Rapeseed Press Cake Immobilization for Removal of HOP in Water

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Introduction

There has been an increasing concern about the release of hydrophobic pesticides to the environment by agricultural activities due to the known toxicity of such substances (Mackay and Fraser, 2000) and the fact that many are already finding their way into drinking water supplies and food products (Margni, et al., 2002). Such compounds have a tendency to be stocked in adipose tissues and are accumulated all along the trophic chain. Previous experiments demonstrated that oilseed press-cakes (PC) have the ability to absorb hydrophobic organic pollutants (HOP) in the residual oil remaining after pressing of seeds (Boucher, 2006). Crude rapeseed PC has a granular structure, but addition of water leads to the formation of a slurry. This causes many problems, such as difficulties to separate the liquid from the solid phase, or clogging when running columns in the case of continuous sorption applications.

An alternative for solving this problem is the immobilization of PC in a matrix, allowing a physical separation between solid and liquid phases. Formation of homogeneous beads containing PC aggregates can be envisaged by mixing an alginate solution with the crude PC powder and then extruding small droplets in a Ca^{2+} solution to cause alginate gelation. The aim of this study is to assess feasibility, kinetics and efficiency of such a system using atrazine as a model pesticide, to envisage a further large-scale application for wastewater treatment in case of local contamination.

Material and methods

Alginate solution 1-5% (w/v) was mixed with crude rapeseed press cake 5-15 % (w/v) and was then extruded through a syringe needle. Droplets were then collected in a gelation bath containing 100mM $CaCl_2$ and 10mM MOPS (pH 7). In certain cases, beads were placed in a drying oven for 24 hours at 64°C to achieve a complete dehydration.

***Figure 1**: Crude rapeseed press cake*

***Figure 2**: Optimal beads (2% alginate, 10% PC)*

To assess kinetics and efficiency, a known amount of beads was then collected and added to a defined volume of atrazine solution 33mg/L. Atrazine was monitored in the aqueous phase by analytical HPLC, using a Luna C18 column (Phénomenex®). The mobile phase was a mixture of acetonitrile and water (70:30) and a diode array detector set to 220 nm was used.

Results and Discussion

Immobilization

Criteria to evaluate the optimal condition for PC immobilizations are the shape of the gelled beads, the homogeneous repartition of PC in the matrix and the mechanical resistance and stability of the spheres formed. From these considerations, the optimal conditions were found using a 2% alginate solution containing 10% of crude PC, leading to 2mm radius beads (Figure 2). To increase the sorption efficiency, a larger amount (up to 45%) of PC can be added to the alginate solution, but extrusion leads to formation of "sticks". Moreover, an increase in alginate concentration (up to 5%) is necessary to avoid PC release.

Kinetics

Initially, experiments without press cake were carried out to assess the effect of alginate matrix on the diffusion of atrazine. The diffusion coefficients determined were from $7.65 \cdot 10^{-6}$ to $1.05 \cdot 10^{-6}$ cm^2/s for alginate solutions ranging from 1 to 5%, while its value in water is $6.18 \cdot 10^{-6}$ cm^2/s (Cornelissen, et al., 2005). It can therefore be assumed that with low concentrated alginate solutions, the effect of the matrix on the diffusion of atrazine is negligible. Experiments with press cake highlighted that immobilized rapeseed presscake shows a significantly slower kinetics compared to the free presscake, and thus that mass transfer limitation occurs (Figure 3). Since increasing the agitation doesn't affect the results, it can then be deduced that the limitation takes place in the bead itself. As it is unfortunately not possible to increase agitate within the alginate matrix, it is not possible to increase the atrazine sorption with particles of this size.

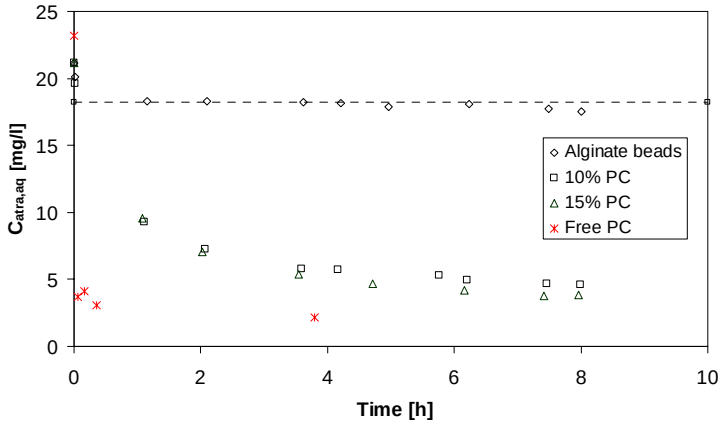

Figure 3: *Concentration of atrazine in aqueous phase as a function of time*

However, after 5 hours, the final equilibrium concentration observed is the same, proving that the efficiency is comparable in both cases.

Sorption Efficiency

Since it is known that the residual micro-droplets of oil in the press cake are responsible for the sorption of atrazine, it is important to compare efficiency of immobilized PC to free PC. Various atrazine solutions of different concentrations were added to the beads, and the concentration of atrazine in solution at equilibrium was measured. From a mass balance, the amount of atrazine in the press cake can be calculated, and the partition coefficient of atrazine ($K_{pc/w}$) between press cake and water was then determined (Figures 4 and 5).

