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Fabrication and evaluation of temperature responsive molecularly imprinted sorbents based on surface of yeast via surface-initiated AGET ATRP

Jianming Pan*, Hui Hang, Xiuxiu Li, Wenjing Zhu, Minjia Meng, Xiaohui Dai, Jiangdong Dai, Yongsheng Yan

School of Chemistry and Chemical Engineering, Jiangsu University, xuefu Rode 301#, Zhenjiang 212013, China

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ABSTRACT

Temperature responsive molecularly imprinted polymers (T-MIPs) were prepared based on the surface of yeast by electron transfer atom transfer radical polymerization (AGET ATRP). The as-prepared T-MIPs were charcterized by FT-IR, SEM, TGA and elemental analysis, which indicated that T-MIPs exhibited thermal stability and composed of temperature responsive imprinted layer. Then T-MIPs were evaluated as sorbents to selectively recognise and release cefalexin (CFX) molecules. The results suggested binding properties of T-MIPs were related to the testing temperature. The maximum adsorption capacity of T-MIPs at 303 K was 59.4 mg g^{-1}, and the maximum release proportion for T-MIPs at 293 K in water for 24 h was 71.08%. The selective recognition experiments demonstrated high affinity and selectivity of T-MIPs towards CFX over competitive compounds, and the specific recognition of binding sites may be based on the distinct size, structure and functional group to the template molecules.

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1. Introduction

Molecularly imprinted polymers (MIPs) are synthetic artificial receptors produced by the cross-linking of functional monomers in the presence of the template molecule. Removal of the template yields imprinted cavity capable of recognizing template molecule under appropriate conditions [1]. The imprinted polymers prepared by this technique have attracted extensive research interest due to the potential applications in many scientific and technical fields, such as separation and pre-concentration, constructing sensors, chromatography stationary phases, pseudo-immunoassay, and catalysis [2]. But the conventional imprinting technique have some disadvantages, such as poor binding capacity and low binding kinetics results from crushing the imprinted polymeric monolith and the diffusion barrier for the template molecules coming from thick matrices, respectively [3]. In order to overcome these drawbacks, surface molecular imprinting technique which fabricates the MIPs layer on a solid support [4] has emerged. Compared to traditional MIPs, surface imprinted polymers are simple and convenient to prepare, not only possessing high selectivity but also avoiding problems with mass transfer and the binding kinetics [5].

Recently, intelligent and functional MIPs aroused widespread interest, such as the response of temperature [6,7], pH [8], magnets [9] and light [10]. In this field, poly(*N*-isopropylacrylamide) (PNIPAAm) has been the focus of significant attention because of its thermo-responsive properties [6]. The use of special functional comonomers (e.g., *N*-isopropylacrylamide (NIPAAm) monomers) in molecular imprinting makes it possible to obtain stimuli-responsive MIPs, which are able to capture and release template molecules in response to environmental temperature changes [11]. At present, the work about the temperature responsive imprinted polymer hydrogels based on the PNIPAM was reported by Liu's group, which suggested that imprinted polymer hydrogels had good temperature response, selectivity and reusability, but with poor adsorption capacity and mechanical strength [6]. Moreover, Pan et al. employed a molecular imprinting methodology to introduce the cell adhesive peptide (Arg–Gly–Asp–Ser) RGDS onto a thermo-responsive cell culture substrate, which was used as a highly efficient system for harvesting cell sheets [12].

Nowadays, controlled/living free radical polymerization (CLRP) has been widely utilized to synthesize MIPs, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), nitroxide-mediate polymerization (NMP) and iniferter [13]. Among them, atom transfer radical polymerization (ATRP) using halogenated Cu(I) as a catalyst holds promise as a useful method for generating

* Corresponding author. Tel.: +86 51188790700.
E-mail address: pjm@ujs.edu.cn (J. Pan).

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MIPs, since various kinds of monomers can be used and the reaction can proceed under mild conditions such as low temperature [14]. However, normal ATRP has some drawbacks because the catalyst complex used in the ATRP system contains a transition-metal compound which is sensitive to oxygen and can be easily oxidized to a higher oxidation state in a lower oxidation state. Thus, polymerization can be easily inhibited by oxygen [15]. To overcome such drawbacks, activators generated by electron transfer atom transfer radical polymerization (AGET ATRP) is an approach that utilizes electron transfer such as by metallic copper and ascorbic acid to consume oxygen, thereby providing a deoxygenated environment for ATRP. AGET ATRP also has other advantages over conventional ATRP, such as reduced catalyst cost and avoidance of use of the unstable catalyst Cu(I) [16].

In this article, we describe the preparation of thermoresponsive-MIPs (T-MIPs) based on the surface of yeast particles by AGET ATRP. Yeast is one of the most important and interesting groups of microorganisms that serve as the ideal model of human and animal eukaryotic cells [17]. Compared with other imprinting supports such as silica gel [18], nanotube membrane [19] and graphene [20], the yeast has the advantages of low cost, easily available source and abundant active biomolecule on the cell wall without further modification process [21]. The T-MIPs were prepared by using antibiotic drug cefalexin (CFX) as template molecule, acrylamide (AAm) as the functional monomer to recognize template molecule, NIPAAm as the temperature responsive monomer, ethylene glycol dimethacrylate (EGDMA) as cross-linking monomer, $CuCl_2$ as catalyst and ascorbic acid (AsAc) as reducing agent. The preparation of the yeast surface-T-MIPs prepared via AGET ATRP was shown in Fig. 1. Bath binding tests were carried out to evaluate the binding characteristics of the T-MIPs. Finally, the T-MIPs were applied for selective recognition and release of CFX from the single solute and dual-solute solutions.

