Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Controlled Release 108 (2005) 132–139

journal of controlled release

www.elsevier.com/locate/jconrel

Controlled release of the herbicide simazine from computationally designed molecularly imprinted polymers

Elena V. Piletska *, Nicholas W. Turner, Anthony P.F. Turner, Sergey A. Piletsky

Institute of BioScience and Technology, Cranfield University, Silsoe, Bedfordshire, MK45 4DT, UK

Received 10 May 2005; accepted 21 July 2005
Available online 19 August 2005

Abstract

The present study describes the development of materials suitable for environmental control of algae. Molecularly imprinted polymers (MIPs) were used as simazine carriers able to provide the controlled release of simazine into water. Three polymers were designed using computational modelling. The selection of methacrylic acid (MA) and hydroxyethyl methacrylate (HEM) as functional monomers was based on results obtained using the Leapfrog™ algorithm. A cross-linked polymer made without functional monomers was also prepared and tested as a control. The release of simazine from all three polymers was studied. It was shown that the presence of functional monomers is important for polymer affinity and for controlled release of herbicide. The speed of release of herbicide correlated with the calculated binding characteristics. The high-affinity MA-based polymer released ~2% and the low-affinity HEM-based polymer released ~27% of the template over 25 days. The kinetics of simazine release from HEM-based polymer show that total saturation of an aqueous environment could be achieved over a period of 3 weeks and this corresponds to the maximal simazine solubility in water. The possible use of these types of polymers in the field of controlled release is discussed.

Keywords: Molecular imprinting; Computational modelling; Simazine; Herbicide; Controlled release

1. Introduction

Simazine is one of the most popular photosynthesis-inhibiting herbicides. It is used in many countries to kill broad-leaved weeds and also to control vegetation and algae in farm ponds, fish hatcheries, swimming pools, fountains, ornamental fish ponds and water-recirculating cooling towers. Although the PAN Pesticide Database (http://www.pesticideinfo.org/Index.html) informs that in some concentrations simazine might be toxic to fish and aquatic ecosystems, simazine is generally considered as non-toxic for most species [1,2]. Although EU directives have banned the use of simazine on non-cropped land, its use is still permitted on cropped land and in orna-

* Corresponding author. Tel.: +44 1525 863534; fax: +44 1525 863533.
E-mail address: e.piletska@cranfield.ac.uk (E.V. Piletska).

0168-3659/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jconrel.2005.07.016

mental water (ponds, aquariums) [3]. According to available literature, simazine is effective at controlling unicellular and attached filamentous algae at a concentration of 0.1–1 mg L^{-1} [2,4].

It is well known that it is extremely difficult to keep pond water in good condition. During the spring when the temperature goes above 10 °C, the water becomes green due to uncontrolled growth of different types of algae (Fig. 1). There are many commercial products which can be used for algae control and most of these products have simazine or 2-chloro-4,6-bis (ethylamino)-*s*-triazine as the only active ingredient. These products are available in liquid, tablet or powder form. It is recommended to add simazine products regularly to the water in order to keep it clear from filamentous (blanket weed) and unicellular algae. Unfortunately, simazine administration in this way is labour intensive, time-consuming and also has one important additional drawback in that it results in fluctuation of the simazine concentration. This could lead on the one hand to uncontrolled algae growth and, on the other, irreversible damage to other organisms or whole ecosystems. The recommendations of the commercial producers tend to underestimate the working concentration of simazine and go for a maximum soluble level, which corresponds to 3.5–5 mg L^{-1}. An innovative solution is required in order to find a user-friendly, simple and controlled method of simazine administration. The ideas presented in this paper work toward this by the design of a specific molecularly imprinted polymer (MIP), which could release the template at required rate.

Fig. 1. A typical view of a pond infested with filamentous and unicellar algae.

Molecular imprinting technology is known as a method of preparation of specific recognition sites by formation of the complex between template and functional monomers [5]. The molecular complex between template and functional monomers is preserved using excess of polymerisable cross-linker. Thermal or photochemical initiated polymerization produces a highly cross-linked insoluble polymer. The extraction of the template from the MIP creates cavities in the matrix, which are complementary in both shape and chemical functionality to those of the template. Traditional fields of MIPs application include separation [6–8], synthesis and catalysis [9,10] and sensors [11,12]. These applications are mainly based on the selective adsorption characteristics of molecular imprinted polymers.

The application of desorption properties of MIPs is a relatively new area. Early studies delivered promising results that showed that these affinity materials could be used for controlled delivery of drugs [13–15]. Although molecular imprinting technology has a potential for creating custom-made carriers for variety of chemicals and biomolecules, intensive development and optimisation is necessary in order to bring the controlled release application into practice. Among the features, which should be included in a "dial-the-MIP" protocol, is the rational selection of the functional monomers, polymer format and increasing the polymer capacity.

In this paper, a feasibility study on the possibility of using a simazine-specific molecularly imprinted polymer for controlled release of simazine into water is described. As far as we know, it is the first report on the application of MIPs for sustained release of herbicides into the environment.

2. Materials and methods

2.1. Materials

Acetonitrile, dimethyl formamide (DMF), water (all HPLC grade), ethylene glycol dimethacrylate (EGDMA), 1,1-azobis(cyclohexanecarbonitrile), MA were purchased from Sigma (UK). HEM was purchased from Aldrich (UK). Simazine was purchased from Riedel-de Haën (Fluka, UK).