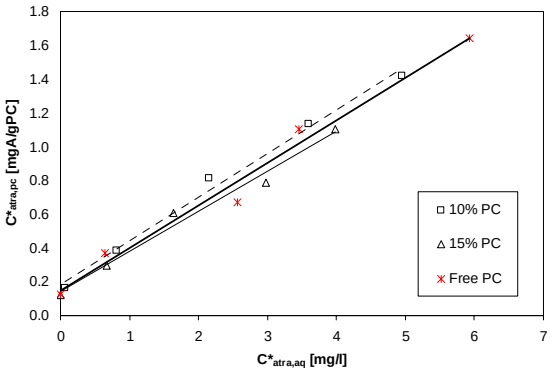

Figure 4: *Sorption isotherm of atrazine between PC and water*

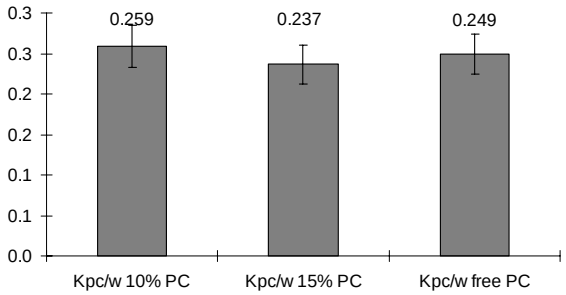

Figure 5: *Partition coefficient of atrazine between PC and water*

From these data, it is demonstrated that the efficiency of sorption and partition coefficient of atrazine for immobilized press cake are as efficient as for the free one.

Large-Scale Process Development

To apply the system previously studied to a large-scale process, the beads could be dried in order to reduce their weight and volume, which would then facilitate transportation. Nevertheless, their efficiency after drying has to be evaluated. The kinetics and efficiency of sorption were compared for fresh beads, dried beads rehydrated before the sorption process, and non-rehydrated dried beads (Figures 6 and 7).

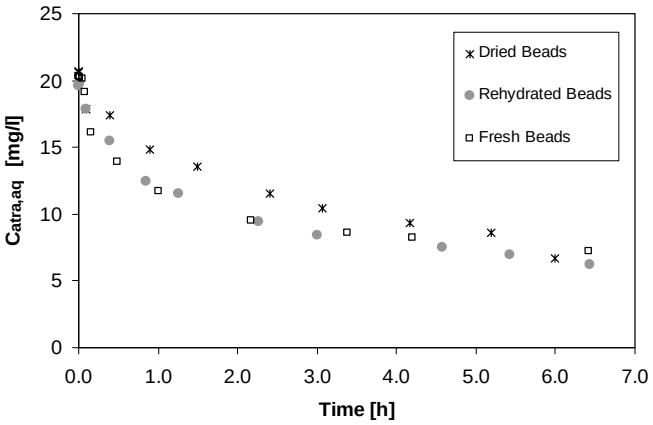

Figure 6: *Sorption of atrazine as a function of time*

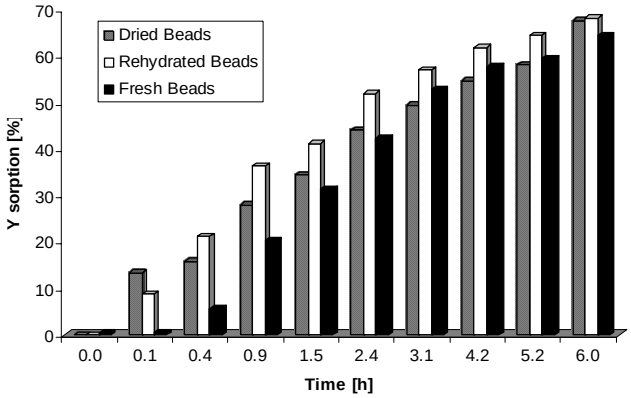

Figure 7: *Sorption of atrazine as a function of time*

Results on figure 6 show that prior rehydration leads to a similar comportment to fresh beads. The kinetics of sorption for dried beads is however slower, but the final equilibrium concentration measured is the same. As a consequence, for a large scale process, dried beads can be used, but it is preferable to rehydrate them before use. Nevertheless, the activity and efficiency remains similar than with fresh beads, which is a great advantage.

Conclusions

This study showed it was possible to immobilize rapeseed press cake in an alginate matrix. The activity of the press cake towards atrazine sorption is preserved, and separation of aqueous phase from the solid one is clearly facilitated.

Compared to free press cake, the kinetics of sorption is slower, and is due to mass transfer limitations within the bead. As it is not possible to induce turbulence inside the matrix containing the biosorbent, it is not then be possible to increase the rate of sorption reaction. However, the total amount of atrazine removed from the aqueous solution is the same with both free and immobilized press cake, showing that the immobilization process does not affect sorption capacity.

Aiming at developing a large scale process, beads were dried in order to reduce their weight and volume, especially to reduce transportation costs. The experiments showed that activity and kinetic were comparable to fresh beads, but that it would be preferable to rehydrate the beads before the sorption process.

References

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