



Macromolecular Nanotechnology

Novel imprinted nanocapsule with highly enhanced hydrolytic activity for organophosphorus pesticide degradation and elimination



Heguang Shi, Ruiyu Wang, Jixiang Yang, Hongqi Ren, Shuai Liu, Tianying Guo*

Key Laboratory of Functional Polymer Materials (Nankai University), Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Weijin Road, No. 94, Tianjin 300071, China

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ABSTRACT

The removal of organophosphorus pesticide residues is of great importance to environment treatment nowadays. In this work, we designed a novel imprinted hollow nanocapsule which could effectively eliminate organophosphorus pesticide residues remained in water environment. The shell of the methyl parathion imprinted nanocapsule was prepared based on a multi-pyridine-ligand functional monomer, N-(4-vinylbenzyl)-di(2-picoly) amine. The obtained nanocapsule showed a high catalytic efficiency towards methyl parathion, with an initial hydrolysis rate of 3.1×10^{-2} mM/h, 355-fold relative to the self-hydrolysis of methyl parathion. And a low K_m value, 0.6 mM, was observed, indicating a good affinity of functional ligand on the nanocapsule towards methyl parathion. Additionally, the obtained hollow nanocapsule could further remove p-nitrophenol generated in the catalytic degradation system, another hazardous substance, by enriching part of p-nitrophenol in its central cavity.

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1. Introduction

Organophosphate compounds (OCs), such as paraoxon, parathion, and malathion, have been widely used as pesticides in agricultural productivity [1,2]. However, they have been proved to be extremely hazardous for human health because they may inhibit main metabolic pathways by inhibiting acetylcholinesterase, the key enzyme in the transmission of nerve impulses [3–5]. Due to their high resistance to spontaneous hydrolysis, OCs may persist in earth for a long time, adverse to the ecology. So pesticide residues in vegetables, fruits, water and earth are drawing more and more attention.

To remove OCs effectively, a number of catalysts to date have been discovered to accelerate their degradation, including inorganic metal ions or metal-oxides [6,7], metal ion complexes [8,9], bio-enzymes [10,11] and so on. Among these catalysts, bio-enzymes have been considered to be the ideal decontaminating agent towards OCs, with the advantages of high catalytic activity, no environment pollution. The typical one is organophosphorus hydrolases, which can detoxify a broad range of toxic organophosphate pesticides [12]. Although owing impressive catalytic capabilities, natural bio-enzymes may possess some disadvantages such as instability of enzyme structure, sensitivity to harsh process conditions, non-recovery of enzyme from the reaction mixture, and high cost of separation, thereby restricting their practical applications for large-scale enzymatic degradation [13]. To avoid these shortcomings mentioned above and

* Corresponding author.

E-mail address: tyguo@nankai.edu.cn (T. Guo).

simultaneously obtain high catalytic capabilities, chemists began to devote to designing molecular structures similar to bio-enzyme several years ago, so mimicking of bio-enzyme by synthetic chemistry gradually became the top subject of organophosphate degradation. So far, outstanding progress has been made to mimic bio-enzyme with several model systems, including synthetic macrocyclic compounds [14,15], molecular assemblies, catalytic antibodies [16], and molecularly imprinted polymers (MIPs) [17–20]. Among these methods, molecular imprinting has been demonstrated to be a promising and facial method, which can effectively mimic bio-enzyme with high catalytic capability towards OCs [20–26]. In comparison with natural bio-enzyme, molecularly imprinted polymers (MIPs) possess many advantages such as low cost, superior stability, easy preparation and storage [27–29].

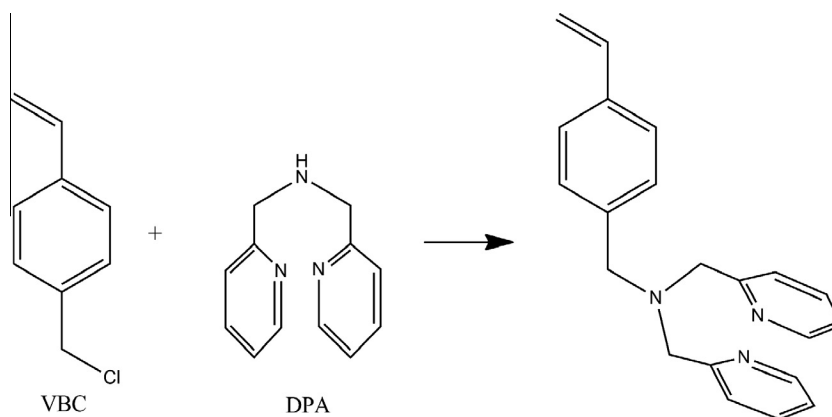
Molecular imprinting is a technique to generate active sites in highly cross-linked polymers with specific shape having functional groups in a defined orientation. The formation of imprinting efficiency is mainly based on the interactions between template and functional monomer such as covalent interactions, non-covalent interactions, electrostatic interactions, and metal ion coordination interactions. It has been demonstrated that constructing active sites by metal ion coordination can remarkably increase the catalytic activity. Recently, much research has been made to deeply investigate the structure of phosphoesterase [30–34] and a series of biomimetic compounds based on multi-pyridine ligands have been synthesized to mimic active functional domain of phosphoesterase, such as 2,6-bis((bis(pyridin-2-ylmethyl)amino)methyl)-4-methylphenol, where the pyridine residues are mimics for histidine, part of phosphoesterase [32]. The obtained Zn(II) complex showed a high k_{cat} , $5.08 \times 10^{-3} \text{ s}^{-1}$, towards bis(2,4-dinitrophenyl)phosphate hydrolysis. Triel and co-workers [35] synthesised 3-(bis(pyridin-2-ylmethyl)amino)propan-1-ol derived from di(2-picolyl)amine and its Zn(II) complex, which also exhibited high catalytic activity towards bis(p-nitrophenyl) phosphate hydrolysis. These results imply that the introduction of pyridine group can help to increase the catalytic activity of mimics. Thus in this work, to improve the coordination interaction between template and functional monomer, a multi-pyridine-ligand functional monomer containing di(2-picolyl)amine was synthesized to prepare MIPs. To the best of our knowledge, this is the first time to investigate multi-pyridine ligand as functional monomer applied in molecular imprinting for organophosphorus pesticide degradation.

Besides, p-nitrophenol, hydrolysis product of methyl parathion, is another hazardous substance to the environment, which has always been ignored by other groups. Herein, to remove simultaneously p-nitrophenol, a methyl parathion imprinted nanocapsule with hollow structure was also designed as similar to our previous work [36,37]. Methyl parathion could be hydrolyzed in the imprinted sites, and the generated p-nitrophenol could be enriched in the void. Therefore the obtained hollow nanocapsule was expected to be able to hydrolyze methyl parathion rapidly and absorb the generated p-nitrophenol simultaneously.

2. Experimental

2.1. Chemicals

Methyl parathion was purchased from Best Reagent Ltd. (Chengdu, China). Di(2-picolyl)amine (DPA), 4-Vinylbenzyl chloride (VBC), azodiisobutyronitrile (AIBN) and γ -methacryloxypropyl-trimethoxysilane (KH-570) were supplied by Heowns Biochem Technologies (Tianjin, China). Tetraethylorthosilicate (TEOS) was purchased from Beijing InnoChem Science & Technology Co. Divinylbenzene (DVB) containing 80% DVB was obtained from Aldrich (Steinheim, Germany) and purified by treating with 5 wt% aqueous NaOH to remove the inhibitor.



Scheme 1. Synthesis of N-(4-vinylbenzyl)-di(2-picolyl)amine.

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