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Molecularly imprinted polymers derived from lignin-based Pickering emulsions and their selectively adsorption of lambda-cyhalothrin

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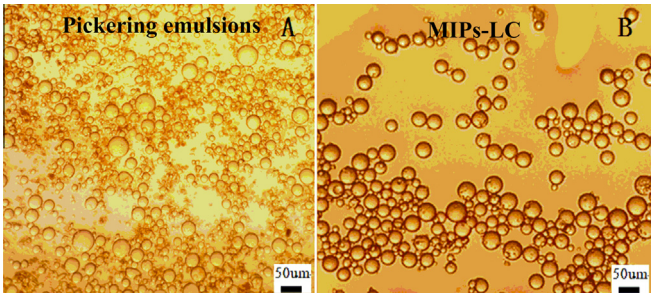
HIGHLIGHTS

- Lignin was utilized as stabilizer to fabricate molecularly imprinted polymers.
- Lignin without modification could irreversible attachment at the oil/water interface.
- Hydrophobic surface of MIPs-LC was benefit for adsorption lambda-cyhalothrin.

GRAPHICAL ABSTRACT



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ABSTRACT

Lignin particles were used as stabilizers to establish a stable Pickering oil–water emulsion, and then the molecularly imprinted polymers (MIPs) were fabricated by radical polymerization in the presence of functional and cross-linked monomers in the oil phase. As-prepared MIPs were observed with a diameter from 10 μm to 65 μm when oil/water ratio increased from 0.11 to 0.68, and exhibited thermal stability and hydrophobic surface. A series of static adsorption experiments were conducted to analyze their adsorption performance for lambda-cyhalothrin (LC). The preliminary results showed that MIPs possessed good recognition toward LC, that is, the adsorption equilibrium time was about 3.0 h and the equilibrium adsorption amount was 72.25 μmol g^{-1} for MIPs and 43.10 μmol g^{-1} for nonimprinted Polymers (NIPs), respectively, indicating the enhanced selectively adsorption of LC. The adsorption process followed pseudo-second-order model by the kinetic analysis and Freundlich equation by the isothermal analysis, respectively. The selective recognition experiments displayed the outstanding selective adsorption effect of the MIPs for target LC. Moreover, the obtained MIPs could be effectively regenerated and recycled at less three times without significant loss of adsorption capacity.

1. Introduction

Industrial interest in environmentally friendly materials has driven research in a variety of products from natural resources [1]. Lignin is found as a natural macromolecule in the cell wall of vascular plants, making it one of the most abundant macromolecules in the biosphere, second to cellulose, and is the only non-petroleum resource that can provide renewable aromatic compounds [2]. Lignin has attracted renewed attention given its anticipated role as a byproduct in biorefinery operations and second generation bioethanol from lignocellulose [3]. However, Lignin is difficult to eliminate or breakdown, and it has long been

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considered as a waste product in the pulp and paper industry. When manufacturing white-colored paper, lignin is traditionally removed by chlorine or chlorine-based compounds as bleaching agents [4]. Tonnes of lignin are readily available from the pulp and paper industries [5], but there were few lignin-based commodity materials because of its complex structure, low reactivity, broad chemical differences depending on source, and poor processability [6]. Thus, about 98% of lignin is directly poured into nearby waters or burned in an energy-recovery step [7,8]. These disposal routes not only waste precious bioresources, but also cause air pollution. Therefore, it is urgent to find an advisable route to utilize lignin without additional waste and pollution.

Recently, Lignin has been studied for two general uses. The first is production of small molecule chemicals by decomposition or refinery process. Catalytic methods used to convert lignin include various types of reduction, oxidation, and catalytic cracking process [9–12]. Typically, softwood lignin has been actively studied by many researchers to produce industrially important vanilline due to its structural similarity with that of lignin. Also, many other industrially important small molecule chemicals can be produced by catalytic decomposition of lignin [13,14]. However, additional research is needed to overcome serious practical issues associated with the huge energy costs and necessary purification process to produce small molecule chemicals from this complex natural material. The second approach to the general use of lignin is as a starting material of a diversity of commercial polymer products such as adsorbent [14]. Lai et al. [15] took alkali lignin as absorbent to remove trametes versicolor laccase, and the adsorption capacity of lignin reached 23.8 ± 0.81 U g^{-1}. Adhikari et al. [16] used kraft mill lignin as adsorbent to remove Au(III) from acidic chloride media and the recovery of elemental gold was obtained by simple incineration of the loaded adsorbent. However, these adsorbents have no selective when faced solution mixing with several competitors. Overall, it is still a difficult but promising task, great endeavors should be done to address this issue.

