Chemical Engineering Journal 198–199 (2012) 503–511

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Surface molecular imprinting onto magnetic yeast composites via atom transfer radical polymerization for selective recognition of cefalexin

Xiuxiu Li [a,b], Jianming Pan [a,b], Jiangdong Dai [a], Xiaohui Dai [a], Longcheng Xu [a], Xiao Wei [a], Hui Hang [a], Chunxiang Li [a,b,*], Yan Liu [a]

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China
[b] State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, PR China

HIGHLIGHTS

- We successfully synthesized the magnetic yeast composites.
- The MMIPs were prepared on the mag–yeast surface by ATRP.
- The MMIPs possessed excellent template recognition capacity.
- The MMIPs were used to selective recognize CFX from the environmental samples.

ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form 29 May 2012
Accepted 29 May 2012
Available online 12 June 2012

Keywords:
Magnetic yeast composites
Magnetic molecularly imprinted polymers
Atom transfer radical polymerization
Cefalexin
Selective recognition

ABSTRACT

In this study, the magnetic yeast composites (mag–yeast) were successfully prepared by coating the chitosan layer containing γ-Fe_2O_3 nanoparticles onto the surface of the yeast. Then, the magnetic molecularly imprinted polymers (MMIPs) based on the mag–yeast were prepared by atom transfer radical polymerization (ATRP) which was occurred in mild reaction conditions. The MMIPs were characterized by Fourier transmission infrared spectrometry (FT-IR), scanning electron microscope (SEM), vibrating sample magnetometer (VSM), thermogravimetric analysis (TGA) and elemental analysis. The results demonstrated that spherical shaped MMIPs particles prepared via ATRP possessed magnetic property (M_s = 1.229 emu g^{-1}) and magnetic stability (especially over the pH range of 5.0–11.0). The MMIPs were adopted as sorbents to selective recognition and separation of cefalexin (CFX). By the batch mode experiments, the results showed that adsorption behaviors of MMIPs were well described by the Freundlich isotherm and the pseudo-second-order kinetics. The MMIPs possessed excellent recognition capacity for CFX (36.86 mg g^{-1} at 298 K), and also exhibited outstanding selectivity for CFX over the other competitive compounds (such as sulfadiazine, tetracycline and ampicillin). Finally, the MMIPs were successfully applied to the selective solid phase extraction of CFX from the environmental samples.

1. Introduction

Molecular imprinting is a well-established and simple technique for synthesizing three-dimensional cross-linked polymers with specific molecular recognition properties, namely molecularly imprinted polymers (MIPs) [1]. Possessing high selectivity and affinity to the target molecule, MIPs have attracted considerable attention in many fields such as chemical sensing, solid phase extraction, antibody mimics, drug development and so on [2]. The imprinting technique prepared with conventional methods 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]. To overcome these drawbacks, the surface molecular imprinting technique has been developed in recent years, which fabricated and situated specific binding sites at the surface or in the proximity of materials surface [4].

Atom transfer radical polymerization (ATRP) is based on the transfer of halogen atom from the initiator to the monomer and the successive transfer to the growing polymer chain catalyzed by a transition-metal complex that mediates the propagation [5]. Since its first discovery in 1995, ATRP has rapidly attracted growing interest because of its versatility in the synthesis of polymers with predictable molecular weights, low polydispersities, and

* Corresponding author at: School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China. Tel.: +86 0511 88790683; fax: +86 0511 88791800.
E-mail address: linxx20@126.com (C. Li).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.05.106

specific functionalities as well as its easy availability of many kinds of initiators, catalysts, and monomers [6]. Surface-initiated ATRP can be used because it ensures preparation of covalently bonded cross-linked polymers provided ATRP initiators are grafted to the substrate [7]. As a typical controlled living radical polymerization [8], ATRP has been proposed to be applied in surface imprinting technology by grafting polymers to various surfaces of the imprinting support such as silica gel [9], gold [10,11], nanotube membrane [5] and graphene [12]. Yeast is one of the most important and interesting groups of microorganisms that serve as the ideal model of human and animal eukaryotic cells [13–17]. Compared with the above imprinting supports, the yeast has the advantages of low cost, easily available source [18] and abundant active biomolecule on the cell wall [19] without further modification process. Further more, most of the imprinting processes combined with ATRP were carried out in organic solvents, such as acetonitrile and dichloromethane, which are relatively expensive and toxic [20]. Recently, Liu et al. [21] had prepared Fe_3O_4@MIP imprinted nanoparticles via surface-ATRP in the binary mixture of methanol and water. Dai et al. [20] had prepared magnetic imprinted nanoparticles sorbents by ATRP emulsion polymerization from aqueous medium. So, in green solvent can be chosen as an environmental reaction solvent in the polymerization process.

Magnetic separation technology has been gradually attracted the eyeballs of many scientists and technicians as a rapid and effective technology for separating magnetic materials. It has been used for many applications in medicine, diagnostics, cell biology, analytical chemistry, mining, and environmental technology [22]. If some magnetic components are encapsulated into MIPs, the resulting magnetic molecularly imprinted polymers (MMIPs) can build a controllable binding process and allow magnetic separation to replace the centrifugation and filtration step in a convenient and economical way [23].

