaceuticals by LECA

A series of batch sorption assays were carried out to investigate how the ibuprofen and carbamazepine sorption capacities by LECA are influenced by some experimental parameters such as the contact time and initial compound concentration (1 ppm upto 50 ppm).

Sorption of clofibric acid by sepiolite and exfoliated vermiculite

A series of batch sorption assays were carried out to investigate how the clofibric acid sorption capacities by sepiolite and vermiculite are influenced by some experimental parameters such as the contact time and initial clofibric acid concentration (1 to 50 ppm).

RESULTS AND DISCUSSION

Characterization of the matrices

Table 1. Main characteristics of the materials tested

Matrix	pH (water)	Conductivity (μS/cm)	X-ray analysis	Porosity (%)	Bulk density (kg/m^3)
LECA 2/4	9.3	188	crystalline	47	417
LECA 3/8	9.7	213	crystalline	40	256
Sepiolite	9.0	177	crystalline	40	631
Vermiculite	7.3	119	crystalline	68	333

Sorption of pharmaceuticals by LECA

The effect of contact time and initial concentrations of the pharmaceuticals on the sorption by LECA was studied. In the range of concentrations studied (1 to 50 ppm), equilibrium is attained within 96 to 144 hours of contact with IB solutions and after 168 hours for CZ solutions. LECA (3/8) showed maximum IB removals between 51% and 100%, while removal efficiencies between 59% and 80% were attained for CZ. Lower initial concentrations had the highest removal efficiencies within the shortest equilibrium period. In comparison with CA (removal efficiencies of 4% – 22%) [1], the results showed that LECA has a significantly higher sorption capacity for these two pharmaceuticals. Assays with LECA (2/4) have reached sorption capacities in some cases triple to those of LECA (3/8).

Sorption of clofibric acid by sepiolite and exfoliated vermiculite

The effect of contact time and initial CA concentrations on sorption behavior by sepiolite and vermiculite was studied. In the range of concentrations studied (1 to 50 ppm), equilibrium is attained within 96 to 120 hours of contact with sepiolite and after 24 hours with expanded vermiculite. AC removal efficiencies obtained with sepiolite varied between 35% and 67%, while with expanded vermiculite removal efficiencies between 35% and 43% were observed. In comparison, the results showed that none of the materials achieves sorption capacities for CA as high as LECA (2/4).

CONCLUSIONS

LECA presents important advantages as support matrix in CWS because it has a high sorption capacity for PhACs tested. Finer particles of LECA achieve higher removal efficiencies due to the larger surface area available for sorption. The other tested support matrices do not show significant improvements in sorption capacity relative to LECA (2/4). In conclusion, expanded clay-based systems seem promising for removing some PhACs from contaminated waters.

REFERENCES

[1] Dordio, A.V.; Teimão, J.; Ramalho, I.; Palace Carvalho, A.J.; Estêvão Candeias, A.J. (2007) *Sci. Total Environ.*, doi:10.1016/j.scitotenv.2007.02.015 (in press).