Nowadays, molecularly imprinted polymers (MIPs) were particularly notable attributed to their high affinity and selectivity towards a given target or group of target molecules. To fabricate MIPs, a monomer-template complex was formed through covalent or noncovalent interactions between the functional monomer and the template molecule in a prepolymerization solution. After polymerization, the template was removed from the polymer matrix to create imprinted cavities with a size, shape, and three dimensional structures complementary to the template [17]. In comparison with antibodies, enzymes or biological receptors, MIPs show inherent advantages: their production is quite simple and economical, moreover the polymers show good physical and chemical stability and applicability in harsh chemical media without loss of binding properties. With their intrinsic properties of selectivity, the application of MIPs was intriguing to improve the response of target molecules. For example, MIPs have extensively been used for the detection and adsorption of various specific molecules such as amino acids [18], pesticides [19], proteins [20], etc. However, few published articles have focused on lignin combining with MIPs to get a selective adsorption material.

It is well-known that in Pickering emulsion, dispersed liquid droplets are stabilized by solid particles instead of conventional surfactants which can cause toxic to fish and aquatic organisms, and eutrophication of water bodies [21]. The stabilizing particles were located at the interface between the two immiscible liquids, thereby preventing coalescence of the droplets [22]. Recently, Ye's group first applied molecular imprinting approach to prepare spherical MIPs based on Pickering emulsion polymerization [23]. In their novel and interesting work, modified silica nanoparticles were allowed to establish a stable oil-in-water emulsion, followed by interfacial imprinting polymerization in the oil phase. However, preparation of silica nanoparticles were time-consuming and would cause environment pollution when silica was modified before used for forming Pickering emulsion. Additional, Lehle et al. [24] demonstrated that for non-spherical colloids at free interfaces capillary interaction appear to be dominant. Hence, it would be better to use a natural material without modified and non-spherical materials as stabilized particles.

Inspired by this body of work, lignin was used for stabilizer in the process of preparation of Pickering emulsion to fabricate molecularly imprinted polymers (MIPs). Lambda-cyhalothrin (LC) was selected as template molecule due to it highly used in cotton plantation and in vegetable production, and the widespread use of these substances has led to serious health problems including neurotoxic effects through voltage dependent sodium channels and chromosomal aberrations, genotoxicity, micronucleus formation in rat bone marrow cells, reproductive toxicity, cardiotoxicity and hepatotoxicity on non-target organisms such as mammals, birds, and fishes. These compounds also interfere with many vital physiological functions and constituently alter the levels of various biochemical and hematological constituents [25–30]. In comparison to the nonimprinted polymers (NIPs) prepared by Pickering emulsion polymerization, the obtained molecularly imprinted adsorbent using LC as template molecule was applied to adsorptive removal of LC from aqueous solutions, and the adsorption properties such as equilibrium, kinetics and recognition were investigation in detail.

2. Experimental methods

2.1. Materials

Enzymatic hydrolysis lignin was obtained from Shandong Longlive Bio-technology Co., Ltd. (Shandong, China). Lambda-cyhalothrin (LC), fenvalerate (FL) and bifenthrin (BT) were purchased from Yingtianyi Standard Sample Company (Beijing, China). Ammonia and hydrochloric acid were received from Hubao Chemical Reagents (Yangzhou, China). Ethanol, methanol, acetic acid (HAC), HPLC-grade methanol, toluene and methacrylic acid (MAA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 4-Vinyl pyridine (4-VP) was received from Aladdin Reagent Co., Ltd. (Shanghai, China). Dimethyl 2,2′-azobis (AIBME) was purchased from Adamas Reagent Co., Ltd. (Shanghai, China). Ethyl glycol dimethacrylate (EGDMA) (Shanghai Xingtu Chemical Co., Ltd., Shanghai, China) was washed consecutively with 10% aqueous NaOH, water and brine, dried over $MgSO_4$, filtered and then distilled under reduced pressure. Deionized water was used in all experiments.

2.2. Instrument

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR (America thermo-electricity Company) with 2.0 cm^{-1} resolution in the range of 4000–400 cm^{-1}, using KBr pellet. The SEM images were examined with JSM-7001F scanning electron microscopy (JEOL Ltd., Japan). TGA was performed for powder samples (about 10 mg) using a Diamond TG/DTA Instruments (Perkin–Elmer, USA) under a nitrogen atmosphere up to 800 °C with a heating rate of 5.0 °C min^{-1}. The morphologies of MIPs-LC were observed by an optical microscopy (OM, Shanghai Peter EM (BM) Optical Instrument Manufacturing Company Limited, China). For (Confocal Laser Scanning Microscopy, CLSM), lignin particle dispersion was stained with rhodamine B fluorophore at 0.5 g L^{-1}. Images of MIPs-LC were acquired using a Zeiss LSM 410 confocal microscope (Zeiss, Gottingen, Germany). Chromatographic analysis was carried out on an Agilent 1200 LC