2. Experimental

2.1. Materials

Yeast powder was purchased from Angel Yeast Co., Ltd. (Yichang, China). Acrylamide (AAm), *N*-isopropylacrylamide (NIPAAm), 2-bromoisobutyryl bromide, triethylamine, ethylene glycol dimethacrylate (EGDMA), *N*,*N*,*N*′,*N*′,*N*″-pentamethyl diethylenetriamine (PMDETA), lomefloxacin (LMLX), tetracycline (TC), sulfadimidine (SMZ) and ampicillin (AMP) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). $CuCl_2$, sodium chloride (NaCl), tetrahydrofuran (THF), ascorbic acid (AsAc), and HPLC-grade methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol, ethanol, and acetic acid were supplied by Nanjing Shuguang Chemical Group Co., China. Cefalexin (CFX) were obtained from Shanghai Shunbo Biotech Co., Ltd. (Shanghai, China). The chemicals for HPLC were at least of HPLC grade, other chemicals were analytical reagent grade.

2.2. Apparatus

Infrared spectra (4000–500 cm^{-1}) were recorded using a Nicolet NEXUS-470 FT-IR apparatus (USA). Scanning electron microscopy (SEM) images were obtained at 15.0 kV on the field emission scanning electron microscope (USA). Thermal stability of the particles was measured using a Diamond TG/DTA instruments (PerkinElmer, USA). Other apparatus applied in this study are listed as follows: Vario EL elemental analyzer (Elementar, Hanau, Germany), Agilent1200 HPLC equipped with a UV–vis detector (Palo Alto, USA), A Unic-2602 UV–vis spectrophotometer (Unic Company, Shanghai).

2.3. Preparation of AGET ATRP initiator

Yeast@initiator was prepared according to the following procedure. An amount of 5.0 g yeast powder, which was washed with 0.9% sterile physiological saline and ethanol each for three times, was dried at room temperature. An amount of 3.0 g the dried yeast was added to a mixture of 30 mL of THF and 1.0 mL of triethylamine under the atmosphere of nitrogen in an ice bath for 30 min. Then, 1.0 mL of 2-bromoisobutyryl bromide as initiator was added dropwise to initiate the reaction and the reaction mixture was stirred at room temperature for 12 h under the nitrogen protection. The obtained AGET ATRP initiator yeast@Br was washed with ethanol and distilled water several times, and then vacuum-dried at 25 °C for 12 h.

2.4. Preparation of CFX surface-T-MIPs via AGET ATRP

The yeast surface-T-MIPs were synthesized by AGET ATRP procedure (Fig. 1) as follows: CFX (0.05 g) and functional monomer AAm (0.28 g) were added to the flask with a mixture solution of methanol and deionized water (20 mL/10 mL, v/v). This solution was sparged with nitrogen gas and stored for 1.5 h, allowing self-assembly of the CFX and the monomer. The temperature responsive monomer NIPAAm (0.40 g) was then dissolved in the mixture solution. After that, EGDMA (3.96 mL) and yeast@Br (0.5 g) were added into the flask under stirring at room temperature, to obtain the pre-polymerization solution. After 0.5 h, $CuCl_2$ (19.2 mg) and PMDETA (30 μL) were added sequentially into the mixture solution pre-heated at 30 °C. Then, 2 mL of AsAc solution (3.775 mg mL^{-1}) was transferred into the flask to reduce the Cu^{2+} to the activator Cu^{+} and start the polymerization. The mixture solution was unceasingly vibrated at 40 °C for 8 h. After the polymerization, the obtained product was washed with distilled water and ethanol several times, and then washed with a mixture of methanol/acetic acid (90:10, v/v) by Soxhlet extraction to remove the template molecules. Finally, the obtained T-MIPs were dried at 50 °C for 24 h. The non-imprinted polymers (T-NIPs) were prepared without the addition of CFX as reference polymer in parallel based on the same procedure.

2.5. Batch rebinding experiment

The effects of experimental parameters such as contact time, initial concentration of CFX and temperature on the adsorption of CFX were studied by batch mode of operations.

In adsorption isotherm studies, 10 mg of T-MIPs/T-NIPs were added into 10 mL of CFX solution with different initial concentrations varying from 5.0 mg L^{-1} to 150 mg L^{-1}, then shaked at temperature of 303 K in water bath. After 24 h, the final mixtures were centrifuged and the concentration of CFX in the aqueous solution was measured by the UV–vis spectrophotometer at 261 nm. In study of adsorption kinetics, 10 mL of aqueous solutions with initial CFX concentration of 50 mg L^{-1} was reacted with the 10 mg of T-MIPs/T-NIPs at 303 K in water bath. After stirred at 350 rpm for the desired time (10–480 min), the mixtures were centrifuged and the amount of CFX in the aqueous phase was measured by UV–vis spectrophotometer. All of the tests were carried out in triplicate under the same conditions, and the average values were chosen.

2.6. Release of CFX

The release of CFX from T-MIPs and T-NIPs was carried out as follows: T-MIPs/T-NIPs were previously loaded by immersion in 10 mL of 5.0–150 mg L^{-1} CFX solution for 24 h at 303 K to reach the adsorption equilibrium. Then, the mixtures captured CFX were centrifuged, washed with distilled water, dried with filter paper, and finally placed into 10 mL of distilled water at 293 K for 24 h.

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