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Immobilization of rapeseed press-cake in an alginate matrix for the sorption of atrazine

V. Breguet[a], J. Boucher[a], F. Pesquet[a], V. Vojinovic[a], U. von Stockar[a], I.W. Marison[b,*]

[a]Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Chemical and Biochemical Engineering (LGCB), Station 6, CH 1015 Lausanne, Switzerland

[b]School of Biotechnology, Dublin City University, Glasnevin, Dublin 9, Ireland

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ABSTRACT

Due to residual oil retained within it, rapeseed press-cake has been shown to be effective for the removal of atrazine from water through an absorption mechanism. However, it is difficult to put this into practice due to the hygroscopic nature of the press-cake resulting in considerable swelling, together with the formation of a thick paste which hinders phase separation. In order to overcome this, press-cake has been immobilized in an alginate matrix. The kinetics and sorption efficiency of this immobilized press-cake to absorb the model pesticide atrazine, has been studied. The results show that the rate of atrazine removal is slower than for free press-cake, although the total amount of atrazine removed is the same ($K_{pc/w} = 0.25$). Phase separation was greatly simplified. The alginate immobilized press-cake could be dried, in order to reduce volume and weight, with no adverse effect on atrazine removal kinetics or sorption properties.

1. Introduction

There has been increasing concern about the release of hydrophobic pesticides and other organic compounds to the environment as a result of agricultural activities due to the high toxicity of these substances (Mackay and Fraser, 2000) and the fact that many are finding their way into drinking water supplies and food products (Margni et al., 2002). Hydrophobic organic pollutants (HOP), are generally characterized by high toxicity and long environmental half-life. As a result, they represent a serious concern for the remediation of contaminated waters and have long been reported to be priority pollutants (Carlsen and Walker, 2003; Eljarrat and Barcelo, 2003; Keith and Telliard, 1979). Due to their poor aqueous solubility, techniques for the treatment of large volumes of weakly concentrated effluents are limited and costly. Notwithstanding the low concentration, HOP may cause serious health and environmental problems, as they accumulate in adipose tissues and all along the trophic chain.

Degradation of HOP (e.g. atrazine) by chemical (Chiron et al., 2000; Ma and Graham, 2000; Saltmiras and Lemley, 2002), physical (Brown et al., 2004; Johnson et al., 2000; Parra et al., 2004) and, above all, biological means (Katz et al., 2000; Masaphy et al., 1996; Schwitzguébel, 2001), has given rise to a prolific literature during the last two decades. Out of the myriad of techniques undergoing research and development, those emerging as potentially real applications are very anecdotic (Felsot, 1996). This arises from the need to preconcentrate very diluted effluents in order to render these techniques viable. Techniques suitable for preconcentration

*Corresponding author. Tel.: +353 1 700 8393; fax: +353 1 700 5412

Abbreviation: AG, alginate; PC, press cake; Aq, aqueous phase; W, water; 0, initial time; ∞, equilibrium.

E-mail addresses: veronique.breguet@epfl.ch (V. Breguet), Julien@balidar.com (J. Boucher), florencepesquet@gmail.com (F. Pesquet), vojislav.vojinovic@epfl.ch (V. Vojinovic), urs.vonstockar@epfl.ch (U. von Stockar), ian.marison@dcu.ie (I.W. Marison).

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Nomenclature

C	Atrazine concentration, $mg\,L^{-1}$
D	Diffusion coefficient, $cm^2\,s^{-1}$
$K_{x/y}$	Partition coefficient between phase x and y, dimensionless
V	Volume of solution, L
Y	Sorption yield, %
a	Bead radius, cm
m	Mass, mg
r	Distance from the centre of the bead, cm
t	Time, s

are very limited, very expensive and require considerable energy. For this reason the need to find cheap, single-use, sorbents, such as biosorbents, has been emphasized in recent years (Aksu, 2005; Volesky, 2002).

