Colloids and Surfaces A: Physicochem. Eng. Aspects 452 (2014) 125–128

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Magnetic molecularly imprinted silica gel for enrofloxacin recognition

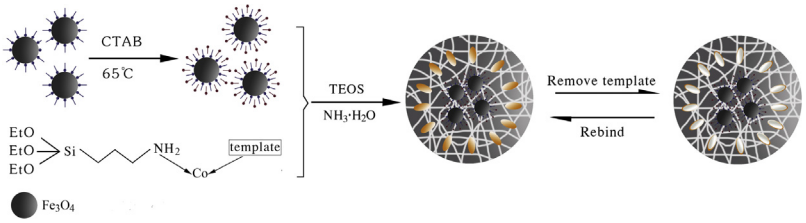
Lijuan An[a,b,*], Jing Wang[c], Zhiyuan Pang[a], Rimo Xi[b,c]

[a] College of Science, Tianjin University of Science and Technology, Tianjin 300457, PR China
[b] Tianjin International Joint Academy of Biotechonlogy and Medicine, Tianjin 300457, PR China
[c] College of Pharmacy, Nankai University, Tianjin 300071, PR China

HIGHLIGHTS

- A novel magnetic molecularly imprinted mesoporous silica gel was prepared by sol–gel processing using enrofloxacin as template.
- The resulting properties of adsorbent are investigated by FTIR, TEM, and SQUID magnetometry.
- The MMIP exhibited excellent recognition towards enrofloxacin.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 September 2013
Received in revised form 17 March 2014
Accepted 22 March 2014
Available online 3 April 2014

Keywords:
Magnetic
Molecularly imprinted polymer
Silica
Metal coordination

ABSTRACT

Magnetic molecularly imprinted mesoporous silica gel was prepared via sol–gel processing method through metal coordinate interaction, and it was applied to the recognition of enrofloxacin (ENRO). The structure and magnetic properties of the gel were systematically investigated by means of FTIR, TEM, and SQUID magnetometry, respectively. The binding characteristics were studied by performing both the static and dynamic adsorption experiments. Our studies suggest that the magnetic molecularly imprinted silica gel was capable of binding ENRO more strongly than the nonimprinted silica.

1. Introduction

In recent years, molecularly imprinted polymers (MIPs) have been demonstrated as one of the most attractive research fields due to their promising applications in the fields of chiral separation, chemical sensors, mimicking antibody, solid-phase extraction, and drug controlled release [1–5]. So far, considerable efforts have been devoted to developing new methods to synthesize MIPs. However, they are mainly acrylate or acrylic type polymers, which are restricted to be used as organic solvent for the dissolution of the organic polymer or template, and usually have been prepared under inert atmospheric conditions [6]. Silica with a highly rigid matrix and hydrophilic surface has a wide choice of functional precursors and structural forms, which makes it ideally suitable for imprinting various organic or biological molecules. The silica based MIPs have been shown to be superior in terms of stable structure, good chemical and mechanical stability [7–9]. In addition, mesoporous silica materials show potential properties as an imprinting matrix due to their high pore volume and nanosized pore wall thickness, which guarantee the generation of recognition sites near to the surface so as to offer a high accessibility for a target molecule [10]. There have been a few reports on the preparation of silica based MIPs. The template can be linked to silica by thermally reversible bond [9,11], covalently bond [12], hydrogen bond [13], and metal coordination [14]. Employment of the high selectivity of metal coordination to molecularly imprinted silica gel may be an easy way to imprint the target molecules.

* Corresponding author at: College of Science, Tianjin University of Science and Technology, Tianjin 300457, PR China. Tel.: +86 22 60601281; fax: +86 22 60601281.
E-mail addresses: anlijuan@tust.edu.cn, anlj513@163.com (L. An).

http://dx.doi.org/10.1016/j.colsurfa.2014.03.075
0927-7757/

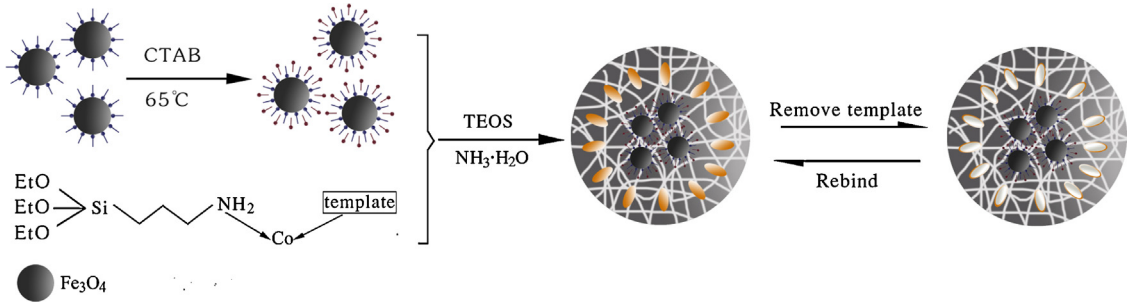


Fig. 1. Scheme of MMIPs preparation.