Cephalosporins, including cefalexin (CFX), are a kind of β-Lactam antibiotics (BLAs) which are widely used to treat respiratory tract infection, prostatitis, urinary tract infection, skin, and soft tissues infection [24]. BLAs are one of the most widely used anti-microbial drugs since 70 years ago, and the wide use of the antibiotics increases the concerns on their environmental exposure [25]. Exposure to BLAs has been shown to induct allergic and toxic reactions in hyper sensitive individuals and to promote the spread of bacterial resistance [26]. Due to concern about the antibiotics as an environmental pollutant, selective recognition and separation of target antibiotic from complex matrices prior to the detection is urgently required.

In this work, the magnetic composites were prepared by coating the chitosan (CTS) layer containing γ-Fe_2O_3 nanoparticles onto the surface of the yeast. And then the obtained mag–yeast was further coated with a thin imprinting film via atom transfer radical polymerization. The ATRP initiators were firstly introduced to the magnetic composites surface. Then, the MMIPs were prepared by using CFX as template molecule, methacrylic acid (MAA) as functional monomer, ethylene glycol dimethacrylate (EGDMA) as cross-linking monomer and CuCl as catalyst. The preparation of surface imprinted mag–yeast@MIPs via ATRP was schematically illustrated in Fig. 1. The characterization, adsorption capacity and selectivity of MMIPs were described and discussed in detail. The MMIPs were also used as sorbents for solid phase extraction (SPE) and separation of CFX from the spiked samples.

2. Experimental

2.1. Materials

Yeast powder was purchased from Angel Yeast Co. Chitosan (CTS) with 98% deacetylation and an average molecular weight of 6.0×10^4 g mol^{-1} was supplied by Yuhuan Biomedical Corp. (Zejiang, China). Sorbitan monooleate (Span-80), paraffin oil, glutaraldehyde (25%, v/v), methacrylic acid (MAA), sodium chloride (NaCl), tetrahydrofuran (THF), and HPLC-grade methanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cuprous chloride (CuCl), γ-Fe_2O_3 (30 nm outer diameters and 99.5% purity), ethylene glycol dimethacrylate (EGDMA), *N*,*N*,*N*′,*N*′,*N*″-pentamethyl diethylenetriamine (PMDETA), 2-bromoisobutyryl bromide, triethylamine, sulfadiazine (SD), tetracycline (TC) and ampicillin (AMP) were obtained from Aladdin reagent Co., Ltd. (Shanghai, China). Cefalexin (CFX) was obtained from

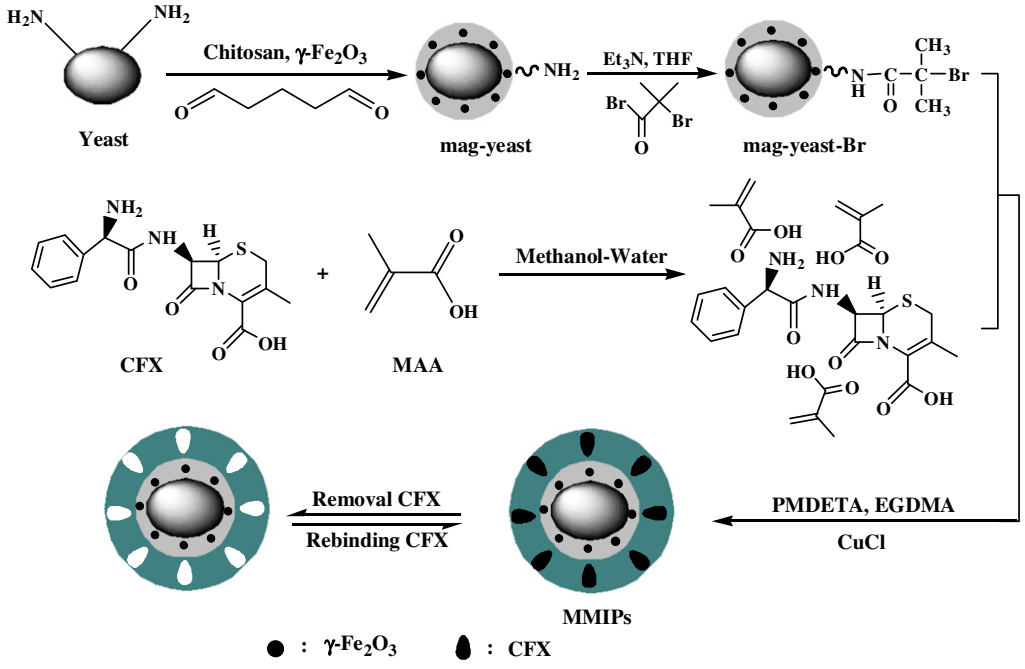

Fig. 1. Schematic route of surface imprinted mag–yeast@MIPs prepared via ATRP.