Biosorbents are materials of biological origin, often composed of secondary industrial or agricultural by-products or organic wastes, such as algae, bacteria, plants, yeast or fungi. Among biosorbents, those originating from agricultural by-products, such as crop wastes, are particularly interesting because of their low-cost and ubiquity. Vegetal material can be considered as very heterogeneous, containing many binding sites, thereby resembling a multichromatographic system with partition (absorption) and adsorption chromatography on varied polarity supports. Indeed vegetal lipophilic phases (waxes, suber, oil) enable absorption of HOP (Briggs et al., 1982; Chefetz, 2003; Raveton, 1992) in addition to adsorption on binding sites of cell membranes, walls or other biopolymers (Antoine et al., 2003). Oilseeds are members of many different plant families and species and are widely used to produce oils and fats for human and livestock consumption, industrial applications and biofuels (Salunkhe et al., 1992). Moreover, among vegetal material oilseeds show the highest content of a lipophilic phase (from 20% to 50% [w/w] oil according to species) and it would therefore seem appropriate to use seeds or oil-containing agricultural by-products as biosorbents for HOP removal from aqueous environments.

Previous work demonstrated that oilseed press-cakes (PC) have the ability to absorb HOP in the residual oil remaining after pressing of seeds (Boucher et al., 2007). The sorption mechanism was demonstrated to be through absorption in the residual oil associated with the PC remaining after pressing of seeds. This residual oil is tightly retained within the fibrous matrix of PC and is not released into the aqueous phase, even under harsh shaking conditions. Thus PC constitutes a promising biosorbent for removing HOP from an aqueous phase. Moreover, PC is a low cost agricultural by-product, often considered to be a waste, that does not need to be reused—as, for example, in the case of activated carbon—to be economically viable. PC can be incinerated (Salunkhe et al., 1992) and organic pollutants, once concentrated in the PC, can thus easily and efficiently be degraded.

However, although crude rapeseed PC has a granular structure, the 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, that would allow for 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 into a Ca^{2+} solution to cause alginate gelation. Successful applications based on alginate immobilization systems have already been developed to remove heavy metals from water, immobilizing fungal species (Bayramoglu et al., 2002), or simply using the alginate gel intrinsic properties (Veglio et al., 2002). It has also been reported that activated carbon may be encapsulated in alginate to remove pesticides from contaminated water (Lin et al., 2005).

The aim of this study is to assess the feasibility of such a system, using atrazine (2-chlor-4-ethyl-amino-6-isopropylamino-1,3,5-triazine) as a model HOP pesticide because of its worldwide use, serious environmental concern (Renner, 2004) and abundant documentation. Atrazine is a hydrophobic molecule ($\log K_{0/w} = 2.5$ at 25 °C), poorly soluble in water ($33\,mg\,L^{-1}$ at pH 7 and 20 °C), and poorly volatile (vapor pressure at 25 °C = 0.039 mPa). Atrazine is known to have a carcinogen potential, and also to induce mutagenesis. According to the World Health Organization, the atrazine threshold limit in drinking water is $2\,mg/m^3$. Kinetics and efficiency have been assessed, in order to determine the feasability of using such a system for the treatment of polluted water.

2. Material and methods

2.1. *Atrazine quantification*

Atrazine (2-chlor-4-ethyl-amino-6-isopropylamino-1,3,5-triazine) was obtained from Riedel de Haën (Seelze, Germany). Stock solutions were prepared by dissolving the hydrophobic organic compound in deionized water at a concentration corresponding to the water solubility (33 mg/L at 20 °C; Tomlin, 1994) with stirring, sonication and gentle warming, followed by filtration on a nitrocellulose membrane (Schleicher and Schuell, NC20, Dassel, Germany) to remove all undissolved material. Standard solutions were prepared in methanol and stored at 4 °C until required for calibration of the HPLC method for determination of the atrazine concentration. Atrazine in the aqueous phase was quantitatively determined using an analytical HPLC, with a Luna C18 column (Phenomenex), a mobile phase of acetonitrile and water (70:30) and a diode array detector set to 220 nm.

2.2. *Press-cake*

Fresh rapeseed PC resulting from cold pressing of rapeseed (*Brassica napus*) seeds was obtained from Eco-Energie SA (Etoy,