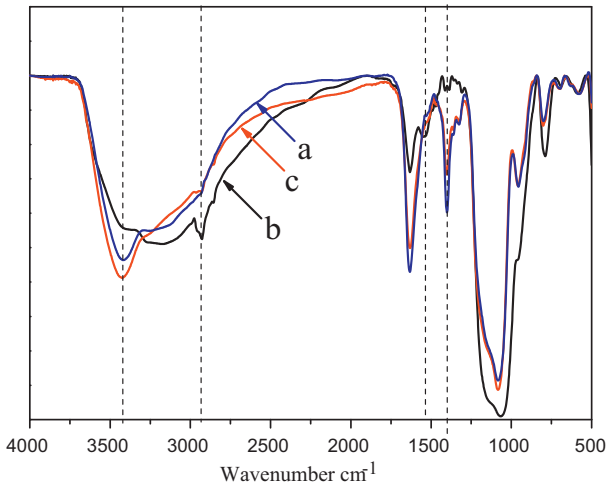


Fig. 2. FTIR spectra of (a) MNIPs, (b) MMIPs before and (c) after extraction of CTAB and ENRO.

Magnetic iron oxide nanoparticles have been used to prepare MIPs, which were called magnetic molecular imprinted polymers (MMIPs). The application of MMIPs would replace the centrifugation and filtration processes in a convenient and economical way. And the phase separation could be conveniently realized by applying an external magnetic field [15,16].

In the present work, we synthesized molecularly imprinted mesoporous silica gel to enwrap magnetic nanoparticles through metal coordinate interaction. Co ion formed a coordinate complex with enrofloxacin (ENRO) and 3-aminopropyl triethoxysilane (APTES), and ENRO worked as template, while APTES worked as a functional monomer in the imprinting process. Then, in the presence of coordinate complex, the sol–gel processing was carried out with CTAB modified iron oxide particles as magnetic cores. After the CTAB was removed by NH_4NO_3, and the template was removed by EDTA extraction, the MMIPs-based mesoporous silica gel was formed, which could capable of selectively rebinding the target molecule ENRO. The characteristics and selectivity of the MMIPs were investigated in details.

2. Experimental

2.1. Materials

3-Aminopropyl triethoxysilane (APTES) was obtained from TCI (Shanghai) Chemical Industry Corporation Limited. Enrofloxacin (ENRO) was purchased from the Sangon Biotech (Shanghai) Corporation Limited. Tetraethylortho silicate (TEOS) was purchased from Tianjin Ruijin chemicals Corporation Limited. All the reagents were used without further purification.

2.2. Preparation of magnetic molecularly imprinted silica gel

2.2.1. Preparation of Fe_3O_4 nanoparticles

Oleic-acid-stabilized magnetic particles Fe_3O_4 were synthesized by the chemical co-precipitation of ferrous and ferric chloride and the prepared nanoparticles were caped with CTAB as described in the literatures [17,18].

2.2.2. Preparation of Co ion formed coordinate complex

Prior to polymerization, Co ion formed coordinate complex was prepared. Briefly, 0.5 mmol of ENRO and 0.5 mmol of cobaltous acetate were dissolved in a component solvent (ethanol:water,

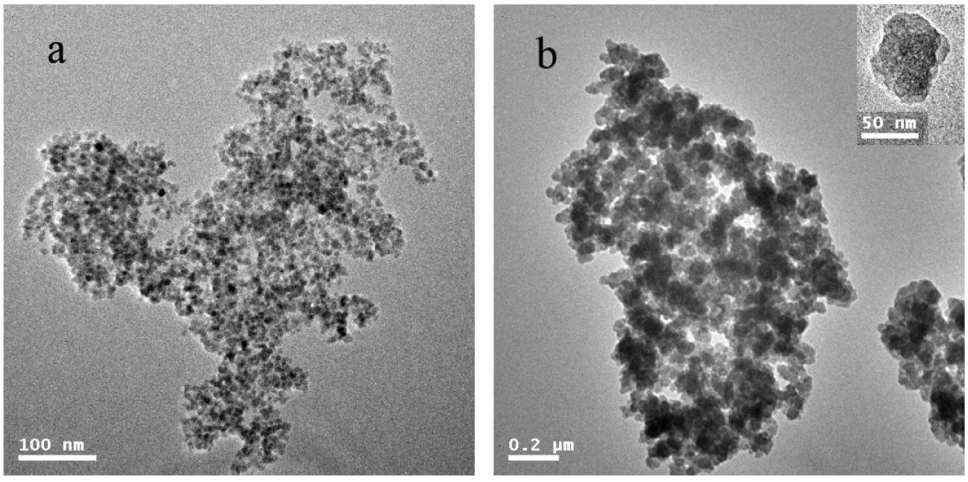


Fig. 3. TEM images of (a) Fe_3O_4 nanoparticles and (b) MMIPs.